



**Mechanisms for Phosphorus Elimination in Constructed Wetlands: A Pilot
Study for the Treatment of Agricultural Drainage Water from Dairy
Farms at the Lower River Murray, South Australia**

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君子不重，则不威；学则不固。

---- 孔子

If the scholar be not grave, he will not call forth any
veneration, and his learning will not be solid.

---- Confucius

For Qunying and Kathy

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Publications during the Candidature

Refereed Journal Paper

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Conference Paper

1. Wen, L. and F. Rechnagel (2002). Use of Creeping Water Plants for Phosphorus Removal from Agricultural Drainage Water. *Proceedings of the 2002 IWA Conference on waste stabilisation ponds*, Auckland, New Zealand, April 2002.
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3. Wen, L. and F. Rechnagel (2001). Phosphorus removal from irrigation drainage water by water plants based systems. *Proceedings of the XXVIII Congress of the International Association of Theoretical and Applied Limnology*. Melbourne, February, 2001.

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.

I consent to this copy of my thesis, when deposited in the University Library, being made available for loan or photocopying.

Li Wen

June 2002

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Mechanisms for Phosphorus Elimination in Constructed Wetlands: A Pilot Study for the Treatment of Agricultural Drainage Water from Dairy Farms at the Lower River Murray, South Australia

Abstract

Phosphorus (P) retention was measured in five pilot-scaled constructed wetlands (CWS) with different configurations in terms of macrophyte species and substrates in order to: 1) evaluate the P removal efficiency of water plants and substrates in experimental ponds with different configuration; 2) assess the contribution of macrophytes to P removal through direct uptake, modification of water chemistry and impacts on the P adsorption characteristics of substrate; and 3) contribute to the optimal design and operation of CWS for the treatment of agricultural drainage water.

Nature of drainage water

The drainage water is comparable to secondary effluent from municipal wastewater treatment plants in terms of average P concentration, P forms and N/P ratio. However, in terms of temporary and spatial changes in both concentration and volume, drainage water has more in common with cropland runoff. These unique characteristics are the main challenges for the purification of drainage water. Moreover, the high salinity in drainage water makes it more difficult to deal with.

Nutrient uptake by water plants

Of the three tested emergent water plant species, common reed was the only one survived the highly saline drainage water and showed robust growth. By trailing the morphometric changes, a highly significant and predictive phenometric model was obtained for catching the growth trajectory of reed ($R^2 = 97.2\%$). The model predicted that the aboveground biomass gradually reaches a plateau after approximately 150 days of growth. P content in reed shoot had clear seasonal patterns with the peak value at approximately 70 days after the beginning of the annual growing circle. Consequently, the maximum P recovery (13.3 g/m^2) can be reach when harvesting is done at about 70 days after the resuscitation, i.e. in later November. In pond one (with emergents), the aboveground biomass P accumulation accounted for 17.6% of the total removed P, which was in contrast to the common conclusion that uptake by macrophytes is a minor pathway in CWS. However, while the

density growth of emergent water plants in CWS can benefit P removal through enhancing the P adsorption by substrate, it impedes other important P pathways such as P co-precipitation with Ca and biofilm P uptake by lower the water column temperature and shading.

Two creeping-stem species performed well in drainage treatment system. Water buttons and water couch had a productivity of $34.2 \text{ g/m}^2/\text{day}$ during the 252 days of cultivation. As a result, a total of 109.6 g of P was incorporated into biomass, which was accounted for 37.5% of total removed P in the pond during the same period, showing the potential use of creeping-stem water plants to recover dissolved P from drainage water.

Performances and annual nutrient budgets of the field pond systems

The average P removal rate of the five ponds ranged from $-0.0 \sim 0.22 \text{ g/m}^2/\text{day}$, and the average P removal efficiency were in the range of $-0.0 \sim 44.2\%$ based on the mass balance during the two years of operation. Pond two (with planted floats) and Pond 4 (with emergents and P Poor soils) had similar higher P removal rate and more stable performances than other ponds. Pond 3 (with submergents) was the least efficient for P processing, and released large amount of the stored P in the low loading season (winter).

Indication for CWS management

Based on the information gained, a conceptional model was proposed to optimise the performance of constructed wetland for P removal. The model focused on the management of the three main and interactive compartments of CWS: vegetation, substrates, and water column.

Key words: Constructed wetlands, Agricultural drainage water, Phosphorus removal, macrophytes, P dynamics

Chapter One Introduction

1.1 ORIGIN AND FATE OF P IN AGRICULTURAL DRAINAGE WATER

1.1.1 P Loadings from Agricultural Land Use

Two broad categories of P source to aquatic ecosystems are used intensively in the literature: nonpoint or diffuse sources (NPS) and point source (PS).

1.1.1.1 PS

Most PS P comes from sewage treatment plants. A normal adult excretes 1.3-1.5 g P per day. Additional P originates from the using of industrial products, such as detergents, toothpaste, food-treating compounds, etc. Primary treatment removes only 10% of the P in the waste stream. Secondary treatment removes only 30%, and the remainder is discharged to the water bodies (Smith, 1990). However, in recent years, in many developed countries, the restricted discharge standards require polishing the secondary discharge by nutrients removal. Tertiary treatment can remove various amount of the remaining P depending on the technology used. Available technologies include biological removal and chemical precipitation.

1.1.1.2 NPS

NPS of P include natural and anthropogenic P.

- Natural: Phosphate deposits and phosphate-rich rocks release P during weathering, erosion, and leaching (Smith, 1990). P may also be released from the lake bottom sediments during seasonal turnover – internal loading (Rossi and Premazzi, 1991).
- Anthropogenic: The primary anthropogenic NPS P includes runoffs from:
 - 1) Lands being mined for phosphate deposits;
 - 2) Agricultural areas;
 - 3) Urban/residential areas.

Anthropogenic P loading from intensive farmland is reviewed in more detail in this thesis.

During the past 20-30 years, most of the efforts to control water pollution have been directed at dramatically reducing of point source discharge to surface waters due to their relative ease

of identification and control. While we have made process in point pollution control, the problems of NPS P - with the dominant source of agricultural land uses - are largely ignored due to its more complicated origins and pathways, and to some extent, the lack of cost-effective methods to manage the problem.

NPS pollution is of substantial quantity and diverse quality to have serious detrimental effects on regional water resources. Agricultural runoffs may contain high concentrations of nutrients and organic pollutants resulting from the use of fertilizers, animal wastes and pesticides in intensive agricultural areas. Nutrient enrichment has been identified as the main cause of impaired surface water quality in the USA (USEPA, 1996^a), in European countries (Ignazi, 1993; UNEP, 1993), in Australia (GHD, 1992), and many other countries (Ongley, 1996). For example, the USEPA's Report to Congress (USEPA, 1987) stated that NPS pollution contributed 76% of the pollutants to lakes. A report of USEPA (1996^b) stated that agricultural NPS pollution is the leading source for inland waters, the third largest source for estuaries, and a major contributor to ground water contamination and wetlands degradation.

In Australia, which is considered by many scientific researchers (such as Harris, 1994; Holland, 1999.) to be a little unusual compared to the Northern Hemisphere continents in terms of the low population density and the relatively low application rates of P fertilizers in some catchments, eutrophication and the subsequent algal blooms are also a concern in inland freshwaters. In Victoria, there were over 100 algal blooms reported in 91 water storages during 1996-97 (Anon, 1996). The surface waters of the Murray-Darling Basin (MDB) - Australia's 'bread basket' - have exhibited toxic blue-green algal blooms that are, in part, the symptomatic of excessive levels of nutrients. A large-scale (>1000 km) blue-green algal bloom in 1991 (the world's largest recorded riverine bloom) focused public attention on the deterioration of Australia's inland waters (Young *et al.* 1996). Subsequently, reduction of nutrient loads became a long-term objective of major catchment management plans.

1.1.1.3 P Forms and Processes

P can enter aquatic ecosystems associated with suspended solids or as dissolved P. Particulate P includes P associated with soil particles and organic materials eroded during flow events, and forms the majority of P lost from most cultivated land via surface runoff. Surface runoffs from non-cultivated lands, such as pastures and forests carry few soil particles, therefore, are generally dominated by dissolved P. The dissolved P is released from soils and plant materials. (Although it is well known that dead plants or plant residues release P quickly, very little is known about the release of P from live plants.) This release occurs when rainfall or irrigation water interacts with a thin layer of surface soil and plant materials before leaving the field as surface runoff or irrigation excess water. To trace the transportation and transformation of P, it is convenient to classify P forms in drainage waters as: (1) dissolved inorganic P (DIP), (2) dissolved organic P (DOP); (3) particulate inorganic P (POP); and (4) particulate inorganic P (PIP). Practically, three P forms are measured by relative easy and sophisticated analysis methods: TP, which is the sum of all P forms in water, total dissolved P (TDP) and DIP (measured and referred in many textbooks as soluble reactive P – SRP). Particulate P (PP) and dissolved organic P can be calculated from them. The differentiation between PIP and POP is difficult, and therefore is rarely carried out.

P may be lost from agricultural lands to water by several processes: erosion, surface runoff, and subsurface flow (leaching). As most soils have a very high capacity to absorb P, usually far above the quantity of P added as manures or fertilizers, it has long been considered that leaching losses of P from soil to water are negligible in most cases. While this is certainly true in terms of economic losses to the farmer, the concentrations of P to trigger eutrophication in freshwater are extremely small (as low as 0.02-0.035 ppm, Vollenweider, 1975). A concentration of 0.15mg/l of TP was proposed by Uunk (1991) as the maximum permissible P concentration in fresh waters. Indeed, the quality of surface waters throughout Europe, North America and Australia, in terms of risks of eutrophication, is a major current concern because of the increasing concentrations of P.

Until the 1980s, the problem of P leaching from soil to water was generally not considered important. Cooke (1986) regarded P concentrations in drainage water to be small (up to 1

mg/l) and not related to fertilizer use but to the nature and pH of the soil parent material and to weather conditions, i.e. factors that farmers can't control, hence management isn't possible. Similarly, Zwerman *et al.* (1972) reported that SRP concentration in drainage water could be less than 0.01mg/l even with moderate fertilizer application. Sharpley and Mentez (1987) also considered that losses of P in subsurface drainage water were small where fertilizers were applied at recommended rates. They quoted P concentrations in subsurface drainage waters from unfertilised and P-fertilized arable and grassland soils in North America ranging from undetectable to 0.064 mg/l, except three soils where it ranged over 0.2 mg/l. These results suggested that SRP concentrations in drainage water were not significantly influenced by fertilizer or management variables.

More recently, it was widely accepted that soil has finite capacity to hold P (Sharpley, 1996; Nash and Halliwell, 2000). As that limit is reached, the P concentration in soil water increases. The application of fertilisers and animal manures increase productivity, the rate of P cycling and the P stored in soil. Consequently, the P losses from land to water increase as well. Many studies reported the positive relationship between soil P and P concentrations in drainage water, although no linear or exponential relationships exist. For example, Brookes *et al* (1997) proposed a critical change point of Olsen soil P of c. 60 mg/kg. Below about 60 mg/kg Olsen-P concentration in soil, the TP concentrations in drainage water were small (c. <0.15 mg/l). When the soil Olsen P exceeds 60 mg/kg, there was a rapid linear increase in the P concentration in drainage water up to a maximum of soil Olsen P concentration of 100 mg/kg. In addition, significant seasonal fluctuations in both concentration and volume are the characteristics of P leaching from agricultural lands. For example, Haygarth and Jarvis (1995) found P leaching from grass monoliths in lysimeter with a peak in spring (>0.1 mg/l SRP). Furthermore, the P leaching from agricultural areas was considered as a regional problem. In the Netherlands, Breeuwsma and Silva (1992) considered that leaching of P was a problem in areas with intensive livestock farming, where high manure application coincided with shallow water-tables and sandy soils.

1.1.2 P Loadings and the Eutrophication of the Downstream Aquatic Ecosystems

One of the major causes of widespread degradation of aquatic systems such as lakes and streams and their associated wetlands is the addition of large quantity of in-organic nutrients, particularly nitrogen (N) and Phosphorus (P), from nonpoint sources (NPS, also referred as diffusion sources) such as land areas receiving fertilizers, agricultural wastes and agricultural drainage waters, and from point sources (PS) such as municipal and industrial effluents. It is estimated that currently 33×10^6 Mg /year of P (Hedley *et al.* 1995) are discharged in the oceans. Nutrient pollution can have impacts on aquatic ecosystems, both directly and indirectly. The most common problem is the stimulation of growth of nuisance plants, i.e. higher water plants, algae and cyanobacteria (blue-green algae), which can dominate and change the structure and function of aquatic ecosystems, a phenomenon known as eutrophication. Eutrophication means the fertilization of surface waters by nutrients that were previously scarce. Over geologic time, eutrophication is a natural aging process via which warm shallow lakes evolve to dry lands. Today human activities are greatly accelerating the process. Freshwater eutrophication has been a growing problem for decades. The net result of the eutrophic conditions and excess plant growth in water is the depletion of dissolved oxygen (DO) in the water due to the increased respiration of microorganisms in order to decompose the organic matter. When macrophytes, algae or cyanobacteria grow to nuisance proportions (referred to “bloom”), they can:

1. Cause a shift in habitat characteristics due to changes in assemblages of macrophytes;
2. Displace endemic and non-endemic species, for example, flagellates compete out diatoms (Bell & Elmetric, 1995);
3. Cause excessive diurnal fluctuations in pH and DO which can stress or eliminate sensitive species, and affect trophic levels due to changing P solubility and P adsorption by sediments (Reddy and Flaig, 1995) and suspended solids;
4. Impede the recreational use of water due to slime, weed infestation, and noxious odour from decaying dead biomass;
5. Increase operating expenses of water treatment and supply in term of:
 - a. Odor and bad taste;
 - b. Extended filtration;
 - c. Disinfectant byproducts with potential human health effects.

6. Deoxygenate the water, which results in:
 - a. Altered fisheries;
 - b. Fish kills.
7. Pose a serious health hazard to animals and humans because of the associated cyanobacteria blooms in freshwaters and dinoflagellate (*Pfiesteria piscicida*) blooms in coast area (Burkholder *et al.* 1992).

Limiting nutrients Although both N and P contribute to eutrophication, management target usually focuses on that nutrient which is limiting. While N is usually the limiting nutrient in saltwater, many studies suggest that P is more important in the majority cases of freshwater and that the acceleration of eutrophication around the world is caused by P input (Schindler, 1977; Sharpley *et al.* 1994). In addition, the exchange of N between atmosphere and water and the fixation of atmospheric N by some species of blue-green algae make it difficult to control the N input into an aquatic ecosystem. Therefore, P control is of prime importance in reducing the accelerated eutrophication. The rationale behind the strategy is illustrated by the statement of Hutchinson (1957): 'Of all the elements present in living organisms, P is likely the most important ecologically'.

In freshwaters, the natural background levels of total P (TP) are generally less than 0.03 mg/l, while the natural levels of dissolved inorganic P (DIP) usually range from 0.005-0.05 mg/l (Dunne and Leopold, 1978). However, the levels of P to accelerate eutrophication and trigger algal bloom can be as low as 0.02 mg/l, which is an order of magnitude lower than P concentration in soil solution critical for plant growth (Sharpley *et al.* 1999). This emphasizes the disparity between critical terrestrial and aquatic P concentrations and the importance of controlling P losses from uplands to downstream water bodies.

1.1.3 P Loadings from Irrigation Drainage Water from Reclaimed Farmland at the Lower River Murray, South Australia

1.1.3.1 Needs for irrigation and drainage

Irrigation and drainage have always played a critical role in Australia. For Australia as a whole, the area of crops and pastures irrigated (2,069,344 ha), is a minute proportion (0.4%) of the total area of land in agricultural holdings (465,953,718 ha). It is only 11.7% of the

total area of crops and pastures. However, the value of irrigated production is out of all proportion to the area of land involved. One source estimated that irrigation accounts for between 25 and 30% of Australia's gross value of agricultural output. This corresponds with a figure of approximately \$7.2 billion. On top of this, there was an estimated four-fold multiplier beyond the farm gate. Today, irrigated agriculture in Australia accounts for 40 percent of the total crop value - from only 15 percent of the total cropland.

In South Australia - the driest state in the driest continent - irrigation is very important to maintain a productive agriculture. In fact, irrigation is, by far, the largest user of water throughout the State. Each year over two-thirds (typically 720 GL) of all water used by South Australians is applied to various irrigated crops. Nearly 60% of the water taken for irrigation comes from the River Murray, 35% from South East groundwater and the majority of the remaining 5% is extracted from smaller groundwater basins around Adelaide. The reclaimed pastures along the LRM are among the most productive systems in the region, and irrigation is one of most important facts contributing to maintaining sustainable development.

Drainage is an integral part of irrigated agriculture. Excess water in the crop root zone is harmful to plant growth. Crop yields are dramatically reduced on poorly drained soils, and prolonged waterlogging will eventually kill plants. Excess irrigation water is recycled back to surface water and/or groundwater through a drainage network, except for the water lost through evapotranspiration.

1.1.3.2 P associated with drainage water

Irrigation-drainage systems in intensively irrigated agricultural areas are traditionally designed and operated mainly to satisfy an agricultural objective - preserving crop productivity. But, as with many other modern agricultural technologies, irrigation-drainage doesn't come without problems. Current environmental constraints demand that the irrigation-drainage should satisfy not only the agricultural objective, but also a second objective: protection of the environment. Several studies have shown that the drainage water from irrigation-drainage systems can in fact cause problems in the downstream environment

related to water quality (Ongley, 1996). The diversion of irrigation drainage back to the River Murray has caused natural resource degradation and increased salinity downstream (Australia EPA, 2000). This impact will further increase unless irrigation drainage will be controlled.

Irrigation can significantly increase P loss potential from both surface runoff and erosion due to the prolonged contact time between water and soil and plant materials. Furrow irrigation, for example, can increase the erosion potential. The irrigation drainage network collects all the surplus water from dairy farms including surface runoff and subsurface leaching, so as the materials contained in the water and transfers them to the receiving waters. Plants, added fertilisers, animal wastes and soil all contribute to the materials contained in the water. When the water (rainfall and irrigation water) comes into contact with the surface layer of the soils and plant materials, P dissolution from soils and release from plant materials occur. The longer the contact time, the more P may enter to the water. As water falls vertically to the deep soil layer, a portion of the dissolved P is sorbed by the P poor deep soils, the remaining P goes to the collection drains and is lost from the pasture.

Most P transported from well-managed dairy pasture in Southern Australia appears to be dissolved P (Nelson et al 1996; Nash and Murdoch, 1997; Fleming et al 1997; Nash, 1998; Nash and Halliwell, 2000). The highest concentrations and loads are found in surface runoff (Small, 1985; Fleming, 1997). Small (1985) reported the highest TP of 21.2mg/l in surface runoff from an irrigated and grazed pasture, of which more than 50% was SRP. However, subsurface transportation may occur, especially in sandy soils (Weaver and Reed, 1998).

1.2 CONCEPTS FOR P CONTROL IN AGRICULTURAL DRAINAGE WATER

Two principal management strategies are distinguished in order to control P losses from land to water:

- A. Sources control to minimise P in drainage. Adoption of best management practices (BMP) by optimisation of fertilization (type of fertilizer, timing, rate and method of application), crop rotation, soil cultivation in a manner that maintains the P balance in soils.
- B. Transport control. Using various ecological engineering technologies such as buffer strips and buffer zones, constructed wetlands, wastewater (drainage) land application to intercept and transform P flow from agricultural land to water.

1.2.1 Prevention of P-loadings

It is the volume of drainage water rather than the concentration that determines the P loading to aquatic systems from pastures (Burwell et al, 1975; Haygarth 1995; Nash et al, 1998). Therefore, the best strategy to control P loss from farmlands is to reduce the drainage produced. Unfortunately, it is difficult to decrease drainage greatly in an irrigation-drainage system. The crop productivity may be negatively affected due to the accelerated danger of waterlogging and salinity buildup in the root zone. Normally, when drainage is reduced, so is the salt removed from the aquifer. Therefore, any management innovation that involves a significant reduction of drainage may cause a salt imbalance in the aquifer, resulting in the presence of more saline shallow water tables than observed in the historically drained areas. Water recycling on-farm may provide an option to reduce the total discharge volume. However, appropriate treatment (such as constructed wetlands), water reuse and disposal systems should be in place. In addition, drainage reduction changes the environmental flows in the upland streams that we aim to protect. Therefore, minimising P availability at the source and then decreasing the P concentration in drainage water could be a suitable approach to address the environmental problems caused by drainage water.

1.2.1.1 Optimum fertilisers management

As most of the P present in drainage water is mobilized from the top few centimetres of soil, an obvious and tempting solution to the drainage problem is to match crop demand and soil P concentration. Optimising fertilization including timing, amount and method of application is

not only the interests of agricultural production, but also of environmental protection. The FAO (2002) estimated that 905 thousand metric tones of phosphate fertilizer were applied to land globally in 2001. However, fertilizers management alone is unlikely to reduce the P losses to environmentally safe levels (Nash and Halliwell, 1999). Studies in southern Australia where fertilizers were applied in autumn and not expected to contribute directly to P loss, TP concentrations in runoff were still as high as 3-5 mg/l.

1.2.1.2 Balance P input and output at farm level

Based on input-output calculation, many studies concluded that many farms had surplus P, especially in animal intensive farms such as pastures and poultry farms. For example, using mass balance calculation, Bacon et al (1990) estimated that P accumulation rate in an intensive dairy farm was 19 kg/ha/year. The long-term accumulation of P eventually leads to high soil P level resulting in P export to aquatic systems via runoff or leaching. For the pasture system, mineral fertiliser and food input are the biggest P inputs. Manipulation of dietary P intake by animals may help balance P at farm level. By reducing daily P intake from 82 to 60 g/day, Morse et al (1992) demonstrated a 17% reduction in P excretion from a dairy cow. Another method is to increase the quantity of P in fodder and other animal foods that is available to animals through plant breeding. Through controlling gene, Ertl et al (1998) reduced the Phytate-P and increased the inorganic P in corn. Feeding this lower phytate-P corn grains to poultry resulted in 23% less P content in litter. Furthermore, breeding plants that are productive at lower soil P levels would require less fertilizer and result in an overall reduction in P cycling, consequently, less P losses. As pointed out by Sharpley (1999), although P builds up rapidly by application of P, available soil P decreases very slowly once further application stopped. McCollum (1991) estimated that without further P application, 16-18 years of corn (*Zea Mays L.*) and soybean (*Glycine max*) cultivation would be needed to deplete soil test P in a Portsmouth sandy loam from 100 mg/kg to the agronomic threshold level of 20 mg/kg. So, balancing P input and output at farm level is the long-term approach or goal for P control.

1.2.1.3 Soil Amendment

Soil modification is also an attractive method to decrease P levels in drainage water, especially for soils with high accumulated P levels due to long-term application of fertilizers

and manures. Summers and Pech (1997) carried out a landscape-scale study at the catchment of the Peel inlet and the Harvey Estuary in Western Australia by using bauxite residues as soil amendments. At an application rate of 20 tonne/ha, the P concentration in drainage dropped 30% in the first year of implementation. By increasing the application rate to 60 tonne/ha in sandy soil, the P concentration in drainage from the treated soils was 75% lower than in that from the untreated control. Anderson et al (1995) tested the application of various soil amendments to reduce soluble P in dairy soils. They found that Fe and Al amendments could increase the P retention capacity by 400% comparing to unamended soils. Ca based amendments, such as gypsum could also reduce soluble P in soils by 63%. However, because of the possible biological toxicities of Fe, Al amendments, and the cost of materials, they recommended gypsum as a favourable soil amendment.

1.2.2 Treatment of P Loadings

Ecological engineering methods have been widely used in pollution control, including NPS and PS pollution in rural areas and other remote regions. As Mitsch and Jorgenson (1989) highlighted in their masterpiece about ecological engineering of "Ecological Engineering: An Introduction to Ecotechnology", the most effective way to control pollution is to reduce pollutants at their sources, the so-called "the beginning-of-pipe-principle" strategy. Ecotechnology can be defined as the design, construction, operation and management of landscape and (or) aquatic structures and associated plant and animal communities to benefit humanity and nature. Ecological engineering offers important potential advantages: better performance, less cost and multiple benefits. It can cost less because structures are not as highly engineered and are durable and self-maintaining. Natural energy sources and self-regulating processes reduce operation and maintenance costs. The multiple ancillary benefits are often environmental. Also, ecological engineering can prove more acceptable to the public and legislating agencies.

The removal and control of P before the drainage reaching the targeted waters by buffering strips, buffer zones and constructed wetlands is one of the most ecologically sound solutions. Two widely utilized methods are vegetated filter strips (VFS, a synonyms for buffering

zone/strip) and constructed wetlands (CWS). Although these systems are distinctly different, both are designed to control NPS pollutions as cost-effective ecotechnologies.

1.2.2.1 Vegetated filter stripes (VFS)

VFS are appropriate for use in areas adjacent to surface waters that may receive runoff containing suspended solids such as soil particles and plant segments, and of course, nutrients. Although VFS can remove dissolved P to some extent, they are most effective in the removal of sediment and other suspended solids, consequently, particulate P, which is associated with solid particles, is separated from water and retained by VFS. VFS need the following essential elements to work properly:

- 1) A device such as a level spreader that ensure that the runoff reaches the VFS as a sheet flow;
- 2) A dense vegetative cover of erosion-resistant plant species;
- 3) A gentle slope;
- 4) A length at least as long as the adjacent contributing area.

If the requirements are met, VFS have been shown to remove a high degree of particulate pollutants, including the P associated with particles. For example, using a vegetation stand of fescue, ryegrass and bluegrass, Schwer and Clausen (1989) demonstrated that the VFS removed 78% of the P in effluent from a milking shed. However, the effectiveness of VFS in removing soluble P is not well documented (Schueler, 1987).

1.2.2.2 Constructed wetlands (CWS)

Like VFS, CWS offer an alternative to other systems that are more structural in design for NPS P control. CWS are typically engineered complexes of substrates (hydric soil), macrophytes, animal life, and water, simulating natural wetlands for human use and benefits (Hammer et al, 1989). According to Hammer and others, CWS typically have four principal components that help in pollutants removing:

- 1) Substrates;
- 2) Plants adapted to saturated (hydric) substrates;
- 3) A water column;

- 4) A microbial population, including aerobic and anaerobic bacteria, epiphytes and periphytes.

There are hundreds of scientific papers and modelling has been in progress about the performances of CWS for wastewater treatment for over two decades. At present, CWS are used increasingly worldwide for the treatment of various sorts of wastewater including urban runoff, agricultural drainage and surface runoff, industrial wastewater and landfill leachate. Although the reported P removal rates vary in the literature from negative to very high P removal rate depending on CWS design and application fields, CWS designed for P elimination in agricultural and urban settings generally display acceptable performance: typical TP removal rates ranged from 50-90% (USEPA, 1999).

1.3 P ELIMINATION FROM WASTEWATERS BY CWS

CWS has grown enormously over the past three decades. According to IWA Specialist Group on Use of Macrophytes in Water Pollution Control (2000), there are more than 6,000 CWS for municipal wastewater treatment in Europe and the United Kingdom. Northern America is the home of over 1,000 CWS. The number of CWS is increasing rapidly in Central and Southern America, Africa, Australia and New Zealand, and in Asia as well.

CWS mimic the optimal treatment conditions found in natural wetlands but provide the flexibility of being suitable for construction at almost any location. CWS are becoming a preferable solution for wastewater treatment for many reasons:

- CWS can be less expensive to build than other treatment options;
- Being solar energy driving systems, operation and maintenance expenses are low;
- Being self-design systems (Mitsch and Jorgenson, 1989), they need only periodic rather than continuous monitoring and maintenance;
- They are tolerant to flow and concentration fluctuations, which is one of most important features in NPS pollution;
- They facilitate water reuse and recycling.

Furthermore, from the point of view of an integrated landscape:

- They provide numerous benefits in addition to water quality improvement, such as wildlife habitats and aesthetic enhancement for open spaces;
- They can be built to fit harmoniously into the landscape;
- They are an environmentally sensitive approach that is viewed with favour by the public.

1.3.1 Types of CWS

Based on the hydrological regions, constructed wetlands can be classified as surface flow and subsurface flow CWS. The free surface flow CWS were firstly investigated in the USA in the early seventies by studying the role of natural wetlands as sinks of chemicals, particularly nutrients. Subsurface flow CWS originated from the idea of using vegetated beds for the purification of wastewater in Germany (Seidel 1976; Kickuth 1977). Subsurface

CWS are dominant in European countries at present (Brix 1994; Cooper *et al.* 1996; Vymazal *et al.* 1998).

1.3.1.1 Free surface flow CWS (FSW)

Free water surface CWS have some properties in common with facultative lagoons, and also have some important structural and functional differences. Within free water surface CWS, processes in deeper water are nearly identical to ponds with surface autotrophic zones dominated by planktonic and (or) filamentous algae, or by floating or submergent aquatic macrophytes. However, in shallow zone of emergent plants, CWS and aerobic lagoons can be quite dissimilar.

CWS are autotrophic systems, which means that carbon and nitrogen fixed from the atmosphere are processed simultaneously with the pollutants such as P, heavy metals introduced from wastewater sources. The net effect of these complicated processes is the general decrease in pollutant concentrations from inlet towards outlet of the system. However, due to the internal autotrophic processes of wetlands, outflow pollutant concentrations are seldom zero, and in some cases, some parameters may exceed inflow concentrations, such as organic P.

Free water surface CWS can be further classified according to the life forms of water plants used in the system:

1. Free floating water plant systems, e.g. water hyacinths hyacinth (*Eichhornia crassipes*) pond, duckweeds (*Lemna spp.*) pond;
2. Emergent water plant systems, including forest wetlands;
3. Submergent water plant systems such as river ribbon (*Triglochin procerum*);

Free surface flow CWS with emergent macrophytes This type of CWS look and function like natural wetlands. It normally has a shallow basin with soil or some other medium such as sand to support the roots of vegetation, and a water control structure to maintain a shallow depth of water from a few centimetres up to one meter. The water surface

is above the sediment and litter, but living plants and standing dead parts of plants are above the water surface.

Inflow wastewater containing particulate and dissolved pollutants flows and spreads through a large area of emergent vegetation. Particulates tend to settle, and are trapped, in the wetland sediments due to the created still environment. These trapped insoluble pollutants, including biological oxygen demand (BOD) components, fixed forms of N and P, trace levels of metals and organics, enter biogeochemical element cycles within the water column and sediment. At the same time, a fraction of the dissolved pollutants is adsorbed by soil particles, and taken up by the active microbial and plant population.

The most commonly used emergents in surface flow CWS are persistent plants, such as bulrushes (*Scripus spp.*), spikerush (*Eleocharis spp.*), sedges (*Cyperus spp.* and *Carex spp.*), rushes (*Juncus spp.*), common reed (*Phragmites australis*) and cattails (*Typha spp.*), etc. Not all wetland species are suitable for using in CWS because plants in CWS must be able to tolerate continuously flooding and relatively high and often variable concentrations of pollutants, for example, high salinity. However, the selection of particular species is less important than the establishment of a vigorous stand of vegetation. Any species that will grow can be chosen, however, native species are often preferred because they are adapted to the local climate, soils, and surrounding plant and animal communities, and therefore, are likely to perform well. A useful method suggested by Mistch and Gosselink (2000) is to introduce as many as possible native local species.

Free surface flow CWS with free-floating macrophytes Free floating aquatic plant CWS consist of one or more shallow ponds in which one or more species of floating plants are grown. The shallower depth and the domination by floating macrophytes instead of algae are the major differences between this type of CWS and stabilisation ponds. As a consequence, the effluents from aquatic ponds are normally of higher quality than those from stabilization ponds for equivalent or even shorter hydraulic residence time (HRT).

The principal floating plant species used in CWS are water hyacinth (*Eichhornia crassipes*) and duckweeds (*Lemna spp.*), although others such as mosquito ferns (*Azolla spp.*), and water lettuce (*Pistia stratiotes*) can occur in any surface CWS. Fast growth and high uptake of nutrients directly from the water column are the advantages of such species. The photosynthetic parts of floating plants exit at or just above the water surface, and their roots extend down into the water column. For growth, the areal parts uptake CO_2 from the atmosphere and their under water roots uptake nutrients from the water column. The roots system provides an excellent support medium for bacteria and for filtration/adsorption of suspended solids. As a result of fast growth, the aquatic pond is frequently covered completely by floating macrophytes. Consequently, the ponds tend to be free of algae and nearly anaerobic. However, part of the O_2 produced by photosynthesis is translocated to roots and keep the root zone microorganisms metabolising aerobically. The development of roots is a function of nutrient availability (the characteristics of wastewater) and nutrient demand (growth rate) of plants. So, in practice, harvesting and wastewater pre-treatment are two management methods for aquatic plants ponds.

Free surface flow CWS with submergent macrophytes In natural wetlands, especially the shallower parts of lakes, reservoirs and rivers, provided that the water is clear enough, submergent water plants such as waterweed (*Elodea spp.*), water milfoil (*Myriophyllum spp.*), river ribbons (*Triglochin procerum*) may dominate these habitats. The utilization of submergent plants for wastewater treatment has also been tested by many researchers (Bavor *et al.* 1988). As many submergents are sensitive to anaerobic conditions, they tend to be shaded out by algae, emergents and floating plants, therefore, their potential utilization in CWS is limited. Furthermore, the turbidity of water has to be kept low to ensure enough light penetrates into the water column to support their photosynthesis. Although submergent plants naturally invade some CWS that have deepwater zones, this kind of CWS has no widespread usage.

To mimic natural wetlands, surface flow systems often utilize a combination of free-floating, emergent, and submergent water plants, and normally include free water zones as well.

1.3.1.2 Subsurface flow (SSF) CWS

In SSF CWS, wastewaters flow through the packed medium (either soil or gravel), on which water plants grow. During this passage, the wastewater makes contact with a network of anaerobic, anoxic and aerobic zones. The aerobic zones occur around roots and rhizomes that leak O_2 into the substrate. Wastewater purification processes, i.e. microbiological degradation, plants uptake, chemical precipitation and adsorption, physical filtration, happen simultaneously.

As there is no standing water, subsurface flow CWS are limited to emergent water plants. The two chiefly used species are common reed (*Phragmites australis*) and Cattails (*Typha spp.*), even though other species such as reed canarygrass (*Phalaris arundinacea*), bulrushes (*Scripus spp.*) are also mentioned in the literature. In fact, the most common term of SSF CWS in Europe is reed bed treatment system (RBTS), because a frequently used plant is common reed (*Phragmites australis*). Maintaining the vegetation stand on the SSF CWS bed is considered to benefit the aeration of the medium and their conductivity. The direct uptake of nutrients by macrophytes is not considered as an important nutrient process in this kind of CWS.

As wastewater has to pass the porosity of the medium in the SSF system, this technology is generally limited to low flow rates such as individual family and small communities. According to the ways of introducing wastewater, SSF systems are divided into horizontal-flow systems (HFS) and vertical-flow systems (VFS).

HFS In HFS, wastewater is fed in at the inlet, and flows slowly through the porous medium under the surface of the bed in a more or less horizontal path until reaching the outlet zone, where it is collected and discharged (or recycled).

VFS VFS have a flat bed of gravel topped by a layer of sand, with emergent plants growing. They are fed intermittently. Wastewater is dosed on the bed in a large batch, flooding the surface, and is then drained vertically down through the bed. Finally, the treated wastewater is collected by a drainage network at the bottom and discharged. The bed drains

completely after each dosage, allowing air to refill the bed. Together with the air caused by rapid dosing and the O₂ leaking from macrophytes' roots, the trapped air leads to good oxygenation of the bed and hence the ability to decompose BOD and process N via nitrification.

1.3.2 Applications of CWS

During the early years (pre- 1985) of the development of the technology, virtually all emphasis was on the treatment of domestic and municipal wastewaters. Nowadays, the CWS encompasses a myriad of water quality applications including municipal wastewater, various industrial effluents, small-scale rural wastewater, acid mining drainage, landfill leachate, nonpoint sources of pollution such as urban storm water and agricultural runoff, and livestock and aquacultural wastewaters.

1.3.2.1 Domestic and municipal wastewaters

There are several roles for CWS in the treatment of domestic and municipal wastewaters. The long history of the application of this technology has accumulated a large amount of information and knowledge. In fact, CWS technology is well defined and is widely accepted in this field of application. At present, utilization of CWS is generally applied in two themes for the treatment of domestic and municipal wastewater: for accomplishing secondary treatment and for achieving advanced (tertiary) treatment.

Secondary treatment Using SSF CWS for secondary treatment of municipal wastewater was first practised in Europe, and was introduced to North America and spread over the world in the late eighties. Effluences from pre-treatment facilities such as septic and Imhoff tanks are introduced into SSF wetlands for further processing. Generally, most SSF wetlands are designed to treat small sources of wastewater (less than 500 population equivalent) and many systems are designed for single household. The systems are simple, effective, affordable, aesthetic and educational. Typically, they are effective in removing BOD, suspended solid (SS) and faecal coliform (FC) but less effective in terms of nutrients removal, even though comparable to conventional treatment systems without a special regime for nutrients removal. For example, results from Northern Regional Corrections Center in USA showed that while the annual removal rates for BOD, SS and FC (in terms of concentration) were

90%, 79% and 99%, respectively, TP and TN removal rates were only 41% and 40% respectively.

In sites with stricter discharge standards, i.e. lower nutrient concentrations, combination of VFS and SSF wetlands provides an option. The medium of the beds should be selected on the base of hydraulic conductivity and P-binding capacity. Of course, such multistage systems are more expensive to construct, run and maintain than one unit VFS or SSF systems, but they may still be much cheaper than other alternatives, such as chemical processes and reversed osmosis (RO) technology.

Surface CWS are typically not used for secondary treatment although there were some trials reported (Hiley 1990).

Advanced treatment Both surface and subsurface CWS are used at this stage of municipal wastewater treatment, although subsurface CWS are more popular in Europe and Australia. Normally, CWS receive municipal wastewater of approximately secondary quality or better. CWS are placed at the end of the treatment chain to polish (removal of nutrient) from secondary or tertiary treatment instead of more expensive conventional treatment facilities. A vast quantity of data on the performance of tertiary CWS is available in the literature. A comprehensive database about the performance of such systems is Northern American Data Base (Kadlec and Knight, 1996). In UK, Green and Upton (1995) described the effluent quality for 29 sites for the calendar year 1993. Cooper *et al.* (1996) present survey data about annual average performance of Leek Wootton subsurface CWS. In addition, Vymazal (1998) summarized the performance of HFS constructed reed beds in the Czech Republic. On the basis of these data, it is clear that CWS can achieve higher standards comparable to “higher technologies” in a much cheaper way.

1.3.2.2 Industrial Wastewater

Phytoremediation is a more “modern” expression for the utilization of CWS in processing industrial wastewater, although phytoremediation has a much broader definition, and was originally introduced as a soil-plant system for restoration of polluted terrestrial ecosystems

(Becker, 2000). CWS has been successfully applied to treat various industrial wastewaters, including mining drainages, food processing water, pulp and paper wastewater, and wastewater generated from petrochemical industry, etc.

The treatment targets of industrial wastewaters are more specific than those of domestic wastewaters, which are normally BOD and nutrients. For example, the contaminants of interests in coal mining drainage are typically pH, Mg and Fe. Therefore, the selection of water plants used in CWS for industrial wastewater treatment is more case-specific: the plant species have to be able to tolerate the toxicity of specific contaminants and conditions which are far from ideal, such as strong alkaline or acidic. Ideally, the species have the capacity of "luxury uptake" of the contaminants of concern.

1.3.2.3 Urban Stormwater

Urban stormwater has been identified as one of the major contributors to NPS pollution. Stormwater runoff originates from a wide range of sources: parking lots, roadways, roofs and other impervious surfaces. A wide variety of pollutants, most importantly sediments, nutrients, trace metals, and organic compounds carried by stormwater, find their way to streams and rivers and finally to lakes and oceans. Increasing urbanization has led to large increases in the pollutant loadings to surface waters. In an average year, for a given surface area, urban land has been estimated to contribute 3 times more N and 13 times more P than forest land, and 1.2 times more N and 2.8 times more P than agricultural land (Silverman, 1983). The types and amounts of pollutants in stormwater vary widely with land use, with higher pollutant concentrations associated with more intensive development and greater surface imperviousness (Livingston, 1989). The quality of stormwater also varies widely with the frequency and intensity of rainfall. However, the pollutant concentrations might not be correlated with the volume of flow (Silverman, 1983). Known as the "first flush", the first few centimetres of rainfall carries *ca* 90% of the pollution load to the receiving waters in a storm event (Livingston, 1989).

Closely linked with rainfall events, both quantity and quality of urban stormwater fluctuate seasonally. The variations can be great enough to deny any method of treatment. However,

with careful design, constructed stormwater wetlands can handle this situation quite well. Before entering the CWS, most stormwater need some kind of pre-treatment to reduce sediment loadings, for example, removing large floating rubbishes by rubbish racks, and decreasing the flow velocity as well. In general, a stormwater wetland consists of densely vegetation stands and a deep zone at the outlet. As the water finds its way through the complex vegetation, an array of pollutant removal processes, such as sedimentation, biological uptake and transformation and chemical precipitation take place.

Schueler (1987) investigated the performance of nearly 60 stormwater wetlands in USA, some of them are natural, and estimated the pollutant removal rates as 75%, 25%, 45%, 75% and 50% for SS, TN, TP, lead and Zinc respectively.

1.3.2.4 Agricultural wastewaters

A very important field for application of CWS is the treatment of agricultural wastewaters. Although many studies and large-scale surveys pinpointed that the nutrient loads from agricultural NPS were the leading causes of degradation of many freshwater systems, the remote locations and variations in quality and quantity make it very difficult, if not impossible, to control the pollution by conventional methods. In addition, intensive land treatment such as conservation practices can be costly and impractical.

Animal wastewater To prevent nutrients and organic matter entering surface waters, many confined animal feeding operations face the challenge to keep the manures in land. Recycling manure in land is very important to maintain high crop productivity. However, when organic matter and nutrients find their way into natural water bodies, they promote algal growth and lead to further problems.

To decrease pollution while maintaining high productivity, confined animal farmers need practical ways to either prevent wastewater entering natural waters or treat the wastewater before it leaves the farm. To fit into a farm system, the wastewater management systems should be reliable, affordable and easy to maintain and operate. Using natural chemical, physical and biological mechanisms and relying on the nature's energies, CWS can be fitted

into most animal farms. A literature review by CH2M Hill (an American environmental Company) & Payne (1997) summarized information from 68 different sites using CWS to treat wastewater from confined animal operations. Overall, the wetland systems reduced the concentrations of wastewater constituents such as BOD, SS, TN, ammonia-N and TP.

Crop runoff One of the most successful cases about usage of CWS for NPS pollution control was a project carried out by the USDA (Department of Agriculture) Natural Resources Conservation Service in Maine. Combining a sedimentation base, a grass filter, a wetland, a pond and a wet meadow, the system removed more than 90% of the SS and TP during all monitored storm events (Huggins, 1993). In particular, CWS have proved to be effective in the control of P losses from agricultural land to natural waters. In the Everglades Agricultural Area in Florida, USA, a 1500 ha constructed wetland (the largest CWS in the world) reduced TP concentrations from 113 $\mu\text{g/L}$ to 22 $\mu\text{g/L}$ (Mitsch, 1993).

1.3.3 Prediction of the Performance of CWS for Pollutants Removal

A vast quantity of operational performance data has accrued for CWS over the last three decades. The data, were collected over a wide range of inflow and outflow concentrations, flow rates, mass loadings, HRTs, water depths, vegetation types and other water quality parameters such as pH, temperature. To summarize the data sets into a small number of defining relationships can help CWS designers to harness the treatment systems being operated in a predictable way. Three types of functions that have been applied to CWS data are removal efficiency, regression equations and first-order mass decrease equations.

Before any of these functions can be adapted to CWS evaluation and design, it is very important to introduce the conception of background concentration, or ambient concentrations, which is denoted as C^* in many scientific papers. Wetland systems include diverse autotrophic and heterotrophic components. Most wetlands are more autotrophic than heterotrophic: a net surplus of the primary products, resulting in an internal release of particulate and dissolved organic matter, nutrients into the water column. Eutrophic wetlands are likely to have higher background concentrations than oligotrophic systems because of the higher productivity promoted by the additions of nutrients and organic carbon.

The removal efficiency is normally calculated from the operation data and used to evaluate the performance. Regressive equations are the most convenient choice for representing intersystem data set, and widely used for the predictions of ecosystem behaviours, either in the form of linear or non-linear equations. The first order equations are based on the assumption that most pollutants decline exponentially to the background levels on passage through a wetland. Table 1-1 summarized the typical pollutants removal efficiencies of CWS for the treatment of various wastewaters all over the world.

1.3.3.1 Basic Equations for Describing Performance of CWS

The fundamental descriptors of wetland performance are influent (C_i) and effluent (C_e) concentrations, volumetric flow rate (Q), surface area (A) and water depth (h). Important design parameters are calculated from the followings:

Wetland water volume (V , m^3):

$$V = Ah\varepsilon \quad (1-1)$$

ε , medium porosity.

Hydraulic retention time (HRT, d):

$$HRT = V / Q = Ah\varepsilon / Q \quad (1-2)$$

The concentration decrease efficiency (EFF, %):

$$EFF = 100 \times (C_i - C_e) / C_i \quad (1-3)$$

The mass removal efficiency (MRE, %):

$$MRE = 100 \times [C_i \times Q / A - C_0 \times (Q / A - ET)] / (C_i \times Q / A) \quad (1-4)$$

Where, ET is the evapotranspiration.

The areal removal rate (ARR, $g/m^2/day$):

$$ARR = [C_i \times Q / A - C_0 \times (Q / A - ET)] / A \quad (1-5)$$

The First-order equations:

$$J = k(C - C^*) \quad (1-6)$$

Where J is the mass decrease rate of particular pollutant, and k , a global rate constant.

By assuming no water loss and gain during pass the wetland, i.e. EP is compromised by precipitation, Q keeps constant, the change of concentration along the wetland length is:

$$-Q \frac{dC}{dx} = JA = kA(C - C^*) \quad (1-7)$$

x , distance from inlet.

Giving a specific influent concentration (C_i), and a targeting discharge concentration (C_e), the area of wetland needed can be calculated by integrating equation (1-7),

$$A = -\frac{Q}{k} \ln \left(\frac{C_e - C^*}{C_i - C^*} \right) \quad (1-8)$$

Equation (1-8) can be modified to give a volumetric equation:

$$\frac{C_e - C^*}{C_i - C^*} = \exp(-k_v \cdot HRT) \quad (1-9)$$

Where $k_v = k/\epsilon h$, a volumetric rate constant.

For those constituents that have C^* value close to 0, equation (1-9) reduces to:

$$C_e = C_i \exp(-k_v \cdot HRT) \quad (1-10)$$

1.3.3.2 SS removal rate

CWS are typically efficient in reduction of SS, with a removal rate frequently over 80%.

Surface CWS The value of k in the first-order equations for SS is theoretically the same as the settling velocity of incoming particles if the growth rate of phytoplankton is low. As the settle velocity of particles varies widely from the very small such as phytoplankton to quite high such as sediment, the values of k range from 0.1 m/d to 10 m/d. A simple regression model by Kadlec and Knight (1996) explains the general trend: $C_e = 1.125C_i^{0.58}$, although the coefficient of determination (R^2) is low (0.38). The model covers influent concentration range 1-800 mg/l.

Subsurface CWS The TSS removal rate constant in SSF CWS is generally very high. For example, Sapkota and Bavor (1994) determined a k value of 31.6 m/d in a large-scale pilot SSF wetland. The high k value corresponds high removal rate in a small wetland.

1.3.3.3 BOD removal rate

Both aerobic and anaerobic degradation of BOD can occur in CWS. As a result of the combined processes the BOD declines along the flow path from inlet to outlet down to background level. For surface CWS, summarising operation data from 36 CWS in USA, Kaldec and Knight (1996) gave a k value of 0.1 m/d with $C^* = 5.5$ mg/l. For SSF wetland systems, on the database of Brix (1994), 70 Danish systems averaged values of $k = 0.16$ m/d for a presumed $C^* = 3.0$ mg/l.

1.3.3.4 N removal rate

Wetlands provide an excellent environment for N processing. N occurs in a number of different oxidation states in wastewaters and in CWS, and various biological and physicochemical processes can transform N between these forms. The most important organic N removal mechanism in CWS is the sequential processes of ammonification, nitrification and denitrification through which the organic N is transformed to gas phase of N_2 and N_2O , and goes to the atmosphere. In addition, inorganic N (mainly NH_4-N) is also taken up by plants and other algal population, incorporated into biomass, and released back into system as organic N after decomposition. Other pathways include ammonia volatilisation and adsorption. On average, these mechanisms are of less importance than nitrification-denitrification, although they can be seasonally important. In CWS, certain species of algae such as blue-green algae can fix N_2 from atmosphere. This add complexity to the overall N cycle in CWS.

N processing in CWS can vary widely depending on the nature of incoming wastewater. For example, if organic N dominates the inflow, mineralization can increase ammonia concentration until nitrification, uptake, and adsorption can decrease it. On the other hand, if NH_4-N dominates the inflow, oxidated N may peak before denitrification decrease NO_3-N concentration.

Table 1-1 Performance (Removal %) of CWS for COD/BOD, TN, NH₄-N, NO₃-N, TP, and FC in CWS

Type of Wastewaters	Type of CWS	HLR ($\text{m}^3\text{d}^{-1}\text{m}^{-2}$)	COD	BOD	TN	NH ₄ -N	NO ₃ -N	TP	FC	Reference
Municipal	SSF	0.04-0.12		97	77.0	97.0	ND	44.0	99.9	House, <i>et al.</i> 1999, USA
	SF	0.08-0.14	63.2	68.0		55.1	-100	36.9	99.9	Okurut, <i>et al.</i> 1999, Uganda
	SSF	0.015	91.9	ND	91.0	95.8	ND	87.9	99.1	Kern & Idler, 1999, Germany
	SSF	0.047	81.2	ND	64.6	59.4	73.2	55.3	99.9	Li <i>et al.</i> 1995, China
	SF	0.1			26.3			11.0		Sakadevan & Bavor, 1999,
		0.04 ^s			48.9			41.7		Australia
		0.013			77.0			22.7		
	SF	0.1215	ND	38.0	38.0	9.0	98.0	-27.0	ND	Greenway & Wooley, 1999 Australia
	SF	0.039	ND	11.0	50.0	29.0	70.0	9.0	ND	Greenway & Wooley, 1999 Australia
	SF	0.0013-0.3583	ND	78.6	66.7	21.8	60.0	51.2	98.2	Gearheat <i>et al.</i> 1999, USA Summary of 20 CWS
Industrial										
Meat processing	SSF	0.046	78.0	ND	21.0	0.0	ND	27.0	-	Oostron & Cooper, 1990, New Zealand
Cheese dairy	SSF	0.029	85.9	ND	35.0	66.6	ND	54.8	96.1	Kern & Idler, 1999, Germany
Cheese dairy	SSF	0.022	82.2		45.3	30.4	0	51.9	98.9	Zust & Schonberon, 1994, Switzerland

Table 1-1 Performance (Removal %) of CWS for COD/BOD, TN, NH₄-N, NO₃-N, TP, and FC in CWS (Continued)

Agricultural								
Dairy Farm	SSF	0.21			75.0*	71.0*		11.2* 93.9 Tanner <i>et al.</i> 1995, New Zealand
Dairy Farm	SSF	0.073			48.0*	34.0*		37.0* 76.2 Tanner <i>et al.</i> 1995, New Zealand
Dairy Farm	SF		70*	78*	78*		54*	Cronk 1996, USA
Swine	SF	0.23 ^a	95*	99*	94*		94*	Cronk 1996, USA
Agricultural runoff	SF	0.01		-49	-86	-193	-43	Carleton et al, 2001, USA
		~		~	~		~	
		0.34		46	88	98.8	89.1	

SSF, Subsurface flow constructed wetlands; SF, Surface flow constructed wetlands;

HL, Hydrological loading; TN, total nitrogen; TP, total phosphorus; FC, faecal coliforms.

§, diluted secondary effluent with TP concentration 3.58mg/l;

*, based on mass removal (%), others are based on concentration reduction (%).

^a, as BOD loading, g/m²/day.

Surface CWS Using regression model, Kadlec and Knight (1996) summarized the input-output N concentrations data from Northern America.

Subsurface CWS A regression equation for TN in Denmark is $C_e = 3.1 + 0.52C_i$ with $R^2=0.68$ (Brix, 1994). In Czech Republic, $C_e = 7.68 + 0.42C_i$ with $R^2=0.72$ (Vymazal, 1998).

1.3.3.5 P removal rate

In CWS, P interacts strongly with wetland soils and biota, which provide both short- and long-term storage of this element.

Surface CWS The amount of data and analysis is much greater than for other pollutants probably because of the importance of P to freshwater ecosystems. There exist hundreds of scientific papers, and modelling has been in progress for over three decades (IWA, 2000).

Surface CWS provide sustainable removal of P but at relatively low rates. The regression of input-output data provides one means of description of the general trends in intersystem performance. One of the best fitted regression equations for TP was given by Kadlec and Knight (1996):

$$C_e = 0.195q^{0.53}C_i^{0.91} \quad (1-11)$$

$$R^2 = 0.77.$$

Where q is the hydraulic loading rate (cm/day).

The first-order areal mass balance model is currently the most supportable level of detail for describing the long-term sustainable performance.

Subsurface CWS In subsurface wetlands, the sorption capacity of medium can be maximized and provide significant P removal (Maehlum *et al.* 1995). However, as the sorption sites eventually become saturated, it is necessary to replace the medium and to re-establish the wetland in order to perform continuous P removal. Data about P removal in SSF wetlands are very sparse.

1.4 BIOCHEMICAL PROCESSES FOR P ELIMINATION IN SURFACE FLOW CWS

P presences in agricultural drainage water can be broadly classified into two groups: particulate P and dissolved P. Both particulate P and dissolved P encounter various forms of organic and inorganic P. The relative proportion of each form depends on soil, vegetation, and land use features in the drainage basin. Most studies about water quality and eutrophication focus their interests on TP, which measures all P present in water, and soluble reactive P, which is the dissolved inorganic P. In addition, total filterable P (TFP) is also a subject of many studies (Maher and Woo, 1998).

Particular P in water passing through wetlands can be removed by sedimentation. Significant quantities of P can be detained by this process as the water pass through the system if the incoming wastewater as runoff from cultivated cropland contains high level of suspended solids due to the still conditions they created (Walbridge and Struthers 1993). However, wind and wave, and the movement of benthic animals can stir up the new deposit sediment, and therefore resuspend the settled solids. In addition, the feed activities of some fish, e.g. carp can also re-suspend the soft sediment due to their feeding habits. The net deposit of suspended solid is always the balance between sedimentation and re-suspension. Furthermore, when the sediment is re-suspended, P bonded by sediment may be released back to water through dissolution and desorption depending on the water SRP concentration.

Dissolved P removal from water in wetlands occurs through three P fixation process:

- Coprecipitation;
- Adsorption;
- Biological uptake.

All the three P fixation processes convert soluble inorganic P into particulate forms (including inorganic and organic P) that can then be buried by sedimentation (Kitchens *et al.* 1975; Spangler *et al.* 1977; Waston *et al.* 1989; Walbridge and Struthers 1993).

Simultaneously, these processes are reversible as they are countered by P mobilization:

- Dissolution;
- Desorption;
- Decomposition.

Microbial removal of P from wetland soil or water is rapid and highly efficient, however, following cell death, the P is released again. Similarly, for plants, litter decomposition causes a release of P with a longer cycling period. Burial of litter in peat, however, can provide long-term removal of phosphorus. Harvesting of plant biomass is needed to maximize biotic P removal from the wetland system. The potential for long-term storage of P through adsorption to wetland soil is greater than the maximum rates of P accumulation possible in plant biomass (Walbridge and Struthers 1988; Johnston 1991). Wetland soils can, however, reach a state of P saturation, after which P may be released from the system (Richardson 1985), therefore, zero removal or even export of P from wetlands may be expected. In most cases, P export is seasonal, normally occurring in late summer, early fall, and winter. During these periods, incoming P concentration is generally lower, and also, dead plant tissue and algal cells begin to decompose and release P, and so, P is released into surface water. The net P retention in the wetland system always depends on the balance of P-fixation and P-mobilization. When mobilization exceeds fixation, the system may become a P source and export the accumulated P. On the other hand, when fixation exceeds mobilization, the wetland can remove P from the water flows through it. Figure 1-1 is a brief diagram of the main P pathways in CWS.

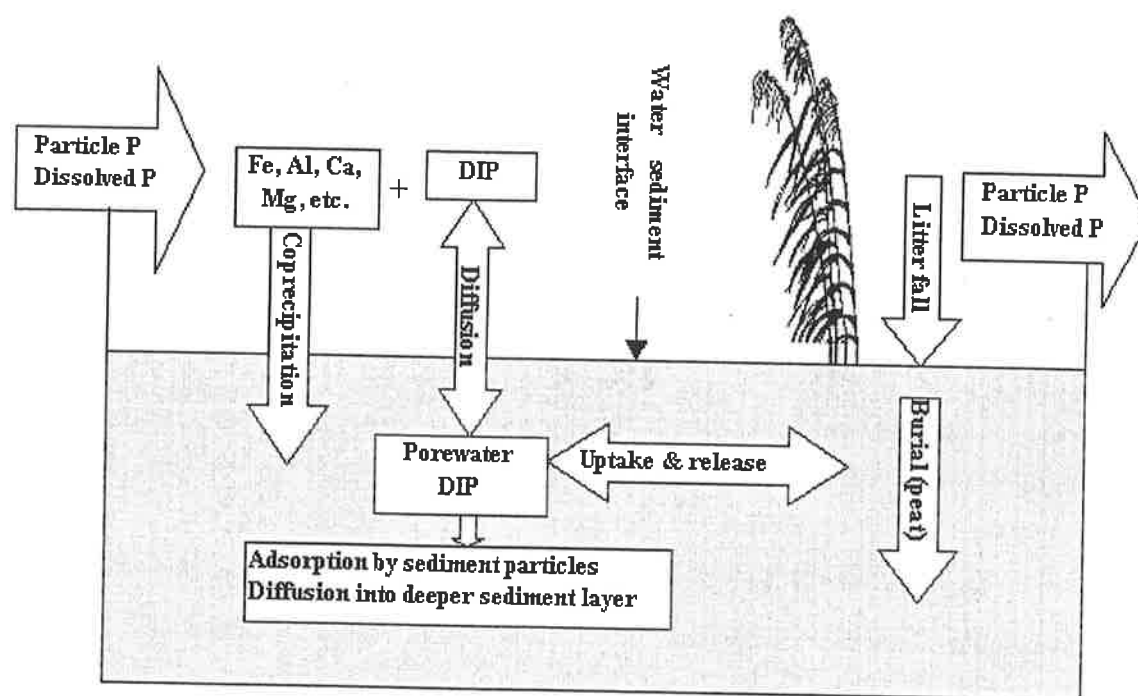


Figure 1-1. Main P pathways in CWS

Both processes of P fixation and mobilization are driven by the specific physical (e.g. temperature), chemical (e.g. mineral concentrations, P forms and levels, pH) and biological (e.g. bacteria, periphyte and macrophyte component and structure) characteristics of the individual wetland. Information and knowledge about the dynamics of these processes and the factors that affect the process rates are useful to manage CWS in a way that optimises their performance.

1.4.1 Water Plants in CWS

Water plants in wetlands are unique in their ability to survive under far from ideal conditions. They must be able to handle flooded conditions as well as dry conditions. In addition, submergent water plants must be able to cope with periodic anaerobic conditions. Wetland plants not only use up nutrients, but also support a diversity of microorganisms that can convert them and other pollutants into less harmful forms. A diverse wetland community will help maintain balance between plants, animals, and insects: providing a self-sustainable system (Mitsch and Jogenson, 1989). The interactions of water plants with other components in wetlands are summarized in Figure 1-2.

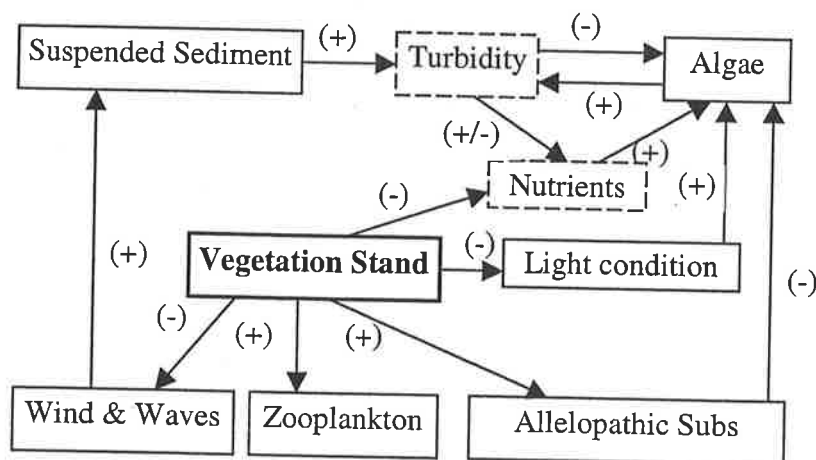


Figure 1-2. The inter-relationships of vegetation stand with other communities and physical parameters: + enforcement, - contraction. Modified from S. Weisner et al 1994.

1.4.1.1 Types of Water Plants

Macroscopic water plants (macrophytes) may be grouped in several ways. A convenient and commonly used one is to distinguish:

- Emergent taxa (such as *Phragmites* and *Typha*);

- Floating-leaved but rooted taxa (*Nuphar* and *Nymphaea*);
- Free-floating taxa with unattached roots (*Lemna*, *Eichhornia* and *Salvinia*);
- Submerged rooted taxa (*Myriophyllum*, *Isoetes*);
- Free floating rootless ferns and mosses (*Azolla*, *Fontinalis*); and, lastly,
- Trees and shrubs (*Salix* spp., *Melaleuca quinquenervia*).

In CWS, water plants play a significant role in P assimilation and storage. The amount of P which can be stored in plant biomass depends on the type of plant species and growth characteristics. Floating plants often occur in the deep zone and uptake DIP directly from the water column. Those plants normally have little supportive structure and lignified tissues, therefore, have rapid turnover rates. The P storage is short-term and much of P is released back into water after decomposition. Emergents have an extensive network of roots and rhizomes. They have more supportive tissues than floating macrophytes and provide ideal anatomical structures for P storage. Although emergents effectively store P, very little of the P in the water column is directly assimilated by them. (e.g. Sculthorpe, 1967; Correll *et al.* 1975; Davis and Valk, 1983). As biomass P is released into water after decomposition, emergents, to some extent, mobilize P that is stored in sediment. However, the active uptake of P 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. Submergents can absorb P from both the water column and the sediments. Like floating plants, they have very rapid turnover rates. In addition, harvesting of submersed plants is difficult comparing with harvesting emergents and floating macrophytes.

1.4.1.2 Utilization of Water Plants in CWS for Nutrients Removal

In theory, all water plants found locally in natural wetlands, river and lake margins, waterways can be used in CWS. Common species used in CWS include emergents, such as bulrush (*Scirpus* spp. and *Schoenoplectus* spp.), Cattails (*Typha* spp.) sedges (*Carex* spp.), free floating water plants such as water hyacinths (*Eichhornia crassipes*), duckweeds (*Lemna* spp.), water lettuce (*Pistia stratiotes*), trees and shrubs, such as willow (*Salix* spp.), paper bark (*Melaleuca quinquenervia*). Submerged water plants are rarely used in CWS as the adverse conditions (e.g. high turbidity, algal blooms) in the early stage of CWS hamper their

propagation. However, relatively few plants can thrive in the high-nutrient, high suspended solid, high BOD waters of CWS. Among these plants are cattails, bulrushes, and reeds. When water is deep enough and emergents' coverage is less, free floating water plants, such as *Azolla*, water hyacinths and duckweeds can dominate CWS.

Table 1-2. Comparison of specific growth rate and nutrient contents of water plants species

Species	SGR	P %	N %	Growth media	Reference
Floating					
<i>Azolla</i>	4	0.68	3.75	Artificial solution (0.18 mgP/l)	Forchhammer,
		0.74	5.04	(6.2 mgP/l)	1999
Water lettuce	10.3	1.02	1.65	Artificial solution	Aoi & Hayashi,
<i>Pistia stratiotes</i>				(6.5 mg P /l)	1996
Water hyacinth	8.0	1.67	2.15	As above	As above
<i>Eichhornia crassipes</i>					
Duckweed	2.1	0.62	2.65	Diluted primary dairy lagoon	Debusk et al.,
<i>L. obscura</i>				wastewater, TP, 6.85 mg/l.	1995
Water hyacinth	36.3	0.55	2.14	As above	As Above
Emergent					
<i>Canna</i>	-	0.384	2.31	Treated sewage	Ayaz & Saygin,
<i>C. flaccida</i>				TP leve 14.4 mg/l	1996
<i>Cyperus</i>	-	0.235	2.61	As above	As above
<i>Paspalum</i>	-	0.294	2.4	As above	As above
<i>P. australis</i>	-	0.12	1.1	Natural Wetland	Ennsbili, 1998
Cattail	9.1	0.19	1.68	Lagoon wastewater*	Debusk et al.,
<i>T. Domingensis</i>	15.0	0.31	1.91	Nutrient enriched wastewater**	1995
Pickrelweed	8.6	0.28	2.02	Lagoon wastewater	As above
<i>P. codata</i>	17.4	0.38	2.32	Nutrient enriched wastewater	
<i>Canna lily</i>	13.2	0.37	1.53	Lagoon wastewater	As above
<i>C. flaccida</i>	39.3	0.44	1.97	Nutrient enriched wastewater	
Bulltogue	1.3	0.32	1.94	Lagoon wastewater	As above
<i>S. lancifolia</i>	14.4	0.41	2.54	Nutrient enriched wastewater	
Arrowhead	2.6	0.44	2.66	Lagoon wastewater	As above
<i>S. Latifolia</i>	8.6	0.61	3.01	Nutrient enriched wastewater	
Reed	21.5	0.17	1.63	Lagoon wastewater	As above
<i>P. australis</i>	16.5	0.19	2.13	Nutrient enriched wastewater	
Bulrush	5.1	0.29	1.63	Lagoon wastewater	As above
<i>S. validus</i>	13.6	0.38	1.84	Nutrient enriched wastewater	
Submergent					
<i>Elodea</i>	0.8	1.93	0.31	Artificial solution (0.18 mgP/l)	Forchhammer,
		4.87	0.96	(6.2 mgP/l)	1999

SGR, shoot growth rate, g/m²/day. For floating water plants, whole plant;

*, TP, 1.7 mg/l; TN, 9.7 mg/l.

**, TP, 29.2 mg/l; TN, 75.7 mg/l.

The utilization of aquatic macrophytes in natural or semi-natural systems for eliminating nutrients from various wastewaters is well documented (Boyd, 1969; Reddy et al, 1982, 1985; Tanner 1996; Aoi and Hayashi 1996). Harvesting the standing crop with its stored nutrients, especially P, is an innovative technique for control of freshwater eutrophication, and the utilization of harvested vegetative biomass can provide economic returns, for examples, biogas, and animal food.

There are at least three approaches for the removal of P by the utilization of aquatic plants. Pond systems with free floating plants such as water hyacinths (*Eichhornia crassipes*), duckweeds (*Lemna sp.*), and pennywort (*Hydrocotyle spp.*) have been investigated since the pioneer works of Boyd (1969) in the late sixties, and are currently in use at a large scale for the treatment of municipal wastewater in Asia (Huub and Siemen, 1998). CWS with emergent plants such as reeds, cattail, and bulrush has become a popular wastewater treatment technology and is increasingly applied (Hammer, 1989; Cooper and Flindlater 1990; Mitsch and Gosselink, 1993; Mitsch *et al.* 1995; Kadlec and Knight, 1996). Finally, the so-called rhizofiltration systems utilize the roots of aquatic or terrestrial plants, e.g. sunflower (Dushenkov *et al.* 1995) to remove heavy metals from polluted soils and waters. In general, constructed wetlands with emergent plants are efficient in trapping particulate phosphorus due to the created favourable conditions for sedimentation of particles; while free floating plant systems are more efficient in eliminating the dissolved forms of phosphorus from the water column. Furthermore, the rooted emergent plants satisfy their nutrient needs from the sediment rather than the from the water column. However, so far, standing crop harvesting has only been carried out in the floating plant systems.

1.4.1.3 Roles of Water Plants on P Removal in CWS

Many studies pinpointed that macrophytes played an important role for P removal in CWS and natural wetlands (Reddy, 1982; Fennessy et al., 1994; Brueske & Barrett, 1994; Brix, 1997; Ennabili, et al 1998; Soto, et al, 1999; Mann & Wetzel, 2000; Liu, et al., 2000). Bix (1997) summarized that water plants presenting in CWS could benefit the P removal by:

- 1) Modifying the physical conditions in the system to encourage settlement of particles;
- 2) Providing surface area for microbial growth in processing P;
- 3) Direct uptake;
- 4) Releasing O₂ from roots increasing P binding ability of sediment;
- 5) Impacting on the sediment hydraulic conductivity (more significant in subsurface CWS).

However, there is still a controversy about the function of macrophytes in wastewater treatment by constructed wetlands. Some researchers have found that an improvement in wastewater treatment occurred in the presence of macrophytes (Rogers et al., 1991; Farahbakhshazad, et al., 1995), while other studies did not detect significant differences between planted and unplanted systems (Tanner et al., 1995). However, comparisons between studies are difficult because they experience different climate conditions, and utilize diverse aquatic plants and water flows. Using a small-scale sub-surface CW, Soto *et al.* (1999) demonstrated that the presence of *Scirps lacustris* improved nutrient removal performance by 30% and 20% for TN and TP, respectively.

However, many other studies concluded that the P incorporated into plant biomass was not an important P removal mechanism in CWS by investigating of the vegetation biomass and analysing plant tissue P concentration (Kadlec, 1996; Tanner et al, 1995). This leads to the belief that sediment is the major P sink in constructed wetlands (CWS) (Axt & Walbridge, 1999; White et al, 2000). Consequently, chemically amended soils and other materials such as industrial wastes were utilized as substrates to enhance the performance of CWS (Anderson, et al., 1995; Brooks, et al, 2000), and the management of vegetation in CWS are not recommended (Kadlec, 1996; USEPA, 1999).

1.4.2 Substrates in CWS

The substrate is important to the overall function of CWS in at least two senses: first of all, the substrate is the primary supporting media for rooted water plants; secondly, the soil plays a significant role in its ability to retain or release certain chemicals, in particular, P. The choice of substrate has to satisfy two criteria: supporting of rooted macrophytes and having

high affinity with the target pollutants. For most CWS for nutrients removal in order to control eutrophication, high adsorption of P is the priority. The soil organic content, texture, P concentration, iron and aluminium concentrations, pH, etc. are factors requiring investigation. Studies in the past several decades led to the conclusion that:

1. In acid sediments, P is retained as Fe- and Al-P, if activities of these cations are high;
2. In alkaline sediment, P retention is regulated by the activities of Ca and Mg cations;
3. P mobilization potentials are high in sediment with slightly acidic to neutral pH.

Reddy *et al.* (1996) derived an empirical relationships between P adsorption maximum and total organic matter, oxalate-extractable Al for stream and wetland sediments:

$$S_{max} = 2.17 \times C_{TOC} + 0.095 \times C_{Fe} + 0.238 \times C_{Al} - 1.2 \quad (1-12)$$

Where, S_{max} is the maximum P adsorption;

C_{TOC} , C_{Fe} , and C_{Al} , are the concentrations of total organic carbon, oxalate-extractable Fe and Al in soils.

However, for CWS designed for nonpoint source nutrients control, the utilization of non-site substrate is limited as CWS is believed to be a cost-effective method. In most circumstances, soils from the site are used as substrates. In the case of converting agricultural lands previously intensively used implemented into CWS, topsoils have to be removed (may be used as constructing materials for banks) or amended to avoid rapid nutrient release once flooded. Ann *et al.* (2000) tested a series of chemical amendments for P immobilization. They found that the order of effectiveness for P fixation was $FeCl_3 > alum > Ca(OH)_2 > calcite > dolomites$. However, as the agricultural soils may also contain high organic matter, high rates of chemical amendments are needed to effectively reduce P levels, as P binding cations (Ca, Fe, and Al) complex with organic matter. In addition, the introduction of chemicals into aquatic systems may cause unexpected ecological consequences.

1.4.2.1 P Forms in Sediments

To determine the role of sediment in P dynamics in the CWS, it is important to distinguish the various P pools in the selected soil. P fractionation, as a method to characterize P binding

to various organic and inorganic sediment components, has been widely used to investigate the internal P loading in shallow lakes (Hietjes and Lijklema, 1988; Sondergaard, et al, 1996; Rydin, 2000). It is believed that some P forms in sediment are sensitive to environmental conditions, thus, under certain circumstances, they may be released to overlying water. For example, the iron associated P is sensitive to low redox potential, when the sediment becomes anoxic due to bacterial respiration or stratification, it has the potential to be mobile (Froelich 1988; Gachter et al 1993). And the Ca bound P is sensitive to low pH value. The most frequently used method in sediment studies is the sequential extraction technique of Hietjes and Lijklema (1980), which was modified from Williams (1971) and Kurmies (1972) or its modifications.

Although it is still an open question which type of P the method actually measures, it is largely accepted by the soil scientific community that the $\text{NH}_4\text{Cl}_\text{P}$ (P extracted by NH_4Cl solution) measures the loosely bound P (P dissolved in pore water, and loosely surface absorbed P), the NaOH_P (P extracted by NaOH solution) relates to the Fe- and Al- P in sediments, the HCl_P (P extracted by HCl solution) indicates the P associated with Ca (mainly apatite), and finally, the difference between TP and extracted P is called residue P, which includes refractory organic P and inert inorganic P. Because this method can't separate Al-P and Fe-P, some researchers add a step between the NH_4Cl and NaOH extractions: the residue from NH_4Cl extraction is extracted by 0.11 M $\text{Na}_2\text{S}_2\text{O}_4/\text{NaHCO}_3$ for one hour (Psenner et al, 1988, Rydin, 2000). The P in the extract is associated with Fe. Until now, there has been a lack of widely accepted methods to qualify the mobile or labile and refractory organic P in sediment, although the difference (NaON-nrP) between digested and non-digested P from NaOH extraction step is considered as organic P with labile character (Penn et al, 1995). Under field conditions, these P pools have different bioavailabilities:

- Loosely adsorbed P represented the labile pool of inorganic P. Although relatively small in most cases, this P pool is very important in rooted water plant growth and in controlling the P concentration of the overlying water column. The labile P pool readily responds to external P loading.
- Fe- and Al- bound P represents the P associated with amorphous oxyhydroxide surfaces and crystalline Fe and Al oxides. P associated with crystalline Fe and Al

oxides are readily desorbed under most conditions, however the P associated with crystalline Fe and Al oxides is desorbed only under extended waterlogged conditions.

- Ca- and Mg- bound P represents the P associated with Ca and Mg minerals. Under most natural conditions, this P pool is essentially unavailable to biological assimilation (Sonzogni et al, 1982).

By combination of P fractionation, release experiment, and P diagenesis, Rydin (2000) concluded that the P pools of loosely sorbed P, Fe-P in Lake Erken surface sediment could be fully mobile, and about 60% of the extracted organic-P (NaON-nrP) was labile. The res-P, Al-P, and Ca-P were permanently bound in sediment.

1.4.2.2 Sediment as P Fixing Media

Sediments in CWS serve as sinks, sources, and transformers of P and other nutrients and contaminants. As such they can have significant impacts on the overall performance regarding to P removal. Laboratory adsorption procedures have been used for many years to qualify and predict P retention capacity of soils and sediments (Olsen and Watanabe, 1957, Logan, 1982; White, 2000). Data (EPC – equilibrium P concentration and S – P adsorbed by soil/sediment) obtained from adsorption experiment have been used to represent P adsorption by standard isotherms such as those of Langmuir and Freundlich (Olsen & Watanabe, 1957; Barrow, 1978; Reddy *et al.* 1995, White, *et al.* 2000). The ability of selected soil to retain P depends on its physico-chemical characteristics. It has been shown that inorganic P added at concentrations considerably greater than those present in the pore water of soil is retained by oxides and hydroxides of Fe and Al, and Calcium carbonate, while at low loading, soil were found to release rather than retain P. In general, in recent created wetlands, P removal can be initially high, but declines as the system “ages” (Kadlec and Bevis, 1985; Mann, 1990), due to saturation of finite adsorption sites (Richardson, 1985; Kadlec and Bevis, 1997).

The following questions are crucial for the management of CWS as P sinks.

- Are sediments sources or sinks for P?
- How much P can be stored in sediment?

- How stable is the stored P and under what conditions will it be released back to water column?
- What is the long-term P assimilatory capacity of wetland sediments?

The questions can be addressed by the following topics:

1. Forms of labile and non-labile pools of P in soils;
2. P sorption capacity of wetland soil.

P sorption by sediment or wetland soil has been described with a Langmuir isotherm (Bache and Williams, 1971):

$$S = [(S_{\max}kC)/(1+kC)] - S_0 \quad (1-13)$$

or by Freundlich equation:

$$S = kC^N - S_0 \quad (1-14)$$

where,

S, P sorbed on solid surface, S_0 , P sorbed under ambient conditions

$S_{\max}$, maximum soil p adsorption capacity

C, P in solution

k, a constant related to bonding energy

N, empirical constant ($N < 1$).

The P adsorption isotherms are used intensively in the literature to determine the direction of P flux. From the Langmuir model, four important factors, which describe the P adsorption characteristics, can be derived:

- Equilibrium P concentration (EPC_0)

EPC_0 is the P in soil pore water in equilibrium with the P sorbed on the solid surface. EPC_0 is referred to the concentration at which adsorption by solid phase equals to desorption. At this point the soil exhibits maximum capacity for porewater P. The EPC_0 value determined by adsorption isotherms have been used to check the direction of P movement between suspended soil particles and the overlying water.

- Buffer intensity: K_d -adsorption coefficient

At low equilibrium P concentrations ($<10\text{mg/l}$), P sorption followed a linear relationship, under both aerobic and anaerobic conditions.

$S = K_d C - S_0$, where,

K_d , buffer intensity for P sorption

C , P concentration in solution

A study by Reddy *et al.* (1995) about the phosphorus dynamics in wetland sediments suggested that the clay soil has higher P buffer intensity, as indicated by the higher K_d value (19.132 kg^{-1} and 44.924 kg^{-1} for sandy and clay soils respectively).

- P Adsorption Maximum ($S_{\max}$)

$S_{\max}$ is a factor determined by the maximal available adsorption sites in sediments or soils. It represents the capacity of sediments to hold P, i.e. the higher $S_{\max}$, more P can be adsorbed by the sediments. However, it should be noted that the $S_{\max}$ determined by laboratory batch experiment assumes that the P is in direct contact with the sediments (a completely mixed system). Under field conditions, however, diffusion of inorganic P from the water column to underlying sediments regulates the amount of P retained in the system. The diffusion is governed by the concentration gradient between P concentrations in porewater and overlying water. Consequently, the $S_{\max}$ is useful only in the context of influent concentration.

- Ambient P concentration (S_0)

The value of S_0 represents the amount of P in the adsorbed phase under ambient condition. It determines the background P levels in a system. The result of $S_0/S_{\max}$ is sometime called P saturation, which is an indicator of available adsorption sites of the sediments or soils.

1.4.2.3 Coprecipitation/ Dissolution and Adsorption/ Desorption

The coprecipitation of P with other free mineral ions, e.g. Fe and Al in acid sediment, Ca, Mg in alkaline environment, is very difficult, if not impossible, to distinct with the adsorption of P onto solid surface. In fact, almost all of the studies reported the two processes as lumped results, which were the sum of adsorption and coprecipitation. Despite

the difficulty to separate and quantify the two processes, P removal rate by mean of adsorption and coprecipitation could be very high. By mending the sediment with bauxite residue (the by-product from the extraction of alumina from bauxite with caustic soda), a sewage treatment pond removed more than 80% of the input P (Summer and Pech, 1997).

In alkaline wetlands, in which both soil and water contains high level of Ca, P precipitates with Ca as calcium phosphate (Novotony and Olem 1994; Walbridge and Struthers 1993). Therefore, co-precipitation is an important P removal pathway. However, the presence of aluminum is the significant predictor of dissolved P sorption and removal from water in most wetland systems (Richardson 1985; Gale *et al.* 1994; Walbridge and Struthers 1993). The capacity for P adsorption by a wetland, however, can be saturated in a few years if it has low amounts of aluminum and iron or calcium (Richardson 1985); or if the incoming water has high level of dissolved inorganic P. Natural wetlands along rivers have a high capacity for P adsorption because as clay is deposited in the floodplain, aluminum (Al) and iron (Fe) in the clay accumulate as well (Gambrell 1994). Thus, floodplains tend to be important sites for P removal from the water column, beyond that removed as sediments are deposited (Walbridge and Struthers 1993).

At high pH, the transformation of Fe/Al- bound P to Ca/Mg- bound P may happen (Ann *et al.* 2000).

1.4.2.4 Sediment amendment as a method to improve P fixation

The precipitation of P as calcium phosphate has been extensively studied by soil scientist to evaluate the fertilization efficiency. Basically, the precipitation of calcium phosphate is preceded by the adsorption of P onto calcite (Cole *et al.* 1953). Similar processes can happen at the interface of sediment/water in the wetland. For example, Reddy *et al.* found (1993) that the long-term P accumulation in the Everglades Marsh was linearly corrected with Ca accumulation giving the evidence of P and calcite interactions.

The accumulative knowledge and increasing evidence of chemical binding of P with cations such as Fe^{3+} , Ca^{2+} and Mg^{2+} , etc. leads to the application of chemical amendments to the

bottom sediment of reservoir, lake and wetland. The presence of high concentrations of functional ions, such as Al, Fe, Ca and Mg oxides in industrial wastes such as steel slag, power station fly ash, suggests that those materials can adsorb P and are potentially valuable for waste reuse for P removal. In fact, the use of industrial waste as soil/sediment amendments is an upsurging technology in recent years. The advantages of chemical amendment are:

- Relative ease of application;
- Wide scope of applicability;
- Reuse of industrial wastes; and,
- Fast and high potential for P fixation.

However, the flocculent hydrous oxides formed could be difficult to settle, and be potentially resuspended by waves and currents in shallow water bodies, such as wetlands and shallow lakes (Sanville et al., 1976). Furthermore, new accumulation of sediment on the top of the amended soil after chemical application may be one of the critical factors in reducing the effectiveness of P entrapment (Cooke, et al., 1986). Lastly, the impacts such as changes in pH on aquatic biota need further investigation.

Many chemical amendments have been tested and practised for P immobilization. Based on the acting ion, they can be broadly classified into four groups: Ca based, Fe based, Al based, and combination of Ca, Mg, Al and Fe. The widely used Ca based additive is calcite (CaCO_3). A common used Fe based amendment is ferric chloride (FeCl_3). Combination based amendments include red mud (Al, Fe, Ca), a by-product from alumina production from bauxite, dolomite ($\text{CaMg}(\text{CO}_3)_2$), power station fly ash (Fe, Al, Ca, Mg) etc. An example of Al based amendment is Alum ($\text{Al}_2(\text{SO}_4)_3$).

The soil science literature shows that the iron/aluminium hydroxide has the capability of binding orthophosphate (Hsu and Rennie, 1962; Lijklema, 1980). P fixation by those materials involves both coprecipitation and adsorption, although it is believed that the later appears to be dominant in short term (Mehadi and Taylor, 1988). The addition of Fe, Al based adsorbents for P removal results in the precipitation of aluminium hydroxy phosphate

($\text{Al}_x[\text{OH}]_y[\text{PO}_4]_z$) and ferric hydroxy phosphate ($\text{Fe}_x[\text{OH}]_y[\text{PO}_4]_z$). However, under anaerobic environment, ferric phosphate compounds dissolve due to the reduction of Fe^{3+} to Fe^{2+} and ortho-phosphate ions are released to the water column – a phenomenon called internal loading, which is responsible for the failure of restoration of eutrophic lakes, by external P reduction. In natural and constructed wetlands, P adsorption and precipitation in sediments is controlled by redox potential, pH value (Reddy, 1995), Fe, Al and Ca minerals concentrations (Khalid *et al.* 1977; Berkheiser *et al.* 1980; Richardson, 1985; Gale *et al.* 1994), total organic carbon (Syers *et al.* 1973), native sediment P level, benthic-bio-film, (Carlton and Wetzel, 1988). A good review of P adsorption to sediments can be found in Reddy *et al.* (1999).

1.4.3 Water Column Processes in CWS

1.4.3.1 Coprecipitation with Ca, Mg in the Water Column

Chemical precipitation of P in the water column can be initiated by pH changes. Temperature fluctuation can also stimulate the reaction. The physiological activities (photosynthesis and respiration) of submerged water plants, periphytes and epiphytes can cause significant pH changes in water column. In sunny summer days, the pH in wetland water can increase to as high as 10. At higher pH, chemical precipitation of P in the water column as calcium (magnesium) phosphate can significantly contribute to P removal where dissolved Ca/Mg is available. However, the importance of coprecipitation of P with Ca/Mg in the water column is still under debate. House (1990) concluded that only 6% of the overall P removal was due to coprecipitation in high Ca^{2+} and moderate alkaline freshwaters, and the others were contributed to biological uptake. Diaz *et al.* (1994) noted that about 75-90% of the precipitated P was solubilized when the pH value decreased to below 8.

The utilization of sediment adsorption and coprecipitation for P removal to restore a eutrophic lake has been practised in Germany (Hupfer *et al.*, 2000). In 1995, the littoral calcareous mud from the highly eutrophic Lake Arendsee was resuspended and distributed over the entire lake surface in the hope of reduce the P level by coprecipitation with calcite. However, no significant changes of the TP concentration in lake water were observed during and after the restoration.

White et al (2000) reported that nearly 60% of the input P was stored in sediment after the restoration of a dried marsh (refilled with agricultural and municipal wastewater).

1.4.3.2 Periphyton Uptake

In the literature, there has been a lot of discussion and controversy about the use of the word “periphyton” (Vymazal, 1995). It has a Russian origin and refers to organisms growing on objects placed in water by man. The term periphyton gradually acquired a broader meaning. Today, periphyton is used by aquatic ecologists to describe communities of microorganisms that are associated with various aquatic substrates, such as sediment and submergent parts of macrophytes. These mats contain a mixed assemblage of microorganisms, including algae, bacteria, and fungi and associated macrophytes, invertebrate grazers and detritus. Periphyton can present in CWS as floating mats attached to macrophytes or as benthic layer at sediment/water interface. Benthic periphyton utilizes P both from sediments and water column (Hansson, 1988). Epiphytic periphyton absorbs P largely from water column and also P released from macrophytes (Riber *et al.* 1983). In general, periphyton mats are very productive. For example, floating mats can produce up to 50% of the vegetative biomass in Everglade sloughs (<http://serc.fiu.edu/periphyton/periphyton.htm>). P content of periphyton was shown in the range of 0.1-4.5 mg/g (DW). High P content is the result of “luxury uptake”, which is commonly observed in P-enriched waters such as CWS (Cotner & Wetzel, 1992). As a result, P removal by periphytes in CWS can be significant in some cases.

Periphyton can assimilate both organic and inorganic P. Through photosynthesis, periphyton can induce significant changes in pH and DO of the water column (Carlton & Wetzel, 1988). These changes in water chemistry are known to mediate the precipitation of CaCO_3 and thus the P coprecipitation. A study from the Everglades in Florida (Scinto & Reddy, 1995) found that less than 20% of the TP in periphyton was present as inorganic Ca- and Mg-P, the remaining P was in organic form. The results shown that both chemical precipitation and biological uptake contributed to P removal by periphyton. In addition, the benthic layer of periphyton influences the P flux between sediment and water column. Large amount of P from sediment can be incorporated into periphytic mat.

1.5 SCOPE AND OBJECTIVE OF THE STUDY

1.5.1 Apprehension of the Problem

One of the major causes of widespread degradation of lakes and streams in Australia is the addition of large quantity of in-organic nutrients, particularly N and P from diffusion sources, such as croplands receiving fertilisers and agricultural wastes, agricultural drainage waters, and from point sources such as municipal and industrial effluent. During the past 20-30 years, most of our efforts to control water pollution have been directed at dramatically reducing of point source discharge to surface waters. While progresses were made in point pollution control, the problems of non-point pollution--with the dominant source of agricultural activities--are largely ignored. Non-point pollution is of sufficient quantity and diverse quality to have serious detrimental effects on regional water resource. For example, the US EPA's Report to the Congress (1986) stated that non-point pollution contributed 76% of the pollutants to lakes. This may be one of the main reasons why the problem of water quality remains, and the degradation of river and lake systems continues.

In the Lower Murray Region, the irrigation drainage waters from reclaimed pasture have been discharged into natural wetlands or river channel at many sites for many years. It's widely recognised that the irrigation drainage water has unacceptable impacts on the river system. Even though the N, P concentrations of irrigation drainage waters are not appreciably high compared with other wastewater, the amount of N, P from the swamp pumped back to the river Murray resulting in a loading of 190 tonnes of N, 50 Tonnes of P, plus bacteria annually. These nutrient loadings are equivalent to 12.2% and 19.6% of total N, and P loading to the river in the Lower Murray, in a dry year, respectively. In wet year, they equal to 1.7%, 2.8% of the total river loading of N, P, respectively. The irrigation drainage waters from the Dairy Swamp have been identified as a major point source of nutrients to the Lower Murray region in South Australia.

Given the characteristics of diffuseness, diversity in quality and variety in quantity, diffuse pollution from agricultural sources can be quite difficult to treat by the conventional methods (by means of cost, operation and maintain). In contrast, the wetland systems provide a natural cost-effective, easy-maintain way to purify this kind of highly variable pollution.

Constructed wetlands have proven to be highly effective for the treatment various wastewaters. They can achieve stringent water quality standards, with BOD removal of 85%, and faecal coliform removal of 99%. Published studies show that they are also effective at removing nutrients such as nitrogen and phosphorous. These systems are being used worldwide to protect groundwater and surface water resources, the simplicity of the design results in low operation and maintenance requirements. The wetland vegetation (ornamental and/or non-flowering) used in these systems give them the appearance of a flower garden. The flowering area of the wetlands provide a natural habitat for birds and other forms of wildlife by attracting worms, bees and other small creatures, thus have an important ancillary function for biodiversity.

Although natural wetland systems have intrinsic abilities to modify and trap a wide range of water-borne pollutants, they should not be used as wastewater water (including irrigation drainage waters) treatment system in most situations. The pollutants should not be intentionally diverted into natural wetlands as very few natural wetlands remain and those that do remain are significant in term of conservation. Moreover, our current understandings of the impacts of wastes on wetlands are far from satisfactory to “wise use” of natural wetlands, and the consequent restoration may take up to several decades. As an alternative, a new category of wetlands--constructed wetlands are beginning to appear on the landscape around the world. The term CWS begins to appear in literature. Today, there are thousands of CWS in the world, which aim to imitate the process of natural wetlands.

1.5.2 Aims and Objectives

With the primary objective of removal phosphorus from irrigation drainage water, the study involves:

- Identify the characteristics of irrigational drainage waters generated from the reclaimed pasture and their environmental concerns;
- To evaluate the P removal efficiency of experimental ponds with different water plants and substrates;
- To identify the native water plants which could be used for the treatment of agricultural drainage water in constructed wetlands;

- To assess the contribution of macrophytes to P removal through direct uptake, modification of water chemistry and impacts on the P adsorption characteristics of substrate;
- To measure P dynamics at the substrate-water interface;
- To monitor pH and dissolved oxygen concentration, and identify their effects on P co-precipitation from water column;
- To assess the impacts of high salinity on the performance of constructed wetlands.
- To contribute to the optimal design and operation of CWS for the treatment of agricultural drainage water.

To achieve the above goals, both growth chamber trials and pilot-scale field study will be conducted to address the following topics:

- The relationship between P removal efficiency and the hydraulic loading rate or detention time;
- Temporal and spatial distributions of P in the experimental ponds;
- The symbiotic relationship for exists in the treatment of wastewater and the roles that plants, substrate, microorganisms have on the processes.

Chapter Two

Methods and Materials

2.1 DESCRIPTION OF THE STUDY SITE

Baseby farm, a flood irrigated pasture is located between Mannum and Murray Bridge in the Lower River Murray (LRM), South Australia (Figure 2-1). The 85 ha reclaimed swamp supports about 250 cattle and produces annually around 1.25 ML milk. Because of the dry climate of South Australia, the pasture needs frequent flood irrigation with water from the nearby River Murray. The overflow and drainage water is collected in a network of irrigation channels (Figure 2-2) and eventually pumped back to the adjacent floodplain wetland-Reedy Creek Lagoon. There are now 23 reclaimed swamps, comprising approximately 4,850 hectares, developed as flood irrigated pasture along the lower River Murray. Approximately 120 farms and 140 families on farm settles within the area (Figure 2-1).

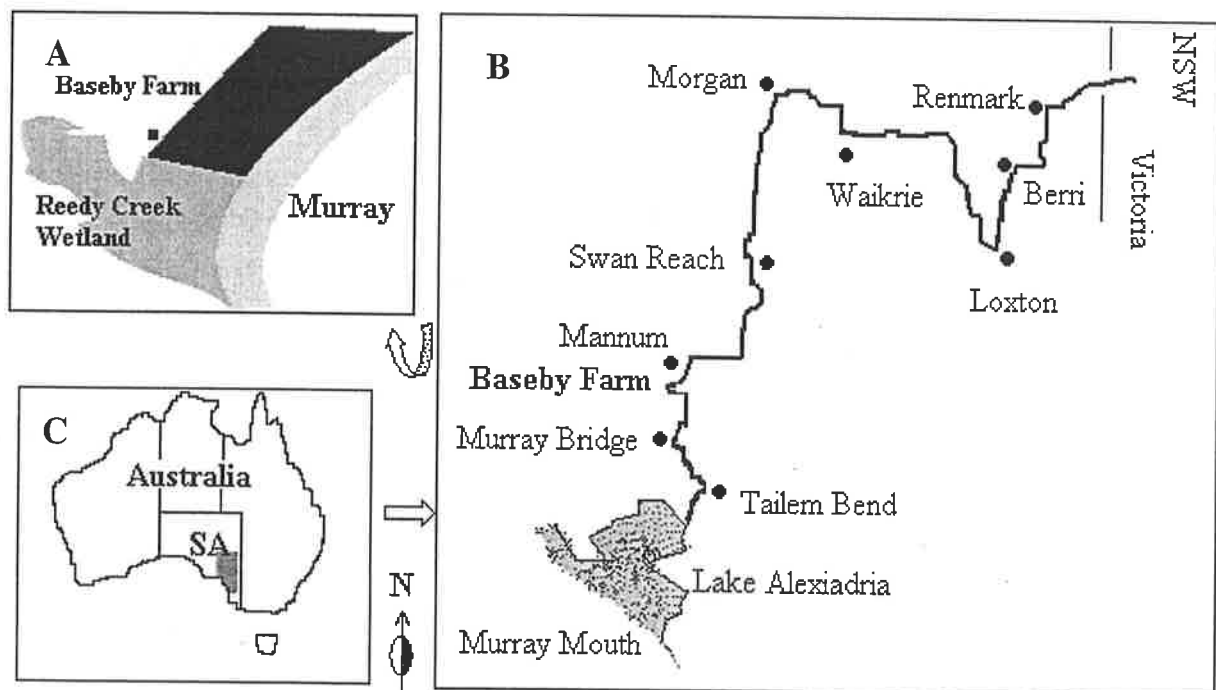


Figure 2-1. Maps of Study site showing: A. The context of Baseby Farm, drainage is currently pumped to the adjacent Reedy Creek Wetland, which is connected to the River Murray; B. Lower River Murray and the main towns; C. Location of Southern Australia, the Lower River Murray catchment is highlighted.

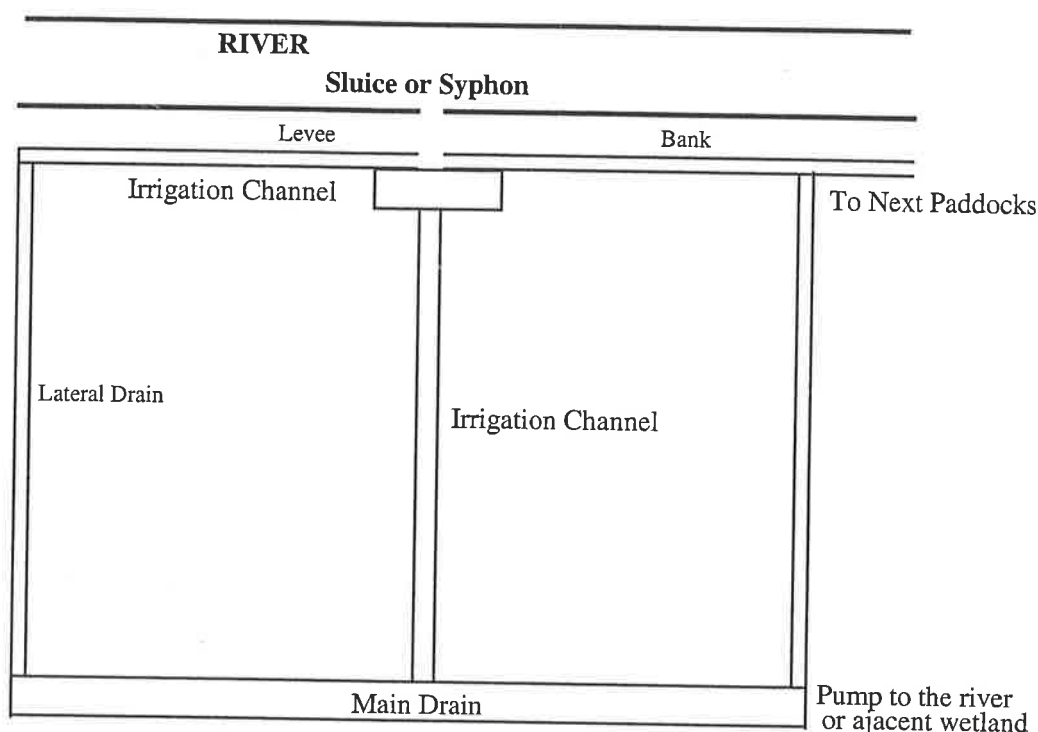


Figure 2-2, Diagram of drainage networks in the reclaimed pasture in South Australia.

2.1.1 Brief History of the Lower Murray Reclaimed Swamps

The credit for the establishment of the first irrigation scheme in South Australia belongs to the famous explorer Edward John Eyre who, in October 1841, in his capacity of resident magistrate and protector of Aborigines, founded the settlement of Moorundie, approximately 5km downstream of Blanchetown. Eyre was able to irrigate an area of river flat on the western bank. Fenced paddocks were laid out to grow lucerne, maize, wheat vegetables and orchards. The purpose of the scheme was to grow food for 43 Europeans and Aborigines. After Eyre left Moorundie in November 1844. Irrigation continued under the supervision of his friend Mr E.P. Scott until June 1856 when the settlement was abandoned. Following the abandonment of the Moorundie settlement, no further apparent effort was made to reclaim and irrigate the lower river flats until 1881. The work was carried out by then governor of South Australia, Sir W. D. Jervois. He reclaimed approximately 1340ha of swampland north of Wellington by the construction of a levee bank to protect the floodplain from flooding. This was followed in 1886 by Mr A. McFarlane, who reclaimed approximately 280 ha on the opposite side of the river, still known as McFarlanes swamp (E&WS, 1986). This initial work was simply a rough, low levee bank to keep out river floods for irregular periods to enable the temporary grazing of livestock, mainly sheep. Pioneering works on permanent

reclamation was undertaken by H. W. Morphett and Co. between 1903 and 1908 at Woods Point Estate. A substantial levee was constructed, drainage channels installed and a drainage pump operated to lower the watertable. The soil proved to be very fertile and was used for growing lucerne, onions, potatoes and pasture. Although the surveyor general at the time had realised the potential value of the swamplands and had recommended to the Government as early as 1887 that some land be withheld for the purposes of reclamation the Government was apparently deterred by the likely costs of such projects until 1904. The early results of reclamation impressed the government so much that they included in 1904 in their land development policy the reclamation and subdivision of the Lower Murray swamps (Carroll and Newbery, 1980; LMIAG, 1993). In 1904-5 the surveyor general was authorised to proceed with the construction of embankments at Mobilong and Burdett (The base of the embankment at Mobilong had been constructed by unemployed persons during 1886.) The area reclaimed in these swamps was 656 acres (266ha), which was let at \$2 per acre per year rental for root crops, lucerne and other grasses. Following a recommendation by the Surveyor general to the Government Long Flat and Monteith were purchased and reclaimed between 1905 and 1909. Other swamps at Mypolonga, Pompoota and Wall Flat were then purchased and work commenced at Mypolonga in April 1909. Construction at Mypolonga was followed by Wall Flat and Pompoota, the latter being completed after World War 1. Pompoota was developed along with Wellington, Cowirra, Neeta, Jervois, Baseby and Swanport as Soldiers Settlement Schemes. By 1929 most of the swamps that were considered suitable had been reclaimed (Carroll and Newbery, 1980; Taylor and Poole, 1931; E&WS, 1986). Reclamation was achieved by constructing levee banks as close as possible to the edge of the river channel, and pumping out the impounded water. Drainage channels were dug and pumps used to maintain the water-table at a sufficiently low level. The banks were later raised to the height of the 1931 flood level. The most significant event which did much to improve the irrigability of the Lower Murray Reclaimed Irrigation Areas was the construction of the barrages at the Murray mouth. After strong representation from land-holders, including from the swamps, the E&WS, acting on behalf of the River Murray Commission, constructed the five barrages at the Murray mouth, commencing in 1935 and finalised in 1940. The purpose of the barrages was to prevent seawater entering the lakes and river, to maintain fresh water as far as Wellington and to keep the river level sufficient to

allow flood irrigation of the reclaimed swamp pastures (Taylor and Poole, 1931; Carroll and Newbery, 1980). [The Above Information was cited from "The History of Reclamation of the Lower Murray Reclaimed Irrigation Area (<http://www.LM.net.au>).]

2.1.2 P Sources in MDB

A study conducted by Murray-Darling Basin Commission (MDBC) indicated that diffuse P was the dominant source for MDB. However, in the LRM Region, the majority P comes from the drainage water (point source) from flat dairy pastures adjacent to the river Murray. The drainage water has been disposed of into natural wetlands and the main channel of the River without any treatment for many years. It is estimated that a total of 75 tonnes per year of P is emitted to the River in the LRM Region, of which 67%, 50 tonne is originated from the drainage water (Environment Australia, 2000).

Water, soil and macrophyte samples used in this study were all taken from the main exit drainage channel, the adjacent Reedy Creek Wetland and the River Murray.

2.2 EXPERIMENTAL PONDS

To test the capability of CWS to remove P from drainage, a pilot-scale constructed wetland, which including three ponds (surface area: 5 m²) in series was built near the exit pump station at the Baseby farm in 1999 (Figure 2-3). A 2,000-litter tank was used to store drainage pumped from the main exit drain, from which drainage flows continuously to a pond that was planted with emergent water plant (pond 1). A valve installed at the tank bottom was used to control manually the flow rate. After the first year of operation, it was found that the topsoil from site released large amounts of P once inundated with drainage. Two additional ponds were constructed beside the first system, and soils from the nearby hills were used as substrate. To prevent the interaction with ground water, all ponds were lined with black plastic sheet (5mm thick).

2.2.1 Ponds with Soil from Site (P rich) as Substrate

2.2.1.1 Pond One: Planted with Emergent Water Plants

This is the pond built on the head of the 3-pond chain. Topsoil from excavation was re-filled and packed to 30 cm in the pond. As a result, the pond has a water storage of about 3 m³ with a water depth of 30 cm. Three locally found emergent water plant species: common reed (*Phragmites australis*), bulrushes (*Juncus spp*), and cattail (*Typha spp*) were planted in the pond before filled with drainage. Pictures of the utilized plants can be found in appendix C. Rhizome cuttings with at least 30 cm shoot were transplanted in the pond with 10 × 20 cm demission. The hydraulic residence time (HRT) in pond 1 was designed to be 5.5 days.

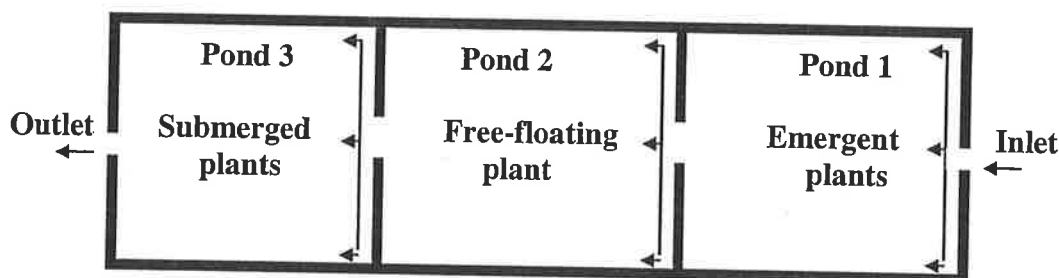


Figure 2-3. Layout of the multistage constructed wetland system (experimental ponds)

Notes:

1. The whole system was lined by plastic sheet to prevent any seepage.
2. Nutrients HRT and loading rate was controlled by the inlet water volume.
3. The average water depth in pond 1 was 30 cm, while in pond 2 and pond 3 were 50 cm and 40 cm respectively.
4. Pond 1 had a layer of soil ca. 30cm, pond 2 had no soil, and pond 3 had 20cm deep soil.
5. All plant materials were collected from the adjacent wetlands and waterways.
6. The initial cover rate of plants in pond 2, 3 was about 10%.

2.2.1.2 Pond Two: with Free Floating Water Plants and No Substrates

The second pond in the chain was free of substrate. At first, *Azolla* and duckweeds (*Lamna spp.*) from Reedy Creek were introduced into the pond in September. After one week, the floating plants died out. Re-introduction of duckweeds and azolla was done in October, again all introduced plants died out. In September 2000, an alternative for floating plants – planted floats was stocked into the pond after growth chamber trial.

Planted floats

The planted floats were designed to replace the free-floating water plants in the pond. In their natural habitats, the procumbent water plants (runners) grow on the edges of water bodies, or any dunes rising out of the water surface, and creep onto the surrounding water surface. As they creep along, roots generate at the nodes and penetrate

into the water. Nutrients are absorbed from the water to satisfy their growth. In the study, floats made from polyethylene-foam were used to initiate the plant growth.

Four species of creeping-stem water plant, water primrose (*Ludwigia peploides*), parrot feather (*Myriophyllum aquaticum*), water couch (*Paspalum paspalodes*), waterbuttons (*Cotula coronopifolia*), were collected from the study site. On the day of collection, the plant materials were cut into 2-5 cm long pieces. Each piece had at least one node. After measuring the initial fresh weights, the plant materials were then planted in a float (10cm×25cm×6cm). A 5-cm layer of washed sand was placed in the bottom of the float. The bottom of the float has ten rows of holes (diameter, 0.5cm and 4 holes per row), through which the roots of plants could elongate into the water. To protect sand drip, the holes were filled with cotton wool. A sand layer of 0.5 cm covered evenly the plant materials. Ten floats were then placed in pond.

2.2.1.3 Pond Three: with Submergent Water Plant

This is the last pond in the chain. The configuration was the same as pond 1. Rhizomes of water ribbons (*Triglochin procerum*) with about 5 cm shoot were transplanted in the pond after filled with effluence from the floating pond for a week.

2.2.2 Ponds with Soils from nearby Hill (P poor) as Substrate

The results from the first year of operation of 3-pond system indicated that the substrates used in the system released large amount of P after flooding. This led to the build of two additional ponds utilizing P poor soil as substrate in September 2000. The two ponds, with surface area of 10 m² each, were filled and packed with soils from the nearby hill to 30 cm, resulting in a water depth of 30 cm. One pond was planted with macrophytes (pond 4) in the same way as in pond 1. The other (pond 5) was left as macrophytes free. The design HRT was 5.5 days.

2.3 WATER QUALITY ANALYSIS

2.3.1 *In situ* Water Quality Monitoring

Water samples from the River Murray, Reedy Creek Wetland, drainage exit drain, and each pond were taken fortnightly in growth seasons (September to May), and monthly in winter (May to September). In the trial of planted float (October 2000 – December 2000), weekly sampling was implemented. At the time of sampling, a multiparameter data logger (YIS 2800) was used to record the temperature, pH, redox, dissolved oxygen (DO), salinity and turbidity.

2.3.2 Laboratory Analysis

Water samples taken from field were carried in an icebox to the laboratory at Waite Campus, Adelaide University for further analysis. Within 48 hours of collection, samples were processed for analysis of total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), nitrate and nitrite nitrogen, and chlorophyll a according to the procedures specified in Appendix A (AHPA, 1992).

2.4 WATER PLANTS GROWTH MONITORING

2.4.1 Field Phenometric Measurement

As common reed was the dominant specie in pond 1, and the growth of other species was obviously depressed, reed was the only one continuously monitored. A non-destructive phenometric technique was adopted for estimating net aboveground biomass. Basically, the method involves following individual tagged plants for changes in biomass, which are estimated using regressive phenometric relationships. Shoots biomass are then summed to determine the total aboveground biomass.

For each tagged shoot, parameters of shoot height (*hght*, m), shoot diameter at base (*dm@b*, cm), number of leaves per shoot (*#lvs*), number of nodes (*#nds*), and number of axillary shoots (*#asht*) were measured monthly. In the same time, ten randomly selected shoot were harvested. After measurement of the above mentioned parameters, the shoots were dried in 70 °C for 48 hours, and the dry weights were recorded using an electronic balance with 4 digits.

2.4.2 Step-wise Multiple Regressive Methods

The dry weight and measured phenometric parameters were then fitted into the following multiple linear equation:

$$B = a \times hght + b \times dm + c \times \#lvs + d \times \#nds + e \times \#asht + f \quad (2-1)$$

Where, B is the shoot biomass (dry matter, g), and a, b, c, d, e, f, are regressive constants.

The number of input of parameters was reduced one by one until the r^2 (coefficient of determination, calculated by software) was optimised. The final regressive equation was used to calculate the growth rate. The areal biomass was calculated using Equation 2-2.

$$B_{areal} = \#sht \times B_{avg} \quad (2-2)$$

Where, B_{areal} is the areal biomass (DW, g/m²);

$\#sht$ is the number of shoot per square meter (1/m²);

B_{avg} is the average biomass of ten tagged shoots (g /shoot).

2.4.3 Shoot P Content Analysis

Shoot P concentration was measured to establish the total amount of P incorporated into biomass, which accounted for the harvestable P. Detail procedures for tissue P analysis was explained in Appendix A. Biomass P was calculated by:

$$P_{bio} = B_{areal} \times C \quad (2-3)$$

Where, P_{bio} is the areal biomass P (g/m²)

C is the shoot P concentration.

2.5 SEDIMENT P DYNAMICS

2.5.1 P Fractionation

P fractionation was carried out according to Figure 2-4. The scheme was adopted from the method reported by Penn et al. (1995) and Rydin (2000). The P concentrations in all extractants were analysed photospectrometrically in the same way as water analysis. Detailed procedures can be found in Appendix B.

2.5.2 P Adsorption/Release

P adsorption/release experiment was carried out according the standard method supposed by Nair et al. (1984). Detail procedure was listed in Appendix B.

2.5.2.1 Langmuir Equation

In the literature, both Langmuir and Freundlich equations are use to describe the relationship between equilibrium P concentrations and P adsorbed, e.g. Olsen and Watanabe (1957); Barrow (1978); Nair (1984). However, the results from our study showed that the Langmuir model fitted better with the data than the Freundlich model, consequently, Langmuir model was preferred. Data obtained from adsorption /release experiment were fitted into Langmuir Equation to find the P adsorption isotherm:

$$S = S_{\max} \times K \times EPC / (1 + K \times EPC) - S_0 \quad (2-4)$$

Where:

S_0 , P present in adsorbed form under ambient conditions, (mg/kg);

$S_{\max}$, Maximum P adsorption (mg/kg);

K , a constant relating to P bonding energy;

EPC , equilibrium P concentration in solution (mg/l).

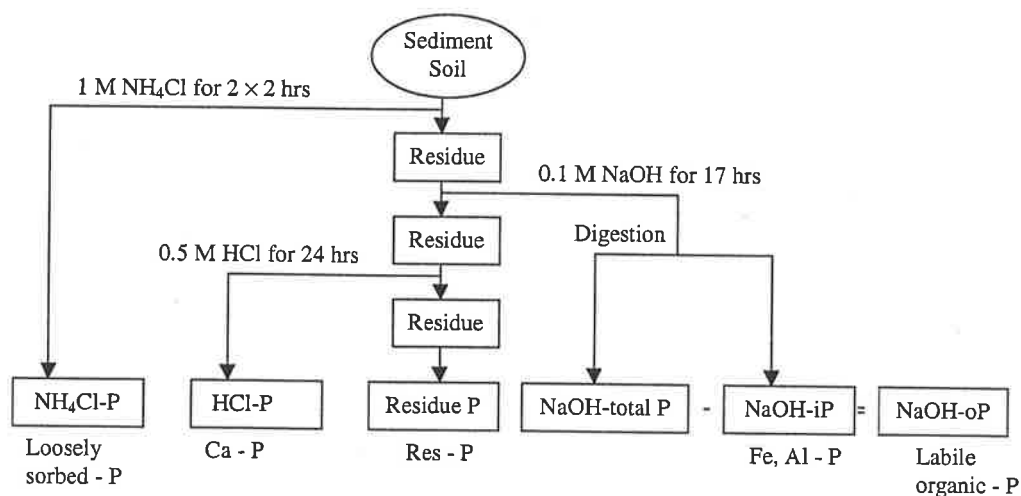


Figure 2-4, P fractionation theme to differential sediment/soil P pools

Non-flux solution P concentration (EPC_0)

EPC_0 can be calculated by assuming $S = 0$.

$$EPC_0 = S_0 / K(S_{\max} - S_0) \quad (2-5)$$

From the fitted Langmuir equation,

2.5.2.2 *P* adsorption index (*PSI*)

The adsorption data at 80 mg/L was used to calculate the *PSI* according to Equation 2-6:

$$PSI = S / \log(EPC) \quad (2-6)$$

Where,

PSI, sediment P adsorption index;

S, *P* sorbed by sediment, g/kg; and *EPC* equilibrium P concentration in solution (mg/l).

2.5.3 Sediment-Drainage Equilibrium Systems

To investigate the impacts of pH on the characteristics of sediment for P retention, laboratory equilibrium experiments were carried out using sediments from natural Reedy Creek wetland (System I), pond 1 (System II) and pond 4 (System III). Filtered drainage water (500ml) was added to glasses containing 10g (dry weight equivalent) fresh sediments (with plant roots and large solid particles removed). Equilibrium was achieved by blowing air through a glass tube (diameter 0.1 cm), which was fixed at the bottom of the glass beaker. Microbial activities were prohibited by adding 5 ml of formaldehyde solution.

At the beginning of the experiment, HCl solution (1M) was added to the beakers to bring the pH down to 3.5. After mixing for 24 hours, the final pH was measured. 10 ml of the solution was removed from the beakers. Following filtration through 0.25µm membrane, the solution was analysed for SRP by the method mentioned above and Ca, Mg and Fe using Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) technique. The procedures were repeated 16 times. Each time, the solution pH increased by 0.5 by adding HCl and NaOH solutions (0.1M). Thus, 16 initial pH levels were tested: 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, and 10.5.

Each system had two replicates, and the average value was used for comparisons.

2.6 COPRECIPITATION: LABORATORY BATCH EXPERIMENT

The investigation involved the sequent measurement of SRP that disappeared from the liquid phase, which was considered as the result of co-precipitation reaction. 4 ml of KH₂PO₄ solution (50 µg/ml) was added as inorganic phosphorus (0.2 mg P) into a 500 ml beaker

which contains 200 ml of filtered water (microbial activities were excluded by adding 1 ml of formaldehyde solution). The solution was mixed entirely by blowing air through a tube which was fixed at the bottom of the beaker. After 24 hours, a portion of solution (10 ml) was removed from the beaker for SRP analysis. Filter water was added to make up the total volume of 200 ml. The procedure was repeated 7 times till the total added P reached 2 mg (from the second step on, 5 ml of KH_2PO_4 solution, 0.25 mg P was added).

Four treatments were implemented in the batch experiment to evidence the coprecipitation: 100ml filtered drainage + 5g washed fine sands (System I), 100ml filtered drainage + 2g washed fine sands (System II), 100ml filtered drainage only (System III), and 100ml filtered natural wetland water (System IV). A blank control was running simultaneously by using double RO water, which contains little Ca and Mg ions. The drainage was taken from pond 3, and the pH was 8.7. The pH in wetland water was 8.6. Both pH values were high enough for co-precipitation. Each treatment was duplicated, and the calculation was based on the averages.

P precipitated was calculation according to equation (2-7):

$$P_{re} = 200 \times (C_i - C_f) - P_{ads} \quad (2-7)$$

Where

C_i and C_f was the SRP concentration at the start and end of each step.

P_{ads} was the P loss due to adsorb onto the surface of beaker, and calculated from the measurements of blank control using Equ.2-7.

2.7 DATA ANALYSIS

2.7.1 Regression Analysis

Regression analysis is a mathematical tool that quantifies the relationship between a dependent variable and one (simple) or more (multiple) independent variables. The parameters for a model is estimated by optimising the value for an objective function, (for example, by the method of least squares), and then testing the resulting predictions for statistical significance against an appropriate null hypothesis model.

In the study, both linear and nonlinear regressions were performed in the data analysis.

2.7.2 Analysis of Variance (ANOVA)

ANOVA is a statistical tool based on F ratios that measures whether a factor contributes significantly to the variance of a response. Also determines the amount of variance that is due to pure error. ANOVA tests the null hypothesis that all the population means are equal:

$$H_0: \mu_1 = \mu_2 = \dots = \mu_a$$

by comparing two estimates of variance (δ^2). (δ^2 is the variance within each of the "a" treatment populations.) One estimate (called the Mean Square Error or "MSE" for short) is based on the variances within the samples. The MSE is an estimate of δ^2 whether or not the null hypothesis is true. The second estimate (Mean Square Between or MSB) is based on the variance of the sample means. The MSB is only an estimate of δ^2 if the null hypothesis is true. If the null hypothesis is false then MSB estimates something larger than δ^2 . The logic by which analysis of variance tests the null hypothesis is as follows: If the null hypothesis is true, then MSE and MSB should be about the same since they are both estimates of the same quantity (δ^2); however, if the null hypothesis is false then MSB can be expected to be larger than MSE since MSB is estimating a quantity larger than δ^2 .

Tukey's test is used for determining statistically significant differences among means, based on the range distribution. In the present study, if the ANOVA reveals that the means are significant different, Tukey's test is performed to determine which means are significantly different from the overall mean.

2.7.3 Software Used

Microsoft Excel 2000 was used to handle (including transform) all the original data. ANOVA was performed using STATGRAPHICS Plus 5.0 (Manugistics, Inc. <http://www.stagraphics.com/>). Regressive fitting for both linear (simple and multiple) and non-linear analysis was performed using Kyplot developed by Toshiba (1999).

Chapter Three Results

3.1 DRAINAGE WATER CHARACTERISTICS

3.1.1 General Physical, Chemical and Biological Characteristics

Table 3-1 shows the comparisons of the mean, median, standard error (S.E.), standard deviation (S.D.) and the range (maximum and minimum) of the measured water quality parameters (nutrients, chlorophyll-a concentrations, pH, temperature, salinity, turbidity and dissolved oxygen - DO) for the Baseby farm drainage water, Reedy Creek Wetland, and the adjacent River Murray. To compare the variances of the main water quality parameters, i.e. nutrients, pH, chlorophyll a, salinity, and turbidity among the three waters, analysis of variance (ANOVA test), a statistical tool based on F ratios that measures whether a factor contributes significantly to the variance of a response, was carried out. If significant difference exists among the three waters, Tukey's analysis, a test to determine the means that are significantly different after an analysis of variance of the differences in the group means, was performed. The results of ANOVA and Tukey's Test (post-test) are presented in Table 3-2. In general, for all of the measured parameters, the differences between river water and wetland water weren't significant. However, the drainage water displayed significant differences from other waters for most of the parameters (Table 3-2).

Drainage waters contained significantly higher levels of nutrients and salinity (Table 3-1, 3-2, Figure 3-1, 3-2). Mean total phosphorus (TP) concentrations in drainage were significantly higher than in wetland water and river water ($P < 0.001$). While the mean in the wetland was higher than in the River but the difference wasn't significant ($P > 0.05$) (Table 3-2, Figure 3-1A). The difference between soluble P, especially soluble reactive phosphorus (SRP) was more obvious (Table 3-2, Figure 3-1B,C). In addition, the dissolved organic phosphorus (DOP) was significantly higher in drainage than in river water, but the difference wasn't significant between drainage and wetland. For nitrogen, the ammonia-N shows the same pattern as P, although the mean difference was smaller (Table 3-1, 3-2, Figure 3-1E). For nitrate-N, the difference between the three waters was less significant statistically than that of ammonia-N (Table 3-2, Figure 3-1F).

The drainage water contained significantly higher levels of salinity than the river and wetland waters (Table 3-1, Figure 3-2C). The mean difference was 3.950 between drainage and wetland and 4.115 between drainage and river.

The pH values were lower in drainage water in most sampling events (M.D = -0.312 and -0.106 for wetland and river water, respectively), and the one-way ANOVA found there were significant differences among the three waters. However, the Tukey's test showed that the difference between drainage and river water wasn't significant (Table 3-2). By contrast, DO concentrations in drainage were higher in most cases than in wetland and river water, but the difference was not statistically significant (one way ANOVA, $P = 0.7654 \gg 0.05$) (Table 3-2). The mean concentrations of chlorophyll-a were significantly different among the three waters ($P = 0.0342$, Table 3-2) at 95% confidence level, and the Tukey's multiple comparison test showed that the difference came from drainage and river water, and drainage and wetland water (Figure 3-2D). The turbidity was significantly lower in drainage than in river ($P < 0.05$) and even lower than in wetland ($P < 0.001$) (Table 3-2, Figure 3-2B).

3.1.2 Seasonal Patterns

In general, all measured parameters showed higher variation in drainage than in river and wetland water except turbidity, which was more constant in drainage (Table 3-1). In Figure 3-3, the seasonal changes of P (TP, TDP, SRP, and PP) over time in the waters are noticeable. The general trend of P in river and wetland was that P concentrations were lower in winter than in summer, and the highest concentrations occurred in late September. For example, the highest TP concentration of 2.48 mg/l in Reedy Creek Wetland monitored during the study period occurred on September 28th, 2000. The all-time lowest TP value of 0.10 mg/l monitored in the river was on June 5th, 2001 (Figure 3-3A). However, P levels in drainage seem to be affected by fertilization and irrigation activities on the pasture, and the seasonal pattern was not clear. For example, the all-time lowest (in 1999) and highest (in 2000) TP values were both measured in summer (Figure 3-3A). All P forms in water generally followed the same seasonal patterns, except for PP in drainage, on one occasion (March, 2000), which was extremely high (Figure 3-3D).

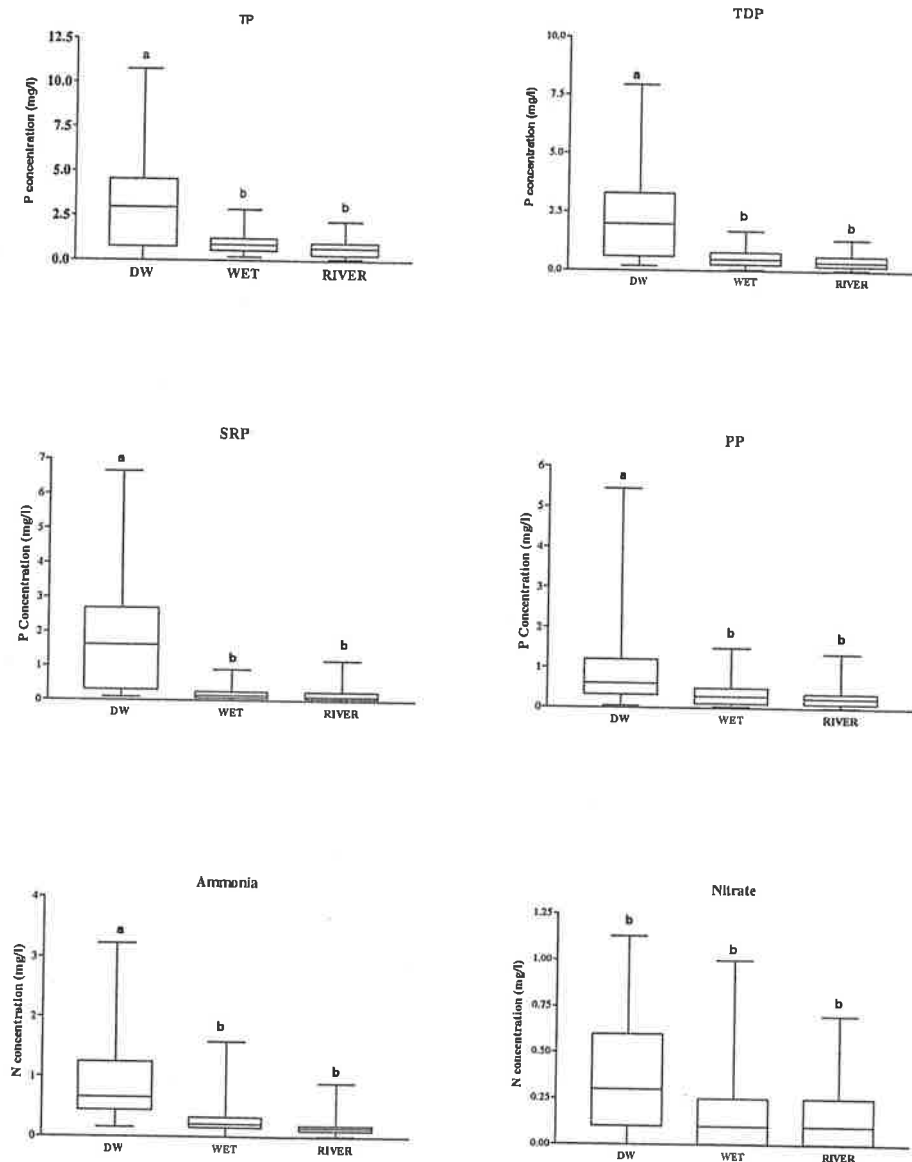


Figure 3-1. Bar and whisker graphs of nutrients in drainage, wetland and river water. DW, drainage water; WET, wetland water. Columns marked with different letters are significant different according to Tukey's test ($\alpha = 0.05$, $n = 38$). TP, total phosphorus; TDP, total dissolved phosphorus; SRP, soluble reactive phosphorus; PP, particulate phosphorus.

N, neither ammonia nor nitrate had clear winter-summer cycles in all three waters (Figure 3-4). This may be because of the low levels in the waters, and the turnover rate was found be quite fast. For pH, a seasonal pattern can't be found for any of the three waters (Figure 3-5). Not surprisingly, pH in drainage water varied dramatically in both frequency and magnitude, but remained relatively stable in river and wetland waters.

Table 3-1. Selected Water Quality Parameters of drainage, wetland and river water over the study period (1999 – 2001)

Parameters	Site	Mean	Median	S.E.	S.D.	Minimum	Maximum
TP	Drainage	3.39	3.38	0.40	2.34	0.35	10.75
	Wetland	1.08	0.96	0.12	0.65	0.27	2.85
	River	0.79	0.76	0.08	0.49	0.10	2.20
TDP	Drainage	2.41	2.30	0.30	1.73	0.20	7.95
	Wetland	0.63	0.55	0.07	0.38	0.05	1.70
	River	0.47	0.44	0.05	0.31	0.05	1.34
DIP	Drainage	1.98	1.71	0.26	1.52	0.10	6.65
	Wetland	0.25	0.18	0.05	0.25	0.00	0.91
	River	0.20	0.14	0.04	0.23	0.00	1.18
DOP	Drainage	0.43	0.34	0.09	0.52	0.06	2.22
	Wetland	0.38	0.31	0.05	0.28	0.02	1.17
	River	0.26	0.18	0.04	0.22	0.00	1.09
PP	Drainage	1.15	0.85	0.20	1.15	0.05	5.45
	Wetland	0.51	0.44	0.07	0.39	0.04	1.50
	River	0.32	0.25	0.05	0.31	0.03	1.37
Nitrate-N	Drainage	0.38	0.30	0.05	0.28	0.00	1.13
	Wetland	0.21	0.13	0.05	0.26	0.00	0.83
	River	0.22	0.10	0.05	0.25	0.00	0.70
Ammonia-N	Drainage	1.11	0.72	0.17	0.91	0.20	3.23
	Wetland	0.33	0.23	0.07	0.35	0.00	1.59
	River	0.18	0.16	0.03	0.16	0.03	0.90
Chlorophyll-a	Drainage	57.83	16.20	22.54	100.78	1.30	352.70
	Wetland	18.47	17.30	1.40	5.95	8.90	29.80
	River	14.60	12.40	1.94	9.12	2.60	33.40
Temp	Drainage	19.35	19.50	0.72	3.60	13.81	26.10
	Wetland	21.04	20.60	1.03	4.26	12.49	28.00
	River	21.50	21.60	0.77	3.86	13.57	28.14
Salinity	Drainage	4.58	5.30	0.60	3.02	0.10	10.28
	Wetland	0.37	0.36	0.05	0.22	0.01	0.84
	River	0.20	0.23	0.02	0.10	0.00	0.30
DO	Drainage	9.43	6.29	2.03	9.29	1.00	36.55
	Wetland	8.34	9.43	0.64	2.41	1.59	10.50
	River	8.10	8.03	0.51	2.35	2.65	13.78
pH	Drainage	7.97	7.90	0.11	0.66	7.04	10.35
	Wetland	8.23	8.25	0.06	0.34	7.59	8.74
	River	8.08	8.02	0.06	0.36	7.34	8.97
Turbidity	Drainage	31.03	26.60	4.92	22.03	0.00	71.90
	Wetland	93.18	65.20	18.88	77.86	8.58	280.00
	River	72.79	79.00	6.57	30.10	15.30	120.10

S.E, standard error; S.D, standard deviation

See Figure 3-1 for explanations of P forms.

Table 3-2. ANOVA table for nutrients, pH, DO, chlorophyll a, salinity and turbidity in drainage, wetland and river waters. If the results of ANOVA were significant, post-test (Tukey's analysis) was performed to compare the individual dataset.

Parameters	ANOVA	DW - Wetland		DW - River		Wetland - River	
		M.D	Significant	M.D	Significant	M.D	Significant
TP	***	2.357	***	2.597	***	0.241	N.S
TDP	***	1.8	***	1.94	***	0.139	N.S
SRP	***	1.737	***	1.772	***	0.035	N.S
PP	***	0.659	**	0.8271	***	0.168	N.S
DOP	*	1.397	N.S	2.779	*	-1.382	N.S
Ammonia-N	***	0.772	***	0.9252	***	0.153	N.S
Nitrate-N	**	0.152	*	0.1688	**	0.017	N.S
pH	*	-0.312	*	-0.106	N.S	0.207	N.S
Chl_a	***	-40.70	**	40.01	***	3.314	N.S
DO	N.S						
Salinity	***	3.950	***	4.115	***	0.166	N.S
Turbidity	***	-62.64	***	-40.23	*	22.11	N.S

***, Extremely significant difference ($P < 0.001$); **, moderately significant difference ($P < 0.01$); *, significant difference ($P < 0.05$); N.S, no significant difference ($P > 0.05$);

$\alpha = 0.05$, $n = 38$;

M.D, mean difference (- means less than).

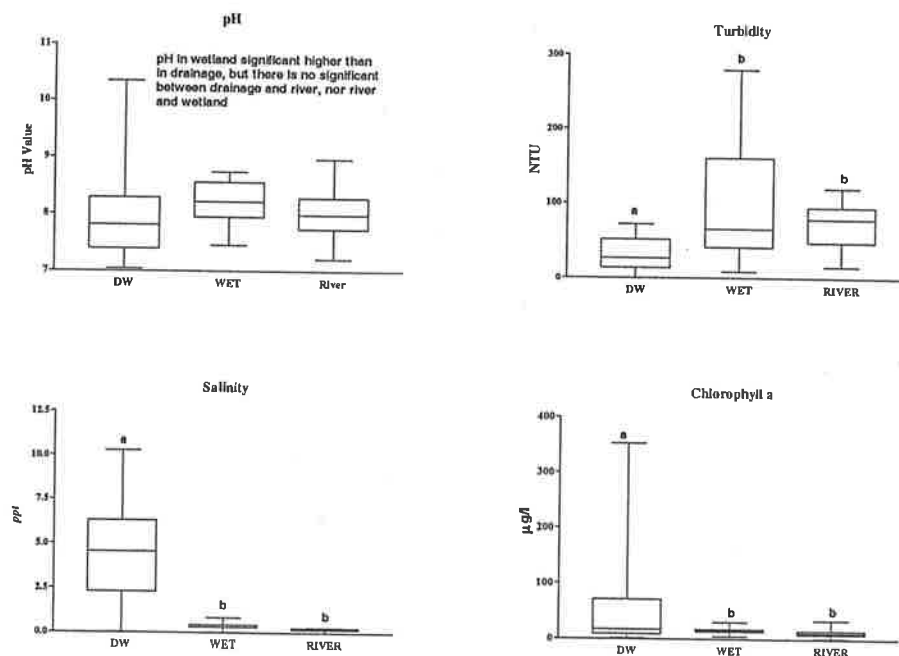


Figure 3-2. Salinity, Chlorophyll-a, pH and Turbidity in Drainage, wetland and river waters: shows the mean, standard deviation and range of the parameters. Values denoted with different letters are significant different ($\alpha = 0.05$, $n = 38$).

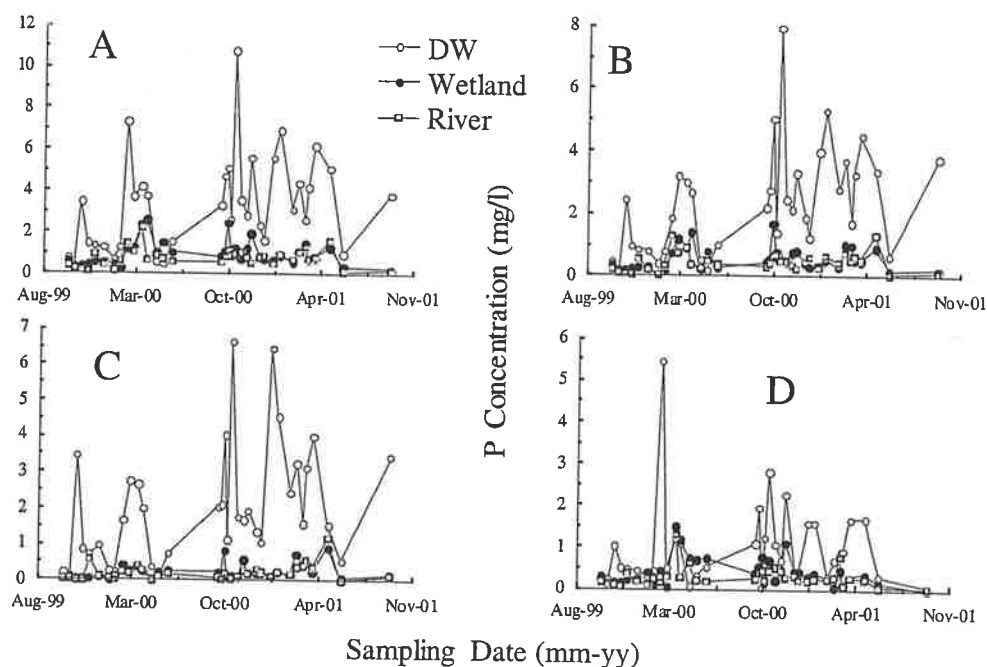


Figure 3-3. TP (A), TDP (B), SRP (C), PP (D) concentrations in drainage, wetland and river waters over the study period.

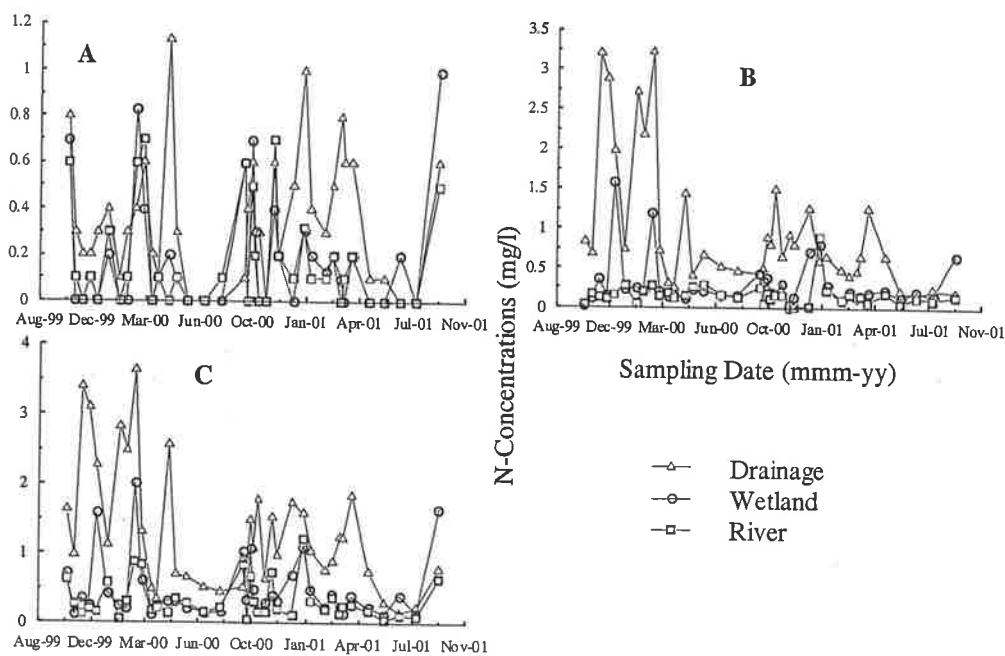


Figure 3-4. Nitrogen seasonal patterns in drainage, wetland and river waters. A, Nitrate N; B, Ammonia-N; and C, inorganic N.

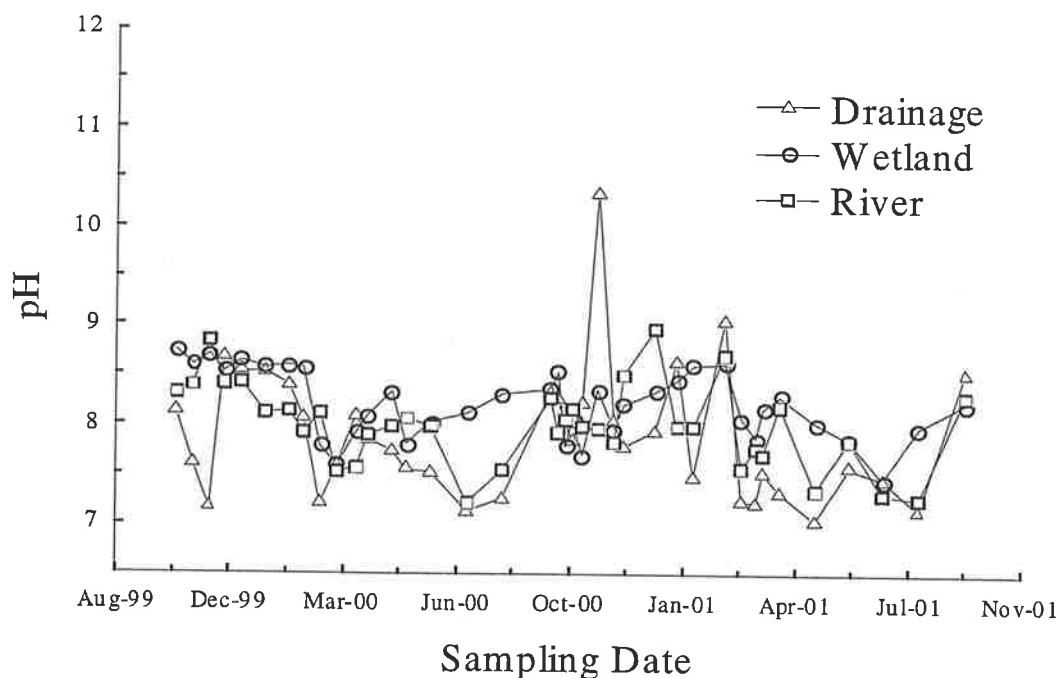


Figure 3-5. pH deviations in drainage, wetland and river waters.

3.1.3 Relationships between P Forms

The relationships between P forms in the three waters gave insight information about the water characteristics regarding P. Simple linear regression, which is a way to describe the relationship between two variables by calculating a best-fitting straight line on a graph, was used to estimate the relationships between different P forms in the three waters. Since the P-values in the ANOVA analysis are less than 0.01 in all the nine fitted models (Table 3-3), there were statistically significant relationships between SRP and TP, SRP and TDP, and TDP and TP in the three waters at the 99% confidence level. However, the goodness of fit as indicated by correlation coefficient and R^2 differ from case to case (Table 3-3). Figure 3-6 shows the fitted curves and the 95.0% prediction intervals (lower and upper 5%) for new observations. From Table 3-3 and Figure 3-6, it was obvious that the models were better fitted for drainage than for wetland and river waters. Moreover, the relationships among the variables were blurrier in wetland than in river water. In addition, TDP was a better predictor for SRP than TP, although there existed reasonably strong relationships between the TP and TDP for all the three waters.

Table 3-3. Linear Model* for SRP-TP, SRP-TDP and TDP-TP in Drainage, wetland and River waters

	Drainage			Wetland			River		
	SRP-TP	SRP-TDP	TDP-TP	SRP-TP	SRP-TDP	TDP-TP	SRP-TP	SRP-TDP	TDP-TP
Intercept (a)	0.022	-0.108	0.141	0.031	-0.026	0.077	-0.008	-0.033	0.056
Slope (b)	0.563	0.845	0.671	0.193	0.431	0.507	0.267	0.511	0.513
C.C	0.894	0.975	0.922	0.541	0.695	0.880	0.587	0.709	0.814
R ² (%)	79.38	95.15	84.59	29.28	48.30	76.76	34.41	50.21	65.36
S.E. of Est.	0.688	0.338	0.686	0.195	0.167	0.178	0.183	0.160	0.182
MAE	0.453	0.194	0.372	0.135	0.115	0.117	0.111	0.106	0.119
P	0.000	0.000	0.000	0.005	0.000	0.000	0.001	0.000	0.000

* Linear equation: $Y = a + bX$.

C.C: Correlation Coefficient;

R² (%): indicates that the model as fitted explains percentage of variability, used to access the goodness-of-fit;

S.E. of Est.: standard error of estimate;

MAE: mean absolute error;

P: the ANOVA P-value of relationship between dependant and Slope (b).

If the Y-intercept (a) was forced to be 0, the percentage contribution of individual P forms to TP can be calculated from the regressive equations. Table 3-4 summarized the ratios of different P forms to TP in the three waters. The majority of P in drainage (70%) was in dissolved forms, of which more than 80% was inorganic P. P associated with particulars accounted only 30% of the TP. The P differentiation was similar for wetland and river waters. The ratio of TDP/PP was around 1.3.

Table 3-4. Ratios of TDP, SRP and PP to TP (%) in drainage, wetland and river waters

	TDP	SRP	PP
Drainage	70.0	56.8	30.1
Wetland	56.4	21.7	43.6
River	56.7	25.9	43.3

3.1.3.1 Drainage

In drainage, SRP can be estimated from:

$$SRP = 0.0251 + 0.601 \times TP \quad (3-1)$$

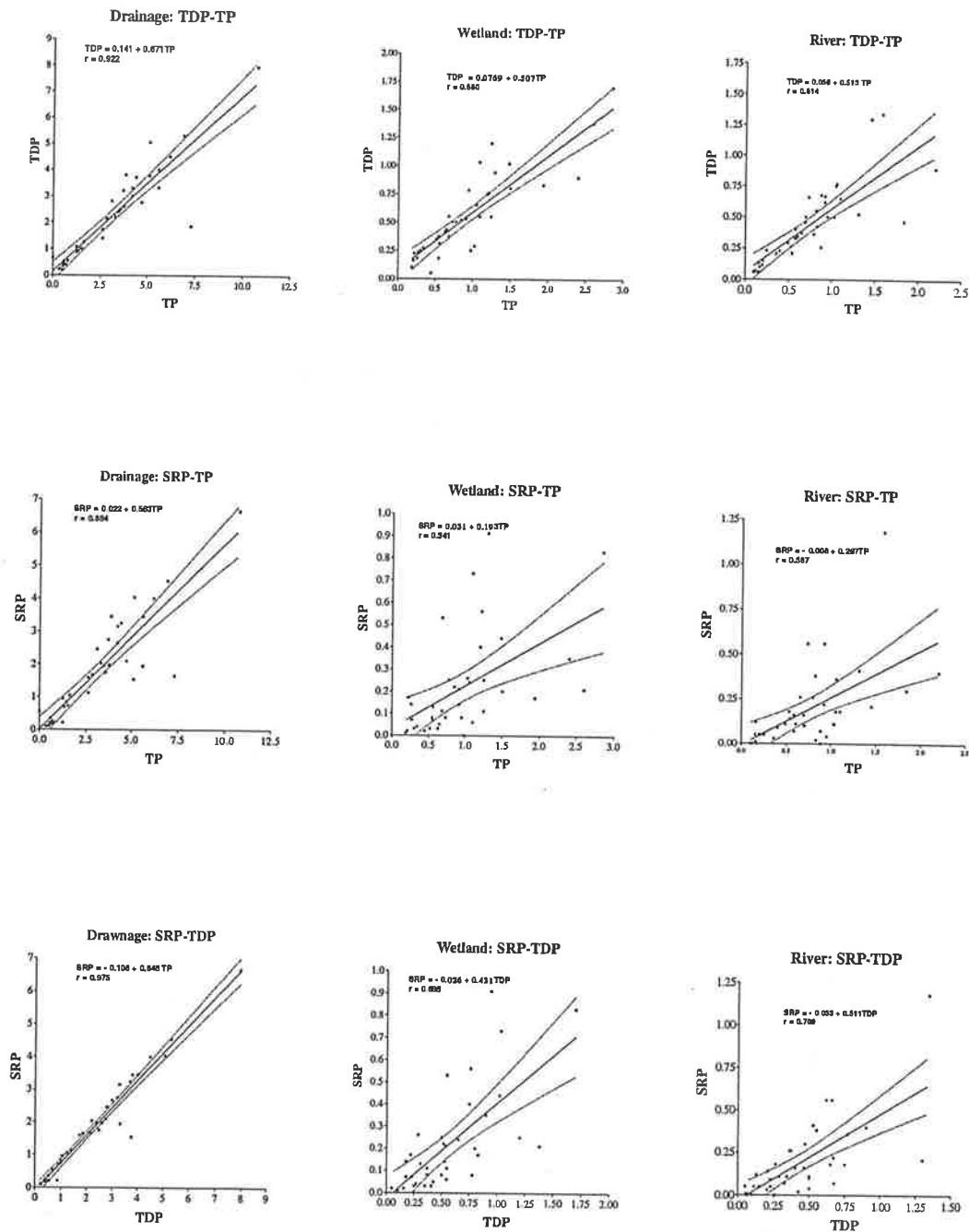


Figure 3-6. Simple regressive models of the relationships between P forms in three waters. Dots were measured data. Solid lines represented the fitted models, and dashed lines were $\pm 5\%$ of the expected limits. The best fitted model was TDP-SRP for drainage, the measured data fell into the 95% intervals. The worst fitted model was TP-SRP for wetland water, whose 95% intervals covered only 50 % of the measured data.

The correlation coefficient equals 0.8757, indicating a moderately strong linear relationship between the two variables. The R^2 statistic indicates that the model as fitted explains 76.68% of the variability in SRP. If TP is replaced by TDP, SRP can be better estimated from:

$$SRP = -0.0674 + 0.8813 \times TDP \quad (3-2)$$

The correlation coefficient is 0.9189, indicating there exists a very strong linear relationship. The fitted model explains 84.43% of the variability in SRP. As indicated by the model, the majority (nearly 90%) of the dissolved P is inorganic P.

TDP in drainage can be estimated from TP by:

$$TDP = 0.0928 + 0.6781 \times TP \quad (3-3)$$

Statistical analysis shows that the function (3-3) explains more than 80% of the variability in TDP and the correlation coefficient of 0.9126 indicating that there is a very strong linear relationship between TDP and TP.

3.1.3.2 Wetland water

For wetland water, SRP can be estimated from:

$$SRP = 0.0419 + 0.1902 \times TP \quad (3-4)$$

The correlation coefficient is less than 0.5, indicating a weak linear relationship between the two variables. As a result, the fitted model explains only 24.83% of the variability in SRP. On average, about 20% of the TP in wetland water is SRP. Replacing TP with TDP can improve the power of prediction.

$$SRP = -0.0083 + 0.4174 \times TDP \quad (3-5)$$

The correlation coefficient is 0.6840, indicating there exists a moderately strong linear relationship. The fitted model explains 46.79% of the variability in SRP. In contrast to drainage, less than half of the dissolved P is inorganic.

Contrary to SRP, the TDP in wetland water can be predicted efficiently from TP by:

$$TDP = 0.03545 + 0.5414 \times TP \quad (3-6)$$

The model explains 75.22% of the variability in TDP and the correlation coefficient (0.8673) indicates that there is a moderately strong linear relationship between TDP and TP. Around half of the TP is in dissolved forms, others are associated with sediment particles and dead and alive biomass (mainly phytoplankton).

3.1.3.3 River water

For water from the River Murray, SRP can be estimated from:

$$SRP = -0.0188 + 0.2942 \times TP \quad (3-7)$$

The correlation coefficient is greater than 0.5, indicating a moderately strong linear relationship between the two variables. However, the fitted model explains only 33.31% of the variability in SRP. In average, about 30% of the TP in river water is SRP. As in wetland water, replacing TP with TDP can improve the power of prediction.

$$SRP = -0.03126 + 0.5055 \times TDP \quad (3-8)$$

The correlation coefficient is 0.6847, indicating there exists a moderately strong linear relationship. The fitted model explains 46.89% of the variability in SRP. About half of the dissolved P present in river water is inorganic.

As in drainage and wetland water, there is a strong linear relationship between TDP and TP in river water, and the fitted equation is:

$$TDP = 0.0154 + 0.5942 \times TP \quad (3-9)$$

The model explains 73.26% of the variability in TDP. For TP present in river water, nearly 60% is in dissolved form.

3.2 P REMOVAL PERFORMANCE OF EXPERIMENTAL PONDS

3.2.1 General Description

3.2.1.1 P removal efficiencies and removal rates in experimental ponds

The performances of the experimental ponds, which were assessed by P removal percentage (%) and removal rate (g/m²/day), were summarized in Table 3-5. In Table 3-5, the P removal efficiency and rate were calculated based on the total P loadings and discharges for the whole operation period according to the following equations:

$$PRE = \frac{\sum (C_i Q_i - C_o Q_o)}{\sum C_i Q_i} \times 100 \quad (3-10)$$

$$PRR = \frac{\sum (C_i Q_i - C_o Q_o)}{A \times D} \quad (3-11)$$

Where, C_i and C_o are P inlet and outlet concentrations (mg/l);

A is the surface area of pond (m²), D is the operation days (day);

Q_i and Q_o are the inflow and outflow (l).

$$\text{And } Q_o = Q_i - ET \quad (3-12)$$

ET is the volumetric evapotranspiration (l).

All forms of P were removed to various degrees in the five experimental ponds except in pond 3, the pond with submergent water plants growing on the P rich substrates. Regarding TP, the most efficient system was pond 4, in which P poor substrate (hill soils) was utilized and planted with emergent water plants, pond 2, the pond cultivated with planted floats and without substrates, ranked the second. The pond with hill soils as substrates and was free of macrophytes (Pond 5) was the third efficient system, followed by Pond 1 (pond with P rich topsoils and emergent macrophytes) and Pond 3. For TDP, the order was the same as for TP: Pond 4>Pond 2>Pond 5> Pond 1> pond 3. For SRP, the order changed to Pond 2>Pond 4> Pond 5> Pond 1>Pond 3. For PP, the order was different with Pond 4 ranked first followed by Pond 3, Pond 2, and Pond 5 remained last. It was obvious that Pond 4 and Pond 2 were more efficient to remove P than other ponds, especially for dissolved forms of P, and pond 3 was the least efficient. In many monitoring events, the pond appeared to be P source.

Table 3-5. Average P removal rate (PRR, g/m²/day), efficiency (PRE, %) and ranks in experimental ponds during the operation period.

	TP			TDP			SRP			PP		
	PRE	PRR	Rank	PRE	PRR	Rank	PRE	PRR	Rank	PRE	PRR	Rank
Pond 4 ^a	44.3	0.220	1	46.6	0.175	1	45.8	0.135	2	57.9	0.104	1
Pond 5 ^a	27.9	0.138	3	41.5	0.156	3	44.8	0.131	3	22.9	0.041	5
Pond 1	24.3	0.108	4	15.9	0.051	4	11.8	0.029	4	57.1	0.093	2
Pond 2	44.1	0.149	2	43.1	0.116	2	73.9	0.162	1	28.6	0.020	4
Pond 3	-0.5	-0.001	5	-2.5	-0.004	5	-37.7	-0.022	5	33.0	0.016	3
Overall ^b	57.5	0.086		51.0	0.054		68.3	0.057		79.5	0.043	

^a, Calculated from one-year data (September 2000 – September 2001);

^b, Overall performance of the three-pond (Pond 1, 2, and 3) system;

Pond 1: with P rich soils (site soils) as substrates and planted with emergent macrophytes;

Pond 2: with no substrates and cultivated with planted floats;

Pond 3: with P rich soils as substrates and planted with submergent macrophytes;

Pond 4: with P poor soils as substrate planted with macrophytes;

Pond 5: with P poor soils as substrate without macrophytes;

Ranks were based on P removal efficiency.

Table 3-6. Results of Tukey's multiple comparisons for the performance of ponds for: A) TP removal efficiency; B) TP removal rate.

A	Pond 2		Pond 3		Pond 4		Pond 5	
	M.D	P value	M.D	P value	M.D	P value	M.D	P value
Pond 1	-29.08	*	20.56	N.S	-30.85	*	-15.84	*
Pond 2			49.65	***	-1.78	N.S	13.24	N.S
Pond 3					-51.42	***	-36.41	**
Pond 4							15.02	N.S
B								
	M.D	P value	M.D	P value	M.D	P value	M.D	P value
Pond 1	-0.003	N.S	0.14	**	-0.12	*	-0.04	N.S
Pond 2			0.14	***	-0.12	N.S	-0.03	N.S
Pond 3					-0.25	***	-0.17	***
Pond 4							0.08	N.S

See Table 3-5 for explanations of ponds.

M.D, mean difference;

For Pond 1, 2 and 3, n = 38; For Pond 4 and 5, n = 20;

***, very significant difference (P<0.001);

**, relatively significant difference (P<0.01);

*, significant difference (P<0.05);

N.S. no significant difference (P>0.05).

The ANOVA test showed that the ponds performed statistically different for both removal efficiency and removal rate (Table 3-6, Figure 3-5). The P removal efficiency and rate in

Table 3-4 were calculated based on a biweekly interval. Results of post ANOVA test - Tukey's multiple comparison revealed that pond 3 had significantly lower TP removal efficiency (Table 3-6A) and removal rates (Table 3-6B) than other ponds. However, the mean differences amongst pond 2, pond 1, pond 4 and pond 5 weren't significant ($P < 0.05$). In addition, the performance of pond 2 was the steadiest compared with the other ponds (the smallest standard error, Figure 3-7), while pond 4 and pond 5 were the most changeable ones.

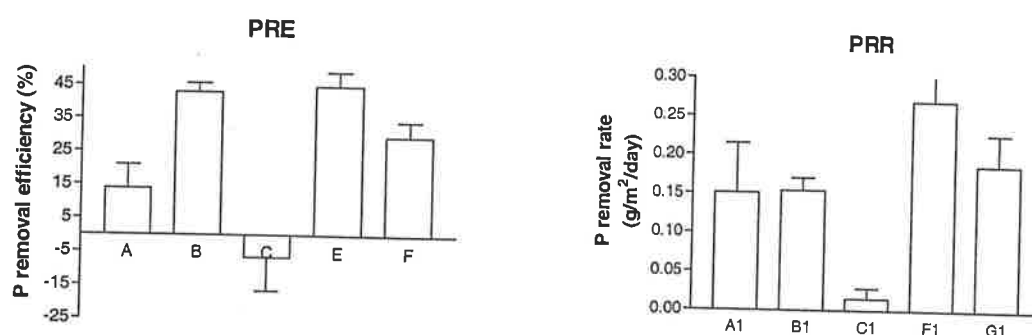


Figure 3-7. TP removal efficiency (PRE) and rate (PRR) in experiment ponds: A, Pond 1; B, Pond 2; C, Pond 3; E, Pond 4; F, Pond 5. Column represents the mean, and bar is the standard error. For A, B and C, $n = 38$, for E and F, $n = 20$.

3.2.1.2 Seasonal Patterns of P removal in experimental ponds

The performance of the experimental ponds changed dramatically during the operation period (Table 3-7). In pond 1, for example, the removal efficiency for TP ranged from -152.0 to 63.4%. In pond 1 and pond 2, SRP was the most variable parameter, while in pond 2, pond 4 and pond 5, PP changed the most.

The ponds displayed distinguishable seasonal behaviours, especially for the ponds with soils from the site as substrates. In general, all ponds had the capacity to remove various P forms in summer except the PP, which increased on many occasions. However, all ponds except pond 2 released the stored P in winter while the P loading was lower, and became net resources of P (Figure 3-8). For example, the peak TP removal efficiency in pond 1 happened in February (62.4%) during the first year of operation, and in October (65.8%) during the second year of operation. In winter, the pond discharged the stored P with the highest release occurring in August (Figure D-1). In addition, the majority of the released P

in winter was SRP. Detailed graphs of the P removal efficiencies and removal rates for TP, TDP, SRP and PP of individual ponds can be found in Appendix D: Figures for P removal efficiency and rate in experimental ponds.

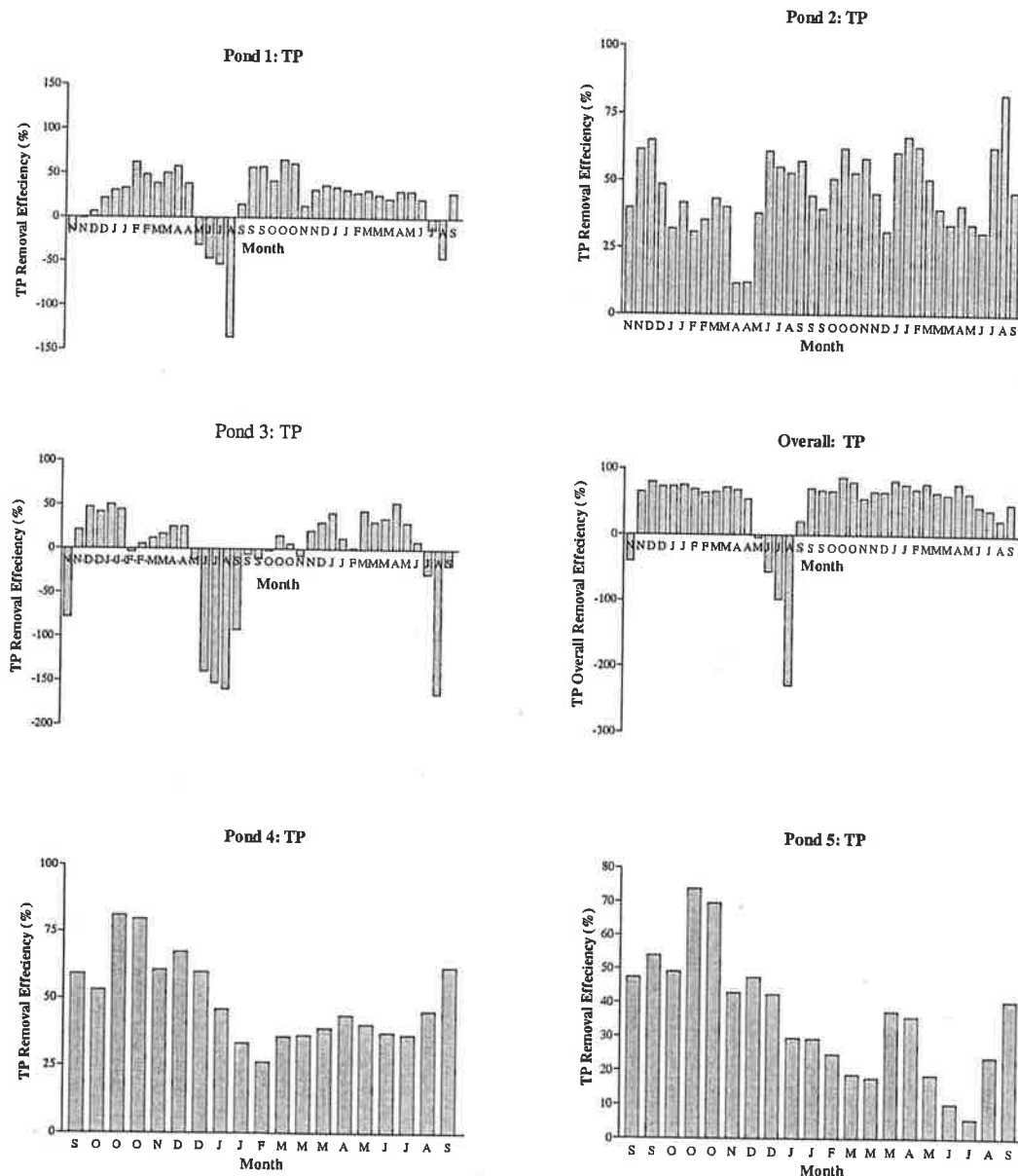


Figure 3-8. TP removal efficiency (%) in experimental ponds. Negative figures mean net P release.

3.2.1.3 Relationships between influent and effluent P

The regressive relationships between inflowing and out-flowing P are useful to assess and predict the performance of ponds. Table 3-8 summarises the results of linear regression

between incoming and out-flowing P for both mass and concentrations in all experimental ponds.

For TP, there existed significant relationships for both concentration and mass (Table 3-8) at 99% confidence level ($\alpha = 0.01$). For other P forms, the situation was different from case to case. In most cases, mass was a better indicator than concentration (larger r and R^2). The details of fitted curves were presented in appendix E: Figures of the linear relationship between influent and effluent P in experimental ponds.

Table 3-7. Minimum and maximum P removal efficiency (PRE, %) and P removal rate (PRR, $\text{g/m}^2/\text{day}$) in experimental ponds

		TP		TDP		SRP		PP	
		PRE	PRR	PRE	PRR	PRE	PRR	PRE	PRR
Pond 1	Min	-152.0	-0.146	-222.7	-0.136	-475.9	-0.188	-27.0	-0.009
	Max	63.4	0.684	57.5	0.456	67.4	0.426	94.9	0.447
Pond 2	Min	5.7	0.014	2.9	0.007	44.2	0.029	-589.4	-0.166
	Max	81.3	0.473	79.9	0.379	98.0	0.380	83.2	0.162
Pond 3	Min	-163.7	-0.210	-202.8	-0.179	-606.0	-0.130	-170.4	-0.036
	Max	53.3	0.206	65.9	0.184	56.2	0.068	90.6	0.157
Overall	Min	-228.9	-0.220	-352.0	-0.216	-1055.6	-0.057	-22.2	-0.006
	Max	87.6	0.944	86.7	0.654	60.1	0.586	97.7	0.452
Pond 4	Min	5.1	0.010	16.9	0.014	-47.2	-0.068	-127.8	-0.267
	Max	79.6	0.772	78.8	0.530	85.2	0.481	90.9	0.316
Pond 5	Min	-26.3	-0.136	-1.0	-0.003	-46.1	-0.067	-236.1	-0.411
	Max	67.4	0.666	74.9	0.458	93.2	0.450	85.2	0.237

See Table 3-5 for explanations of ponds.

From Table 3-8, it was interesting to notice that most of the fitted models had significant relationships with both slopes (b) and Y-axis intercepts (a) except in pond 2 indicating the complicated P dynamics in ponds with substrates. The Y-axis intercepts, which could be explained as background P levels in systems, were higher in ponds with P poor substrates. The reason for this may be the poor buffer capacities of the soils.

As the HRT in ponds was 5-6 days, it was long enough for P transformation to take place. The utilization of individual P forms i.e. TDP, SRP, PP as independents for regressive fitting may not be appropriate in systems where P transformation was active. The replacement of

incoming TDP, SRP and PP with influent TP may improve the prediction power of the models. Table 3-9 showed the results of linear fitting of individual effluent P forms with influent TP. Comparing Table 3-8 with Table 3-9 revealed that the influent TP was a better predictor for effluent P in all ponds for both mass and concentration, especially for ponds with substrates. For example, in pond 4, the replacement of incoming SRP with TP increased the correlation coefficient from 0.399 to 0.616. The results indirectly explained the transient characteristics of these P forms in aquatic systems.

The nonlinear regression (Eq. 3-10) was more appropriate to describe the relationship between the influent and effluent P Concentrations (Table 3-10). However, the degree of improvement was different from system to system. For example, for pond 4, R^2 , which means the percentage of variability in effluent TP concentration, can be explained by the model fitted increased more than 50% from 21.2% to 38.6%. In pond 3, however, R^2 increased only marginally, from 45.3% to 46.4%. In addition, the fitted constants (A and B) in the power models were very close for ponds with substrates, i.e. pond 1, 3, 4 and 5, revealing the similar P behaviours in these systems. In pond 2, the differences were much bigger, indicating the distinguishing P dynamics (Figure 3-9).

Fitted model: $C_o = A \times C_i^B$;

(3-10)

Where, C_o and C_i are the TP concentrations in inlet and outlet, respectively, mg/l; A and B are model constants.

Table 3-10. Power fit of effluent and influent TP concentrations for each pond

	Pond 1	Pond 2	Pond 3	Overall	Pond 4	Pond 5
A	1.27***	0.62***	1.07**	0.86**	1.17***	1.45***
B	0.56**	0.92**	0.62**	0.32**	0.47**	0.48**
R^2	66.7	70.0	46.4	19.4	38.6	45.6

Refer to table 3-5 for explanation of ponds.

Table 3-8. The linear relationships ($P_{\text{output}} = a + b \times P_{\text{income}}$) between the incoming and output P

		TP		TDP		SRP		PP	
		Concentration Mass		Concentration Mass		Concentration Mass		Concentration Mass	
Pond 4 ^a	a	1.038*	0.096 ^{ns}	0.859**	0.074 ^{ns}	NS	0.097**	NS	NS
	b	0.262**	0.346***	0.227**	0.326***	NS	0.198*	NS	NS
	r	0.522	0.595	0.495	0.628		0.399		
	R ²	21.2	31.6	20.3	35.9		11.0		
Pond 5 ^a	a	1.281**	0.119 ^{ns}	0.941**	0.093*	NS	NS	NS	NS
	b	0.345***	0.449**	0.262**	0.348**	NS	NS	NS	NS
	r	0.597	0.662	0.521	0.602				
	R ²	32.2	40.8	23.3	32.7				
Pond 1 ^b	a	0.871***	0.124***	0.805***	0.123***	0.795***	0.124**	0.276***	0.030 ^{ns}
	b	0.423***	0.452***	0.432***	0.448***	0.358***	0.373**	0.139**	0.219***
	r	0.776	0.828	0.674	0.765	0.553	0.636	0.394	0.541
	R ²	59.4	67.7	44.0	58.5	28.7	38.7	13.2	27.3
Pond 2 ^a	a	0.063 ^{ns}	0.018 ^{ns}	0.111 ^{ns}	0.014 ^{ns}	0.199 ^{ns}	0.006 ^{ns}	NS	NS
	b	0.539***	0.511***	0.488***	0.496***	0.179**	0.218***	NS	NS
	r	0.835	0.842	0.733	0.728	0.621	0.697		
	R ²	68.7	70.0	52.4	51.7	36.8	47.1		
Pond 3 ^b	a	0.418**	0.082***	0.343**	0.070***	0.226**	0.033***	0.166***	0.024***
	b	0.598***	0.510***	0.604***	0.495***	0.699***	0.699***	0.170**	0.202**
	r	0.684	0.607	0.670	0.585	0.429	0.450	0.368	0.391
	R ²	45.3	35.0	43.4	32.7	16.1	22.8	11.1	12.9
Overall ^c	a	0.754***	0.043***	0.338*	NS	0.280**	0.048***	0.170**	NS
	b	0.131***	0.217**	0.50*	NS	0.110**	0.083**	0.07*	NS
	r	0.426	0.407			0.364	0.325		
	R ²	15.9	14.2			10.9	8.0		

^a, n = 20, one year data; ^b, n = 38, two years data; ^c, overall of the three ponds (Pond 1, 2 and 3) in series;
R²(%), determination coefficient, indicating that the fitted equation explains the percentage of variability in P_{output};
r, Correlation Coefficient;

*** Significant relationship at 99% confident level; ** Significant relationship at 95% confident level; * Significant relationship at 90% confident level; ns, no significant relationship at 90% confident level.

Table 3-9. Linear relationships between effluent P (TP, TDP, SRP and PP) and incoming TP

		TP		TDP		SRP		PP	
		Conc.	Mass	Conc.	Mass	Conc.	Mass	Conc.	Mass
Pond 4 ^a	a	1.038*	0.096 ^{ns}	0.788**	0.012 ^{ns}	0.716**	0.080**	ns	ns
	b	0.262**	0.346***	0.188**	0.306***	0.118*	0.235*	ns	ns
	r	0.522	0.595	0.533	0.778	0.397	0.616	ns	ns
	R ²	21.2	31.6	24.5	58.3	11.1	34.3		
Pond 5 ^a	a	1.281**	0.119 ^{ns}	0.857**	0.014 ^{ns}	0.556 ^{ns}	0.084*	ns	ns
	b	0.345***	0.449**	0.217***	0.306**	0.168**	0.276***	ns	ns
	r	0.597	0.662	0.559	0.776	0.449	0.648		
	R ²	32.2	40.8	27.7	58.0	16.0	38.8		
Pond 1 ^b	a	0.871***	0.124***	0.644***	0.105***	0.549***	0.092***	0.227***	0.018 ^{ns}
	b	0.423***	0.452***	0.359***	0.352***	0.282***	0.271***	0.064**	0.10***
	r	0.776	0.828	0.762	0.818	0.683	0.726	0.383	0.581
	R ²	59.4	67.7	56.9	65.9	45.2	51.3	12.3	31.9
Pond 2 ^a	a	0.063 ^{ns}	0.018 ^{ns}	-0.023 ^{ns}	0.007 ^{ns}	0.035 ^{ns}	0.026 ^{ns}	0.064 ^{ns}	0.01 ^{ns}
	b	0.539***	0.511***	0.454***	0.419***	0.146***	0.60***	0.145***	0.063**
	r	0.835	0.842	0.788	0.780	0.669	0.746	0.470	0.372
	R ²	68.7	70.0	61.0	59.7	43.2	54.4	19.9	11.4
Pond 3 ^b	a	0.418**	0.082***	0.247*	0.058***	0.106 ^{ns}	0.012 ^{ns}	ns	0.023***
	b	0.598***	0.510***	0.550***	0.445***	0.296***	0.304***	ns	0.070*
	r	0.684	0.607	0.682	0.595	0.537	0.617		0.303
	R ²	45.3	35.0	45.1	33.5	26.9	36.2		6.6
Overall ^c	a	0.754***	0.043***	0.593***	0.103***	0.265*	0.042***	0.160***	0.023***
	b	0.131***	0.217**	0.108**	0.086*	0.067*	0.060**	0.023*	0.028**
	r	0.426	0.407	0.382	0.346	0.348	0.364	0.294	0.363
	R ²	15.9	14.2	12.2	9.5	9.7	10.8	6.1	10.7

See Table 3-8 for explanations of denotes.

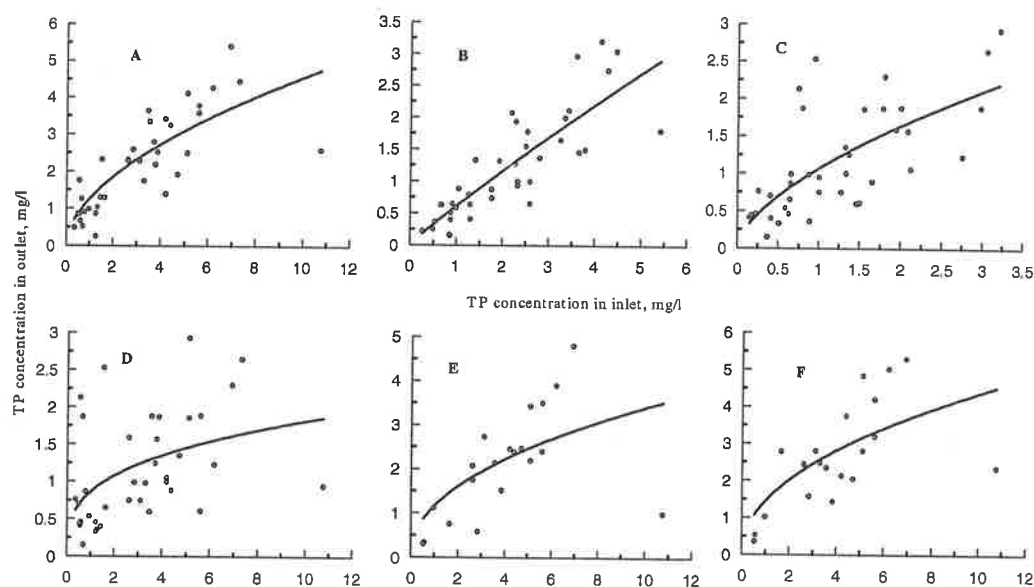


Figure 3-9. Power fitting of the relationships between influent and effluent TP concentration in A) pond 1; B) pond 2; C) pond 3; D) overall for three ponds; E) Pond 4; F) Pond 5. Curves represented the fitted models in table 3-10, and dots were measured data. Notice the different curve shape for pond 2.

3.2.1.4 Water pH and Chlorophyll-a Concentrations

Water pH

The pH in the water column is one of the master parameters that controls a series of chemical reactions, many of which are related to P removal, e.g. coprecipitation with CaCO_3 . The order of mean pH values in ponds was Pond1 < Pond2 < Pond 4 < Pond 3 < Pond5 (Figure 3-10), and the ANOVA test indicating that there was a significant difference among the means ($P < 0.0001$). Table 3-11 summarised the post Tukey's test to compare the paired means. Amongst the experimental ponds, pond 1 had significantly lower pH than any other pond, and the pond 5 had the highest pH value. While pH in pond 2 was significantly lower than in pond 3 and pond 5, the Tukey's test showed that the mean wasn't significantly different from pond 4. The Tukey's test also indicated that there were no significant differences among the means in pond 3, pond 4 and pond 5.

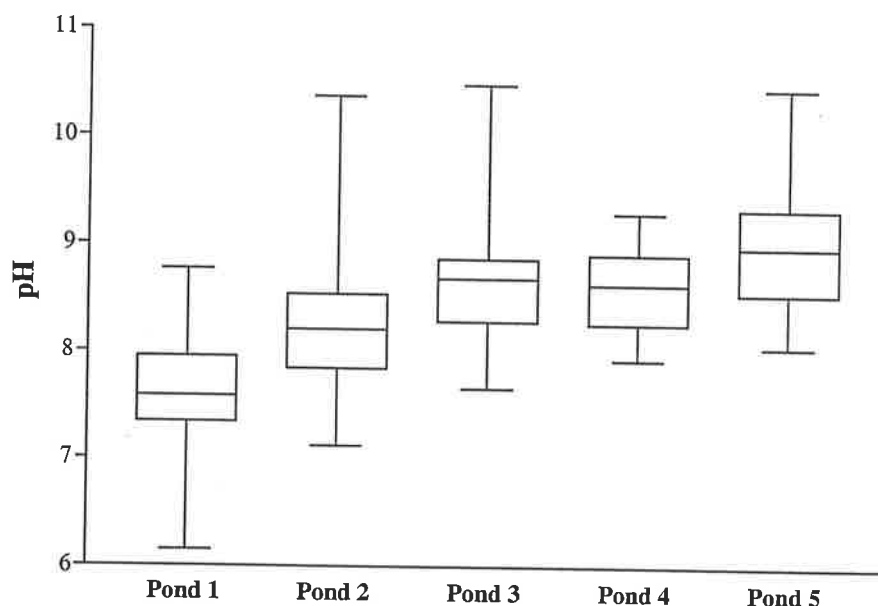


Figure 3-10. The variations of pH in pond systems, means and ranges (bar) are showed

Table 3-11. Results of Tukey's multiple comparison for pH in experimental ponds

	Pond 2		Pond 3		Pond 4		Pond 5	
	M.D	P	M.D	P	M.D	P	M.D	P
Pond 1	-0.616	***	-1.057	***	-0.993	***	-1.373	***
Pond 2			-0.442	**	-0.378	N.S	-0.758	***
Pond 3					0.064	N.S	-0.316	N.S
Pond 4							-0.380	N.S

Chlorophyll-a concentration

The chlorophyll-a concentration, which is the lump indirect indicator of phytoplankton in water, displayed distinguishing behaviours among the experimental ponds (Figure 3-10). The pond 5 had noticeably higher phytoplankton than others and changes dramatically over time (mean = 104.3, standard deviation = 158.3). This characteristic made the pond 5 stood out from other ponds and can blur the Tukey's multiple comparison test. The results of Tukey's test excluding pond 5 indicated that emergent pond had significant lower chlorophyll-a level amongst the experimental ponds. The difference among floating, submergent and pond 4 wasn't significant.

Relating chlorophyll-a level with water pH

The graphs of temporal variations of chlorophyll-a and pH (Figure 3-12) in pond 2 displayed that the two parameters changed simultaneously, although the peaks and valleys

didn't meet exactly. The patterns revealed that an intrinsic relationship between the two variables might exist.

Chlorophyll a - Summer

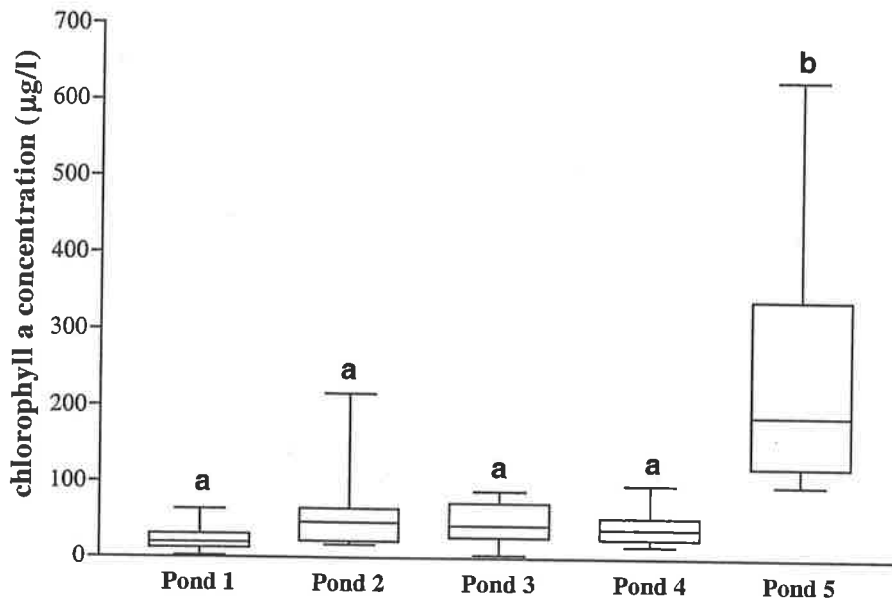


Figure 3-11. Chlorophyll-a level in ponds in the growth season of 2000-2001, graph showed the means and ranges (bar). Figures denoted by different letters means significant difference among the means ($\alpha = 0.05$).

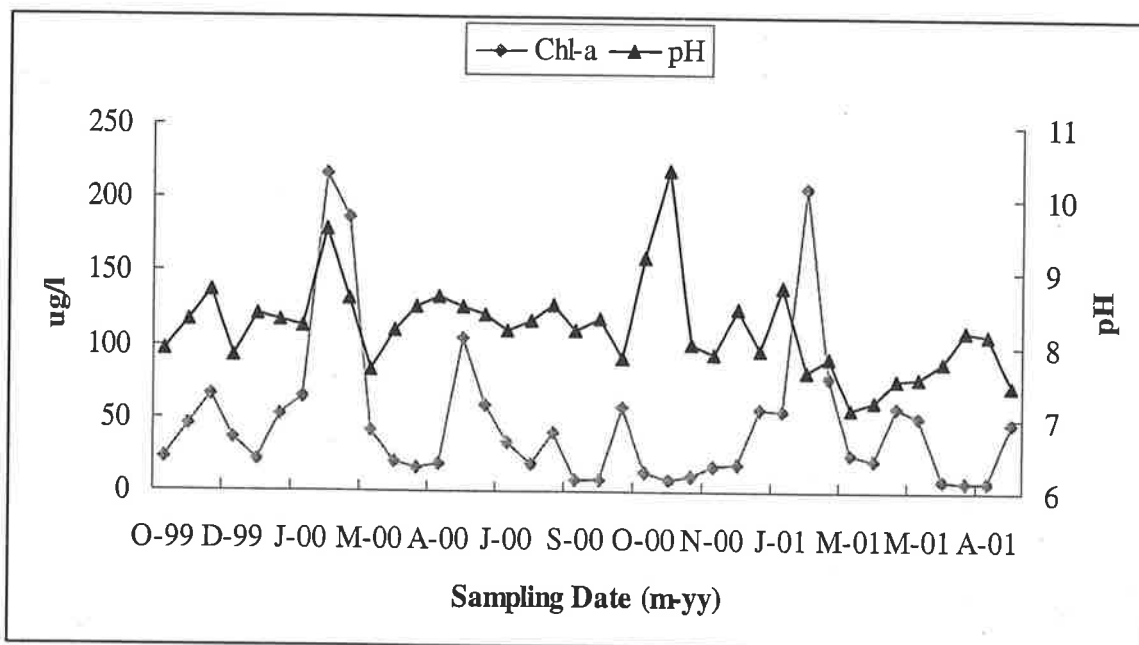


Figure 3-12. Chlorophyll a concentration and pH in pond 2

3.2.2 Performance of Individual Pond

3.2.2.1 Pond 1: with P rich topsoils as substrates and emergent macrophytes

P removal efficiency and removal rate

Comparing with other ponds, this system was effective in removing PP, but less effective with dissolved P (Table 3-4). More than half (57.1%) of the incoming PP was detained in the marsh. The removal rate for PP was $0.093\text{g/m}^2/\text{day}$. However, as dissolved forms of P predominated in the drainage, it was the second least efficient pond to remove TP, better only than pond 3. In the two years of operation, a total amount of 1555.9g of TP entered the pond, and 1178.2g of TP flew out of it. The difference, about 24.3% (377.7g) of the incoming TP was retained in the marsh. The breakdown of total phosphorus discovered that most of the retained P was PP (323.8g or 85.7% of TP). For SRP, the dominant P form in drainage, the marsh only retained $0.029\text{g/m}^2/\text{day}$, and the removal efficiency was 11.8%.

The pond was a net TP resource within the first 4 months of operation (Figure D-1, D-7). It also released large amounts of (e.g. in August 2000, a net release of $0.15\text{g/m}^2/\text{day}$) the stored P during the first winter (from May to August). During the second year, however, the TP removal efficiency was relatively stable for the growth season although the pond released SRP in one monitoring occasion (early November). In winter, the marsh released the stored P again although on a much smaller scale ($0.05\text{g/m}^2/\text{day}$ in August) and for a shorter period (from June to August) than in the first winter. In addition, the TDP and SRP removal patterns were identical, and SRP removal was less than the TDP removal on most occasions, indicating the release and transformation of organic P wasn't an issue in the pond even in winter.

Relationship between influent and effluent P

The influent P (P in drainage) was more erratic than the effluent P for all P forms for both concentration and mass (Table 3-12, the SD and SE were less in the 'out' column than in the 'in' column), meaning that the pond harmonized the incoming P, i.e. buffering the changes in influent P, and discharged more stabilized P. As indicated in Table 3-8A, the influent concentrations for all the P forms departed significantly from normality, as did the effluent concentrations (except TP). The transformation of LN(X) normalized both the

influent and effluent concentrations for all P forms (Table 3-13): the skewness or Kurtosis was in the range of (-2, +2). However, the mass variables followed a normal distribution in most cases (except the PP loading) (Table 3-12B). Consequently, the simple regression analysis was performed based on mass.

Table 3-12. Summary of description statistics for influent and effluent P in emergent Pond

A	TP		TDP		SRP		PP	
	In	Out	In	Out	In	Out	In	Out
Mean (mg/l)	3.090	2.177	2.196	1.754	1.748	1.421	1.057	0.424
Median (mg/l)	2.966	2.235	1.996	1.635	1.621	1.375	0.617	0.275
Standard Error	0.385	0.210	0.284	0.182	0.246	0.159	0.181	0.064
Standard Deviation	2.375	1.292	1.748	1.119	1.514	0.981	1.117	0.395
Standardized Skewness	2.59*	1.34	2.82*	2.13*	2.84*	2.80*	5.37*	3.73*
Standardized Kurtosis	1.70	-0.60	2.03*	1.04	1.85	1.73	7.08*	2.06*
n	38	38	38	38	38	38	38	38

B	TP		TDP		SRP		PP	
	In	Out	In	Out	In	Out	In	Out
Mean (g/day)	2.508	1.640	1.645	1.320	1.307	1.070	0.807	0.320
Median (g/day)	2.745	1.657	1.708	1.358	1.281	1.026	0.661	0.244
Standard Error	0.251	0.128	0.171	0.101	0.149	0.087	0.099	0.040
Standard Deviation	1.527	0.779	1.042	0.615	0.903	0.531	0.601	0.244
Standardized Skewness	0.72	0.82	0.96	0.63	0.98	1.06	2.43*	2.93*
Standardized Kurtosis	-1.04	-0.41	-1.01	-0.32	-1.10	-0.12	0.22	1.07
N	37	37	37	37	37	37	37	37

*, As the standardized skewness or Kurtosis was out of the range of (-2, +2), the terms were significant departure from normality, which may invalidate any of the standard statistic analysis. To perform further analysis, transformation, such as LN(X), LOG(X), and 1/X, is needed to make variables more normal; A, Concentration; B, Mass.

As shown in Table 3-8, the influent and effluent P had a moderately significant linear relationship for all P forms. The fitted models were presented in Figure E-1 and Figure E-6. The linear model fitted best for TP: 67.7% of variability in the output TP could be explained, and more than 95% of the measured data fell into the range of +/-5% prediction limits. The poorest fitted model was for PP: $R^2 = 27.3\%$ for mass and 13.2% for concentration. However, the effluent PP could be established from influent TP, and the relationship was moderately significant ($r = 0.581$, Table 3-9). In addition, as the model as fitted wasn't affected by the Y-axis intercept (a), and the intercept wasn't significantly

departure from zero, the intercept could be explained as background PP discharge, i.e. $C_{PP}^* = 0.030 \text{ g/m}^2/\text{day}$.

Table 3-13, The normalization test of LN(X) transformed data of influent and effluent P concentration in emergent pond

	TP		TDP		SRP		PP	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT
Mean	0.772	0.568	0.407	0.326	0.039	0.088	-0.443	-1.322
Variance	0.868	0.505	0.939	0.563	1.420	0.635	1.158	1.180
Standard deviation	0.931	0.711	0.969	0.750	1.192	0.797	1.076	1.086
Standardized Skewness	-0.957	-1.624	-1.072	-1.358	-1.471	-1.509	-0.736	-1.633
Standardized Kurtosis	-1.400	-0.099	-1.149	-0.545	-1.130	0.137	-0.091	0.338

The linear relationship between effluent P and influent TP concentrations was presented in Figure 3-13. Results of ANOVA analysis showed that all fitted models had significant relationships with both the slope and the Y-axis intercept, and the Y-axis intercepts were significantly different from zero (Table 3-8), revealing the relatively complicated P dynamics in the marsh. Consequently, the Y-axis intercept, a , can not simply be explained as background levels of P. The use of non-linear models with a constant denoted as background concentrations would be more appropriate to estimate this parameter.

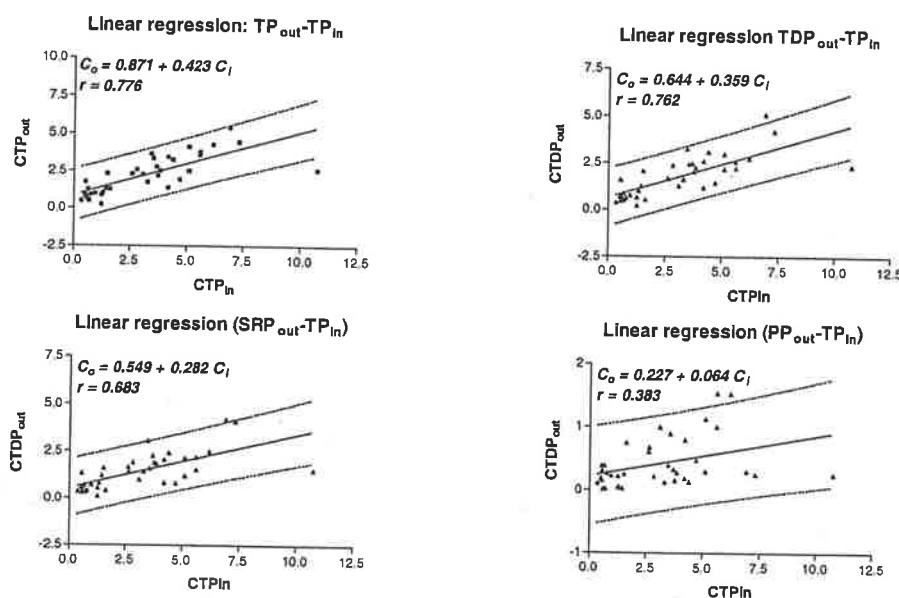


Figure 3-13. P removal in pond 1: relationships between effluent P (TP, TDP, SRP and PP) concentrations and influent TP levels. Dots, measured data; solid line, fitted linear relationship; dashed curves, the +/- 5% prediction limits.

3.2.2.2 Pond 2: no substrate and with planted floats

P removal efficiency and rate

As the introduced free floating water plants such as *Azolla* and duckweeds couldn't survive the drainage conditions, and simply died out, planted floats were introduced into the pond as an alternative to floating plants since September 2000 (See chapter three Methods and Materials for details of planted floats). Data from September 2000 to September 2001 were used to assess the performance of this pond.

During the operation period, the effluent concentrations of TP, TDP and SRP were statistically significant lower than the influent levels, while the difference for PP wasn't significant, showing that significant TP, TDP and SRP were removed by the pond. During the operation period, in total, 763.7g TP entered into the pond, of which 368.7g (48.3%) was detained by the pond, resulting in an average removal rate of $0.20\text{g/m}^2/\text{day}$.

The P removal rates had no clear seasonal pattern (Figure 3-14). However, the peak P removal happened in January to February, which is the hottest summer month in South Australia, and then decreased toward the valley value in July to August, which is close to the end of winter. The TDP and SRP removal pattern was identical to that of TP, indicating the intrinsic relationship between these variables. In other words, the removal of SRP contributed the most to the overall performance of the pond. Moreover, more SRP was removed than TDP when it was approaching the end of the growing season (Figure 3-14), providing indirect evidence of the transformation of SRP to soluble organic P. PP removal was more complicated with negative values at the start of growing season and peak value at full growth.

As there was no substrate in this pond, there was no problem of P release from sediments. It was shown clearly in Figure 3-14: there were not any negative values for PRE and PRR for TP, TDP and SRP, although there were some occasions when the effluent PP concentration was higher than the incoming PP.

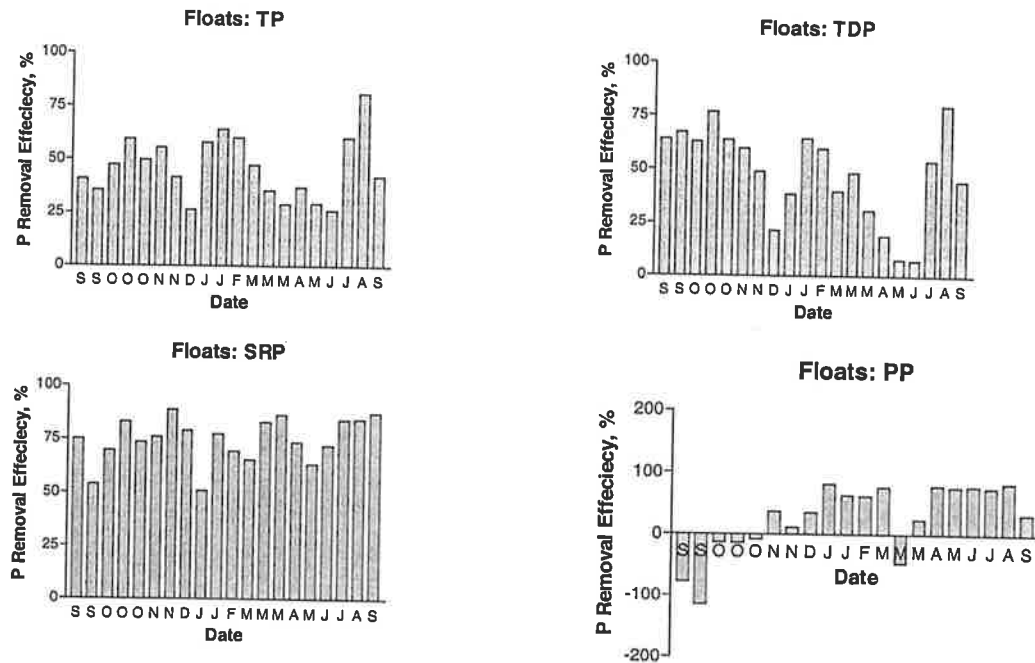


Figure 3-14. P removal in pond 2 during the implementation of planted floats (September 2000 – September 2001)

Relationships between influent and effluent P

From Table 3-8 and Figure E-2 and E-8, it was clear that the models as fitted had significant relationship with slope (b), but not with the Y-axis intercept (a), making pond 2 stands out from the experimental ponds. This means that the incoming P (in terms of both concentration and mass) was the governing factor for the performance of the system. A relatively constant fraction of the incoming P was retained by the system.

The effluent TP concentrations could be adequately predicted by the influent TP levels by the following linear regressive equation (3-14).

$$C_{out} = 0.06 + 0.54 C_{in} \quad (3-14)$$

C_{out} and C_{in} are the influent and effluent TP concentration.

The correlation coefficient $r = 0.835$, indicating a moderately strong linear relationship between the two variables. The determination coefficient statistically indicated that the fitted model explained 68.7% of the variability in effluent TP concentrations ($R^2 = 68.7\%$). In addition, as the Y intercept was statistically close to zero (0.063), it was safe to estimate

the TP concentration removal efficiency from the slope (a) by $(1-a) \times 100$. The result of 46.1% was very close to 42.3%, which was calculated from the annual average influent and effluent TP concentrations.

The replacement of concentration with mass marginally improved the power of prediction ($r = 0.842$, $R^2 = 70.0\%$). The effluent TP (mass) can be estimated from influent TP (mass) by equation (3-15).

$$M_{out} = 0.02 + 0.51 M_{in} \quad (3-15)$$

M_{out} and M_{in} are the influent and effluent TP in $\text{g/m}^2/\text{day}$.

The TP mass removal efficiency estimated from equation 3-15 was 48.9% $[(1-0.511) \times 100]$, which was close to 44.1% (Table 3-4) calculated from the total incoming and outputting TP for the whole operation period.

For other P forms, the effluent P (both mass and concentration) could also be estimated linearly by influent P. For example, the correlation coefficient (r) for the linear equation between influent and effluent SRP was 0.780, indicating a moderately strong linear relationship between the two variables. However, for PP, there were no significant linear relationships between influent and effluent P for both concentration and mass, indicating that rapid transformations of P forms may occur.

3.2.2.3 Pond 3: pond with P rich substrates and submergent water plants

Performance of pond

The overall performance of this pond was the poorest amongst the experimental ponds (Table 3-5). During the operation period of two years, the system actually released 3.1g TP and had a negative removal efficiency of -0.5%. Figure D-3 and D-9 showed that the pond released TDP most of time. In addition, as shown in these figures, the release/removal of TDP and SRP wasn't synchronized, i.e. while on some occasions the system removed TDP, the SRP was actually released, and on other occasions, the opposite situation would occur. This phenomenon indicates the fast transformation of the dissolved organic P to dissolved inorganic P in the system. The pond was less efficient to remove P even when it was on full

operation (summer). During the second summer, the mean TP removal rate was $0.058\text{g/m}^2/\text{day}$ (18.6%) with a peak of $0.206\text{g/m}^2/\text{day}$ (53.3%) in April. Furthermore, a large amount of SRP was released in winter.

Relationships between influent and effluent P

The goodness-of-fit of the linear models for influent and effluent P in pond 3 was poorer than in pond 1 and pond 3 (Table 3-8, 3-9). However, a moderately strong relationship existed between the influent and effluent TP for both concentration and mass (Figure E-3 and E-9, $r = 0.684, 0.607$ for concentration and mass respectively). In addition, the relationship for TDP was also significant.

3.2.2.4 Performance of the three-pond system

Performance of the system

In terms of P removal efficiency, the whole system including the three ponds i.e. pond 1, 2 and 3 in series performed well. As drainage flowed through the three ponds, 57.5% of the incoming TP was retained in the ponds (Table 3-5). The pond system was especially effective to trap particulate P: nearly 80% of the incoming PP was retained in the system. The processing of SRP was also effective: the effluent SRP was only 31.7% of the incoming SRP. However, in terms of P removal rate, the system was less efficient to remove TP than most of the individual ponds except pond 3. Moreover, for SRP, the majority P in drainage, the system was more efficient than pond 1 and pond 3 but less effective than pond 2 and ponds with P poor soil as substrates.

As the lump effectiveness of three ponds, the performance of the system displayed clear seasonal patterns for all P forms (Figure 3-14, D-4): the system was more effective in summer and less efficient in winter. For example, in the second summer (September 2000 – April 2001), significant amount of P were removed by the ponds. The removal rates of 0.186, 0.135, 0.135 and $0.068\text{g/m}^2/\text{day}$ were achieved for TP, TDP, SRP and PP respectively. From April to September 2001, these numbers dropped more than half for TP, TDP 0.067 and $0.046\text{g/m}^2/\text{day}$. The decrease for SRP was more significant, in winter the SRP removal rate was less than 1/5 of that in summer. However, the decrease for PP removal was less significant (Table 3-14). As the P loadings were less in winter, the

comparison of P removal efficiencies, which are relatively independent of P loadings, could be more realistic. The P removal percentages also dropped in winter for TP, TDP and SRP although the reductions were less significant. However, the PP removal efficiency increased. An obvious explanation was that the processing of SRP depends on the biological activities of biota especially water plants in ponds, while the retention of PP, to some degree, was a physical filtration process.

Table 3-14, Comparison of the performance for 3-pond system in summer and in winter.

	TP		TDP		SRP		PP	
	g/m ² /day	%	g/m ² /day	%	g/m ² /day	%	g/m ² /day	%
09/00 - 04/01	0.186	68.3	0.135	67.5	0.135	82.2	0.065	75.2
05/01 - 09/01	0.069	52.8	0.046	45.1	0.025	36.1	0.056	91.5

The identical patterns of TP, TDP and SRP removal (Figure 3-14) revealed the importance of dissolved P in drainage. To achieve better P removal performance, processes that are involved in the transformation and retention of dissolved P, such as plant uptake, sediment adsorption, and coprecipitation, should be emphasized.

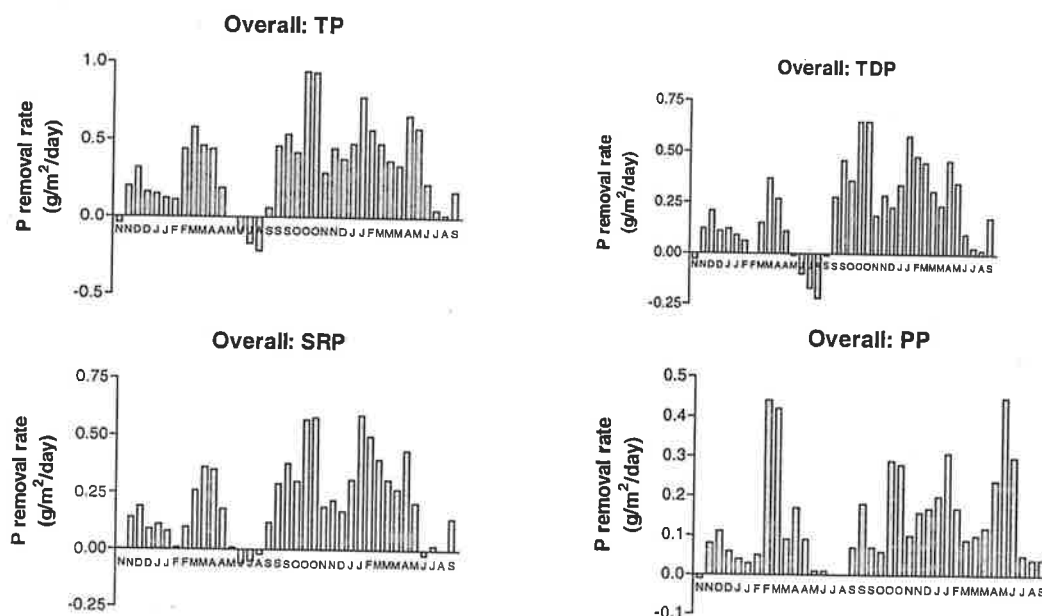


Figure 3-15. P removal rate in the 3-pond system.

Relationships between influent and effluent P

There were weakly significant linear relationships between influent and effluent TP and SRP for both mass and concentrations (Table 3-8, Figure E-4, E-10). For TDP and PP,

there were no significant relationship for mass, but weakly relationship for concentrations. The application of non-linear models could improve the power of prediction marginally (Table 3-10).

Nevertheless, the P retained by the system could be estimated from incoming TP concentration by a modified Langmuir equation (Equation 3-16):

$$S = S_{max} \times K \times C_{TPi} / (1 + K \times C_{TPi}) - S_0 \quad (3-16)$$

Where S , P retained in system $\text{g/m}^2/\text{day}$; and S_0 , the background P in the system;

C_{TPi} influent TP concentration (mg/l);

S_{max} , Maximum P could be retained by the system ($\text{g/m}^2/\text{day}$);

K , constant, which is associated with the various pathways of P in system.

The equation plotted with the measured data was presented in Figure 3-16. The constants for the equation (3-16) were:

$$S_{max} = 0.391 \text{ (g/m}^2/\text{day)},$$

$$K = 0.211, \text{ and } S_0 = 0.027 \text{ (g/m}^2/\text{day)}.$$

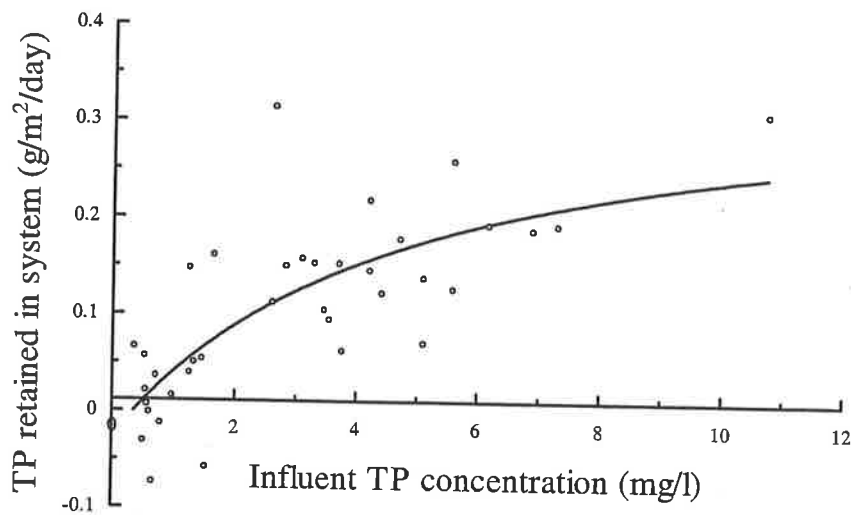


Figure 3-16. A model describes the relationship between P retained by system and influent P concentrations. Dots were measured data, and the curve represented the fitted model. Negative value shows that the system exports P when P loadings are low.

The multiple correlation coefficient (r) of the model as fitted was 0.753, which indicated a relatively strong relationship between the influent TP concentration and P retained by the system. The coefficient of determination, $R^2 = 56.8\%$ showed that the model as fitted could explain 57.2% of the deviation in P retained by the system. The ANOVA results revealed that the fitted model has no significant relationships with the three constants listed above. Consequently, these constants can be treated as the intrinsic characteristics of the system, defined by the regional climate, substrates and water plants used, and are independent of influent P levels.

The S_{max} , which was defined as the maximum P retention capacity of the system was $0.391 \text{ g/m}^2/\text{day}$. During the two years of operation, the highest value of P removal rate was $0.315 \text{ g/m}^2/\text{day}$ on October, 2001, which fell into the region of predicted value. However, the lowest value of $-0.073 \text{ g/m}^2/\text{day}$ was slightly out of the predicted region $-0.027 \text{ g/m}^2/\text{day}$.

P mass balance

During two years of operation, 1555.9g of TP entered the system with drainage water, as the water flowed through the three ponds, 894.7g or 57.5% was retained in various components i.e. sediment, biofilm and water plants of the system. For SRP, 591.2g out of 865.6 (68.3%) was removed by the system. Of the incoming TP, 865.6g or 71.5% was in dissolved forms and about 36.4% was associated with particles, e.g. soil and plant materials. The effluent, however, contained less PP (17.6%) and the percentage of dissolved P increased to 82.4%. Furthermore, the ratio of SRP to TDP decreased sharply from 77.8% in the drainage to 50.3% in the effluent, indicating the system was effective in transforming SRP to organic P. As the organic P in PP was difficult to distinguish from inorganic forms, it was hard to evaluate the overall transformation rate of soluble inorganic P to organic P. However, the dramatically increased chlorophyll a concentrations in the effluent indicated indirectly that the PP in effluent might be organic P associated with living phytoplankton biomass.

3.2.2.5 Pond 4: the Pond with P Poor Substrates and Macrophytes

Amongst all the experimental ponds, pond 4 was the most efficient system for TP, TDP and PP removal. For SRP, it was second only to pond 2 (Table 3-5). From September 2000 to

September 2001, a total of 1802.7 g of TP entered the pond, carried by drainage, of which 921.1 g (44.3%) was retained in the system, resulting in an average TP removal rate of 0.220 g/m²/day.

The seasonal P removal pattern was very clear with the peak value happening in summer (October) and the valley in winter (July and August) (Figure D-5 and D-12) for TP, TDP and SRP. However, for PP, this pattern was missed: the valley removal rate was in February and March (-0.06 and -0.02g/m²/day for February and March, respectively) corresponding to the hottest month in South Australia.

The all-time highest TP removal rate for the five experimental ponds of 0.772g/m²/day was achieved in this pond in late October. During the same period, the highest SRP removal rate of 0.481g/m²/day was the all-time highest amongst the ponds.

3.2.2.6 Pond 5: the Pond with P Poor Substrates and Free of Macrophytes

The pond 5 was less efficient than pond 4 and pond 2 but was more effective than pond 1 and 3 for the P forms of concern, i.e. TP, TDP and SRP (Table 3-4). It was the least efficient pond for PP removal. During the period of operation, 1785.3 g of TP entered into the pond, and 1285.3g flowed out of it, resulting in a removal rate of 0.138 g/m²/day (removal efficiency, 27.9%, Table 3-5).

The seasonal P removal patterns in pond 5 were not as clear as in other ponds (Figure D-6 and D-12). However, the pond was a net source of PP from early January to late March corresponding to the growth of phytoplankton (Figure 3-17). As phytoplankton stays within the water column and flows out of the pond with the effluent, it might be the main contributor of PP.

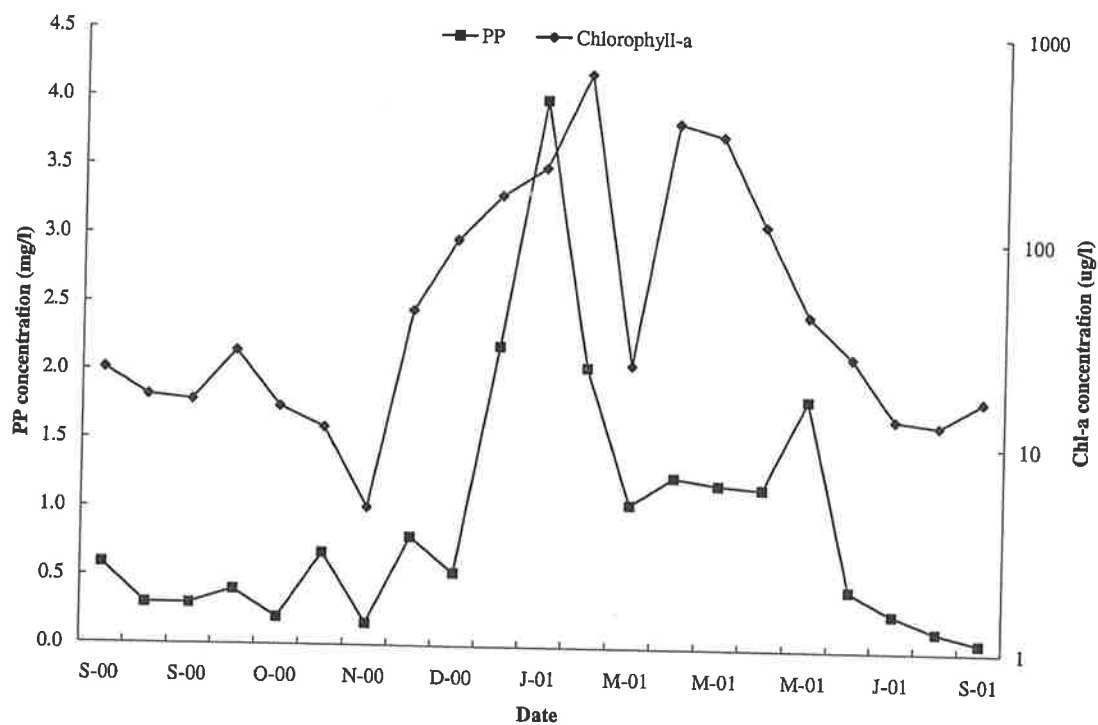


Figure 3-17. The relationship between PP and chlorophyll-a concentrations in pond 5. Note the synchronized trends of the two parameters.

3.3 P INCORPORATED INTO WATER PLANT BIOMASS

3.3.1 Planted floats

3.3.1.1 Growth Chamber Trial

Growth of water plants

Three (parrot feather, water couch and waterbuttons) of the four test species showed positive growth on the water surface under all treatments. As water primrose showed only negligible growth in all floating floats, and therefore, it was excluded from further analysis. After 70 days of growth, the mean float biomass ranged between 51.8 g and 192.0 g dry matter per float (Table 3-15). At high nutrient level, the biomass composition of each float ranged as follow: water couch>waterbuttons>parrot feather. At low nutrient levels, however, the waterbuttons was the main contributor, followed by parrot feather and water couch.

Table 3-15. Biomass produced and growth rate of the tested water plants during 70 days cultivation under 4 treatments

Species	HNLS		HNHS		LNLS		LNHS	
	DW	GR	DW	GR	DW	GR	DW	GR
Water Couch	82.32 ^a	13.07	76.22 ^a	12.10	8.88 ^b	1.41	12.64 ^b	2.01
Parrot feather	44.87 ^a	7.12	31.38 ^a	4.98	12.66 ^b	2.01	11.18 ^b	1.77
Waterbuttons	64.81 ^a	10.29	68.63 ^a	10.89	30.24 ^b	4.80	30.16 ^b	4.79
Total	192.00		176.23		51.78		53.98	

HNLS: high nutrients low salinity, HNHS: high nutrients high salinity, LNLS: low nutrients low salinity, LNHS: low nutrients high Salinity;

DW: dry weight (g), GR: plant productivity (g/m²/day);

Means (n=2) in the same row followed by the same letter indicate no significant difference (P=0.05) from each other according to paired sample t-test.

As expected, nutrient enrichment had positive influence on plant growth. Under low salinity treatment, dry matter at high nutrient treatment was 9.3, 3.5, and 2.1 times higher than those at low nutrient level for water couch, parrot feather and waterbuttons, respectively. At higher salinity level, there was a smaller difference in biomass between the high and low nutrient treatments, where the dry weight of high nutrient level was 6.0, 2.8, and 2.3 times higher for water couch, parrot feather and waterbuttons, respectively. While nutrient enrichment increases growth of all species, the differences in biomass and plant

productivity between the salinity treatments were not significant for the three species at each nutrient level.

Plant tissue P concentrations

The P concentrations in plant tissue are presented in Table 3-16. At both salinity levels, waterbuttons had the highest tissue P concentration, and P content in water couch was the lowest. The tissue P concentrations in water couch increased with TP level in solution, but P concentrations in waterbuttons and parrot feather were very close under different treatments, indicating that the water TP concentrations had no significant effects on P level in waterbuttons and parrot feather. However, comparing with plants growing in wetlands, the cultured plants had significant higher tissue P concentrations, except for water couch grown under low nutrient conditions.

P bioaccumulation rate

Table 3-17 presents the results of P bioaccumulation in tested plants. After 70 days' growth, P incorporated into plant biomass ranged from 0.27 g per float under low nutrient and high salinity (LNHS) to 1.08 g per float under high nutrient and low salinity (HNLS).

Table 3-16. P concentration in plant tissue (%) cultivated in four treatment solutions*

Species	HNLS	HNHS	LNLS	LNHS	Wetland
Water Couch	0.50 ^a	0.46 ^a	0.26 ^b	0.27 ^b	0.26 ^b
Parrot feather	0.54 ^a	0.57 ^a	0.50 ^a	0.43 ^a	0.24 ^b
Waterbuttons	0.65 ^a	0.64 ^a	0.63 ^a	0.62 ^a	0.43 ^b

Means (n=2) in the same row followed by the same suffix indicate no significant difference (P=0.05) from each other according to paired sample t-test.

* See Table 3-14 for explanations for treatment solutions.

Table 3-17. Floats P removal mass (g) and rate (g P m⁻² day⁻¹) after 70 days cultivation and the contribution of species

Species	HNLS		HNHS		LNLS		LNHS	
	g	%	g	%	g	%	g	%
Water Couch	0.41	38	0.35	36	0.02	8	0.03	12
Parrot feather	0.24	23	0.18	19	0.06	22	0.05	18
Waterbuttons	0.42	39	0.44	45	0.19	70	0.19	70
Whole float	1.08	100	0.97	100	0.27	100	0.27	100
Bioaccumulation	0.086		0.073		0.044		0.043	

* See Table 3-14 for explanations for treatment solutions.

P removal rate ranged from 0.043-0.086 g/m²/day. Of the total P removed by float, waterbuttons accumulated more P compared with water couch and parrot feather. Under low nutrient levels, waterbuttons contributed up to 70% of the total removed P due to its ability to uptake P at low P concentration (waterbuttons had the highest tissue P concentration of 0.62-0.63% under low P treatment). Under high P level, water couch's contribution increased (38%, 39% at low and high salinity level, respectively) as both biomass and tissue P content increased. In addition, salinity had little impact on the performance of waterbuttons and water couch, while reducing the growth of parrot feather.

3.3.1.2 Field pilot experiment

Waterbuttons and water couch were the two species which grew robustly in the pond. It is worth to point out that aboveground parts of the plants were alive in the pond during winter although the growth was ignorable while they died in their native habitats. The other two species died in the first month of experiment. The seasonal change of vegetation was noticeable: the floats were colonized by Waterbuttons until early December (about 90 days). In other months, Waterbuttons was replaced by water couch (about 152 days). Although the lifecycle of Waterbuttons is shorter, it contained significant higher level of P than water couch (Table 3-18). In addition, the production of the species was similar. As a result, the P removal rate by crop harvesting was higher in the phase of Waterbuttons domination (0.103 and 0.082 g/m²/day for Waterbuttons and water couch, respectively, Table 3-18).

Table 3-18. Biomass, tissue P concentrations and P removed by floats

	Biomass kg per float	P concentration G/kg	Biomass P g	P Removal rate g/m ² /day
Waterbuttons	1.09 ± 0.388	4.25 ± 0.044	46.36 ± 0.699	0.1030
Water Couch	3.05 ± 0.523	2.07 ± 0.074	63.26 ± 1.239	0.0819
Total	8.054		109.62	0.0906

Mean ± Standard Deviation, n = 5;

The overall P removal rate was calculated by: total biomass P divided by surface area and growth days.

A total of 80.54 kg dry biomass was harvested from the floats during the growth season of 2000 – 2001 (242 days). Correspondingly, 109.62 g of P was removed from the pond through biomass harvesting (Table 3-18). At the same period, the total incoming TP was

603.29g, of which 292.05g was removed by the pond (Figure 3-12). Biomass harvesting contributed 37.53% of the overall TP removal.

3.3.2 Emergent Plants in Pond 1

3.3.2.1 Plant performance

Growth characteristics of reed

Of the three introduced plant species, only common reed had measurable growth during the three years of operation. The growth of bulrush and cattail was obviously stressed and suppressed. Consequently, reed was the only specie closely monitored in the study. Figure 3-18 represented the average growth of individual tagged shoots. The shoot elongated rapidly in late October and then kept stable towards the end of the growth season in May (Figure 3-18A). The diameter at base, however, remained relatively unchanged for the whole growth season (Figure 3-18B). The increase in axillary shoots stopped in late December (Figure 3-18C). As a result, the shoot biomass increased quickly in late October and remained its peak value until the plant finished its lifecycle (Figure 3-18D).

Multiple regressive equation

Results of stepwise multiple regression analysis were summarized in Table 3-19. The first step included all measured phenometric parameters: height (*Hght*), diameter at base (*Di@base*), number of axillary shoots (*#Asht*), number of leaves (*#lfs*) and number of nodes (*#nds*). Since the highest P value was 0.9317, belonging to *#nds*, it was reasonable to remove the variable from the equation in order to simplify the model. Exclusion of the parameter of *#nds* slightly improved the prediction power of the multi-regressive model (R^2 -adjusted increased to 97.13% and the standard error of estimation decreased to 0.5603). However, the highest P value was 0.3764, belonging to *#lfs*, greater than 0.1, indicating the term wasn't statistically significant at 90% or higher confidence level. Excluding *#lfs* could simplify the model, and may not undermine the power of prediction. Results showed that the R^2 -adjusted increased marginally and the standard error of estimation decreased a little (Table 3-18). The third step of analysis included three independents, i.e. *hght*, *Di@base* and *#Asht*. The highest P value was 0.0403, belonging to *#Asht*. Since the P value less than 0.05, *#Asht* was significant to the DW at 95% confident level. Consequently, removing any

of the variables from model could reduce the prediction power. The final fitted regressive model was shown in equation (3-17) ($r = 0.9653$) as follow:

$$DW = -7.43371 + 9.16109 \times Hght + 5.44155 \times Di@base + 0.523671 \times \#Asht \quad (3-17)$$

Where,

DW , dry biomass (g); $Hght$, shoot height (m); $Di@base$, diameter at base (cm);

$\#Asht$, number of axillary shoots, dimensionless.

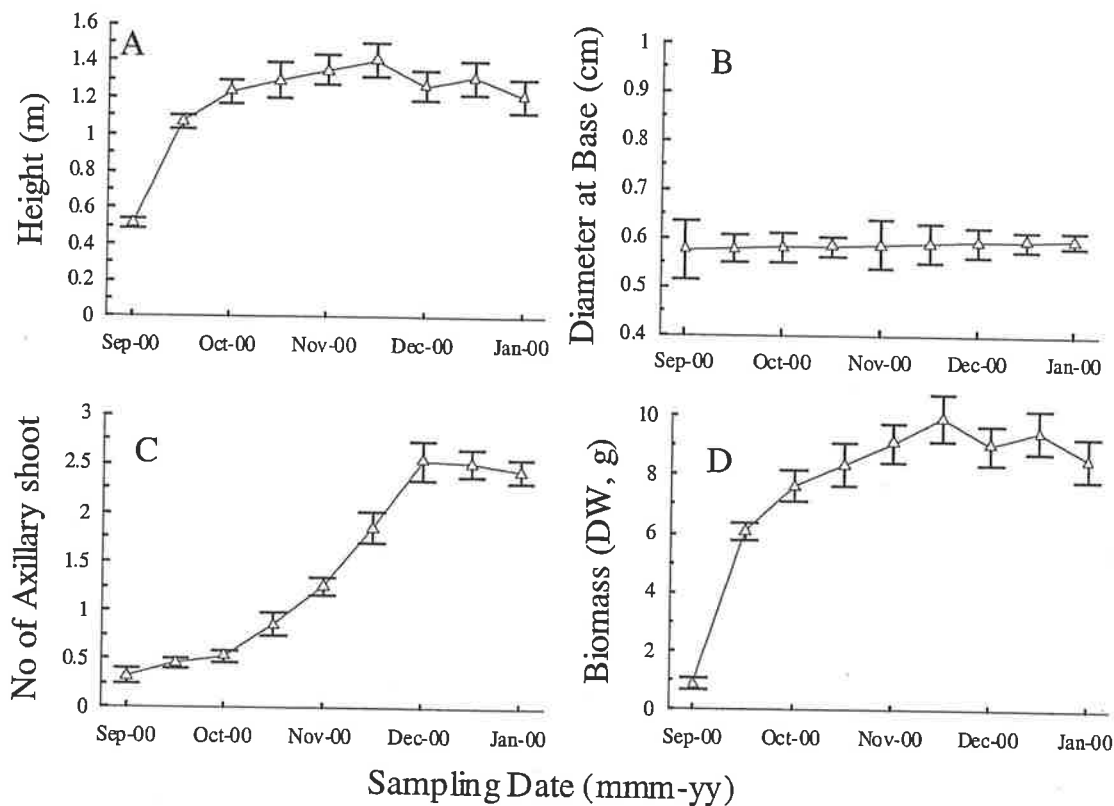


Figure 3-18. Graphs show temporal variations in shoots height (A), diameter at base (B), number of axillary shoots (C), and aboveground biomass (D). Triangles were the means of ten samples and bars were the standard errors.

Together with the number of shoots, which was surveyed in monthly intervals in a fixed plot (0.25m^2) during one growth season of 2000-2001, equation (3-17) was used to estimate the aboveground biomass of reed in the pond. The results, together with tissue P concentrations and P stored in aboveground biomass, were presented in Figure 3-19. The aboveground biomass had no clear peak. Following a rapid increase from early spring to

the start of summer, the aboveground biomass stayed quite stable from late November until the end of growth season.

Table 3-19. Stepwise multiple regression between biomass (DW, g) and the measured phenometric parameters.

Step No.	1					2				3		
Variable	H	D	Asht	Lfs	Nds	H	D	Asht	Lfs	H	D	Asht
P-value	0.014	0.015	0.167	0.409	0.932	0.008	0.007	0.137	0.376	0.000	0.004	0.040
R ² (%)	96.7					97.1				97.2		
SE of Est.	0.599					0.560				0.557		

H, shoot height (m); D, diameter at base (cm); Asht, number of axillary shoots; Lfs, number of leaves per shoot; Nds, Number of nodes per shoot.
SE of Est., standard error of estimation.

3.3.2.2 Tissue P concentration

The change of P contents in shoot was of particular interest if harvesting of the standing crop would be implemented for stopping the P cycle in ponds. In one lifecycle, the shoot P concentration in reed peaked (0.35%) once in late November, after which the P levels dropped sharply to the middle of December (0.20%): decreased nearly one-third within half a month. From late December, reed entered the phase of slow decrease of its shoot P concentration (about 0.09% in late May) (Figure 3-19).

3.3.2.3 P incorporated into aboveground biomass

P incorporated into aboveground biomass was calculated by multiplying the P concentration with aboveground biomass. Figure 3-19 summarises the temporal change of aboveground biomass, shoot P concentration and P incorporated into shoot biomass. As P concentration had a peak in late November and the aboveground biomass had no clear peak, the P stored in shoot biomass had a peak coincident with tissue P content. Consequently, to remove the maximum P from the system by harvesting, the best harvest timing was late November, and about 13.5g/m² of P could be removed.

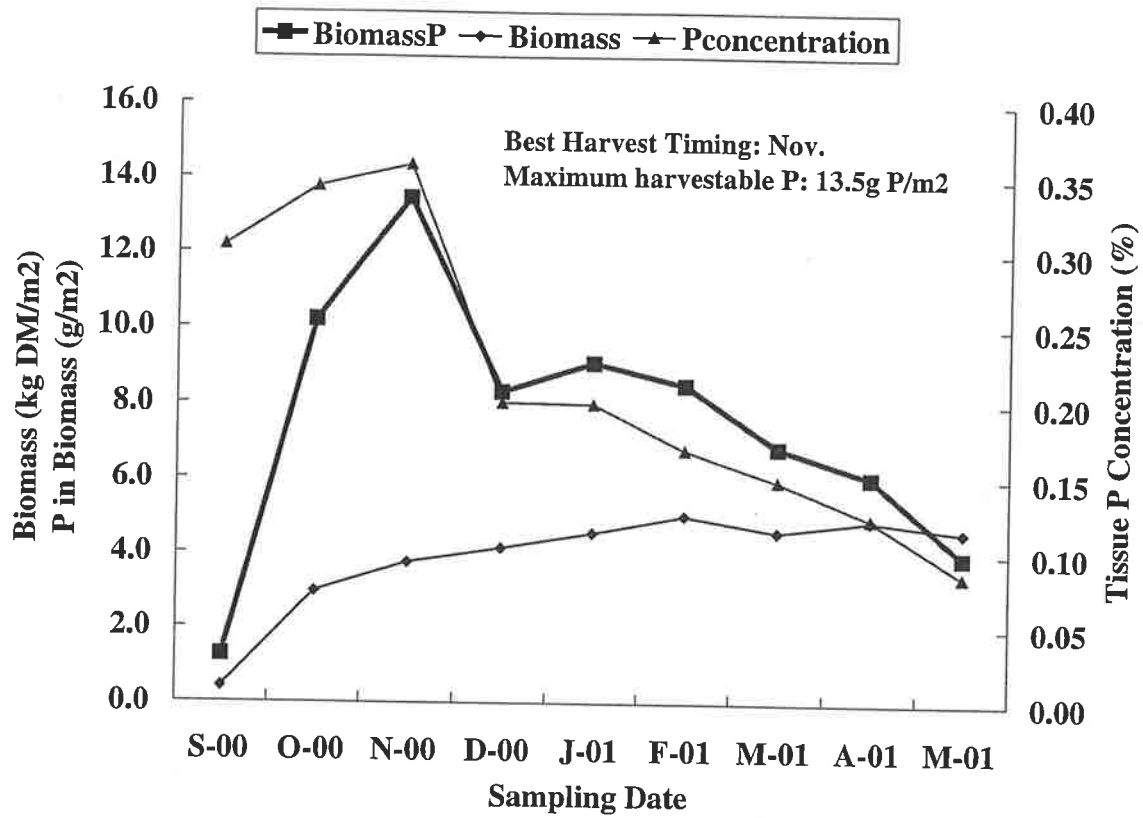


Figure 3-19. The aboveground biomass, tissue P concentrations, and aboveground biomass P of reed during the growth season of 2000 – 2001

3.4 SEDIMENT P DYNAMICS

3.4.1 P fractionation

The soil/sediment P fractionation procedure distinguished the TP into five P pools: loosely adsorbed P, labile organic P, Fe/Al-P, Ca/Mg-P and residual P, based on their solubility in NH_4Cl , NaOH and HCl extracting solutions (Figure 3-20).

The topsoil from the site had a relatively high TP concentration of 828.2 mg/kg as result of the long-term agricultural usage (Figure 3-20A). The majority (62.6%, 518.5mg/kg) of P was bonded by Fe, Al, which is sensitive to the redox potential. Interestingly, the labile organic P pool was not significant, only accounting for 9.6% of the TP or 79.5mg/kg accumulated in soil. However, the Res-P pool, which contains mainly the resistant organic P accounted for 14.5%. The loosely bonded P, extracted by NH_4Cl solution, which is believed to represent the readily bio-available P pool (Psenner *et al*, 1988), was relatively small (0.8%).

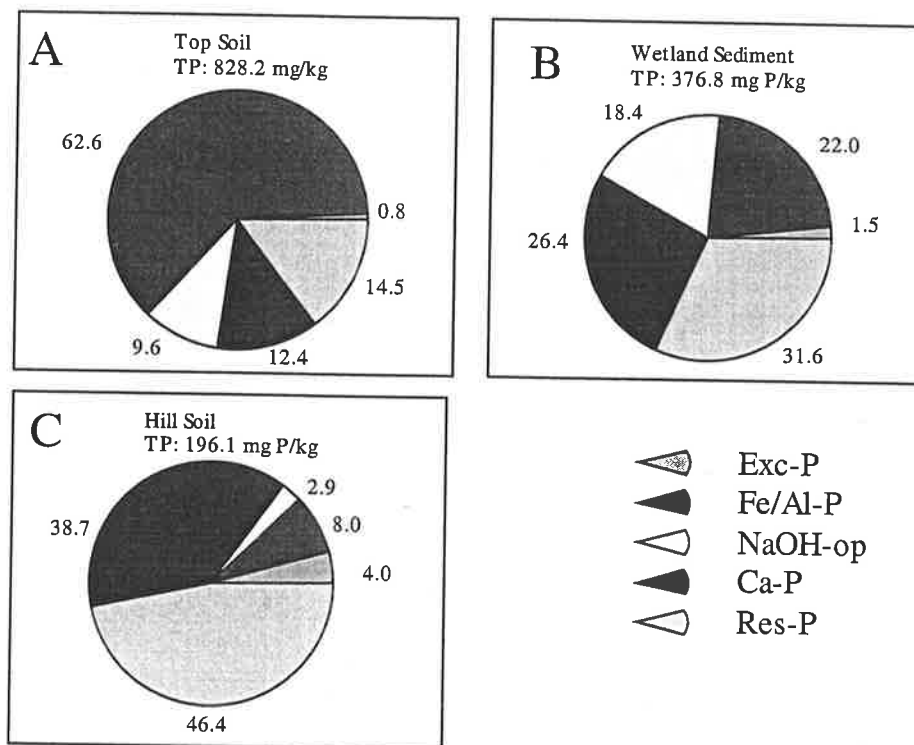


Figure 3-20. P pools in Soils/sediment: A, Topsoil; B, Sediment from Reedy Creek Wetland; C, Soil from nearby hill. Data are showed as percentage of the TP. Exc-P, loosely absorbed P; Fe/Al-P, Fe/Al bound inorganic P; NaOH-op, labile organic P; Ca-P, Ca, Mg bound inorganic P, Res-P, resisted organic and inorganic P.

The soils from the hill had significant lower P (ANOVA, $P < 0.0001$) concentration than the soils from the site (Figure 3-20). Contrasting to P-rich soils, the dominant P pools were Ca-P (38.7%) and Res-P (46.4%) other than Fe/Al-P (8.0%) (Figure 3-20C). This characteristic may mean that the P-poor soil had distinguishing behaviors compared with P-rich soil after inundation as the Ca/Mg-P isn't sensitive to the redox potential but to pH.

The sediment for natural wetlands contained moderate TP level, with residue P as the dominated P form and almost equal amounts of Ca/Mg-P and Fe/Al-P and LOP (Figure 3-20B). Only a small fraction of the TP was loosely bound P, which is believed to be biological active.

3.4.2 Dynamics of sediment P pools

3.4.2.1 Soil/Sediment P Dynamics in Pond 1 and Pond 2

After flooding, the TP levels dropped rapidly in the first 3 months, 51% and 36% reduction for pond 1 and pond 3, respectively (Figure 3-21). As mentioned above, large pool of P bonded by Fe released to the overlaying water under flooding condition (anaerobic). Regarding P loss, the Fe/Al-P pools contributed the most, which may indicate that this P pool is mainly associated with Fe, as the Al-P was considered as relatively stable in environment. In pond 1, Fe/Al-P reduced by 269.7 mg/kg, contributed the most P release of 63%, followed by Ca-P (77.4 mg/kg, 18%), NaOH-orP (54.3 mg/kg, 13%) and Res-P (26.0 mg/kg, 6%). In pond 3, the order of contribution was Fe/Al-P (152.3 mg/kg, 51%), Res-P (68.6 mg/kg, 23%), Ca-P (51.6 mg/kg, 17%) and NaOH-orP (36.2 mg/kg, 12%).

After the pulse release of P, P release slowed down. For pond 1, in the next 3 months, TP in sediment dropped only 13% from 402.3 to 372.3 mg/kg. The Fe/Al-P was still the biggest contributor (43.0 mg/kg, 84%), followed by Res-P (25.2 mg/kg, 49%). The Ca-P pool increased 10.7 mg/kg by 42%, and NaOH-orP (labile organic P) pool increased by 43% (10.9 mg/kg), indicating that coprecipitation of P with Ca and (or) Mg may occur in the system, and the increased organic P pool in sediment. For pond 3, the trends were similar. TP dropped 107.1 mg/kg (20%). However, the release of Fe-P was still significant (from 366.4 to 177.2 mg/kg). A drop of 189.2 mg/kg, which was bigger than the reduction of TP,

means that there were other mechanisms adding P to sediment, i.e. coprecipitation and the settlement of phytoplankton. The increases in Ca-P, and labile organic P pools were more obvious than in pond 1 (increases of 54.0, and 46.4 mg/kg for Ca-P and NaOH-orP, respectively).

After the release of the original accumulated P, the P levels in sediment increased slowly. From March to June, TP level in pond 1 increased slightly (6.3%), while the P pools were barely changed except the Res-P (increased 35.2%). However, the TP increase was significant in pond 3 (21.2%). The increases for labile organic-P, Ca-P and Res-P were 26.5%, 19.6% and 152.2%, respectively.

Sediment TP in both ponds shared the same trend although the magnitudes differed: decreased in the first 6 months after flooding and then increased slowly (Figure 3-21). The dynamic of sediment TP could be divided into three phases: pulse release, stabilization and build-up.

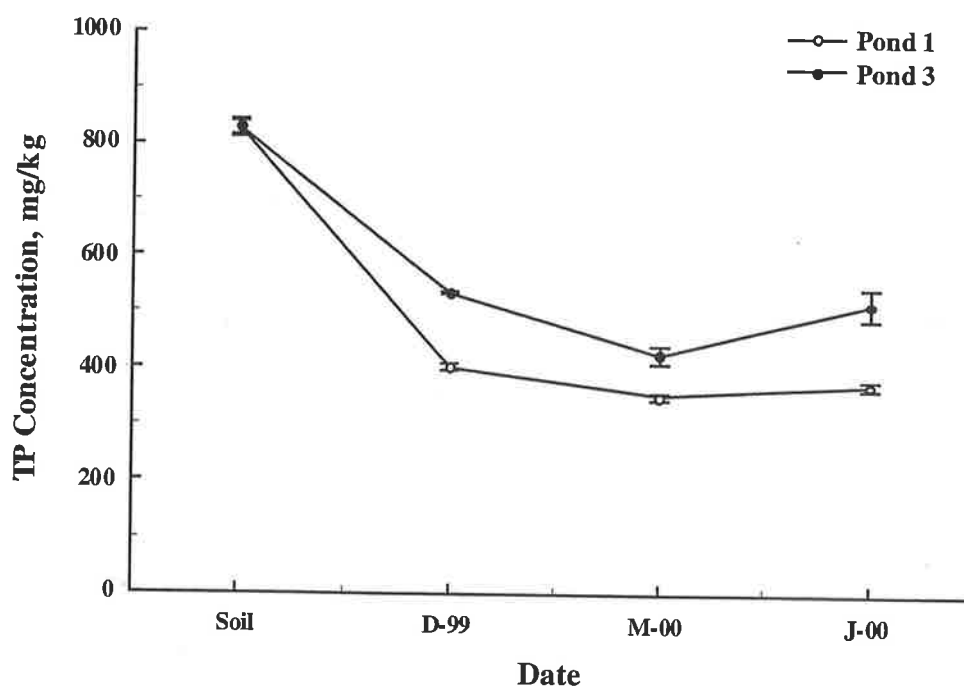


Figure 3-21. Temporal patterns of TP concentrations in sediments: means $\pm$ SE ($n = 3$). Soil means the initial TP level before the introduction of drainage.

Phase I was the first 3 months after flooding. During this period, the TP levels dropped rapidly, 51% (from 828.2 to 402.3 mg/kg) and 36% (from 828.2 to 533.4 mg/kg) reduction for the pond 1 and pond 3, respectively. One of the most obvious features in phase I was that all sediment P pools decreased except the loosely adsorbed P (Figures 3-22 and 3-23). In pond 1, Fe/Al-P reduced by 269.7mg/kg, contributed the most P release of 63%, followed by Ca-P (77.4 mg/kg, 18%), NaOH-orP (54.3 mg/kg, 13%) and Res-P (26.0 mg/kg, 6%). In pond 3, the order of contribution was Fe/Al-P (152.3 mg/kg, 51%), Res-P (68.6 mg/Kg, 23%), Ca-P (51.6 mg/kg, 17%) and labile organic P (36.2 mg/kg, 12%). As Fe/Al-P was the dominant P form in the soils (Figure 3-20), the sediment TP dynamics were identical to that of Fe/Al-P (Figure 3-22A). Furthermore, the Fe/Al-P pools reduced the most, which may indicate that this P pool is mainly associated with Fe, as the Al-P was considered as relatively stable in the environment, and P bonded by Fe released to the overlaying water under flooding conditions (anaerobic). As for the loosely absorbed P, the most dynamic P pool that include P in the porewater in sediment, marginally increased from 6.6 to 8.0 mg/kg in pond 1 (21%), from 6.6 to 20.4mg/kg (210%) in pond 3.

Phase II was the following 3 months: a period of stabilization featured by the increase in some P pools and decrease in others. After the pulse release of P, TP level drops slowed down: in pond 1, TP in sediment dropped only 13% from 402.3 to 372.3 mg/kg, and in pond 3, the decrease was much higher: TP level decreased 20% (107.1 mg/kg reduction). During phase II, some P pools continuously decreased, i.e. Fe/Al-P (Figure 3-22A), loosely absorbed P (Figure 3-23A) and residual P (Figure 3-24). Other P pools, i.e. Ca/Mg-P (Figure 3-22B) and labile organic P (Figure 3-23B), however, increased. In pond 1, Fe/Al-P decreased by 43.0 mg/kg (17%), and was the P pool that dropped the most. The residual P also decreased 25.2 mg/kg (27%). However, the Ca-P and labile organic P pools increased (10.7 mg/kg by 42% and 10.9 mg/kg by 43% for Ca-P and labile organic P, respectively) indicating coprecipitation of P with Ca and (or) Mg might occur in the system, and the increased organic P pool in sediment. In pond 3, the trends were similar. Interestingly, the reduction of Fe-P (from 366.4 to 177.2 mg/kg, a decrease of 189.2 mg/kg) was bigger than the reduction of TP (107.1 mg/kg) indicating the importance of P adding processes, i.e. coprecipitation and settlement of phytoplankton. In fact, the increases in Ca-P and labile

organic P pools were more obvious than in pond 1 (increases of 54.0, and 46.4 mg/kg for Ca-P and NaOH-orP, respectively).

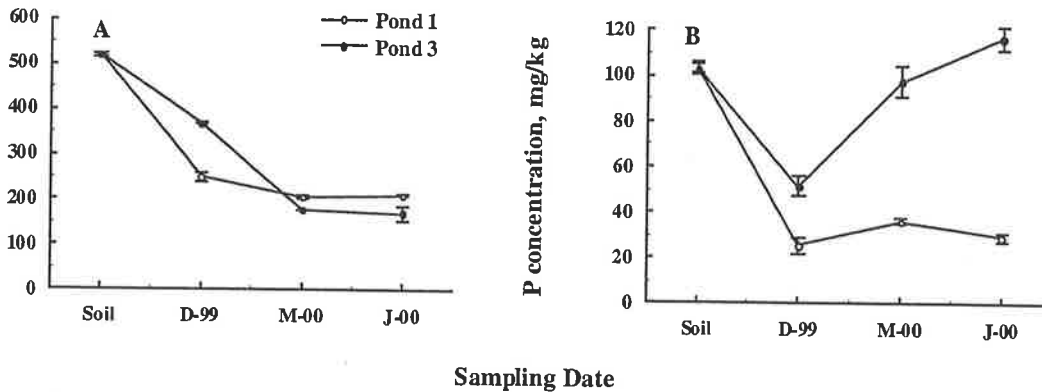


Figure 3-22. Temporal patterns of Fe, Al-P (A) and Ca-P (B) concentrations in sediments: means $\pm$ SE ($n = 3$).

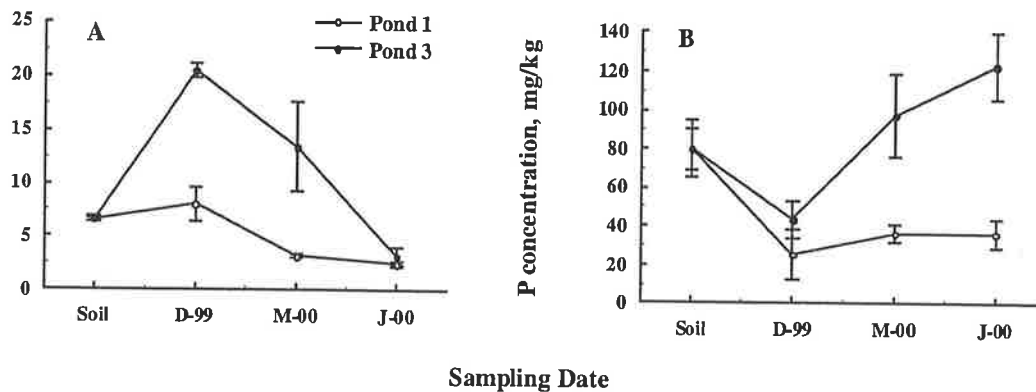


Figure 3-23. Temporal patterns of Loosely absorbed P (A) and labile organic P (B) concentrations in sediments: means $\pm$ SE ($n = 3$).

Following the phase of stabilization, the P levels in sediment built up slowly (phase III). From March to June 2001, TP level in pond 1 increased slightly (6.3%). In pond 3, the increase was more obvious: after three months, the sediment TP concentration increased 90.3 mg/kg from 426.3 to 516.6 mg/kg (21.2%). As the sediment TP built-up, the components of TP between the two ponds became significantly different, indicating the divergence of P removal processes as the results of the water plants employed. For example, in pond 1, the Ca/Mg-P and labile organic P pools were 7.9% and 9.8% of TP, respectively. In pond 3, however, 22.6% and 23.9% of TP were Ca/mg-P and labile organic P (Table 3-20).

In both ponds, Fe/Al-P, which was once the dominant P pool in soils and sensitive to redox potential, barely changed (2% and -3% in the pond 1 and pond 3, respectively, Figure 3-22A). In addition, although it was still the dominant P in sediment from pond 1, Fe/Al-P was only slightly higher than Ca-P and labile organic P and residual P in sediment from pond 3 (Table 3-19). Different from in pond 1, the labile organic P and Ca-P increased rapidly in pond 3 (Figure 3-22B, 3-23B).

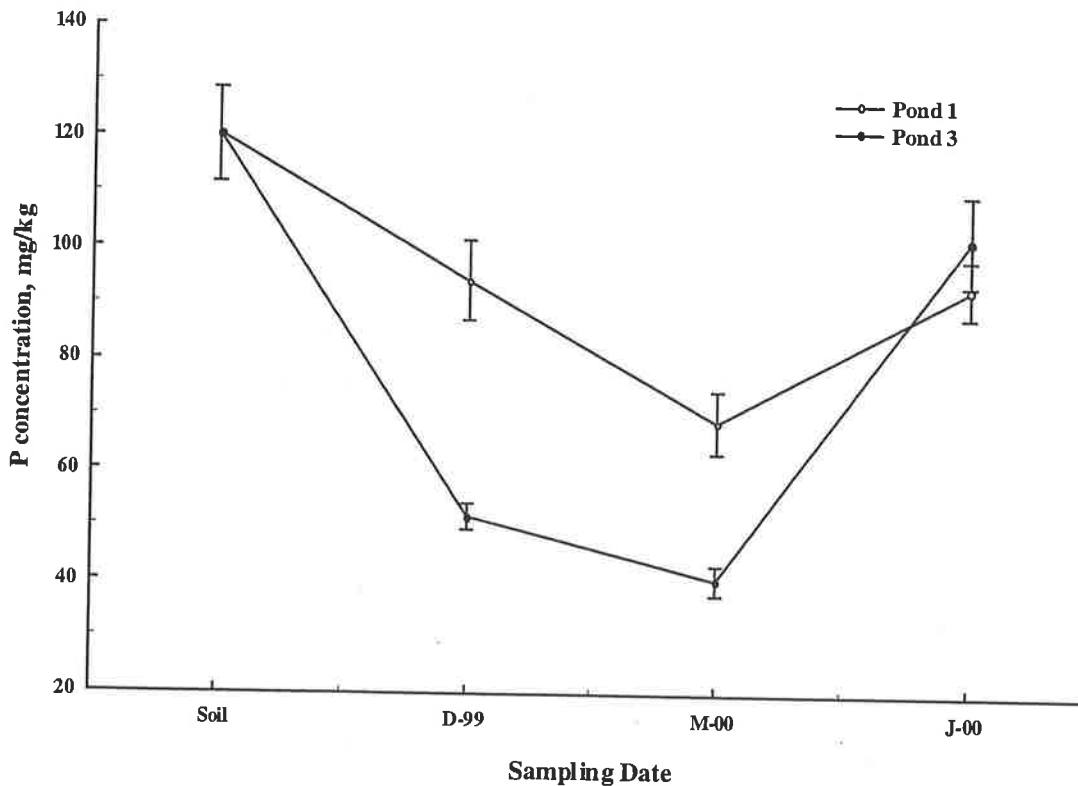


Figure 3-24. Temporal patterns of residual P concentrations in sediments from pond 1 and pond 3: means $\pm$ SE ($n = 3$).

In phase III, the residual phosphorus, which represented the refractory P in soil/sediment, and was non-sensitive to chemical changes, e.g. redox, pH, began to increase. In both ponds, the fraction of res-P became significant (25.1% and 19.7% in the pond 1 and pond 3, respectively). In addition, from Figure 3-21, it was clear that sediment TP levels were always higher in pond 3 than in pond 1, especially during the period of P build-up indicating that the sediment P increased faster in pond 1 than in pond 3.

P flux calculated from the sediment P concentration changes was presented in Table 3-21 to summarize the dynamics. In phase I, 1.85 and 1.28 g/m²/day of TP was released from sediment to water in the pond 1 and pond 3, respectively. Of the released P, Fe/Al-P contributed the most: 1.17 and 0.66 g/m²/day in the pond 1 and pond 3. During phase II, the P flux was also from sediment to the overlying water but at a much lower rate than during phase I, 0.22 and 0.46 g/m²/day for the pond 1 and pond 3, respectively. During this period, the Fe/Al-P in both ponds continuously decreased (0.19 and 0.82 g/m²/day in the pond 1 and pond 3, respectively). However, the labile organic P and Ca/Mg-P increased, especially in pond 3. As the res-P in both ponds decreased, it was difficult to quantify the amount of P which entered into sediment from water as a portion of the increased Ca/Mg-P and labile organic P may have come from the residue P. In phase III, P flux was from water to sediment. The TP flux was 0.09 and 0.39 g/m²/day in the pond 1 and pond 3, respectively. In addition, the difference between the ponds became significant. Investigation of the individual P pool revealed that all P pools except loosely absorbed P had a much higher flux in pond 3 than in pond 1, especially the labile organic P, Ca/Mg-P and residual P.

Table 3-20. P pools in sediment

	Exchangeable P		Fe/Al-P		Labile organic P		Ca/Mg-P		Residual P	
	mg/kg	% of TP	mg/kg	% of TP	mg/kg	% of TP	mg/kg	% of TP	mg/kg	% of TP
Pond 1	2.5	0.7	210.5	56.5	36.5	9.8	29.5	7.9	93.3	25.1
Pond 3	3.2	0.6	171.0	33.1	123.4	23.9	116.9	22.6	102.0	19.7

Table 3-21. P flux (g/m²/day) in pond 1 and pond 3

Phase	P flux		Exc-P		Fe/Al-P		LOP		Ca-P		Res-P	
	P1	P3	P1	P3	P1	P3	P1	P3	P1	P3	P1	P3
I	1.85	1.28	-0.006	-0.06	1.17	0.66	0.24	0.16	0.34	0.22	0.11	0.30
II	0.22	0.46	0.02	0.04	0.19	0.82	-0.08	-0.23	-0.05	-0.20	0.11	0.05
III	-0.09	-0.39	0.003	0.04	-0.02	0.03	-	-0.11	0.03	-0.08	-0.10	-0.27

Exc-P, loosely absorbed (exchangeable P); LOP, labile organic P.

P1: pond 1, the pond with emergent macrophytes; P3: pond 3, the pond with submergent.

-, means P from water to sediments.

3.4.2.2 P dynamics in Ponds with substrates from the nearby hill (P poor soil)

In pond 4, the sediments P concentrations increased slightly after flooding with drainage water for 6 months (6.0%, Figure 3-25A), and the change wasn't significant at 90% confident level (ANOVA, $P = 0.3487 > 0.1$). However, for the individual P pools, the changes were significant. In the six-month period, the labile organic P pool increased the

most (56.2 mg/kg, 997.2%), followed by Fe/Al-P (13.0 mg/kg, 83.1%) and Ca-P (11.1 mg/kg, 14.7%), while the res-P dropped 71.8 mg/kg, 79%).

For the Pond 5, TP in sediment increased rapidly (44.0 mg/kg, 22.4%, Figure 3-25B). All P pools increased except the res-P, which was similar to pond 4, decreased by 24.2% (22.1 mg/kg). Ca-P increased the most (37.5 mg/kg, 49.4), with Fe/Al-P the second (13.24 mg/kg, 84.8%), followed by labile organic P (6.1 mg/kg, 108.1%). Unlike in the ponds with P rich soil, the exc-P pool increased in both ponds even though the scales were different (47.6% and 120% increase in pond 4 and pond 5 respectively), indicating that the soil from the hills wasn't saturated with P.

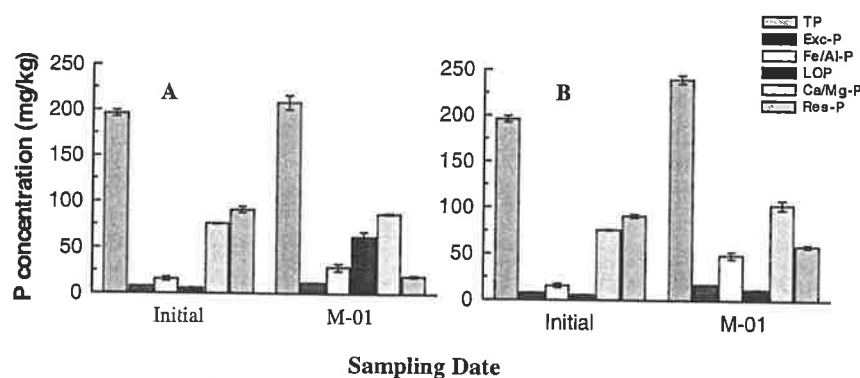


Figure 3-25. P pools dynamics in (A) Pond 4; (B) Pond 5. Exc-P, exchangeable P (loosely absorbed); LOP, labile organic P; Res-P, residual P. Initial represents P component before introduction of drainage water. The second data set (M-01) represents P fractionation after flooding for 6 months.

3.4.3 Soils and sediments P adsorption characteristics

Table 3-22 summarised the amounts of P sorbed by soils and sediments and the EPC. In Table 3-22, positive values denote adsorption, and negative values indicate desorption from the solid phase. The fitted Langmuir curves were drawn in Figure 3-26. The constants of the fitted Langmuir equations and calculated variables (EPC₀, S₀, P saturation and PSI) were listed in Table 3-23.

3.4.3.1 Natural Soils and Sediments

Of the three tested natural soils/sediments, the sediment from the natural wetland exhibited the best P adsorption, which had obvious higher S_{max}, lower K and EPC₀, and this can be explained by the lower P saturation, S₀ and higher PSI (Table 3-23). Although it's TP level

was more than 4 times higher than the hill soil (Figure 3-20), the soils from the site exhibited better P sorption than the hill soils. The P bonding constant (K) and EPC_0 were identical for the two soils, however, the S_{max} for site soils was much higher than the hill soils (783.78 mg/kg and 272.63 mg/kg for site soil and hill soil respectively). As a result, the fitted Langmuir isotherms (Figure 3-26A, B) had the same shape but differed in magnitudes compared with others.

3.4.3.2 *Sediments from Experimental Ponds*

After inundation and with macrophytes growing on it for two years, the P adsorption of sediments in pond 1 was enhanced indicated by a lower K value, EPC_0 and a higher S_{max} . The S_{max} increased nearly 60%, the S_0 decreased almost 40% and the EPC_0 halved. In addition, the P saturation decreased from 8% to 3%, and the PSI increased from 19.2 to 42.3 (Table 3-23). The P adsorption for sediment from pond 3 was also improved, although the enhancement was less significant than sediment from pond 1. Furthermore, the EPC_0 actually increased.

For P poor soils, the P adsorption decreased to some extent as the result of P accumulation. In pond 4, where the P accumulation rate was lower, the degradation of P adsorption was less than in the pond 5 (without macrophytes). After 6 months of operation, the P adsorption in pond 5 saturated faster (increase from 5% to 29%) than in pond 4 (from 5% to 8%) (Table 3-23).

Table 3-22. Equilibrium P concentration and P absorbed to soil and sediment

Initial P concentration (mg/l)	Site Soil		Hill Soil		Sediment Pond 1 ^a		Sediment Pond 3 ^b		Sediment Wetland		Sediment pond 4 ^c		Sediment pond 5 ^d	
	EPC	P +/-	EPC	P +/-	EPC	P +/-	EPC	P +/-	EPC	P +/-	EPC	P +/-	EPC	P +/-
0	0.24	-7.39	0.18	-2.79	0.19	-4.66	0.22	-4.82	0.15	-3.90	0.12	-3.19	0.18	-5.63
0.2	0.27	-4.86	0.17	-2.54	0.19	-2.28	0.24	-3.18	0.16	-1.44	0.16	-1.41	0.19	-2.83
0.5	0.29	-2.58	0.17	-2.34	0.21	-0.30	0.26	-1.62	0.16	1.29	0.16	0.90	0.21	-0.13
1	0.30	6.35	0.18	-2.01	0.22	6.87	0.29	6.05	0.16	9.26	0.17	7.92	0.21	9.63
2	0.32	21.94	0.24	0.07	0.42	14.23	0.38	17.31	0.24	21.70	0.18	20.50	0.23	19.93
5	0.33	56.79	0.47	9.36	0.78	28.87	0.55	36.14	0.29	39.46	0.44	35.86	0.31	41.03
10	0.69	116.87	1.46	46.56	0.87	101.13	0.67	117.42	0.36	153.59	0.80	97.78	0.68	113.13
50	1.36	187.26	2.15	76.57	1.43	158.87	1.25	170.82	0.84	161.74	1.88	123.79	1.39	180.87
80	56.19	684.20	74.25	243.13	29.78	1246.71	46.10	1039.88	45.54	1113.05	69.02	261.30	69.84	270.79

EPC, Equilibrium Solution P Concentration (mg/l);

P +/-, P adsorption/desorption ($\mu\text{g/g}$);^a Sediment from pond 1 after 2 years' inundation;^b Sediment from pond 3 after 2 years' inundation;^c Pond 4, Sediment from pond with P poor soils and macrophytes after 6 months flooding;^d Pond 5, Sediment from pond with P poor soils and without macrophytes after 6 months flooding.

Table 3-23, P adsorption characteristics of soil/sediment

	Site Soil	Hill Soil	Sediment Wetland	Sediment Pond 1	Sediment Pond 3	Sediment Pond 4	Sediment Pond 5
TP	828.2	196.1	372.3	376.8	516.6	208.5	240.1
K	0.379***	0.211***	0.075**	0.268*	0.193***	0.664**	2.164***
S _{max}	783.78***	272.63***	1849.42***	1247.58***	1221.57***	287.16***	388.13***
S ₀	65.262**	13.003***	32.749*	40.541 (N.S)	58.228**	21.959*	114.102**
EPC ₀	0.239	0.237	0.072	0.125	0.260	0.125	0.192
P Saturation	8	5	2	3	5	8	29
PSI	19.2	7.0	32.0	41.3	30.0	7.1	7.4
r ²	0.998	0.999	0.996	0.986	0.973	0.986	0.999

N.S, no significant relationship ($p > 0.05$); * significant relationship ($P \leq 0.05$); ** moderate significant relationship ($P \leq 0.01$), *** very significant relationship ($P \leq 0.001$);

r²: Coefficient of determination;

S₀, P already adsorbed in solid phase; K, a constant related to binding energy;

S_{max}, maximum P adsorption under ideal conditions;

EPC₀, equilibrium P concentration, at which the net flux of P is 0;

PSI, P adsorption index;

P saturation, calculated from S₀ and S_{max}, theoretical indicator how many more P may be retained;

See table 3-22 for explanations of soil/sediment types.

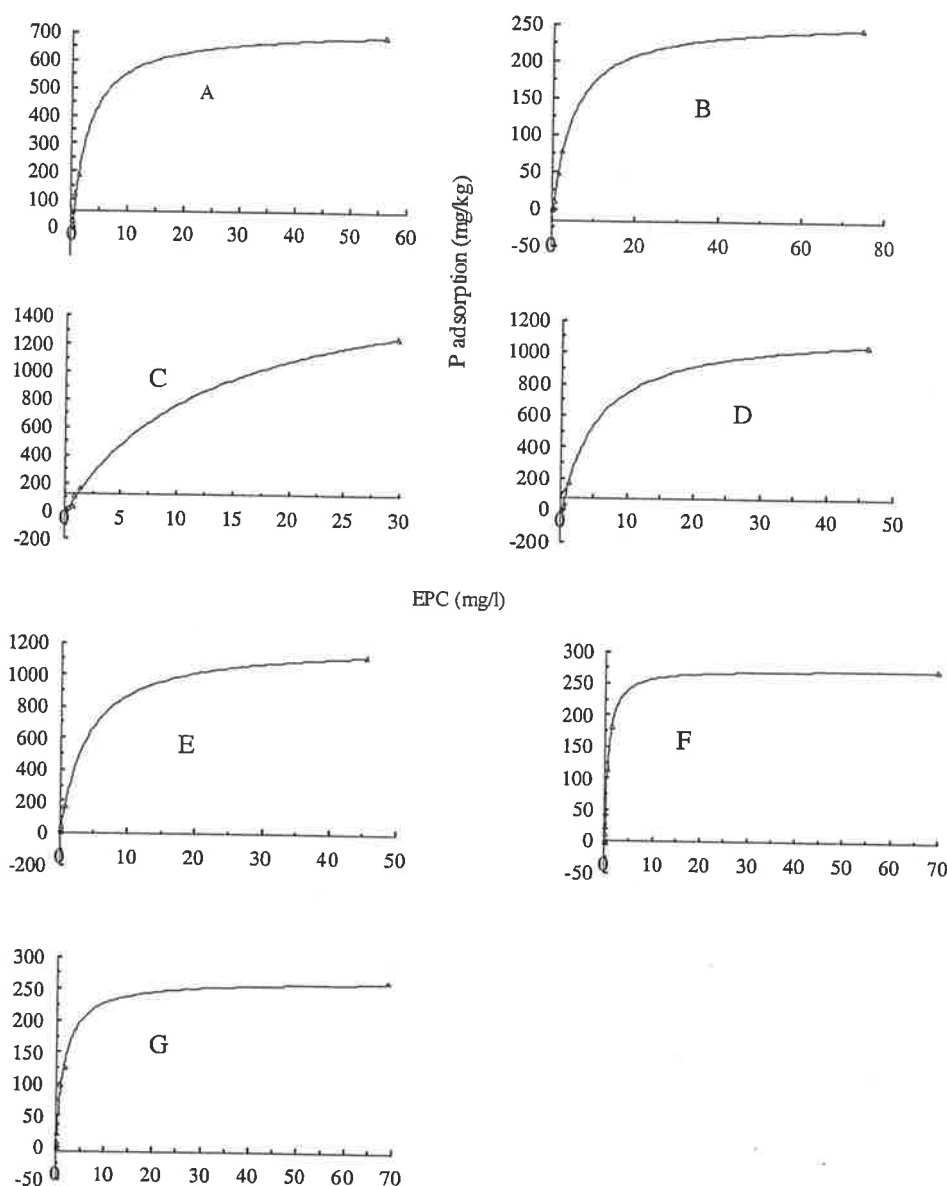


Figure 3-26. P adsorption isotherms (Langmuir fit). Dots present the measured data, and lines are the fitted curve. A, Topsoil from site; B, Soil from hill; C, Sediment from emergent pond after 2 years' inundation; D, Sediment from submergent pond after 2 years' inundation; E, sediment from natural wetland; F, Sediment from pond with P poor soil and free of macrophytes after 6 months of inundation; G, Sediment from pond with P poor soil and macrophytes after 6 months of inundation.

3.4.4 Ca^{++} , Mg^{++} , Fe^{++} and SRP in solution from sediment-drainage equilibrium systems under different pH regimes

To investigate the sediment P retention under different acid-base conditions, laboratory equilibrium experiments were carried out using sediments from natural Reedy Creek wetland, pond 1 and pond 4. Filtered drainage water (500ml) was added to glasses

containing 10 g (dry weight equivalent) sediments (with plant roots and large solid particles removed). Equilibrium was achieved by blowing air through a glass pipe (diameter 0.1 cm), which was fixed at the bottom of the glass beaker. Microbial activities were prohibited by adding 5 ml of formaldehyde solution. HCl and NaOH solutions were used to adjust pH levels. At each pH level, the systems were left mixing for 24 hours to achieve equilibrium. A portion of the solution (10 ml) was then taken out and filtered through 0.25 μ m membrane for SRP and Ca, Mg, Fe analysis. As P concentrations of all extracts from the drainage-natural sediments system were below determination limits (Table 3-24), it was omitted from further discussion.

The two sediments with different origins displayed distinguishing behaviours regarding P release and retention under different pH regimes. In general, the sediment originating from the site soils (P-rich soil) was sensitive to pH change with the maximum P retention occurring at pH range of 6-8 (Figure 3-27A). On contrast, sediments originated from the hill soils (P-poor soil) were insensitive to pH change: the SRP concentrations in solution kept relatively constant in the pH range of 5-9 (Figure 3-28A).

For other ions that are important to sediment P holding capacity, Ca^{++} and Mg^{++} performed differently for sediments from different sources: they are sensitive to pH changes for sediments originated from site soil with the maximum solution concentrations occurring at pH 5-8 (Figure 3-27B). For sediments developed from hill soils, however, no clear patterns can be discovered, although the minimum solution concentrations happened at pH = 7, i.e. neutral conditions (Figure 3-28B). In addition, the solutions had significantly higher Ca^{++} , Mg^{++} concentrations. For Fe, there was no clear difference for the two. Under acid (pH<6.5-7) conditions, the solution concentration ranged from 1.6mg/l to 31mg/l for systems with sediments originating from site soils and from 0.03mg/l to 6.7mg/l for systems using sediments with hill soil origin. As pH value increasing to about 7, the solution Fe concentrations fell to below the determination limit level (0.03mg/l).

Table 3-24. Fe, Ca, Mg and SRP concentrations (mg/l) at equilibrium.

Initial pH	System I					System II					System III				
	Final pH	Fe	Ca	Mg	P	Final pH	Fe	Ca	Mg	P	Final pH	Fe	Ca	Mg	P
3	4.03	23.90	249	233	-	3.52	31.46	309	202	2.81	5.58	4.24	1680	520	1.18
3.5	4.91	15.66	346	233	-	3.54	23.89	317	206	2.68	6	2.22	1640	520	0.59
4	5.01	9.70	396	253	-	4.58	22.11	321	207	1.11	6.43	0.27	2360	520	0.76
4.5	5.07	2.23	440	259	-	4.67	17.48	325	208	0.69	6.61	0.04	2640	560	0.60
5	5.12	1.56	500	262	-	4.67	17.03	327	212	0.61	6.8	0.03	2680	580	0.64
5.5	5.85	0.99	660	272	-	4.71	13.77	420	321	0.5	7.15	-	2760	600	0.74
6	6.28	0.75	680	260	-	5.6	5.26	480	323	0.45	7.16	-	2700	620	0.64
6.5	6.4	-	720	243	-	5.83	2.50	500	343	0.45	7.35	-	2410	620	0.74
7	6.85	-	740	242	-	6.37	-	520	377	0.43	7.36	-	2680	640	0.53
7.5	6.87	-	620	236	-	6.75	-	500	367	0.36	7.49	-	2660	640	0.54
8	7.13	-	540	232	-	7.43	-	500	365	0.36	7.62	-	2640	640	0.45
8.5	7.16	-	520	223	-	7.47	-	480	356	0.36	7.65	-	2620	640	0.79
9	8.01	-	460	218	-	8.25	-	460	346	0.36	8.33	-	2560	620	0.74
9.5	8.31	-	440	213	-	8.31	-	440	194	0.59	8.37	-	2480	620	0.70
10	9.05	-	420	119	-	9.03	-	298	189	0.76	8.68	-	2080	500	0.79
10.5	9.1	-	319	102	-	9.17	-	258	86	0.83	8.73	-	1620	379	0.36

System I, Drainage – sediment from natural wetland;

System II, Drainage – sediment from pond 1;

System III, Drainage – sediments from pond 4.

-, under determination limit.

3.4.4.1 Relationship between SRP Concentration and pH Value in System II

The equilibrium solution SRP and Ca concentrations had an obvious relationship with pH values (Figure 3-27). The data fitted very well with the heat-capacity equation. There was a strong relationship between SRP and pH ($P < 0.0001$). In addition, the fitted model (equation 3-19) explained 94.9% ($R^2 = 0.949$) of the variations in SRP concentration with a multiple correlation coefficient of 0.974 ($r = 0.974$).

$$SRP = -0.5129 + 0.545 \times (pH) + 71.377/(pH)^2 \quad (3-19)$$

Where, SRP and pH are SRP concentration (mg/l) and pH value of solution.

The fitted model (Equ.3-20) was less efficient in predicting Ca concentration. However, the coefficient of determination and the multiple correlation coefficient were 0.7303 and 0.8546, respectively, indicating a moderately significant relationship between the two variables.

$$SRP = 872.531 - 42.674545 \times (pH) - 3505.121/(pH)^2 \quad (3-20)$$

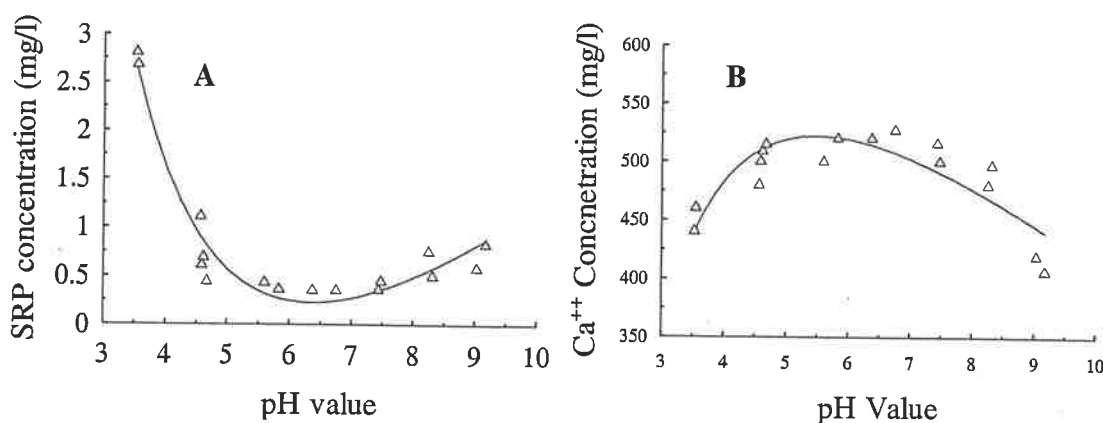


Figure 3-27. Non-linear relationships (heat capacity function) between solution pH value and SRP (A), Ca^{++} (B) concentrations for system II (sediments from emergent pond). Curves represent the fitted model, and triangles are measure data.

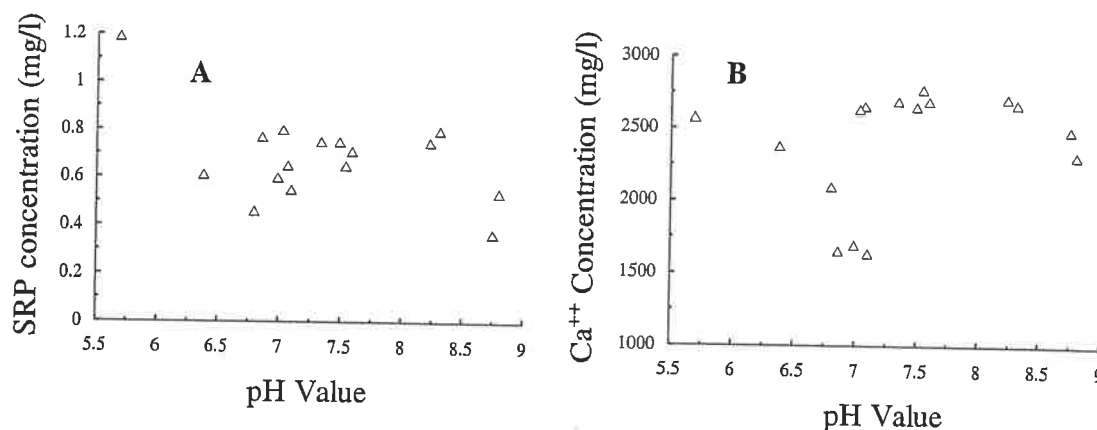


Figure 3-28. Relationships between solution pH value and solution SRP (A), Ca^{++} (B) concentrations for sediments from Pond 4. SRP and Ca^{++} concentrations were not related to pH values

3.5 WATER COLUMN COPRECIPITATION: LABORATORY INVESTIGATION

Significant amount of the added inorganic P was disappeared from the liquid phases, indicating precipitation of P occurred in all systems (Table 3-25). The results showed clear that the raw water from natural wetland had less buffering capacity for P addition. Although the addition of sand into the solution increased the amount of P disappeared from solution, the differences between system 1, 2 and 3 were marginal.

Table 3-25. P coprecipitation from water column: data show the initial and final solution P concentrations, and the accumulative P added and disappeared.

P_{ad}	System 1				System 2				System 3				System 4			
	C_i	C_e	P_{re}	%	C_i	C_e	P_{re}	%	C_i	C_e	P_{re}	%	C_i	C_e	P_{re}	%
200	1.53	1.33	39.5	12.7	1.53	1.11	83.9	26.9	1.53	1.26	54.3	17.4	1.53	1.25	55.0	17.6
450	2.42	1.60	209.2	39.6	2.23	1.31	272.9	51.1	2.36	1.22	286.5	54.0	2.36	2.24	81.4	18.4
700	2.79	1.75	412.9	54.1	2.52	1.89	393.0	51.0	2.44	1.71	426.6	55.5	3.41	2.94	170.6	22.5
950	2.94	2.06	583.1	58.6	3.07	2.27	548.8	54.8	2.90	2.31	538.9	53.8	4.07	3.23	333.6	34.1
1,200	3.21	2.45	735.1	60.0	3.40	2.57	716.0	58.2	3.44	2.72	684.2	55.7	4.31	3.47	502.8	42.0
1,450	3.64	3.25	800.4	55.2	3.75	3.27	800.7	55.1	3.90	3.44	762.6	52.6	4.63	4.43	525.6	37.2
1,700	4.42	3.92	884.3	53.0	4.43	3.90	891.3	53.3	4.60	3.89	887.9	53.3	5.57	5.30	557.3	34.5

System 1, 200ml filtered drainage + 10g washed fine sand;

System 2, 200ml filtered drainage + 5g washed fine sand;

System 3, 200ml filtered drainage only;

System 4, 200ml filtered water from Reedy Creek Wetland;

P_{ad} and P_{re} are added P and P disappeared from solution, mg;

C_i and C_e are initial and equilibrium inorganic P concentrations, mg/l;

% represents the percentage of the disappeared P.

Precipitated P has strong linear relationship ($P < 0.0001$) with the P added into solution (Figure 3-29, R^2 ranged from 92.9 – 98.6%). The fitted equations suggested that the drainage water systems had the capacity to precipitate more than 50% of the added inorganic P, while the wetland water was less capable (34.6%).

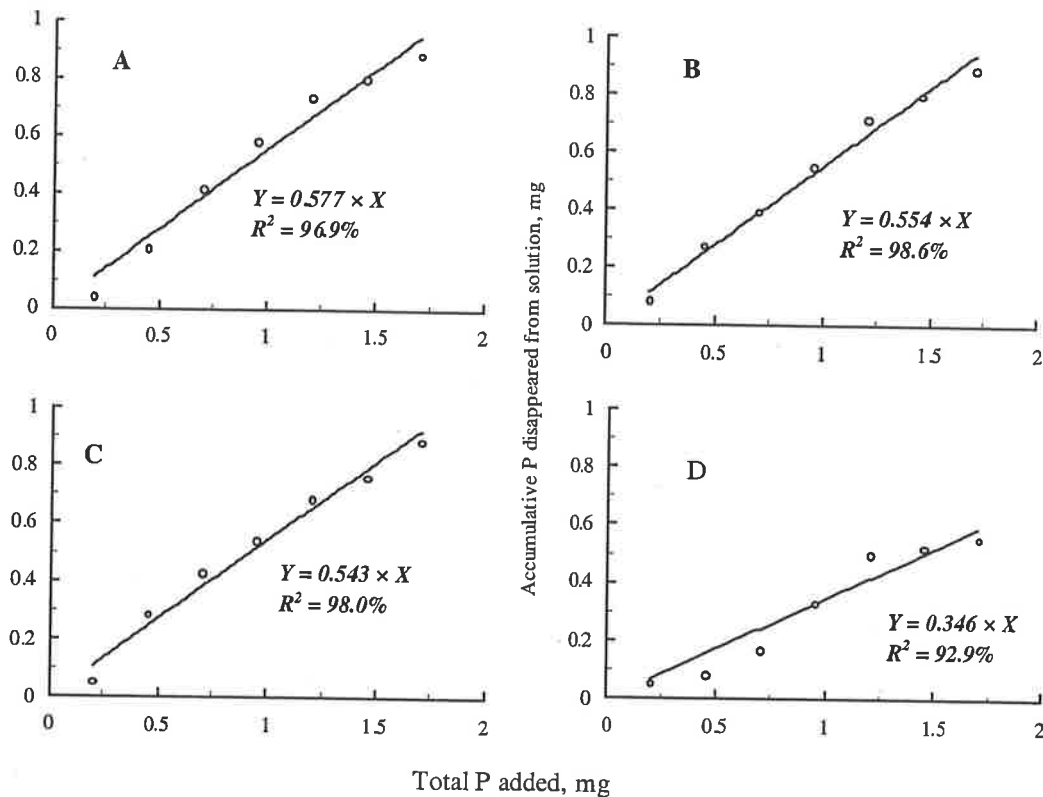


Figure 3-29. The linear relationships between P precipitated (g) and P added in equilibrium systems of A, filtered drainage + 10g sand; B, filtered drainage + 5g sand; C, Filtered drainage only; and D, Raw water from Reed Creek wetland. Lines are fitted equations, and circles represent the measured data.

Chapter Four Discussion

4.1 POLLUTANTS IN DRAINAGE WATER

Surface and subsurface drainage water from irrigated agricultural areas is normally degraded compared with the quality of the original water supply. Drainage water that flows through the soil will pick up a variety of dissolved and suspended substances including salts, nutrients, organic compounds and soil particles. Management for safe reuse or disposal requires an understanding of the characteristics of the drainage water and a matching of those characteristics to the environmental protection needs of the reuse and disposal area. As the drainage water from Baseby Farm is a collection of surface runoff and subsurface drainage, the potential pollutants include:

- i. Substances purposely introduced into the pasture, e.g. nutrients, pesticides;
- ii. Materials mobilized by the practices of irrigation and drainage, e.g. salts, soil particles;
- iii. Salts and trace elements concentrated as a result of evaporation;
- iv. Other microorganisms such as *coliform* generated from animal growth, blue-green algae and associated toxins in the drain network as result of eutrophication in ditches.

4.1.1 Trace elements

The results of ICPAES (inductively Coupled Plasma Atomic Emission Spectrometry) revealed that most of the trace elements in drainage water were within the irrigation water acceptable contaminant concentrations recommended by the Australian and New Zealand Environment and Conservation Council (ANZECC) and the Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ) (1999). They were also within the aquatic life protection limits proposed by Marshack (1993) (Table 4-1).

4.1.2 Turbidity

There are several reasons why turbidity in drainage water is significantly lower than in river and wetlands. Comparing with river water, the average hydrological residence time (HRT) of drainage is relatively longer. Longer residence time and the shallowness of the drains create a favourable environment for the settlement of large soil particles and plant materials,

resulting in a significant lower turbidity level than river waters. Comparing with wetland, the configuration of canals and drains can reduce the wind energy dramatically, thus the chance for sediment to re-suspend is less. In addition, the density of large benthic fish such as carp is much lower than in natural floodplain wetlands (Bowmer et al, 1994). The high degree of self-purification in drains systems regarding turbidity provides a kind of preliminary treatment of drainage water. However, the process of settlement of particles in channels can't replace the pre-treatment facility in a full-scale constructed wetland as the degree of settlement is depended upon the time that drainage stays in the canals. During heavy rain seasons and intensive irrigation, HRT of drainage in channels maybe very short and the particles maybe have no chance to settle. For example, in December 3, 1999, the turbidity of drainage was as high as 71.9 NTU.

Table 4-1, Measured concentrations of trace elements in the drainage water from Baseby Pasture and established US water quality for aquatic life protection (Marshack, 1993) and Australian irrigation (ANZECC and ARMCANZ, 1999)

Constituents	Measured	Criteria	
		mg/l	
		Irrigation guideline	Aquatic life protection
Al	N.D	20	-
B	0.67	0.5	-
Cd	N.D	0.05	0.0005
Co	0.021	0.1	-
Cu	N.D	5	0.0054
Fe	0.025	10	-
Mg	460	10	-
Mn	7.4	10	-
Mo	N.D	0.05	-
Ni	N.D	2	0.65
Zn	N.D	5	0.047

N.D, Not detectable; -, No data.

4.1.3 Salts

Salt concentrations are expected to be high in arid or semi-arid areas where evaporation usually exceeds precipitation. As water evaporates from pasture, salt concentrations increase. These salts may be carried in irrigation return flow or in overland flow resulting a high level of salinity in drainage water. In the dairy farms of the Lower River Murray region, the high salt concentrations may come directly from the saline groundwater. The pastures were reclaimed from natural wetlands, these wetlands were historically the intersections of saline

groundwater and surface freshwater – the groundwater recharge and discharge points. To maintain a productive pasture, the depth of the main channel is below the groundwater level. Consequently, saline groundwater mends with the drainage from irrigation resulting in a very high level of salinity in drainage. Although salinity is not the issue of the study, it does make the P problem more complicated and more different to deal with.

4.1.4 Nutrients

4.1.4.1 N

Inorganic N concentrations (ammonia and nitrate) in drainage water were very low although significantly higher than those in river and wetland waters. In their experiments on subsurface tile drainage, which contained high level of nitrate, Bowmer et al (1994) showed that the nitrate dissipated very quickly as the water flow through the channel, maybe due to denitrification. The channel is a favourable site for N processing featuring the co-existence of aerobic and anaerobic conditions, which are ideal for nitrification and denitrification.

4.1.4.2 P

In comparing the reliable data on nutrient exports of Australian catchments with Northern American data sets, Young et al. (1996) concluded that the P export rates from Australian catchments were lower than those estimated in Northern American. In disturbed Australian catchments, the more recent results of Lewis et al. (1999) and Downing (1999) showed that P exports were much lower than in the Northern Hemisphere. Considering Australia as a whole, this is true. This results from the lower atmosphere deposition (Holland et al. 1997), lower fertilizer input (Carco, 1995) and lower population density (Howarth et al. 1996). However, in pastures, especially in irrigated pastures, Australia isn't an exception (Table 4-2). The drainage water from pastures contains similar P levels. In addition, the ratios of SRP:TP are also comparable.

SRP is 26% and 22% of the TP in the River Murray and Reedy Creek Lagoon, respectively. In a broad context, SRP represents about 10-30% of the TP in Australian river waters (Harris, 2001). In drainage water, however, the ratio of SRP:TP is much higher (56%). This can be partly explained by the lower Turbidity level in drainage, and the application of inorganic P fertilizers.

Table 4-2, P concentration in drainage (runoff) and export rates from pasture under different management

Country	Production	P export (kg/ha/yr)	TP range (mg/l)	SRP/TP	Source
Australia	Sheep grazing	0.22	0.44-2.0	<70%	Tham (1983)
Australia	Mown pasture	0.02-0.45	0.36-6.75	>50%	Greenhill et al (1983)
Australia	Grazed irrigated pasture	4	1.3 – 21.2	>50%	Small (1985)
Ireland	Intensive grassland	0.4-2	0.094- 0.295	36-45%	Jordan & Smith (1985)
England	Intensive grassland	3			Haygarth & Jarvis (1996)
USA	High density beef		2 - 10		Campbell et al (1995)
	Low density beef		0.2 - 2		
Australia	Grazed irrigated pasture	4.8	0.35 – 10.75	>55%	This Study

The main factors influencing P movement from land to water can be separated into the transport, P source, and P management factors (USDA, 1994). Transport factors include flow rate, landscape topography, soil texture. Factors which influence the source and amount of P available are soil P content and the P applied. P management factors include the method of application, timing, and placement in the landscape. As a result of historical dairy production, a layer of about 20 cm of mixture of alluvial soil, cattle excretion, plant residues and P fertilizer is formed as the topsoils in the dairy pastures. The topsoils from the site have relatively high level of P. In addition, most of the P is bonded by Fe/Al, which is sensitive to redox potential (Eh) condition. When flooded, large amount of soil P can be released as dissolved inorganic P. The significant high alluvial clay content of deep layer soil prevents fast infiltration. Consequently, surplus irrigation water, which contains high level of dissolved P, enters into drains and become drainage water.

4.1.5 Design Considerations for Constructed Wetland Systems (CWS) to Remove P from Drainage Water

The goal of this study is to evaluate the prospects for using CWS to remove P from drainage water. There is considerable experience in utilization of CWS as tertiary treatment for municipal wastewaters (e.g., Kadlec and Knight, 1996), as well as published information on the efficacy of using wetlands (constructed, restored or natural) for NPS pollution control

(e.g. Mitch, 1989). However, there are relatively little literature findings on the using CWS for irrigation drainage treatment. Therefore, a useful starting point is to address the question: How does the drainage differ from the other wastewaters and what are the implications of these differences in considering the potential of CWS to remove P from drainage? For this comparison, Table 4-3 summarized the nutrients conditions in effluent from municipal wastewater treatment plants (Gakstatter, et al., 1978), in streams located within agricultural areas of the "Corn Belt and Dairy Region" in USA (Omernik, 1976), and in drainage water from Baseby Farm. As the differences between cropland runoffs and drainage from irrigated pasture are obvious, it is necessary to address these two kinds of water separately although they are generally classified as non-point pollution in literature.

Table 4-3, Comparison of nutrients levels (mg/l) in drainage, steam water from agricultural catchment and secondary effluent from municipal wastewater treatment plants

	Secondary effluent ^a	Corn Belt Cropland ^b	Drainage from Baseby ^c
TP	6.8 ± 0.4	0.14	3.4 ± 2.3
Soluble P	5.3 ± 0.4	0.06	2.4 ± 1.7
TN	15.8 ± 1.2	4.4	11.7 ± 7.9
Inorg-N	8.4 ± 0.45	3.4	1.3 ± 0.9
N:P	2.4	31.6	3.7

^a, Data from Gakstatter, et al., 1978. Means and standard deviations represent effluent from 244 activated sludge treatment plants throughout the USA;

^b Omernik, 1976, data are means of 80 sampled streams in agricultural land;

^c, Data from this study. Means and standard deviations represent monitoring results of 40 sampling events; TN is based on 5 samples.

As a first consideration, the drainage contains comparable N and P levels as secondary effluent but much higher than cropland runoffs, especially for P, higher by an order of magnitude. Moreover, the N:P ratio in drainage and secondary effluent is similar while it is much higher in cropland runoff. Therefore, drainage and secondary effluent are strongly N limited, while the cropland runoff is generally P limited as in natural waters. The discharge of drainage and secondary effluent into natural waters may alter the trophic status, and cause environmental consequences. Second, the nutrients concentrations of secondary effluent are relatively stable (spatially), with standard deviations around 10% of the means. Although there are no data to make similar statistical calculation of the uncertainty of the drainage water, it seems that annual nutrient loadings from irrigation drainage systems may vary by one order of magnitude similar to runoffs from croplands (Novotny and Chesters, 1981).

Thus, a CWS for municipal wastewater treatment could be designed based on published data, but site-specific data would be needed to design an efficient CWS for cropland runoffs and drainage. Third, the chemical components of drainage water from Baseby Farm vary dramatically (temporarily), with standard deviations around 70% of the means, while nutrients in the secondary effluent were very constant (Gakstatter, et al., 1978). The temporal uncertainty is also a characteristic of cropland runoffs (Nash and Halliwell, 1999; Harris, 2001). In addition, not like secondary effluent, the amount of drainage and runoff is well known as stochastic, event-driven (Skaggs, et al. 1994). This may be the most critical difference. Therefore, CWS for polishing secondary effluent could be designed in a more predictable manner, while CWS for irrigation drainage and cropland runoffs has to have a large buffer capacity. Fourth, in cropland runoff, the majority of P is associated with the solid phase. The calm condition and shallowness in CWS encourages the settlement of particles with their associated P resulting in a good performance for CWS treating agricultural runoff. However, most of TP in drainage and secondary effluent is in dissolved forms, sedimentation is no longer the major P removal pathway. CWS design should emphasize on other mechanisms, such as substrate adsorption, plant uptake, and co-precipitation.

Because of these differences, the design of CWS to optimise the P removal processes from drainage water would be different. First, to address the dissolved P, maximizing soil adsorption and maintaining a favourable environment for P coprecipitation in CWS are the priority in wetlands for drainage treatment. In wetlands receiving secondary effluent, however, P coprecipitation is minor as the availability of Ca and Mg is limited. Therefore, utilization of substrates that have high P affinity is always a priority in municipal wastewater wetlands. By contrast, sedimentation of particles is a major process for P removing in wetlands receiving cropland runoff. Second, the low N:P ratios in drainage suggest that plant uptake would be relatively less important as a long-term P retention mechanism in drainage and secondary effluent treatment wetlands than in wetlands for cropland runoff processing, because P is grossly oversupplied relative to N. Third, the stochastic and event-driven feature of drainage and cropland runoff, with extreme variations in both concentration and flow, demand a larger design size to ensure a predictable treatment efficacy.

4.2 PERFORMANCES OF POND SYSTEMS

The performance evaluation of ponds has been analysed at three different levels. The first level includes a summary analysis of all the monitoring data about influent and effluent P concentrations in the ponds, determining the mean values and the range over the period of operation. The annually averaged influent and effluent P concentrations were used to calculate the overall P removal efficiency and rate. The first level of evaluation is useful only in the context of summarizing the range of operation conditions of the ponds and their response in terms of effluent concentrations.

In the second level of performance data analysis, the performance of the ponds with the most extensive in/out concentration and mass data at the fixed sampling intervals were compared. This level of analysis is displayed in terms of cumulative probability over the period of data collection. The third level of evaluation is designed to determine how individual system perform in terms of effluent concentrations, mass discharge and retention over the range of its loadings. In the third level of analysis, loading versus effluent concentration, discharge and retention for each pond are compared, thus demonstrating the expected variability within a single system.

4.2.1 General Description

The P dynamics in CWS involve many processes in a complex biogeochemical cycle, which is discussed in details by Kadlec and Knight (1996). Principal mechanisms of P elimination include sedimentation, adsorption of soluble P on to sediments, co-precipitation, and uptake by aquatic biota. Although these processes normally co-exist in most wetland ecosystems, the importance of a particular pathway can be different in any specific wetland. In addition, the stability of P compounds, e.g. Ca-P, Fe-P, varies. Under certain conditions, P in the solid phase dissolves and is released to the water column. Consequently, there is considerable variability in the amount of P that could be removed and retained by wetlands from water flowing through them reported in literature. It's hard to compare as the designed loading rate, influent concentration and hydrological residence time were different, therefore, optimisation design is hard to achieve. As the influent, HRT and P loading rates were similar in the five experimental mesocosms, the investigation of ponds' performances can provide inside

information about P dynamics and P elimination processes. Thus, provide a chance to optimise the P elimination pathways in surface flow wetlands.

Most of the data regarding the P removal performance found in literatures were calculated based on the mass balance according to equation (3-12 and 3-13). There were also many reports based on the annually average I/O concentrations, $(C_i - C_o)/C_o \times 100$ (e.g. Schierup et al. 1990; Green and Upton, 1992). Although the evapotranspiration can condenses the P in field pond and causes discrepancy between the two approaches, results of the two approaches agreed with each other quite well in the present study (Table 4-4). Consequently, only mass balance data were discussed in this study.

Table 4-4. The comparison of P removal efficiencies (%) calculated by mass balance equation (M. B) and annual average I/O concentrations

	Pond 1	Pond 2	Pond 3	Overall	Pond 4	Pond 5
M. B	24.3	44.1	-0.05	57.5	44.3	27.9
I/O	29.4	43.8	6.8	62.9	48.1	33.6

The average P removal rates of the five ponds ranged from $-0.0 \sim 0.22 \text{ g/m}^2/\text{day}$, which are well above the average performance of $0.022 \text{ g/m}^2/\text{day}$ summarized from the North American Wetland Treatment System Database (Knight et al., 1993). However, Knight's data represent combined performance data for surface flow and subsurface flow wetlands, derived from wetland treatment systems that collectively represent a wide range of wastewater types (municipal, industrial and agricultural) and loading and design characteristics. As a result, cautions must be taken to directly compare between the two data sets. Greenway and Woolley (1999) summarized the performance of eight surface flow CWS for secondary sewage treatment in Queensland, Australia. In their data set, the TP loading rates ranged from $0.19 \sim 1.0 \text{ g/m}^2/\text{day}$, which is comparable to the loading rates of $0.025 \sim 1.153 \text{ g/m}^2/\text{day}$ in the present study. The TP mass retention rates ranged from $-0.22 \sim 0.40 \text{ g/m}^2/\text{day}$, a comparable though broader range performance to our study. A general pattern can be seen that when the TP loading rates is in the same range, the performance may be compatible giving the almost same climate conditions.

The maximum P removal efficiency of 44.3% was achieved by pond 4 (pond with P-ppor soils and planted with emergents). Pond 2 had a slightly less efficient performance (44.1%). In an annual base, pond 3 exported P, although the amount was ignorable (-0.05%) based on the mass balance calculation. The performance data were in agreement with those found in the literatures. For example, in summarization of the operational data from more than 100 Danish constructed wetlands, Schierup et al. (1990) reported the P removal efficiency ranged from -111.4 to 97.9%, with an average of 35.6%. Green and Upton (1992) reported the operational data for five CWS in the Great Britain. The average TP removal efficiency was 20.9%, which ranged from 3.0 to 40.9%.

4.2.2 Seasonal Patterns and System Performance Prediction

Although the lumped black-box approach is useful for the general description of the performance of individual ponds, it gives little information about the seasonal changes. Consequently, more detailed P removal efficiency and rate were calculated according to the sampling intervals using similar mass balance equations (Equation 3-12, 13). At the breakdown level of data interpretation, correlations between system operating variables may be made possible via regression equations. Thus, performance predictions become possible.

4.2.2.1 Time series: the unsteady state

Constructed wetlands typically need a few months for vegetation and biofilm establishment, and one or two years for the development of the litter compartment (Kadlec, 1997). The stabilisation of P in substrates after inundation can take as long as a year although the maximum P solubilization occurs only several days after wetting (Turner and Haygarth, 2001). In this regard, the data used for evaluation of performance are taken after three months of operation. When calculating the input and output P, the transport lags caused by detention time were also taken into account. However, due to the changes of P components in the drainage, the fluctuations in internal wetland P storage, and mechanistic variability, the input changes do not necessarily produce similar trends in the output (Figure 4-1). In pond 1 (the pond with emergent water plants planted on the site soils as substrates), the system became a net P source during the period from April to September in the first year of operation. In the second year, the period of P generation was shorter (from May to August). Furthermore, the magnitude of P release was less in the second year as well. This

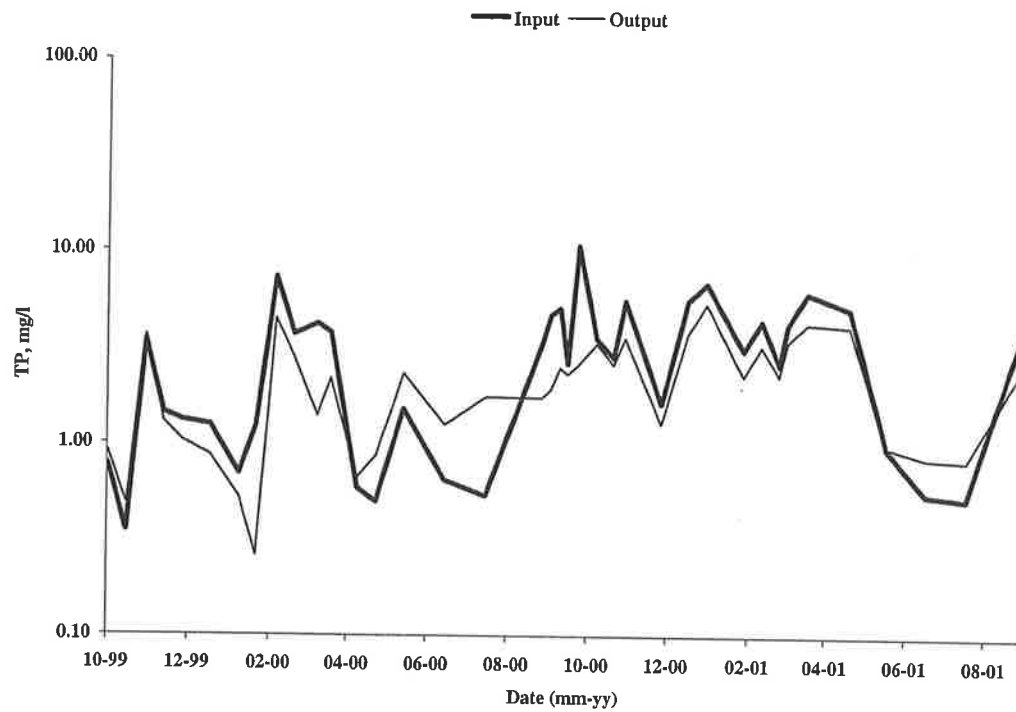


Figure 4-1, Time sequences of inlet and effluent TP concentration in pond 1.

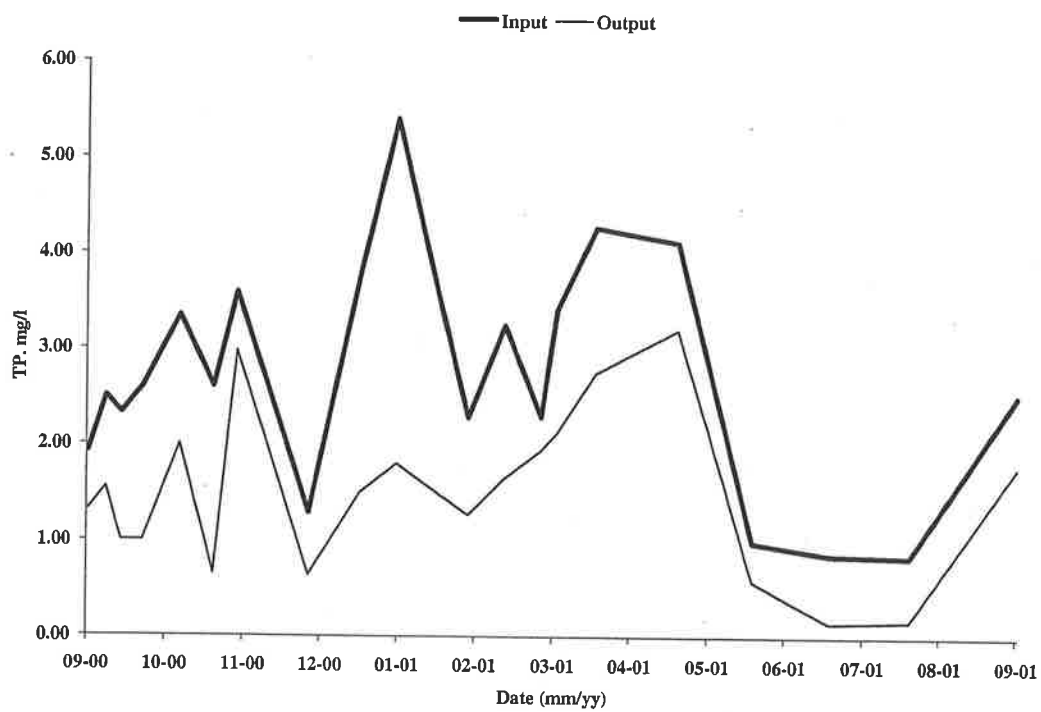


Figure 4-2, Time sequences of inlet and effluent TP concentration in pond 2.

phenomenon supported the conclusion of many other reports (e.g. Kaldec and Knight, 1996; Gearhert, et al., 1999) that new constructed wetlands need at least one year to function stably.

In the pond with floats (pond 2), as there was no sediment utilized, the P cycles were relatively simpler than those in other ponds. Excluding the interruption of P-flux to-and-from sediments produced a more predictable and stable performance (Figures D-2, D-8, D-13 and D-14), especially for SRP. In summer, the warmer climate encourages the growth of creeping-stem water plant and the associated epiphytes, which promote the SRP uptake. In return, the P removal rates were higher than those in winter. Consequently, the trend of input TP concentrations reflects, to some extent, the trend of output concentrations (Figure 4-2). It is obvious that the effluent has always-lower TP than the influent resulting an all year around P removal in such system.

4.2.2.2 *Seasonal Variation in performance*

The stochastic nature of natural or semi-natural systems means that the annual average of I/O concentrations may be not enough to describe the behaviours of ponds regarding the P removal. Temperature and solar radiation are the primary determinants of the activity of the photosynthetic processes in wetlands, it is therefore intuitively plausible that these variables would be of importance in the removal of P (Kadlec and Knight, 1996). The P present in drainage water is predominantly in dissolved forms, thus, the performance of pond systems largely depends on the processing of dissolved P, i.e. uptake by macrophyte and other biota, chemical precipitation, and adsorption by sediments. As all of these processes are temperature depended, it is not surprising that the ponds were more efficient in summer than in winter, especially in pond 1 and pond 3 (Figures D-1, D-3, D-6 and D-7).

The operational data for the second year in pond 1 and pond 4 (the pond with emergents planted on P poor hill soils) were re-organized to illustrate the different P removal behaviours in summer and winter (Figures 4-3 and 4-4). As there is no clear spring and autumn in South Australia, a year was loosely divided into summer (late September to April) and winter (May to early September). In both ponds, P removal rate was higher in summer than in winter. For individual P forms, the SRP had the biggest variations between summer

and winter values. The differences for PP were not significant. It is understandable, as the removal of PP was physical progresses such as sedimentation and filtration, which are relatively independent to temperature and solar radiation. In addition, the phytoplanktonic activities in these ponds were insignificant (refer to Figure 3-11, the chlorophyll-a in ponds).

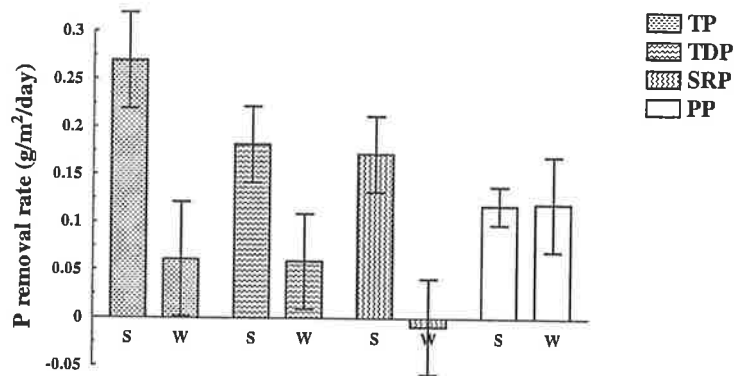


Figure 4-3. Comparison of P removal rates (Mean $\pm$ S.E) between summer (S, n = 15) and winter (W, n = 5) in pond 1 for the second year of operation.

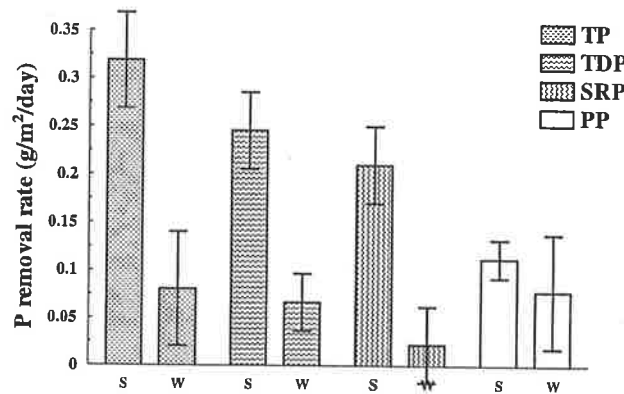


Figure 4-4. Comparison of P removal rates (Mean $\pm$ S.E) between summer (S, n = 15) and winter (W, n = 5) in Pond 4.

4.2.2.3 Probability Frequency Distribution of Effluent Concentrations

As the regulatory requirements for wastewater discharge place a maximum on a given percentile, normally 80th or 90th in most countries (including Australia), the probability frequency distributions of input and output concentrations acknowledge the requirements. In addition, it provides substantial description of CWS performance. The monitored I/O concentrations data for each pond were utilized to construct the possibility distribution graphics (Figure 4-5 and 4-6).

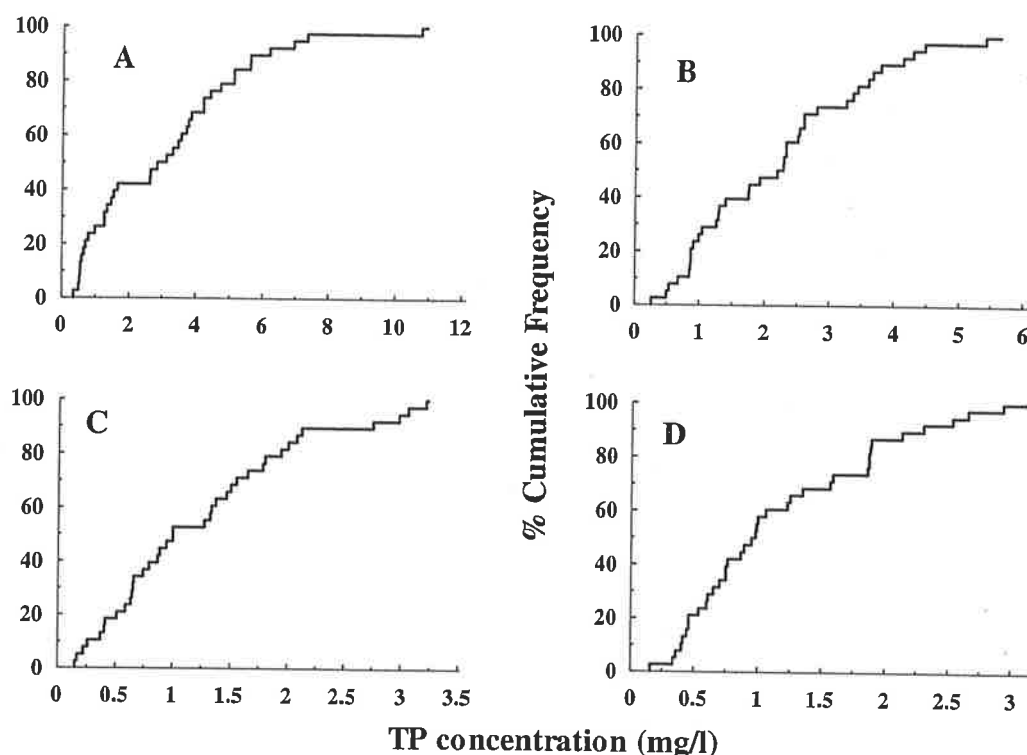


Figure 4-5, TP concentration probability distribution for: A) Influent; and Effluents from B) Pond 1; C) Pond 2; and D) Pond 3.

According to Figure 4-5, the 90ile distribution of input TP concentration was about 6.5mg/l. For the output concentrations from the pond 1, 90% of the effluent TP concentrations were below 3.5mg/l. The opportunity for achieving effluent concentration below 1mg/l, which is the discharge standard for advanced wastewater treatment in some European countries, was less than 20%. For the effluent from the pond 2, the 90th percentile concentration was 2.1mg/l. The probability of discharge concentration less than 1 mg/l was 48%, an enhanced performance compared with the pond 1. The last pond in the treatment chain, pond 3 didn't increase the performance: the 90th percentile discharge concentration was 2.0 mg/l and the percentile for 1mg/l was 40th. Overall, for the 3-pond system, it achieved the 90ile effluent concentration of 2.0 mg/l, which is twice as much as the targeting discharge standard of 1mg/l for tertiary treatment.

The situation in pond 4 and pond 5 (the pond with P poor hill soils as substrates but free of macrophytes) was not better. The 90th percentile for pond 4 and pond 5 were 3.4 mg/l and

4.2 mg/l, respectively. The accumulative frequencies for less than 1mg/l discharge TP concentration were 21% and 16% for pond 4 and pond 5 (Figure 4-6).

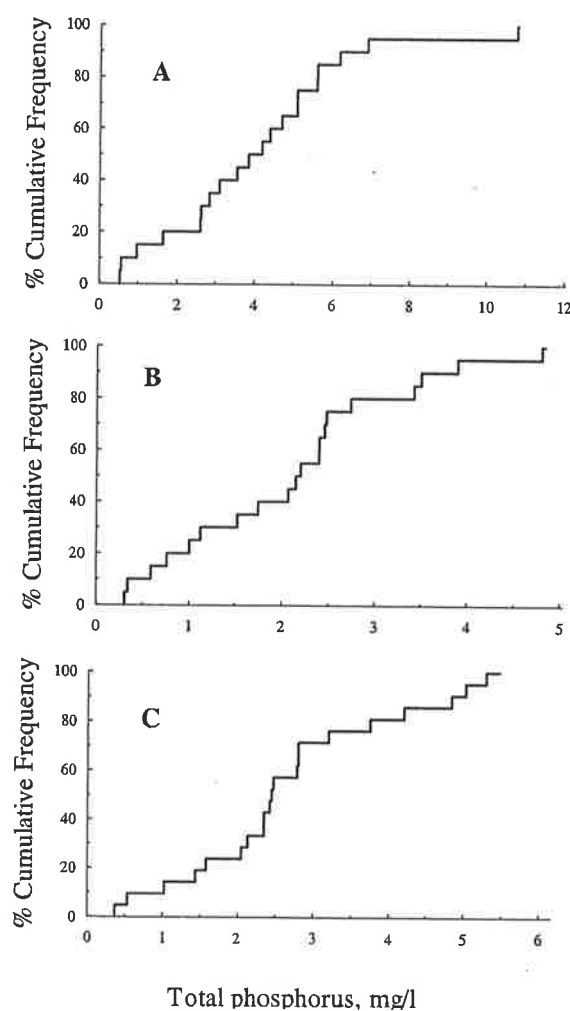


Figure 4-6, TP I/O probability distribution for Ponds with P poor substrates. A, Input; B, Pond 4; C, Pond 5

4.2.3 Relationships between Input and Output P Concentrations

The nonlinear power models fitted better for influent and effluent P concentrations in ponds than the simple linear models (Table 3-10), consequently, increased the power of prediction for the performance of ponds. In an attempt to predict the P removal efficiency of the emergent marshes, Kadlec and Knight (1996) plotted the in/out P concentrations from 49 wetlands in the USA, which range from reed canary grass in Oregon to cattails in Florida to sphagnum/Labrador tea in Quebec, they found the best regressive equation as $C_o = 0.34 \times C_i^{0.96}$ with $R^2 = 73\%$. Only the pond 2 produced the similar I/O behaviour as the

American model (Figure 4-8), the others are more erratic (Figures 4-7, 4-8, 4-9, 4-10, 4-11 and 4-12). The figures presented are the revised graphics of Figure 3-9, in which the power-law correlation of the inlet and outlet TP concentrations for individual pond are logarithmically transformed. These figures provided more visible information about the behavior of the ponds than Figure 3-9.

In pond 1 (Figure 4-7), pond 4 (Figure 4-11) and pond 5 (Figure 4-12), the power models as fitted are more accurate at higher P loading period. In the pond 2, the power model can be applied to almost any incoming P concentrations. In pond 3 (Figure 4-9) and the three-pond system (Figure 4-10), however, the prediction power is quite low for both low and high influent P concentrations.

Most of pond systems provide sustainable P removal except in the pond 3, in which the TP concentration in outlet exceeds concentration in inlet at 17 out of 40 sampling events (Figure 4-9). Not like in the pond 1, pond 4 and pond 5, which only released P during lower loading period in winter, pond 3 exported P during high loading period, making the prediction more difficult. The pond 2, however, can remove substantial P even in winter, although at a lower rate.

4.2.3.1 *P Loading and CWS Performance*

Pollutant loading rate is one of the most important conceptions in wastewater treatment. To ensure a good performance of any wastewater treatment facility, a suitable loading rate should be designed to match the treatment capacity and waste generation. CWS are not exception (US EPA, 1988; Gearheart et al., 1999). In the present study, as the flows were kept constant during the whole operation period, TP loading difference was only reflected in the input concentrations. As mentioned above, the TP concentrations fluctuate dramatically. In return, the TP loading into pond systems changed all the time with a general pattern of being lower in winter and higher in summer. The TP loading rate for the ponds covered a wide range from $0.025\text{g/m}^2/\text{day}$ in winter up to $1.153\text{g/m}^2/\text{day}$ in summer, which is approximately within the loading rate of $1\text{g/m}^2/\text{day}$ recommended by USEPA (1999).

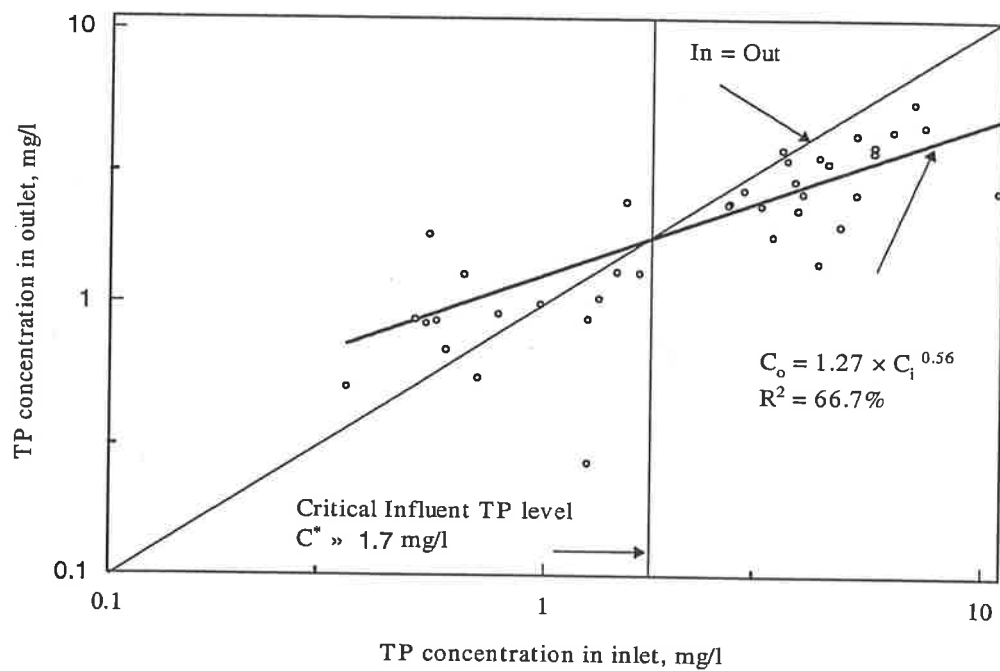


Figure 4-7. Black-box approach of P removal in pond 1, C_o and C_i are the TP concentrations in outlet and inlet respectively.

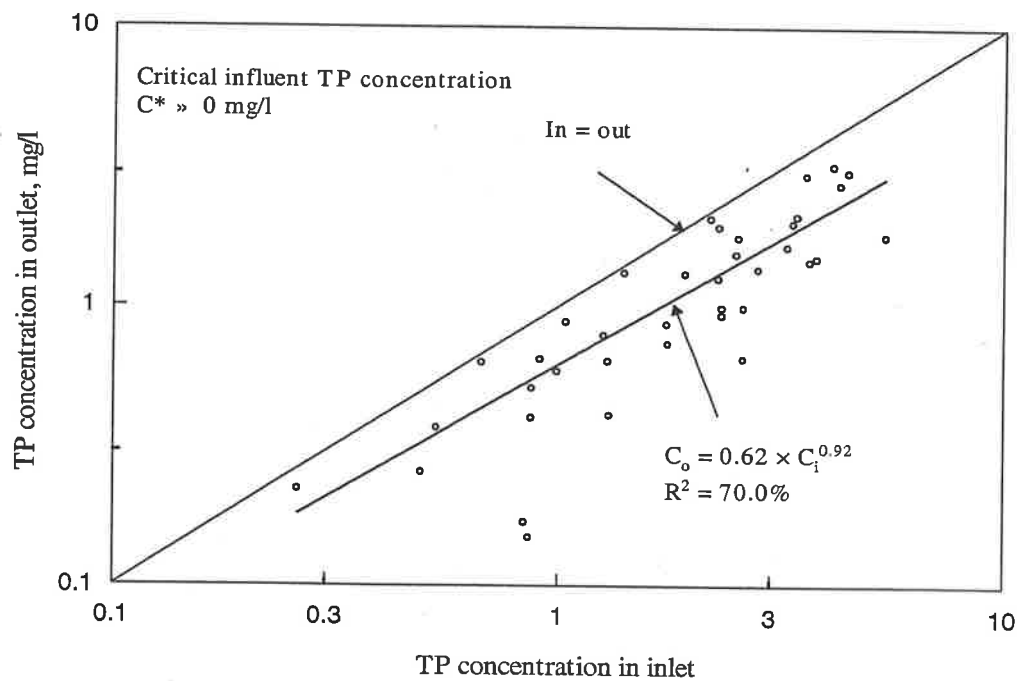


Figure 4-8. Black-box approach of P removal in the pond 2

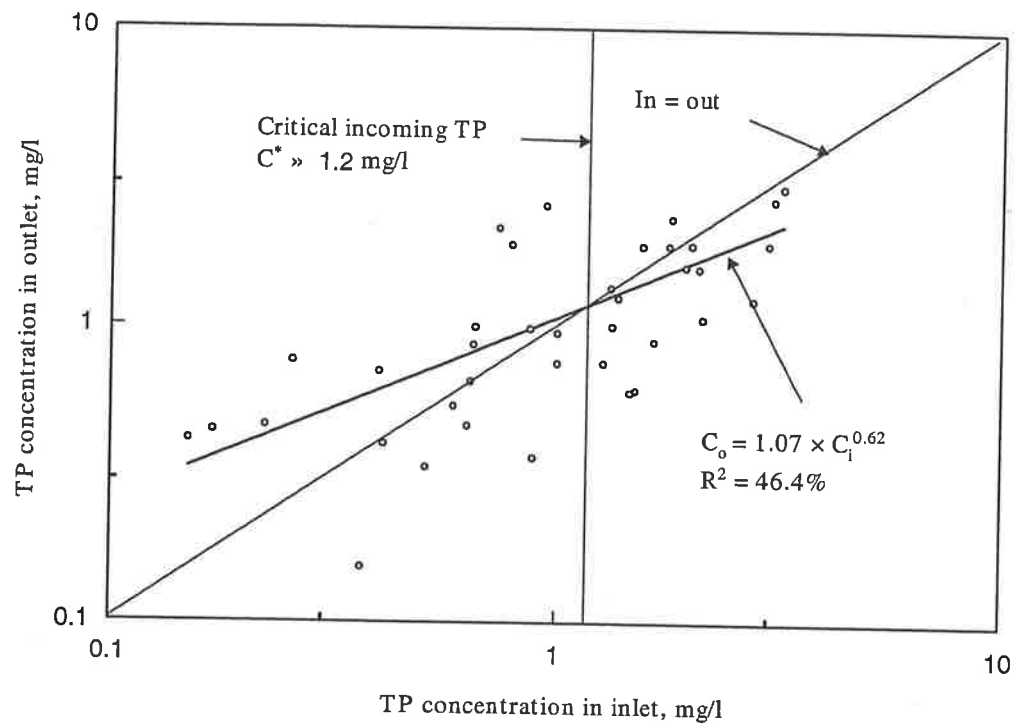


Figure 4-9. Black-box approach of P removal in the pond 3

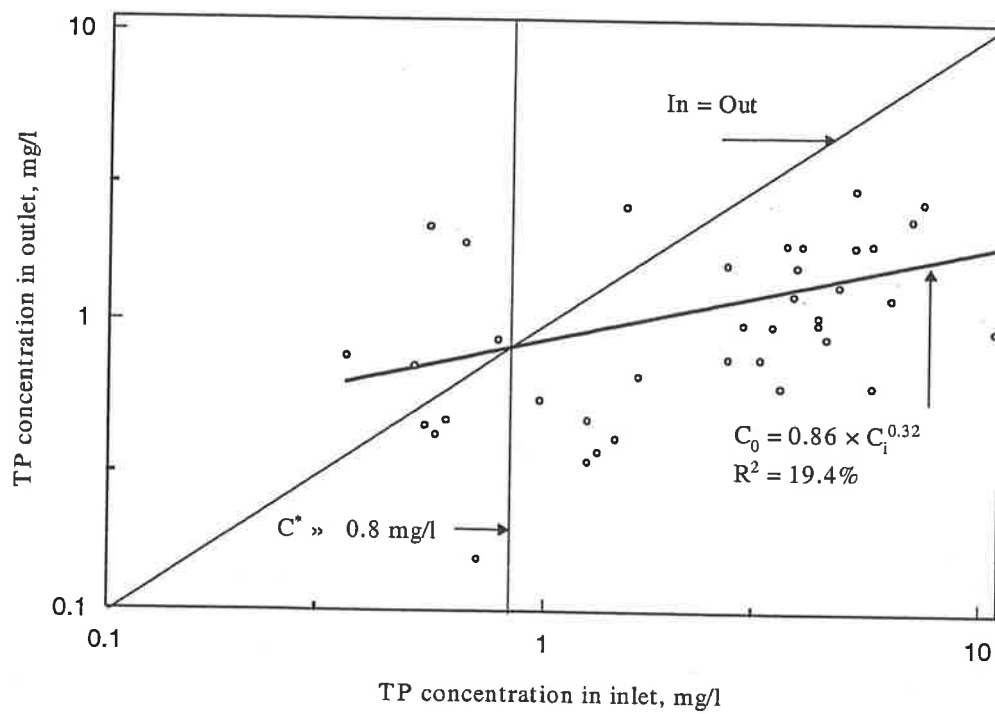


Figure 4-10. Black-box approach of P removal in the three-pond system

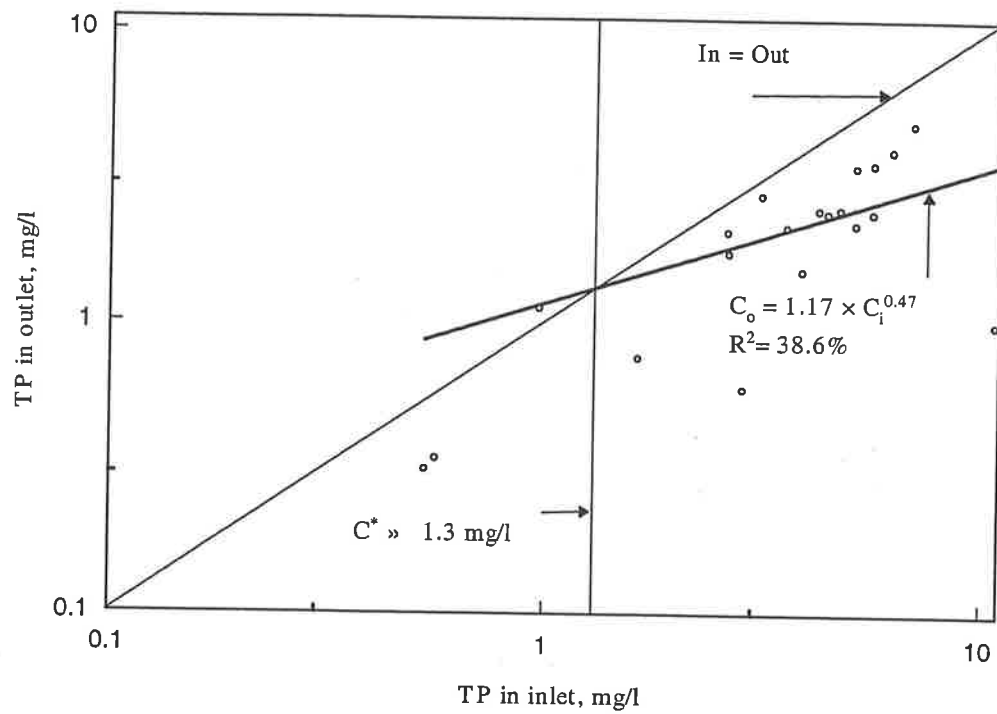


Figure 4-11. Black-box approach of P removal in Pond 4

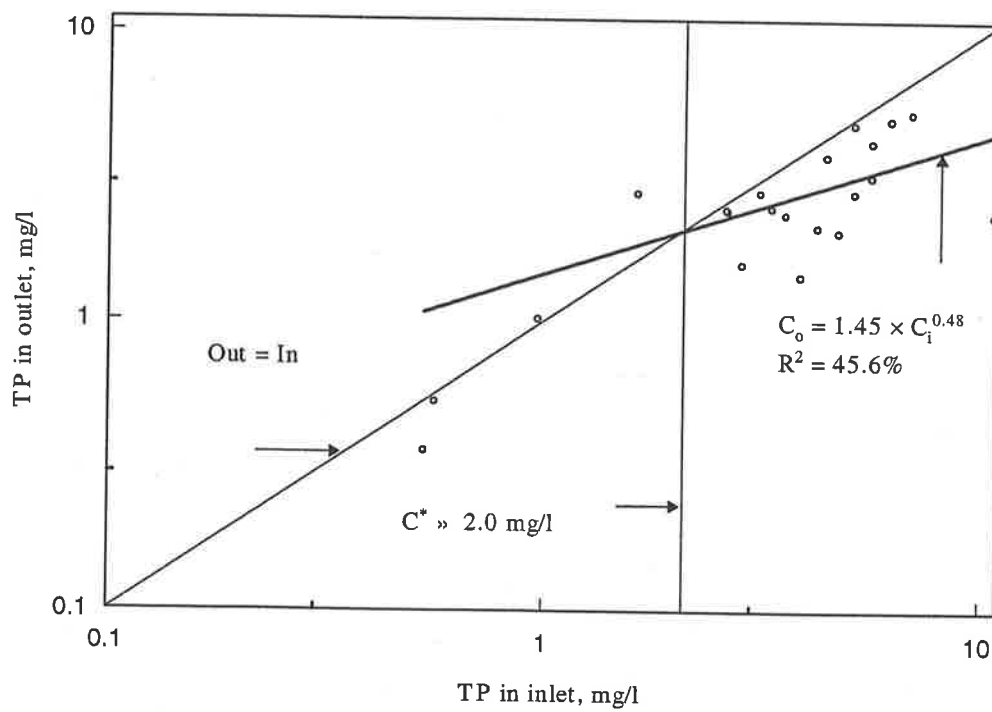


Figure 4-12. Black-box approach of P removal in pond 5

Figure 4-13 is the linear regressive fitting between TP loading rates and TP retained by the pond systems. Fitted parameters and the goodness-of-fit are listed in Table 4-5.

Table 4-5. Linear fit between TP loading rate and retention ($\text{g/m}^2/\text{day}$) in pond systems

	Pond 1	Pond 2	Pond 3	Overall	Pond 4	Pond 5
Intercept (a)	-0.125***	-0.016**	-0.083**	-0.042***	-0.096 ^{N.S}	-0.119 ^{N.S}
Slope (b)	0.545***	0.481**	0.414 ^{N.S}	0.885***	0.651***	0.551**
C.C	0.871	0.823	0.595	0.961	0.814	0.735
R ² (%)	75.8	67.8	35.5	92.4	66.2	54.0

The measured data fitted well the linear models (the collation coefficient ranges from 0.601 – 0.952, $P < 0.001$). However, both the fitted Y-axis intercept (a) and slope (b) differ from system to system, which means that each system has its own intrinsic characteristics to shape the fitted curve. The correlation between loading and retention was slightly stronger than that between loading and discharge for individual pond (Table 4-9). For the three-pond in series, the relationship between P loading and retention is much stronger than that between the incoming and outgoing P ($R^2 = 92.1\%$ and 14.2% respectively), suggesting the regressive equation for loading and retention may be more appropriate for prediction the system performance. It is obvious that the retention was positively related to loadings for all the pond system. This result suggests that the range of TP loadings into ponds in the present study failed to test the upper limits of water and chemical loading, which is in agreement with the observations of Mitsch et al. (1990), but contrast to the design guideline for P loading rate limitation of $1\text{g/m}^2/\text{day}$ proposed by the USEPA (1999).

Like the correlation between influent and effluent TP concentrations, the power model satisfactorily describes the relationship between P loading and retention in pond systems, especially for the three-pond system (Table 4-6). In addition, the power model produced visually better fit to the measured data than did linear regression (Figure 4-14), and the correlation coefficient (C.C) and coefficient of determination (R^2) are slightly higher than the linear fits except for pond 3 (Table 4-5), in which correlation was not significant.

$$\text{Fitted model: } Y = a \times X^b + C$$

(4-1)

Where, X and Y represent the TP loading to and retention by systems, $\text{g/m}^2/\text{day}$;

a, b and C are the intrinsic constants related to the characteristics of individual system.

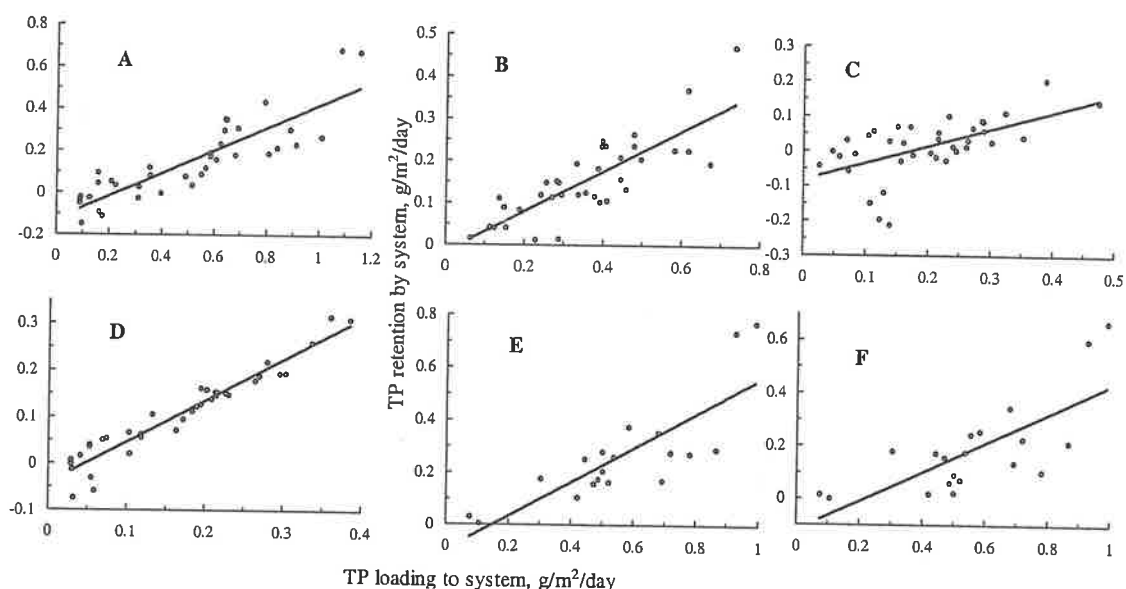


Figure 4-13. The linear relationships between TP loading and retention in A)Pond 1; B)Pond 2; C)Pond 3; D) Three ponds in series; E)Pond 4; F)Pond 5 . Circles are measured data, and lines represent the least-square linear regression fittings.

The power models also fail to test the saturation point of TP loading for the pond systems (Figure 4-14). However, not like the linear regression, it produced two groups of curves with distinct shapes (Figure 4-14). The ponds with P-rich soils from the sites had similar loading-retention patterns no matter what type of macrophytes employed, while the ponds using P-poor hill soils shared another analogous curves. Correspondingly, for system with site soils, the models as fitted have no significant relationship with the constant C , and C was not significant different from 0. For systems with hill soils as substrates, the constant C is important for the models as fitted.

Table 4-6. Parameters of the fitted power model between TP loading and retention by experimental ponds

	Pond 1	Pond 2	Pond 3	Overall	Pond 4	Pond 5
A	0.504***	0.525***	1.569 ^{N.S}	1.209***	0.646***	0.611***
B	1.585***	1.448**	2.805 ^{N.S}	1.398***	4.674**	6.10*
C	-0.05 ^{N.S}	0.03 ^{N.S}	-0.0 ^{N.S}	-0.0 ^{N.S}	0.152**	0.105**
C.C	0.882	0.829		0.958	0.866	0.842
R ² (%)	77.8	68.7		91.3	75.0	71.0

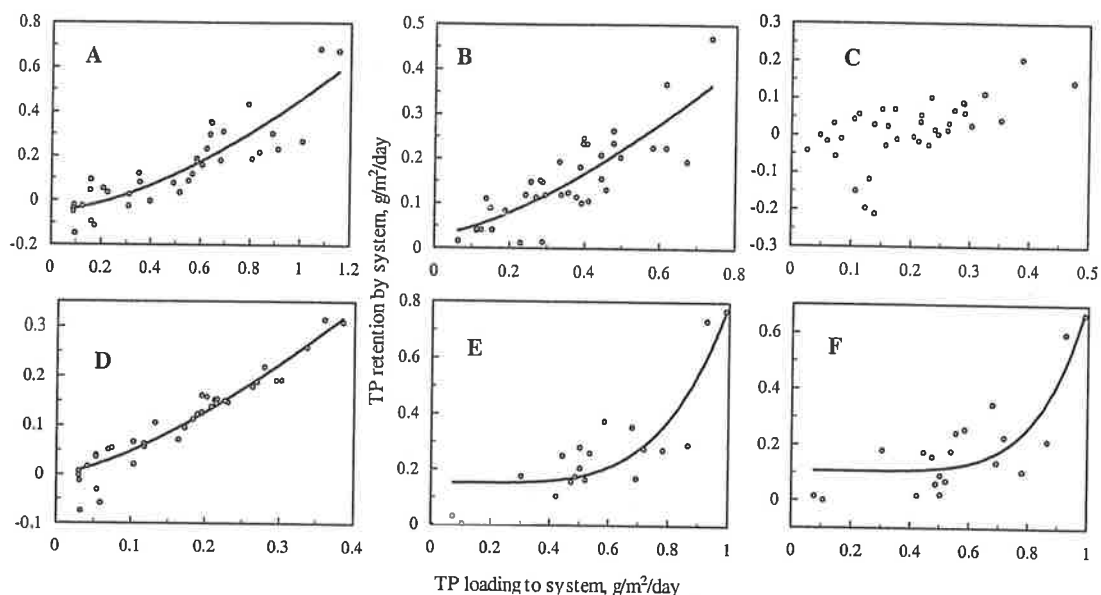


Figure 4-14. Power relationship between TP loadings and retention in A) Pond 1; B) Pond 2; C) Pond 3; D) Three ponds in series; E) Pond 4; and F) Pond 5. Circles are measured data. Curves represent the nonlinear regression fit of power models (Equation 4-1).

4.3 CONTRIBUTION OF MACROPHYTES TO P REMOVAL

One of defining characteristics of wetlands is the presence of macrophytes (US EPA, 1987), and as such macrophytes are an indispensable component of wetland systems. Many papers concluded that the role of macrophytes in constructed and natural wetland is critically important and their management will contribute to the level of performance achieved by the system and its long-term viability. Mann and Wetzel (2000) addressed the importance of the small aerobic rhizosphere created by rooted macrophytes by releasing oxygen into the surrounding sediments on the chemical composition of interstitial water and bacterial productivity. By comparing the differences between vegetated and unvegetated wetlands, they suggested that the releasing of oxygen from roots into sediments could facilitate microbial and chemical oxidation of reduced species present in interstitial waters, therefore, affect substrate utilization rates by bacteria, metabolic pathways and nutrient availability. Harlin et al. (1982), Carpenter and Lodge (1986) and Stevenson et al. (1988) reported that vegetation increased the deposition of particulate matter by slowing water velocities. Based on nutrient mass balance, some papers concluded that the macrophytes uptake could be a dominant removal mechanism for treatment wetlands (Breen, 1990; Rogers et al., 1991; Busnardo et al., 1992). In addition, the stems and leaves and debris of macrophytes that are

submerged in the water provide a huge surface area for biofilm (Gumbricht, 1993; Chappell and Goulder, 1994). The biofilm is responsible for the majority of the microbial processing that occurs in wetlands.

However, macrophytes may also have adverse impacts on P removal. For examples, vegetation patterns can lead to preferential flow patterns in CWS (Bowmer, 1987), which can reduce the sediment-trapping capacity (Johnston et al., 1984). Rooted macrophytes could pump nutrients from deep sediments and release into water column (Tanner, 1996). Lower temperature caused by vegetation shading reduces the bacterial activity. Density growth of emergent causes light limitation for the growth of epiphytes, phytoplankton and filamentous (Wen and Recknagel, 2001). As for the direct uptake, many reports thought that the macrophytes contributed very little for P removal (Gersberg et al. 1986, Tchobanoglous, 1987; Kruzic, 1990; Tanner, 1996, USEPA, 1999).

4.3.1 Floats Planted with Macrophytes as a Temporary P Storage

4.3.1.1 Growth Chamber Trial

Biomass removal with its accumulated P appears to be an efficient technique to control freshwater eutrophication, as it terminates the nutrient cycles in aquatic systems. The rates of P uptake by vascular plants have been the subjects of some studies (Boyd, 1969; Tanner, 1996, Greenway and Woolley, 1999). The published data are limited to those plants commonly used in constructed wetlands, mainly rooted emergent water plants, such as common reed, Typha, bulrush, or in floating-plant systems, for example, water hyacinth, duckweed, etc. The proportions of P potentially removable by stand biomass cropping depend upon plant growth rate and tissue P concentration. The current study is the first approach to explore the potential of procumbent water plants (runners) to remove P from wastewater. The plant productivities of the tested plants ($1.77 - 13.07 \text{ g/m}^2/\text{day}$) were in the range of reported wetland species (Table 4-7). The tissue P concentrations were at the upper range of spectrum of the reported. Aoi & Hayashi (1996) reported the highest P concentration of 1.67% in water hyacinths. In duckweed, Reddy and DeBusk (1985) reported the highest tissue concentration of 1.52% of P. Combining plant productivities and tissue P concentrations, the planted float showed a promising P removal potential of $0.086 \text{ g/m}^2/\text{day}$

under the controlled conditions. Under HNHS (high nutrients and high salinity), which was similar to the actual drainage water from the study site, the P removal rate reached $0.073\text{mg/m}^2/\text{day}$. Although it is difficult to assess the nutrient removal rate at system level due to the limitation of experiment design, the tested plants show high P bioaccumulation rate. While less than the highest removal rate of water hyacinth system reported by Reddy (1985), the float removed as much P as ($0.086\text{g/m}^2/\text{day}$) the duckweeds cultured on agricultural drainage water (Table 4-8).

In addition, compared to other ecotechnologies, such as floating-plants systems, constructed wetlands, buffer strips and buffer zone, the float method has several advantages: (1) It directly takes up nutrients from water column, and doesn't remobilise the nutrients in sediment. Any P bioaccumulated in water plant accounts for the mass P removed from water; (2) It enables the use of a diversity of aquatic plants; (3) It could be used in any waterbody regardless of its depth and bottom characteristics, for example, in some concrete channels which prohibit any other methods using rooted water plants; (4) The growth of plants is under control, minimizing the potential for impediment drains, and eliminating the problem of over-growth (such as occurs with water hyacinth); (5) Biomass harvesting is relatively easy; (6) There are no land costs if used as in-channel treatment of drainage water.

Table 4-7. Comparison of the relative growth rates of procumbent water plants with some reported data

Species	GR ($\text{gDM/m}^2/\text{day}$)	Reference
Water hyacinth	45.2	Westlake (1982)
Typha	53	Boyd (1970)
Carex stricta	11	Bernard (1974)
Carex stricta	12	Jervis (1969)
C. aqualitis	4	Gorham and Somers (1973)
Juncus effusus	14.2	Boyd (1970)
Sedge	2.5	Barnard (1974)
Sedge	1.4	Gorham and Somers (1973)
Sedge	0.9	Van der Walk and Bliss (1971)
Water Couch	1.41-13.07	This study
Parrot feather	1.77-7.12	This study
Waterbuttons	4.79-10.89	This study

However, although the study demonstrated the potential for P removal of floats under a controlled environment, some critical questions needed to be answered before application to

the field. Firstly, the effects of water movement on plant growth. The water movement caused by wind, wave and flow in field circumstances has a two-blade effect on the plant growth: while it brings more nutrients and other elements to the rhizomes, it may also cause physical damage to plant's root. The actual effects on plant growth may depend on the intensity of water movement. Secondly, in any natural or engineered ecosystem for wastewater treatment, plant bioaccumulation is only a fraction of the overall P removal. The P removal at system level, which involves both water plants and microorganisms should be investigated. Thirdly, the potential of rapid spread of water plants has to be tested. For the plants used in our study, water couch and waterbuttons are native plants, however, parrot feather is considered as exotic species in South Australia. The possible ecological and economic impacts of parrot feather need further research.

Table 4-8. Comparison of P retention in various ecotechnologies for wastewater treatment

System	Retention (g/m ² /day) ^a	Reference
Free water surface wetlands for polluted river water	0.004-0.14*	Mitsch (1993)
	0.0205	Nairn and Mitsch (2000)
Free water surface wetlands for effluent from anaerobic lagoon	0.37-0.43 (0.104)	Tanner (1996)
Floating plant-water hyacinth	0.371 (0.243)	Reddy and DeBusk (1985)
Floating plant-duckweed	0.234 (0.087)	Reddy and DeBusk (1985)
Floating plant-Azolla	0.128 (0.033)	Reddy and DeBusk (1985)
Floating plant – duckweed	0.082 (0.020) in winter 0.109 (0.019) in summer	DeBusk et al., 1995
Free floating – water hyacinths	0.10 (0.059) in winter 0.166 (0.20) in summer	DeBusk et al., 1995
Sub-surface wetland	0.03-1.37*	Mitsch and Gosslink (1993)
Sand/plant filter	0.18	Mander and Mearing (1997)
Bio-ditch	0.29	Mander and Mearing (1997)
Grassland	0.6*	Kuusemets and Mander (1999)
Alder forest	0.16*	Kuusemets and Mander (1999)
Planted floats	(0.043-0.086)	This study

^a figures in parentheses represent the removal rates due to plant uptake only;

* in g/m²/year.

4.3.1.2 *Field Pilot Study: Comparing with Floating Plant Pond Systems*

Fast growing floating water plants are used commercially all over the world in aquaculture systems to produce protein-rich feed for animals (Duran, 1994; Leng et al., 1994), green manure (Lumpkin and Plucknet, 1980), and biogas (Taheruzzaman and Kushari, 1989; Jain et al., 1992). These plants are also cultured as the major component in an integrated, advanced wastewater treatment system to remove nutrients (Eighmy et al., 1987; Tripathi et al., 1991). Floating-plant systems are shallow ponds with floating aquatic plants. The most thoroughly studied systems are those use water hyacinths or duckweeds (USEPA, 1988). The major characteristics of water hyacinths that make them an attractive biological support media for bacterial processing of pollutants are their extensive root system and rapid growth rate. The major characteristic that limits their widespread use is their temperature sensitivity (i.e., they are rapidly killed by winter frost conditions, Kadlec and Knight, 1996). In addition, their aggressive growth rates make them a pest and threaten to natural water bodies in Australia. The major advantage of duckweeds is their lower sensitivity to cold climate, while their major disadvantages have been their shallow root systems and sensitivity to wind and salinity, which is a widespread threaten to Australian inland freshwater systems. The planted float pond is an analogous system to floating-plants pond. It inherits the advantages of water hyacinths and duckweeds systems but could be utilized in a manner to overcome the intrinsic disadvantages originated by the characteristics of the water plants employed.

Under the field conditions, Waterbuttons and water couch can tolerate the high salinity level in drainage water. However, the parrot feather, which grew well in growth chamber, failed to survive the field conditions. A possible reason is that although the average salinity levels were comparable in the two experiments, the extreme salinity in drainage of 10.28‰ is fatal. During the operation period (242 days), the average salinity level was 4.58 ‰ with maximum of 10.28 ‰ (Table 4-1), which is far from optimal for most freshwater macrophytes.

In field, the growth rate of water couch was much higher than in growth chamber (25.21 and 13.07 g/m²/day for growing in field and growth chamber, respectively). However, the tissue (whole plant) P concentration of 0.207% was much lower than 0.46% when cultured in artificial media of high nutrient and high salinity, and comparable to low nutrient and low

salinity conditions (0.26%). The lower tissue P concentration may be due to the dilution effect of the fast increased biomass. Another possible explanation is that the artificial growth solution used in growth chamber was nutritionally balanced while the drainage water may be far from ideal, i.e. the N:P ratio. For waterbuttons, while the growth rate was slightly lower (9.01 vs. 10.89 g/m²/day), the tissue P concentration was much lower under field conditions (0.425% vs. 0.65%). Nevertheless, the planted floats were slightly more efficient for P removal in field than under stable environment (0.0906 and 0.086 g/m²/day for field and growth chamber conditions, respectively). As the two species are both native plants and acclimatize to the local environment, it is not surprising that they grew better in the natural condition.

The total productivity of planted floats (34.2 g/m²/day) can match that of water hyacinths system (36.3 g/m²/day, Debusk et al., 1995, refer to Table 1-2). As the plant P tissue concentrations were lower than that of duckweed and water hyacinths cultured in wastewater, the biomass P accumulation was lower in planted floats system (Table 4-X). However, as P uptake by macrophytes is only a fraction of the total removed P in such systems, the maximum P removal in the planted floats systems was 0.47 g/m²/day, which was higher than that of the water hyacinths system (0.371 g/m²/day) reported by Reddy and DeBusk (1985).

4.3.2 Emergent water plants in CWS

4.3.2.1 Biomass Production

The high potential productivity, deep rhizome and root system, ready propagation and wide distribution of giant reed, which was the only species that survived the drainage condition in the study, have made it the most common planted in CWS all over the world. This is particularly so in Europe, where it has become the key species specified in design guidelines (Cooper and Findlater, 1993).

System theory predicts that the development of an ecosystem is a function of initial conditions and the forcing functions to that system (Jorgensen and Mitsch, 1989). Vegetation successional trend is, in part, a function of changes in the physical environment, a qualitative model described by van der Valk and Davis (1978). In this model, the physical environment behaves as a sieve, allowing the persistent species to adapt to the conditions at hand. Changes

in the plant community in pond 1 show good agreement with this model. Community structure developed within the physical confines of the systems using the introduced plant sources. The development of the macrophyte community was a function of the initial “available” plants species and the “sieve” effect brought about by inundation with drainage. In the present study, as all the introduced macrophytes are native wetland species, they are wet-adapted and highly productive. One of the most important selective forces in this case may be the high salinity level. Only those wet-adapted species, which are tolerant to the high salinity can, persisted, their productivities rise as their coverage expanded, and become the dominant species. Reed, *Typha* and bulrush, all introduced before the flooding, are perennials which can persist and spread vegetatively for many years. However, only reeds showed rapid establishment and spread, increasing its mean shoot density to around 520/m² during the first growth season. Other species, as observed in the study, their growing was obviously suppressed, and contributed little the overall biomass production. Besides the high salinity, water depth may be another “sieve” which contributed to the dominance of reed, as *Typha* and bulrush prefer relatively deeper water levels.

Using alluvial gravels as substrates and fed with anaerobic pond effluent, Tanner (1996) demonstrated that the reed density could reach 758 /m² in 90 days. Although the shoot density was lower in the present study, it had a relatively higher maximum aboveground biomass value of 5.02 kg/m² in February. In Tanner’s study (1996), the corresponding value was 1.8 kg/m². Hofmann (1986) investigating reed growth in nutrient-rich sewage sludges, reported maximum aboveground biomass of 2-3 kg/m². Adcock and Ganf (1994) have recorded a lower aboveground biomass of 0.8 kg/m² in Australia.

The maximal shoot height of 1.5 m was much shorter than those found in the literature, while the basal diameter (0.6 cm) was slightly higher. Similar tendencies, i.e. the forming of a greater number of shorter shoots as an effect of flooding with nutrient high wastewaters, were noted by Hardej and Ozimek (2002) and Reinhofer (1998).

By trailing the morphometric changes, a highly significant and predictive phenometric model was obtained for catching the growth trajectory of reed ($R^2 = 97.2\%$). The step-wise regression also indicates that the measurements of shoot height, diameter at base and number

of axillary shoot is sufficient to catch the majority of biomass variation. The model is more accurate than the commonly used shoot height-biomass model, such as that used by Hosoi et al (1998). However, as the measured parameters are tripled, the amount of labour required also increased. The established growth pattern was in accordance with the observations of Hocking (1989), although the biomass was less than half in our study.

4.3.2.2 *Tissue P Concentrations in Reed*

Shoot P content in reed showed distinct seasonal pattern. The maximum value of 0.39mg/g was recorded at its early growth stage followed by a sharp decrease as growth continued. Hosoi et al (1998) also observed that the highest P content was in spring (Japan). Many other researchers found that the tissue P concentration was different in plants collected at different time of the year (e.g. Boyd and Balckburn, 1970; Handoo and Kaul, 1982). Vegetation nutrient contents tend to be highest in the early growth stage, and decrease as the plant matures and senesces (Boyd, 1970; Bernard and Solsky, 1977). It is generally attributed to the translocation from the nutrient stocks in the rhizomes in early growth. Approximately 40% of P required for growth was transferred from rhizomes according to the calculation of van der Lindin (1986). The decrease of P levels in shoot as reed approaching mature and towards senescence was due to the reverse translocation from shoot to rhizomes, and the dilution effect as biomass increase.

As the P contents in the shoot of reed is always in a dynamic state, most of the reported P concentrations are mid-season levels. In our study, the mid-season tissue P concentration was around 0.20 mg/g, which was less than those of the other tested species and the average P content (0.25 mg/g) of wetland plants (Kadlec and Knight, 1996). Greenway (1997) also found that reed had relatively lower P concentration among 12 macrophyte species planted constructed wetlands treating secondary domestic sewage. Similar P levels have been recorded for reed growing in gravel-bed wetlands for secondary sewage (Adcock and Ganf, 1994) and for settle domestic sewage (Burgoon et al., 1991). Records for reed cultured in fertilized tank (Ulrich and Burton, 1985), for mature natural communities (Hocking, 1989) have shown considerably lower levels.

4.3.2.3 P Recovery by Harvesting

The dynamic states of accumulated aboveground biomass and shoot P content have profound effects on the amount of P could be removed from constructed wetlands by biomass harvesting. The ultimate amount of removed P is the product of shoot P content and aboveground biomass. As the tissue P levels decrease sharply after reaching the peak value at approximately 70 days after the beginning of the annual growing circle, furthermore, the aboveground biomass gradually reaches a plateau after approximately 150 days of growth, the P recovery is maximum (13.3 g/m^2) when harvesting is done at about 70 days after the resuscitation, i.e. in later November. By investigation the biomass accumulation and tissue P content dynamic, Hosoi et al. (1999) recommended the best harvest timing was about 90 days after regrowth. The longer growth period may due to the difference between temperate (Japan) and Mediterranean climate (South Australia).

Table 4-9. Advantages and disadvantages of emergent and planted-floats systems

	Advantages	Disadvantage
Emergent	• Longer storage; • Easy management; • Modification of substrate, enhancing the capacity of substrate adsorption; • Large surface area for attached biota	• Costly to harvest; • Pump nutrients from deep sediments; • Density growth shades out epiphytes, periphytes and phytoplankton; • Cooling down water temperature; • Causing short-circuits; • Unstable P removal rate
Planted-floats	• Easy to harvest; • Directly uptake nutrient from water column; • Stable performance; • Encouraging coprecipitation	• Shorter storage; • Shallower water depth

The optimal biomass P recovery of 13.3 g/m^2 in the present study was within the range of 3-15 g/m^2 for wetland plants cited by Brix (1997), but much higher than the 1.4-5.3 g/m^2 summarized for reed by Kadlec and Knight (1996). Macrophyte uptake accounted for 17.6% of the P removed by the pond 1. Our result of relatively high biomass P accumulation is contrast to the general conclusion that the amount of nutrients that can be removed by harvesting was insignificant comparing with the overall performance (Gersberg et al., 1986; Tchobanolous, 1987; Brix, 1994; Brix, 1997). Moreover, multiple harvesting could increase

P removal. For example, by examining the regrowth behaviours after harvest, Hosoi et al. (1998) demonstrated that P removal could be doubled if harvesting twice a year. In addition, if the wetlands are not harvested, the vast majority of standing stock of P will be return to the water by decomposition processes. Despite of the evidences, the regular harvest of emergents from constructed wetlands has not been successful in full-scale applications because of cost and sustainability. Table 4-9 summarizes the advantages and disadvantages of emergent plant and planted floats systems.

There is a misconception that the uptake by rooted vegetation contributes little to the P removal in CWS because sediments are the major source of nutrients (Vymazal, 1995; Kadlec and Knight, 1996; Tanner, 1996). It is true that rooted emergents do get most of the P from sediments (Sculthorpe, 1967), but the uptake reduces the ortho-P concentration in the porewater, thus, fastens the diffuse of water P towards the sediment (see discuss in section 4.2).

4.3.3 Submergent Plants

Submergent water plants are either suspended in the water column or rooted in the bottom sediments. Typically, their photosynthetic parts are in the water column. The fact that they can take up nutrients from both the water column and sediments makes the potential for use of them for polishing effluent at least theoretically an attractive option. The tendency of these plants to be shaded out by algal growths and to be killed or severely harmed by anaerobic conditions limits their practical usefulness. So for, the utilization of submergent plants for water treatment is not implemented in full-scale, and the studies on the topic are scarce.

Although the river ribbons developed well in the pond, their contribution to P removal is questionable. Pond 3 had the most disappointing performance among all the experimental ponds. In addition, the pond was, sometimes, a net P sources even in the summer season, especially for the dissolved inorganic P. One possible reason is that the quick release of accumulated P upon the decay of plant biomass.

4.4 SUBSTRATES' ROLE IN P REMOVAL

The bottom sediments of large natural water bodies, such as lakes, represent a natural record of their history because most substances entering the water body eventually find their way to the sediments (Fishman et al., 1994). It is not only true for particles that sink directly to the bottom but also for substances dissolved in water. With time, the dissolved substances can be retained in the sediments by various processes, including adsorption to particles and chemical precipitation, and biological transformation and the consequent sedimentation. In constructed wetlands, all the processes also occur although in a smaller scale for some processes due to the shorter hydrological residence time.

In Wetlands, the topsoil layer (normally 0-30 cm), in which the activities of plant roots and microorganisms and chemical reactions such as desorption and adsorption is very active, is sometimes called *acrotelm*. In contrast, soils below the root zone are relatively inactive and are the *catotelm*. Although both zones contain available and unavailable P, it is the *acrotelm* that affects the P flux between water column and substrates. Researches have repeatedly attributed the major loss of P from water column to the soils and bottom sediment (Reddy, 1999). However, chemical compounds that reach the sediments do not necessarily remain there permanently. Sediments can function as a reservoir, or temporary storage place, for certain elements, which can be released back to the water column (resolubilized) with changing environmental conditions, such as pH, redox potential and temperature (Mitsch and Gosselink, 2001). Substances associated with sediments can also be released by biological activities, such as burrowing of worms of aquatic insect larvae, algal productivity near the sediment surface, microbial activity that causes biodegradation, etc. P is a good example of an element that can move in both directions between water and sediments. P exists in various forms in both sediments and water, but it tends to move towards the sediments when it is incorporated into various kinds of particulate matter. However, most of the particulate associated P is relatively unstable. Under certain environmental conditions, it can be released to the water from the solid phase.

The capacity of wetland soils to retain P depends on the physico-chemical characteristics. For a particular wetland soil, under certain environmental conditions, inorganic P added at considerable greater concentration than those present in the porewater is retained by oxides

and hydroxyoxides of Fe and Al and by calcium carbonate. At low P loadings, wetland soils release rather than retain P (Logan, 1982; Richardson, 1985).

4.4.1 P Pools in Soils Utilized in the Experiment Ponds

The hill soil used in the experimental ponds is Calcarosol according to the Australian soil classification system. It contains calcium carbonate as soft or hard fragments. The top layer of soil has about 10% of clay, less than 5 % of silt and more than 80% of sand (Peverill et al. 1999). The TP concentration of 196.1 mg/kg is on the lower end of 134-554 mg/kg for Australian soil (Ruan and Gilkes, 2000). On contrast, the soils from the site are developed from the historical fluvial sediments and has large amount of clay. It can be anticipated that the highly organic heavy clay soils, with associated high cation exchange capacity and high levels of iron and calcium, will have good potential for P immobilization. However, the long-term of dairy production alters the soil structure and chemical components. A significant change is the increased levels of nutrients (N, P) and organic matter. TP concentration of soils from the site of 828.2 mg/kg is relatively high. The potential of P release once inundated with drainage is also high. The sediments from the natural wetland receiving drainage have a moderate TP level of 376.8 mg/kg. Ruan and Gilkes (2000) analysed sediments of ponds and dams from a wide range of trophic states in East-South of Australia and found that the sediment TP levels ranged from 29 to 1101 mg/kg.

To determine the role of sediments on P cycles in CWS, it is important to develop a fundamental understanding of the forms of P in the system. Major inorganic P pools identified by the modified P fractionation scheme used in this study included: 1) loosely adsorbed P or labile inorganic P (LIP), 2) Fe/Al- bound P and 3) Ca-bound P. In addition, the method quantified organic P into two pools: labile organic P (LOP) and residual or refractory organic P (any P not extracted). This fractionation scheme was originally developed for mineral soils, and it only roughly characterizes the organic P pool. Although it is still an open question which type of P the different fractionation methods actually measure (Pettersson et al., 1988; Jauregui and Sanchez, 1993) due to hydrolysis of P forms when extracting with different solutions, there is a lack of alternative methods. Moreover, as the relationships between P release and the various P fractions are largely unknown, their potential usefulness in predicting sediment-water interactions is presently limited

(Sondergaard et al. 1996). Trying to link Phosphorus fractions and phosphorus sorption characteristics of freshwater sediments, Borovec and Hejzlar (2001) found that maximum sediment P-sorption capacity was the only sorption parameter correlated with P-fractionation, and none of the other sorption parameters (initially adsorbed P, adsorption/desorption equilibrium concentration) were correlated with the results of fractionation analysis.

Among the three identified inorganic P pools, the loosely adsorbed P is considered labile and is important for plant growth and controlling the P balance between soil particles and porewater. Although this pool of P is relatively small (0.8%, 1.5% and 4.0% for soils from the site, wetland sediments and hill soils, respectively), it readily responds to external P loading, and is the most dynamic P form in soils and sediments. The relatively higher level of LIP in hill soils suggests that this pool of P may be loosely bound to CaCO_3 , as the hill soils contain high level of calcium carbonate. Many studies measured LIP in soils or sediments (Gale et al., 1994; Reddy, 1990; Martin, et al., 1995; Reddy et al., 1998), but the effects of LIP on adsorption of P onto the soil particles is hard to distinct due to its short turnover rate. By examination of P pools in 32 shallow lakes, Sondergaard (1996) found that the LIP was positively correlated to the external P loadings, to sediment organic contents and to phytoplankton, but not to TP and Fe suggesting its role on governing the balance between sediment and water.

The P extracted with 0.5 M HCl represents Ca/Mg-bound P. Hieltjes and Lijklema (1980) and Olila et al. (1994) extracted 98 –100% of P associated with synthetic Ca phosphate using 0.5 M HCl. Many papers reported the significant correlations between HCl-P and the extracted Ca and Mg concentrations in soils and sediments (e.g. Reddy et al. 1996). The highest levels of Ca-P (38.6% of TP) were measured in soils from the hills. In contrast, Ca-P only accounted for 12.4% of TP in soils from the site. As Ca-P was believed to be stable under anaerobic conditions and sensitive to lower pH, the hill soil could be a better substrate for CWS than the site soil. In natural wetland sediments, more than 20% of the TP was Ca associated. This may be the evidence that the P accumulation in the drainage-affected wetland was mainly in the Ca-P pool, as the Ca concentrations are relatively high in drainage water.

The total NaOH extracted P was analysed for organic P (as labile organic P) and inorganic P (as Fe/Al-bound P). As NaOH probably hydrolysed a portion of organic P, the results may elevate the levels of Fe/Al-P and underestimate the level of the LOP pool, especially for soils from the site and wetland sediments due to their high organic matter contents. The Fe/Al-P not only represents the P associated with hydroxyoxide surfaces, but any P associated with crystalline Fe and Al oxides (Hieltjes and Lijklema, 1980; Olila et al. 1995). P associated with hydroxides can be desorbed under most conditions, but the P associated with crystalline Fe and Al oxides is only desorbed into solution under extended waterlogged condition (Patrick and Mahapatra, 1968). The high level (62.6%) of Fe/Al-P in soils from the sites, albeit including part of the LOP, indicates that large amount of P may be released into water once flooding with drainage. This hypothesis was substantiated by the evidence of the sharp drop of TP in soil in Pond 1 and pond 3. The hill soil, by contrast, has lower NaOH extracted P (10.9%, including Fe/Al-P and LOP).

4.4.2 Soil P Dynamics

4.4.2.1 Ponds with Soils from the Site as Substrates

As P level in soils was relatively high and dominated by Fe/Al-P, P dynamics in the sediment were more complicated. The Fe-P pool may mobilize and dissolve under anaerobic conditions (Wildung *et al.* 1977). Not surprisingly, the Fe/Al-P pool decreased dramatically as the soil was flooded. The trends of TP in pond 1 and pond 3 were identical (Figure 3-21), but the dynamics of the individual P pool had obvious differences (Figures 3-22 and 3-23). In pond 1, the Ca-P maintained consistently lower levels than in pond 3 for all the sampling dates (Figure 3-22B). This may be explained by the significant lower pH value (Table 4-10, 4-11A) in the water within pond 1. As the difference of chlorophyll-a concentrations in the two ponds was not significant, the higher pH value in pond 3 may be mainly caused by the photosynthesis of submergent macrophytes, which also contributed to the significant higher DO level (Table 4-11D). The submergent macrophytes also contributed to the always-higher concentration of labile organic P in sediments (Figure 3-23B). Unlike the emergent water plants, submergent macrophytes are very short biomass P storages. However, the Fe/Al-P pool, which showed fast response to inundation, was identical in the two ponds (Figure 3-22A).

Table 4-10. Selected water quality parameters in ponds

System	pH	Chl-a ($\mu\text{g/l}$)	Temperature ($^{\circ}\text{C}$)	DO (mg/l)
Pond 1	7.66 (0.75)	36.98 (43.35)	19.71 (3.81)	4.23 (2.86)
Pond 3	8.72 (0.48)	53.93 (47.67)	19.91 (3.75)	8.19 (3.76)
Pond 4	8.66 (0.44)	28.98 (25.62)	19.39 (3.82)	10.46 (3.93)
Pond 5	9.08 (0.61)	130.67 (180.64)	18.97 (3.62)	12.25 (4.87)

Data for one growing season, results as means ($\pm$ S.D), n=22.

The P build-up in pond 3 was faster than in pond 1 (Figure 3-21), consequently, the sediment P adsorption was less efficient (Tables 3-21 and 3-22). As the exc-P was always higher in pond 3 than in the pond 1, the value of S_0 , which is the indicator of P in soil/sediment under ambient conditions, was also higher. Reddy *et al.* (1993) also found a positive relationship between S_0 and exc-P.

Table 4-11. Comparisons of the selected water chemical and biological parameters in ponds with different configuration

A				B			
	Pond 3	Pond 4	Pond 5		Pond 3	Pond 4	Pond 5
Pond 1	*** (P<0.001)	*** (P<0.001)	*** (P<0.001)	Pond 1	N.S. (P>0.05)	N.S. (P>0.05)	* (P<0.05)
Pond 3		N.S. (P>0.05)	N.S. (P>0.05)	Pond 3		N.S. (P>0.05)	N.S. (P>0.05)
Pond 4			N.S. (P>0.05)	Pond 4			* (P<0.05)
C				D			
	Pond 3	Pond 4	Pond 5		Pond 3	Pond 4	Pond 5
Pond 1	N.S. (P>0.05)	N.S. (P>0.05)	N.S. (P>0.05)	Pond 1	* (P<0.05)	** (P<=0.01)	*** (P<0.001)
Pond 3		N.S. (P>0.05)	N.S. (P>0.05)	Pond 3		N.S. (P>0.05)	N.S. (P>0.05)
Pond 4			N.S. (P>0.05)	Pond 4			N.S. (P>0.05)

A: pH; B, Chlorophyll-a; C, temperature; D, Dissolved oxygen.

*** highly significant; ** moderate significant; * significant difference; N.S, difference not significant based on Tukey's test at confidence level of 0.05.

4.4.2.2 Ponds with soils from hill as substrates

As the soils used were dominated by Ca-P and res-P, which are less sensitive to redox potential, furthermore, the labile organic P was also negligible (2.9%), it could be expected that anaerobic conditions caused by flooding would not cause a large amount of P flux from the sediment to the water column. In fact, the results of P fractionation showed that all the P pools, except the res-P, increased after inundation with drainage in both ponds (Figure 3-25). Although P fractionation can't provide information about P transformation in sediment, the

changes of P pools indirectly gave evidence about the P removal mechanisms and their relative importance in CWS.

In pond 5, the Ca-P pool increased the most, which reflected that co-precipitation might be the dominant P removal mechanism in the system. House (1995) suggested that the co-precipitation would take place when the pH in water was higher than 8.5, and Ca was available. As planktonic algae dominated the system (Table 4-10, average chlorophyll-a concentration 130.67 µg/l, which was significant higher than other systems, Table 4-11B), the algal photosynthesis utilised the dissolved CO₂ and drove the pH to a very high level (average 9.02, Table 4-10). In addition, the Ca concentration is relatively high in drainage water. As a result, co-precipitation was promoted. The dense growth of planktonic algae caused very high turbidity in the water (data not shown), and the chance of benthic algae and epiphytes to develop was light limited. Additionally, as planktonic algal cell does not settle easily and most of the algal cells were flushed out of the system, its contribution to P removal was less important. Consequently, the accumulation of labile organic P (6.1 mg/kg) in sediment was much less than that of Ca-P (37.5 mg/kg) (Figure 4-25). Contrast to the observation of Ann *et al.* (2000), there was no evidence of the transformation of Fe/Al-bound P to Ca/Mg-bound P at high pH, as Fe/Al-bound P increased faster in pond 5 (higher pH) than in pond 4 (lower pH).

In pond 4, on the contrary, the increase of Ca-P was less important compared with the build-up of labile organic P (56.24 mg/kg and 11.18 mg/kg for labile organic P and Ca-P respectively, Figure 3-25). As shown in Table 4-10 and 4-11B, the chlorophyll-a level was significant lower than in pond 5, correspondingly, pH and dissolved oxygen were also lower although the differences were not significant. The relatively clear water and P-rich conditions encouraged the quick colonization of epiphytes and benthic organisms on the surface of the sediment and the submergent parts of macrophytes, which in turn competed out planktonic algae. Many benthic algal and epiphytic species are known as "luxury P uptakers" (Wetzel, 1983, 1996), and P uptake by these organisms may be an important P removal mechanism in this specific system.

4.4.3 P Adsorption Characteristics of Soils

The mobility of P in wetland sediments is governed by P retention capacity and P buffer intensity. P retention capacity refers to the maximum available sorption sites, which is determined by the physico-chemical properties and P already present on solid phase. This is also referred to as buffer capacity of the soil analogous to pH buffering (Froelich, 1988). Buffer intensity refers to the strength of adsorption. Maximum P retention capacity is generally reached following saturation of all sorption sites. The sorption capacities of soils and sediments measured in studies reported were based on the soil/sediments mixed continuously with P-enriched water. P adsorption can only occur when inorganic P is in direct contact with adsorbents. In CWS, water column P must diffuse into underlying sediments before it can be retained. This happens only when there exists a concentration gradient between porewater and water column P levels. Thus, in field, areal P retention by wetland sediments depends on P diffusion from water column to underlying soil/sediments, the physicochemical characteristics at the sediment-water interface. The laboratory sorption data alone are not readily useful in predicting the P retention capacity in a dynamic wetland system, unless consideration is given to the P concentration of the influent, water depth, hydrological residence time, and the effects of vegetation.

Although the handling of the sediments and soils may have altered the P adsorption capacity, it seems unlikely that the relative sorption capacity would differ between samples. Samples exposed to oxygen during the spiking experiments may differ to those *in situ*. Consequently, the results were not inferred to the actual maximum sorption capacities of soils and sediments. In fact, the amount of P adsorbed by soils after 2 hours may represent only 60% of the maximum capacity of the adsorbents (Kadlec and Hammer, 1982), because long term processes bind sediment with greater amounts of P over time (Barrow and Shaw, 1975; Van Riemsdijk, et al., 1977). However, the results gave valuable information about the adsorption characteristics of soils and sediments.

The P retention capacity of sediment and soil was significantly related to the content of amorphous and poorly crystalline forms of Fe and Al (Lijklema, 1980; Richardson, 1985; Gale *et al.*, 1994), total organic carbon (TOC) (Reddy *et al.*, 1995) and particle size (Sanville *et al.*, 1976). In the present study, the sediment/soil compounds other than P were not

analysed, the discuss will focus on the impacts of rooted macrophytes and P pools on the P adsorption characteristics of sediments.

There is a considerable controversy over the proper use of the Langmuir equation for adsorption studies and interpretation of the parameters fitted, arising from the fact that the Langmuir model was developed from the assumption that adsorbed gases form a monomolecular film on uniform surfaces, whereas the adsorption of P on minerals involves adsorption to non-uniform surface (Barrow, 1978). The biggest advantage in the application of the Langmuir equation is that it enables the calculation of theoretical P adsorption maximum. Therefore, the model is being most frequently used so far. In the present study, the Langmuir model is extended to include a state constant S_0 , which refers to the initially adsorbed P (Reddy et al., 1995). Based on the fitted models, a series of parameters to describe the P adsorption characteristics were calculated.

4.4.3.1 P Adsorption of Initial Soils and Sediment from Natural Wetlands

The results of P adsorption/release experiments indicated that the sediments from natural wetland had the highest P adsorption capacity, i.e. higher value of P adsorption maximum, lower binding energy, EPC_0 and P saturation. This was in agreement with the results of one-point measurement of PSI, which was highest for natural wetland sediments (Table 3-23).

Table 4-12. P adsorption characteristics of different soils, sediments and substrates

Substrates	TP (mg/kg)	LIP (mg/kg)	S_{max} (mg p/kg)	K	References
Pasture soil	828.2	6.9	783.78	0.379	This study
Hill soil	196.1	7.9	272.63	0.211	This study
Wetland sediment	372.3	5.1	1849.42	0.075	This study
Stream sediment	347	0.35	575	0.525	Reddy et al. 1995
Wetland sediment	190	2.1	98	0.233	As above
CWS	485	-	1153	0.0235	Sakadevan and Bavor, 1998
Wetland soil	873	-	5208	0.219	As above
Zeolite			2150	0.046	As above
Furnace Slag			44247	0.044	As above

LIP, Labile inorganic P; -, no data

Furthermore, the fitted Langmuir models had significant relationships with all the three parameters, i.e. S_{max} , S_0 and K, indicating the importance of these parameters for governing

the P adsorption. As mentioned above, the interpretation of parameters in the Langmuir model should be with caution. The reported values of maximum P adsorption and binding energy cover a wide range (Table 4-12).

Comparing with the soils from hill, the pasture soil had higher P adsorption maximum and PSI whereas the much higher TP concentration. It confirmed the conclusion that the P adsorption depends on the soil compound and soil texture other than the P levels providing both soils were far from saturated with P (8% and 5% for pasture soil and hill soil, respectively).

4.4.3.2 P Adsorption of Soils after Operation as Substrates in CWS

P Rich Site Soils A significant change in soils after inundation with drainage was that the TP levels dropped (See discuss on P dynamics). Coincidentally, the P adsorption capacity was enhanced in both pond 1 and pond 3, indicated by the increased P adsorption maximum and PSI, and decreased S_0 , EPC_0 and K. Although the pulse release of P from soils may benefit the P adsorption, it is more likely due to the root activities. As the rooted macrophytes take up P from the soil porewater, the concentration gradient between solid and liquid phase increases and forces the adsorbed P enters into liquid phase, resulting in available sites for P binding. This is in agreement with the decreased S_0 value.

In field, as the P level in porewater decreases, the concentration gradient between porewater and overlying water column increases, thus enhance the downwards diffusion of P. Also important is the release of oxygen from roots. Oxygen from the roots of macrophytes raises the redox potential of their surrounding sediments, resulting in a high concentration of Fe^{2+} in sediment and increase of the P adsorption capacity. By investigating the P retained by vegetated and unvegetated sediment cores, Christensen and Andersen (1996) demonstrated that the vegetated sediment core had higher P retention than the bare sediment core. A study conducted by Carlto and Wetzel (1988) on the influence of benthic microalgae on ^{32}P release from a surface sediment from a hardwater, oligotrophic lake gives strong evidence of the importance of oxygenation on P retention. In the study, they observed that P release decreased during illumination and increased during dark. The dark release was attributed to

the lower biological uptake and reduced oxidising effect resulting from the lack of benthic microalgal photosynthesis.

Although sediments in both pond 1 and pond 3 had better P adsorption than the original soils, the sediments in pond 1 exhibited better adsorption characteristics than those from pond 3 for every parameter (Table 3-23). The maximum P adsorption was higher for sediments from pond 1. The slower P build-up rate in pond 1 (TP concentrations were 376.8 mg/kg and 516.6 mg/kg for sediments from emergent and pond 3, respectively) resulted in lower P saturation (3% vs. 5%), EPC_0 (0.125 vs. 0.260) and S_0 (40.541 vs. 58.228 mg/kg). Thus, there were more available adsorption sites in sediments from pond 1. There are two possible reasons. Firstly, the emergents have longer roots which can have effects on a thicker layer of sediments. Secondly, the emergents have a longer turnover than the submergent macrophytes. While the submergents take up inorganic P from sediments and water column, they continuously release P into the environment as organic P, which was evidenced by a higher labile organic P in sediments. The higher level of labile organic P may impair the efficiency as P adsorbents. Consequently, pond 1 was more efficient for P retention than pond 3.

P Poor Hill Soils On contrast to pasture soils, the sediment P adsorption in both ponds was degraded (Table 3-23, Figure 3-26) as P built up. Because P adsorption (S) was significantly related to S_{max} , S_0 , and K in both ponds (Table 3-23), the increase of S_0 and K indicated that the sediment was less efficient as P adsorbents after being fed with drainage, especially in pond 5. It was obvious that the sediment from pond 5 became saturated with P very quickly (rise from 5% to 29% in six-month time), corresponding to the quick increase of TP. The constant K in the Langmuir equation increased to 2.164 indicating that the potential for desorption was high. The poor P adsorption and quick saturation may be due to the fact that more than 85% of the hill soils are sand, and the clay content is less than 10%.

4.5 COPRECIPITATION IN CWS

The precipitation of P as calcium phosphate has been extensively studied by soil scientists in evaluating applied fertilizer reactions. The process is believed to be two sequent steps: the initial P adsorption onto calcite is followed by precipitation as calcium phosphate (Cole et al.

1953; Griffin and Jurinak, 1973). Similar reactions can occur at the sediment-water interface of calcareous water bodies.

Because of the ecological importance in the control of eutrophication, P coprecipitation in aquatic systems has been widely studied in recent years (Hartley et al. 1997). The so called self-purification is considered to operate directly by the co-precipitation with calcite (House, 1990) as what happens in soils and indirectly by the association of nucleated minerals with algal cells (Hartley et al., 1995). The initiation of the precipitation reaction is normally triggered by increase in pH (Otsuki and Wetzel, 1972). Water column photosynthesis and respiration can initiate significant changes in water pH on a diurnal basis (Wetzel, 2001). These processes can drive pH to as high as 10 (in the present study, the highest pH recorded was 10.75 in pond 5 on a hot summer day). In the present study, Ca-P in sediments from all ponds increased overtime (except from March 2000 to June 2000 in pond 1) suggesting the P coprecipitation with Ca from water column.

4.5.1 Water Column P Coprecipitation: Laboratory Evidence

As the drainage contains high concentration of Ca, it has high buffer capacity than water from Reed Creek Lagoon. The results also suggested that added sand had little effect on the P precipitation reaction as the slopes of the fitted linear equations were identical for the three systems. The experiment did not test the maximal buffering capacity of drainage, but at lower inorganic P concentration, approximately 55% of added inorganic P could be removed from the solution phase.

Figure 4-15 represents the plot of accumulative P removal (%) against the P added (mg). The associated exponential equation (Eq. 4-2) effectively (R^2 ranges from 73.4 to 92.3%) described the relationship between P removal and P added.

$$Y = a \times (1 - e^{-bX}) \quad (4-2)$$

Where Y represents the accumulative P removal (%); and X is the added P (mg).

The associated models gave the maximal P precipitation rate of the systems: 60.1%, 56.0%, 56.1% and 40.3% for systems 1, 2, 3, and 4, respectively. These values are in accordance

with the estimates from linear equations (Figure 3-29). Despite the high precipitation rates estimated from laboratory batch study, they are rarely realized under field conditions. First, unlike in the laboratory systems, the predominant P species are H_2PO_4^- and HPO_4^{2-} , the P forms in natural waters are far more complicated (Stumm and Morgan, 1996). Second, the pH in the study was maintained relatively stable over the range of 8.7-8.9, which was ideal for the coprecipitation of P with calcite. In field ponds, the water pH varies on a day-night base, and may have impacts on the solubility of phosphate compounds.

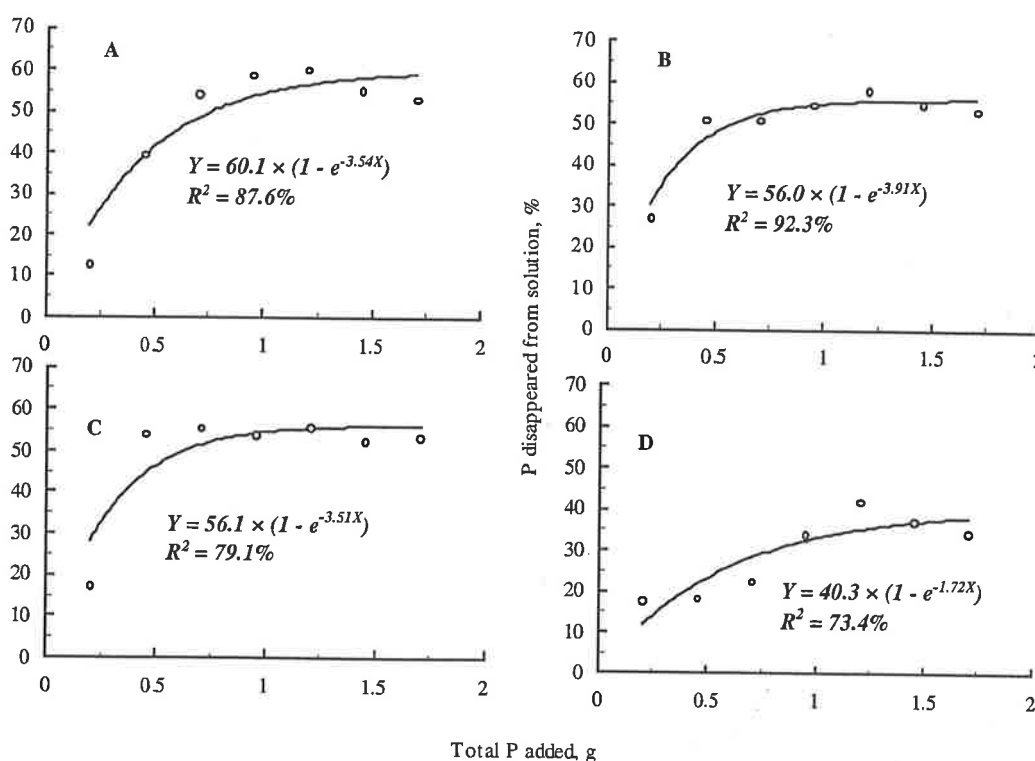


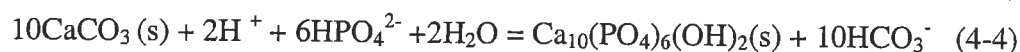
Figure 4-15. Associated exponential models to estimate the P coprecipitation (%) based on total added inorganic P (mg). Curves are fitted equations, and circles represent the measured data. A, filtered drainage + 10g sand; B, filtered drainage + 5g sand; C, Filtered drainage only; and D, Filtered water from Reed Creek wetland.

4.5.2 Water pH as a Master Parameter Controlling P Coprecipitation: Laboratory Equilibrium Systems

It is well known that the sediment acts as reservoirs in natural aquatic systems, and the P concentration in waters overlying sediments, i.e. buffered by solubility and adsorption or ion exchange equilibria at the sediment-water interface. The nature of P control is not fully understood although there is a general agreement that chemical interactions of phosphate

with Fe^{3+} , Al^{3+} (clays) and Ca^{2+} are relevant. Microbial activities influence the extent of these actions, perhaps to a large extent indirectly, by (1) transforming P forms, i.e. inorganic P to particulate or dissolved organic P, and (2) through control the microenvironmental conditions which determine solubility equilibria, such as pH, redox potential, and type of organic matters.

The plot (Figure 3-27) of SRP against pH were similar to the results of a study on the equilibration of P with oxidized lake mud as a function of pH conducted by Macpherson et al. (1958). Qualitatively, the general shape of the curve describing the pH dependence of the residual P suggests that in the pH range of 4.5 – 6.5, P tends to be bound to the solid phase by Fe^{3+} and Al^{3+} , either by precipitation or by adsorption (Eq. 4-3). At higher pH values, the tendency for precipitation as calcium phosphate (Eq. 4-4) becomes enhanced.



4.6 IMPLICATION FOR THE DESIGN AND IMPLEMENTATION OF CONSTRUCTED WETLANDS FOR THE TREATMENT OF IRRIGATION DRAINAGE WATER

To enhance the performance of CWS for the treatment of drainage, in which dissolved inorganic P is the predominant form, processes such as plant and microbial uptake, coprecipitation, and substrate adsorption should be emphasized.

A conceptional model for design and maintenance of CWS for the treatment of irrigation drainage water was presented in Figure 4-16. The mass balance calculation of pond systems suggested that the substrates in ponds (except the pond 2, which was free of substrates) played an important role to govern the P movement in system, which corresponds with the statement of Hammer (1994) and others (e.g. Reddy, 1999). Consequently, in the model, the start point and the core are how to manage and maintain the maximal P adsorption of substrates in CWS. There are four main processes adding P into sediment: sedimentation of particles, decay of dead algal and water plant biomass, coprecipitation with Ca/Mg, and adsorption. These processes all decline the capacity of substrates as P storage, i.e. the 'ageing' process of CWS (Kadlec, 1996). When the P accumulation in the sediments reaches a critical value, P releases from sediments - the indication of the needs for sediments replacement. In a short term, only one process removes P from the sediments and then enhances the P storage capacity: uptake by rooted water plants. To maintain good sediment P adsorption, two management tools were highlighted in the model: a) Harvesting of standing P stock; and b) Sediment replacement.

The model starts with the question of the clay component in sediments as it is believed that clay was responsible for P adsorption. If sediments are dominant with clay and its TP level is less than 300mg/l (a pragmatic value based on laboratory experiment in this study), the sediments have good P affinity. Providing with proper hydraulic residence time (HRT), a good P removal performance could be expected. If the TP level is greater than 300mg/kg and the EPC_0 lesser than 0.5mg/l (a pragmatic value), the sediments can adsorb P in most cases and support the vigorously growing of rooted water plants. In return, the rooted water plants take up P from the sediments and the consequent harvesting of standing biomass could help to maintain the P adsorption capacity providing with that the vegetation is dominated with

emergents, i.e. cropping of the standing stock P could delay the “ageing” process of CWS. As it lacks of practical methods to harvest submergents, the decomposition of biomass and the following P remineralization returns P into sediments, their growth is of limited benefits to sediment P adsorption. However, if the sediments have a higher TP level ($>300\text{mg/kg}$) and EPC_0 ($>0.5\text{mg/l}$), the risk of P release from the sediments is high. To ensure good P removal, the replacement of sediments to rejuvenate the system is necessary.

One the other hand, if the sediments contain mainly sand, their capacity to bind P is limited. The P removal may mainly due to the uptake by floating water plants, biofilm, and planktonic algae. Nevertheless, if the incoming wastewater contains high Ca concentration ($>100\text{mg/l}$, according to House, 1990) and the water column pH is high enough (>8.0 , according to Diaz, 1994), P coprecipitation can be a substantial P pathway in any CWS.

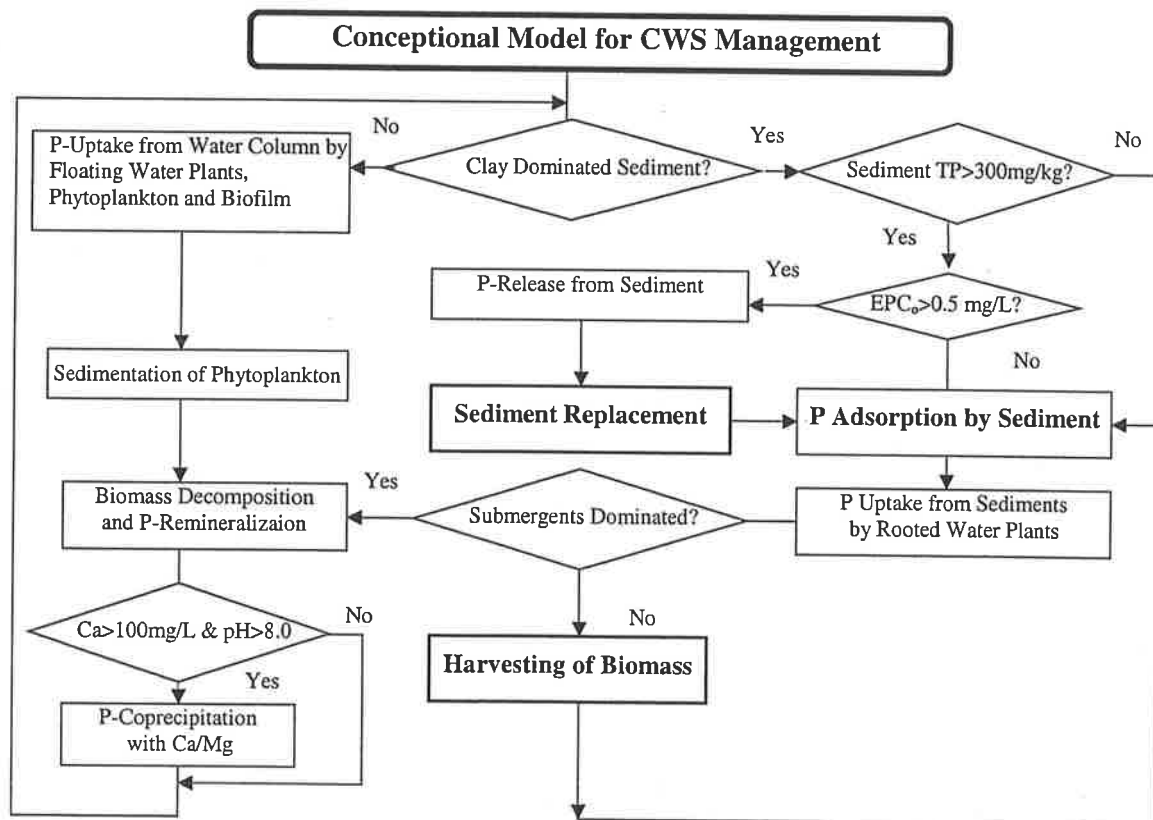


Figure 4-16. A conceptual model for design and maintain CWS for the treatment of irrigation drainage water. TP, total Phosphorus; EPC_0 , Equilibrium P concentration at zero release

4.6.1 Substrate Utilized in CWS

To keep the construction costs low, local materials are preferred in CWS as substrates. Laboratory batch experiments showed that the soils from the site were superior to the soils from the nearby hills despite the relatively higher P content. The maximum P adsorption of site soils was 3-4 times higher than that of the soils from hill indicating a longer lifespan for CWS with site soils. In addition, the development of macrophytes on the site soils was faster than on the hill soils. In the first year of operation, the vegetation coverage in pond 1 reached 100%, but less than 10% in pond 4. However, as proven in this study, the site soils released large amount of P in a short period once being inundated. The initial release of P must be addressed when constructing a full-scale treatment wetland. This is of critical importance when restoration of the riverine wetland upon the abandoned pastures.

As the P release is rather quick (less than three months), one possible option is to wash away the soil P which is sensitive to the low redox potential caused by flooding. River water can be introduced into the newly built systems to "rinse out" the original P, and the P rich effluent can be re-used for land application. Another option is to remove the topsoils and use for the construction of banks and barriers.

4.6.2 Management of Macrophyte in CWS

In this study, three functional groups of macrophytes were tested in CWS. The submergent water plants were not recommended based on the I/O data from pond 3. The submergent plants may be efficient for taking up P from water column growing on the P poor substrates, however, they are known to experience more or less continuous senescence and sloughing of a portion of their foliar and rooting tissues (Wetzel, 1996). As a result, harvesting the standing biomass may be of little benefit to the overall P removal. In addition, methods for harvesting of submergent are difficult to implement in field.

Float planted with runners is an innovative technology for utilization of water plants for nutrient cropping (Wen and Recknagel, 2002). The creeping-stem water plants can accumulate significant amount of P into their biomass, and contribute to direct P removal. Beside the direct uptake, the coprecipitation of P with Ca/Mg in the pond 2 was also a P pathway which contributed considerably to P removal. To promote P precipitation, the water

pH has to be sustained to over 8.5 according to House (1995). The water pH was closely linked to the CO₂ concentration, which is a function of the primary productivity in water column. As the algal photosynthesis is the main driving force for maintaining a higher water pH, keeping a portion of pond surface as open water was critical for precipitation to occur. Because the growth was restricted on the floats and their surrounding water surface, an appreciate ratio of open water to plant covered area can be maintained easily by controlling the amount of floats introduced.

As discussed in section 3, rooted emergents implicated the P adsorption of sediment by increasing the concentration gradient between water column and sediment porewater and promoting the downward diffusion of P from water to sediment. The P fractionation results indicated that while the dense growth of emergent helped to sustain the capacity of P adsorption of sediments, it seemed to be an obstruction for P co-precipitation and uptake by attached biofilm in pond 1. The density coverage shaded out the chance for phytoplanktonic and epiphytic development. In return, the water pH was the lowest among the five ponds. The P dynamics in the sediments from pond 4 gave indirectly evidence. In the pond 4, Ca-P and labile organic P increased notably indicting the active co-precipitation and microbial P uptake.

In the design stage, deep-water zones (normal >1.5 m) in CWS are helpful for prevention the invasion of macrophyte, therefore, provide niche for the growth of planktonic algal. However, the harvesting of standing biomass at an appreciate timing is the most promising method as harvesting 1) removes P from the system, and terminates the P cycles; 2) keeps the macrophytes in r-growth stages, and maximize the direct uptake; 3) promotes the growth of attached microbial consortia.

Chapter Five Conclusion

This study, conducted over 3 years, has involved the collection and analysis of enormous experimental field data, several laboratory batch experiments, as well as a comprehensive statistical data analysis. CWS at pilot scale were constructed on the Baseby Dairy Farm to conduct research concerning the drainage quality and P dynamics in CWS. The study focused on three major objectives: 1) to evaluate the efficiency of CWS as a cost-effective technology to remove P from agricultural drainage; 2) to assess the contributions of macrophytes and substrates to P removal in CWS; 3) to contribute to the optimal design and operation of CWS for the treatment of agricultural drainage.

5.1 DRAINAGE WATER CHARACTERISTICS

5.1.1 Comparisons between the Secondary Municipal Effluent and Drainage

The source and quality of the wastewater are an important factor which should be seriously considered when proposing CWS as a cost-effective alternative for conventional treatment facilities. Although experimental studies have been made on the use of CWS for treatment of nonpoint source pollutions such as urban and rural runoff, the majority of the successful applications are designed for polishing municipal wastewaters (advanced wastewater treatment). Thus, the design and operation guidelines developed based on the operational data of the CWS for municipal wastewater treatment should be reconsidered before using them in CWS for irrigation drainage water.

Despite the fact that the drainage water appeared to be comparable to the secondary municipal effluent in terms of P levels, P forms, and N/P ratio, there is one major difference between the domestic wastewaters and drainage, namely, the higher organic components in the former. The organic matters in domestic wastewater are the main energy source for bacterial processes. Thus, in domestic wastewater treatment, bacterial processes are always the key for operation. In drainage, however, the content of organic matters is normally relatively lower. The energy source for bacterial growth may mainly depend on the photosynthesis of water plants and algae, which contributes to P removal by its own. This has fundamental impacts on the treatment processes in CWS. The emphasis of the treatment wetlands for municipal wastewater and drainages should be addressed separately. While the

bacterial removal may be an important mechanism in CWS for municipal wastewater treatment, the other processes as sedimentation, precipitation, plants and algae uptake, and adsorption by substrates should be emphasized in CWS for drainage water, at least at the development stage. The stochastic and even-driven nature of drainage is another important discrepancy between the two.

5.1.2 Comparison between Cropland Runoff and Drainage

Compared with agricultural runoff, the drainage has much higher P concentration and much lower N:P ratio. In addition, while the majority P in agricultural runoff is associated with soil particles resulting from erosion, the P in drainage is mainly in dissolved forms. Consequently, while sedimentation may be the most important P removal mechanism in CWS for runoff, it contributes little to the overall performance of CWS for drainage treatment.

5.2 CONSTRUCTED WETLANDS AND AQUATIC PLANT SYSTEMS FOR IRRIGATION DRAINAGE WATER TREATMENT

Constructed wetlands and aquatic systems are among the recently proven efficient technologies for wastewater treatment. One of the main objectives of this study was to investigate the suitability of the application of CWS technology to the treatment of irrigation drainage. The wetland ponds except pond 3 were proven to be effective compared with the operational data for CWS treating municipal and industrial wastewaters in terms of P removal efficiency and rate. However, none of the systems reached the advanced discharge standard of 1 mg/l at the 95% probability.

The operational data showed that pond 2 (with floats and no substrates employed) performed better than other systems in terms of P removal rate and stability. The 90ile effluent TP concentration of 2.1 mg/l was much lower than that from pond 1 (pond with emergent water plants and site soils as substrates), pond 4 (with emergents and hill soils as substrates), and pond 5 (with hill soils as substrates and no water plants).

Pond 1, which is the commonly used type of CWS for wastewater processing, seemed to be inefficient for P removal during the first year of operation. The P removal efficiency and rate

were 15.4% and 0.05 g/m²/day, respectively. Moreover, it exported P during the first two months of monitoring and winter. In the second year, the performance was enhanced: the efficiency for P removal reached 27.6% and P removal rate increased to 0.152 g/m²/day, comparable to the performance of pond 4, and much higher than the average value of 0.022 g/m²/day for the Northern American treatment wetlands (Knight et al., 1993). The sediment P data indicated that the original P accumulated in the soils was responsible for the poor performance in the first year. Once the sediment P stabilized, the marsh can achieve good P removal.

Pond 3 (with submergents and site soils as substrates) was the least efficient among the five pond systems. Operational data showed that it released P even in the rigorous growing season. The mass balance data indicated that the pond was a net P exporter over the operation period. The main function of submergent water plants in aquatic systems maybe structural, and the contribution to nutrients removal is negligible.

The ponds with P poor soils demonstrated to be efficient for P removal even without macrophytes at least at the first year of operation. However, the quick saturation with P in the substrates, especially in the pond 5 (without water plants), may indicate the questionable sustainability.

The main mechanisms for P removal differed from system to system. In pond 1, P removal was realised by adsorption to substrate and accumulation in plant and biofilm biomass. In the floating pond, plant biomass accumulation and coprecipitation with Ca/Mg were the major P pathways. In PWM, substrate adsorption, coprecipitation and uptake by the attached microbial consortia contributed to the majority of P removal, evidencing by the increased TP, Ca-P and labile organic P in the substrates. In PMF, however, coprecipitation and adsorption were the main mechanisms responsible for P loss from water.

5.3 CONTRIBUTION OF MACROPHYTES

Based on their performance in the field, three native water plant species were recommended for utilisation in CWS and aquatic systems for drainage treatment: common reed (*Phragmites australis*) is emergent, and water couch (*Paspalum paspalodes*) and

waterbuttons (*Cotula coronopifolia*) are runners. They survived the extreme salinity level of up to 10.75 ppt. They can also cope with the trophic conditions, i.e. N limited (lower N:P ratio), and showed relatively high tissue P contents.

Macrophytes contribute to P removal in CWS by 1) direct uptake; 2) effecting the P adsorption capacity of substrates; 3) providing energy and attaching surface for microbial consortia. The first two functions were addressed in this study.

5.3.1 Emergent Water Plants

The phenometric model, developed from stepwise multi-parameter linear regression, can be used to accurately obtain the growth trajectory of the aboveground biomass of reed. While the aboveground biomass was relatively stable following a rapid increase in the late spring to early summer, the P content of tissue fluctuated widely. Consequently, timing of harvest is critical if P cropping is considered to maximize the P removal efficiency of such systems. The results suggested that the optimal harvest time was in late November, i.e. 70 days after the resuscitation under Southern Australia conditions.

The standing stock of P of (13.3 g/m^2) in reed was higher than the reported values found in literature. P recovery by in the aboveground biomass accounted for 17.6% of the total P loss from water, suggesting that the direct uptake by emergent water plant is a mechanism of P removal which could not be ignored, contrasting to many investigations in the literature.

The growth of macrophytes on the substrates can improve their P adsorption capacity probably due to the oxygenation by O_2 released for roots and the increased concentration gradient from water column to sediment. The P adsorption isotherms (Langmuir Model) showed that the presence of macrophytes decreased the EPC_0 and increased the S_{max} of the substrates. Moreover, sediments for pond 1 had better P adsorption than the sediments for pond 3.

The effect of macrophytes on substrates was better illustrated in pond 4 and pond 5. The sediments from pond 5 degraded faster than sediments from pond 4. Without rooted

macrophytes, the P saturation in substrates increased from 8% to 29% in six-month time. The P saturation was barely changed when planted with emergent.

5.3.2 Creeping-Stem Water Plants

The cultivation of planted floats in the growth chamber demonstrated that the creeping-stem water plants have the potential to remove significant amounts of P from wastewater. The technology used was analogous to the floating-plant systems, but allows utilization of procumbent water plants. The P removal rate by floats was much higher than that of the emergent marshes, and matched that of floating plant systems. Because the growth of plants is restricted on the floating float and its surrounding water surface, and therefore under control, the potential of rapid spread was minimized. The method described overcomes the intrinsic disadvantage of floating plant system and keeps their advantages such as reliability and high efficiency.

In the field pilot scale experiment, the pond stocked with planted floats was more effective for P removal than pond 1 due to a number of reasons. Firstly, the plants get their nutrients directly from water column, this is very important for wastewaters that are predominated by dissolved P, such as irrigation drainage waters. Secondly, as no sediment employed in the floating pond, the systems can be operated more stably. Comparing with other commonly used ecological engineering methods, the overall P removal rate by pond stocked with planted floats is promising. Supported by floats, they could replace water hyacinths, duckweeds that are nowadays utilised predominated in floating plant systems elsewhere they are not suitable, e.g. in landscapes where native plants are preferred. As the growth of plants is restricted on the float and its surrounding water surface, the problem of overgrowth is limited.

Water couch survived the high salinity of drainage water and grew robustly in both lotic (irrigation channel) and lentic (pond) environment. It can be a "suitable robust species" (BOWMER et al, 1994) for in-channel nutrient remover. The floats performed well in irrigation drain with a P removal rate of $0.098 \text{ g/m}^2/\text{day}$. As the rafts float freely on the water surface, nutrients removing would not affect the main hydrological function of irrigation

drain. The 7900 km irrigation drains in the MDB (ROBERTS, J. 1998) could provide a capacious space for control of nutrients loss from farmland to aquatic systems.

5.4 SUBSTRATE FUNCTIONS

By combining the sediment P fractionation and P adsorption, the study provided insights into the sediment P dynamics in CWS. The results showed that macrophytes, especially the emergents, could promote P removal by enhancing the capacity of P adsorption of the sediment. However, the dense growth of emergent may reduce the efficiency of P removal by restricting the growth of periphytes and benthic algae and the coprecipitation of P, which are also important P elimination pathways in CWS. Maintaining the emergent macrophytes in a moderate coverage may be important for the successful operation of CWS.

In pond 5, blooms of planktonic algae increase water pH to a high level of 9.02. As a result, P co-precipitated with Ca cation was the dominant P removal mechanism. The accumulation of Ca-P reduced the capacity of sediment P adsorption, and P saturation increased to 29% in 6 months. However, the PSI remained barely changed.

In pond 4, the presence of macrophytes prohibited the colonization of planktonic algae and encouraged the development of periphytes and benthic algae. Consequently, both co-precipitation and biological P uptake were active in the system, and contributed to the overall P removal. As the increase of P was coincident with the build-up of organic matter and the oxygenation of the root system, the sediment P adsorption capacity was barely changed, as indicated by the Langmuir isotherm.

In pond 1, where the initial soil P was high and supported the robust growth of water plants, both co-precipitation and the growth of periphytes and benthic algae were restricted. The TP level in the sediment was relatively stable after the pulse release of P upon inundation. The uptake and a relatively longer storage (comparing with submergents) of P in emergent macrophytes slowed down the P build-up in sediments. As a result, the sediment maintained relatively good P adsorption characteristics. However, in pond 3, the build-up of Ca-P in sediment was quick as the result of the elevated water pH causing by the underwater photosynthesis. Furthermore, the short return of biomass P from submergent macrophytes

resulted in a large pool of labile organic P in the sediment. The faster P build-up meant that the sediment was less effective for P adsorption than the sediment in emergent pond.

5.5 CHEMICAL PRECIPITATION FROM WATER COLUMN

In the water column, photosynthetic activity of algae (attached or planktonic) and other aquatic plants can drive the pH value to a high level. In all ponds except pond 1, average pH value was greater than 8.0, which was significant higher than the pH value in the drainage. As the drainage has relatively high concentration of Ca/Mg ions, precipitation of P as Ca/Mg phosphate compounds was an important process involved in P removal, which was in agreement with the P fractionation results in the sediments.

5.6 CWS AS INTEGRATED ECOSYSTEMS

The implications from preceding remarks are that effective constructive wetlands must be regarded as, and designed and maintained as, natural integrated ecosystems. P retention in CWS is regulated by a variety of biological, physical and chemical factors. The design and operation of CWS should equally consider all the important components. These dominant features can be summarized as follows:

- The organisms present in CWS are interdependent. The macrophytes depend on microbial activities for nutrient regeneration from organic detrital and sediment sources, and the microbiota rely on macrophytes for organic matters.
- The rooted macrophytes promote the P adsorption of sediment, upon which they grow and obtain nutrient from, through increasing the concentration gradient and release of O₂ from rhizomes.
- Living and dead macrophytes provide surface area for the growth of epiphyton (biofilm), which is the assemblage of algae, bacteria, fungi, and mircoinvertebrates. Together with planktonic algae, biofilm determines the water column productivity – the key factor responsible for diurnal pH change. The diurnal fluctuation is the driving force for P coprecipitation.

5.7 SYSTEM CONSTRAINTS, LIMITATIONS, AND OPPORTUNITIES

Any ecosystem, natural or artificial, has limits of capacity to accept disturbances, for example, pollutant loadings. This capacity is a function of the intrinsic characteristics of the

particular system, such as the evolution stage, and the extrinsic geographic settings, e.g. the climate conditions. The wetland ponds were efficient for P processing in terms of P removal rate, but the effluent TP concentration failed to reach the advanced discharge standard, although the loading rates were moderate. It seems that the poor quality in effluent was caused by the system background concentration as relatively high TP levels were monitored during winter when the load rates were low.

Three years is relatively short for study on a newly developed ecosystem. The lack of long-term operational data creates uncertainties when generating guidelines for system design and operation. In addition, the seasonal variability in treatment performance may cause serious operational constraints. However, in spite of such limitations and uncertainties, the potential for realizing low-cost, reliable treatment of irrigation drainage seems worth additional effects to gain scientific foundations in the application of CWS.

5.8 FUTURE CONSIDERATIONS

5.8.1 Processing Issues

Most evaluations of the use and efficacy of wetlands (natural or constructed) to improve water quality are little more than I/O analysis. Very little is understood about the control and regulatory capacities of the physical and biological properties within the “black box” (Wetzel, 1993). The systems are biologically mediated and the scientific foundations of the biological control in an integrated ecosystem are essential to design and manage these ecosystems effectively and maximize their treatment capacities. As pointed out by Wetzel (1993), unless a greater understanding of the regulatory processes is known, highly efficient utilization of CWS for wastewater treatment is unlikely to emerge. The present study is an attempt to go beyond the black-box approach by investigations into the three main compartments in CWS, which are responsible for P removal, i.e. macrophyte, sediment and water column. There are a number of critical issues requiring additional information and data analysis, especially about the role of biofilm and water column processes.

5.8.1.1 *The Contribution of Attached Microbial Consortia*

A notable feature in CWS is that their functions are almost solely regulated by microbiota and their metabolism. First, the retention capacity of soil and sediment particles is governed by the microenvironmental redox conditions, which in turn are controlled by bacterial metabolism. That metabolism is in turn regulated by the chemical composition of organic matter loadings, the quantities of organic matter and essential nutrients, the hydrology, and other factors. The geochemical structure of the soil/sediment particle is only one factor, and often subordinate to other factors at regulating adsorptive and exchange properties. Second, the microbial biomass is an important sink for nutrients. The collective mass of microbiota, with high reproductive and growth rates, on the surface area of detritus and sediment particles of wetlands is very large. Under anaerobic conditions, a significant portion of this mass is interred and decomposed at very slow rates. Third, the attached microbiota function as efficient recyclers of nutrients. The photosynthetic productivity of attached algae and cyanobacteria can be very high. Once obtained, nutrients are intensively retained by the community, incorporated into the organic/inorganic detritus (soil), and recycled.

5.8.1.2 *Methods to Measure the in situ P Dynamics between Water Column and Sediment*

Soil/sediment P adsorption estimated by laboratory experiment is of limited merit when applying to real world field conditions as this method excludes diffusion constraints and biological contributions. The adsorption Langmuir isotherms are far from of practical usefulness because the three constants in the model make the direct comparison difficult. The PSI measured from high level of EPC (80 mg/l), which is too far from the real conditions, is also a questionable gauge for soil/sediment P assimilation. Kinetic studies using sediment-water column are probably better measurement of the abiotic assimilation.

5.8.1.3 *Application of Soil Amendments*

The site soils have good P adsorption characteristics but they release the original accumulated P once flooded. On contrast, the hill soils have low P content, also the low P affinity. The limitations can be overcome by the application of chemical amendments. These measures may become even more important if the allowable discharge TP concentration is reduced. Two specific topics about soil/sediment amendments must be addressed before full-scale application:

- The impacts on the survival and growth of macrophytes;

- The lifespan of amended soil/sediment for P adsorption.

5.8.1.4 Water Column Productivity, Calcite Precipitation, and P removal

It is well known that the photosynthesis and respiration of attached and planktonic algae can cause significant diurnal changes in water chemistry, and can increase pH enough to trigger the coprecipitation of P together with calcite in aquatic systems. This phenomenon is observed in this study evidenced by the remarkable increase of sediment Ca-P, especially in pond 3 and PMF. Nevertheless, the relationships between water column productivity, pH, and P and Ca concentrations were not investigated. Importantly, the solubility of the newly formed Ca-P at lower pH (decrease at night) is wealth for further study.

5.8.2 Design and Management Issues

5.8.2.1 The Appropriate Open Water/Vegetation Ratio

The importance of open water areas in CWS was demonstrated in this study. The optimal ratio of open water to vegetation cover can facilitate the growth of biofilm and planktonic algae, in turn, promote P coprecipitation with Ca/Mg through sustaining a relatively high pH value. Detailed researches about optimal ratio of open water/vegetation cover and/or vegetation density are helpful to quantify the system and water column productivity, and their contributions to P reduction.

5.8.2.2 The Response of Macrophytes to Harvesting

To ensure maximal removal of P from CWS, harvesting should be done at the early stage of growth. The study suggested that the best harvest time for reed under South Australia climate condition was at about 70 days of growth after resuscitation. But a number of questions remain. First, and maybe the most important one is how the emergents response to harvest. Can they recover from this early harvest? Second, does harvesting promote nutrient uptake? Previous studies proved that the nutrient stored in rhizomes supported the early growth. Taking away the previous stored nutrient may or may not stimulate the nutrient uptake rate of root system. Third, does the harvesting have side effects on microbial activity? Along with P, organic carbon, which is the main food and energy source for the microbiota, is also removed from the system. Further studies are needed to balance the demands of various functional groups in the system.

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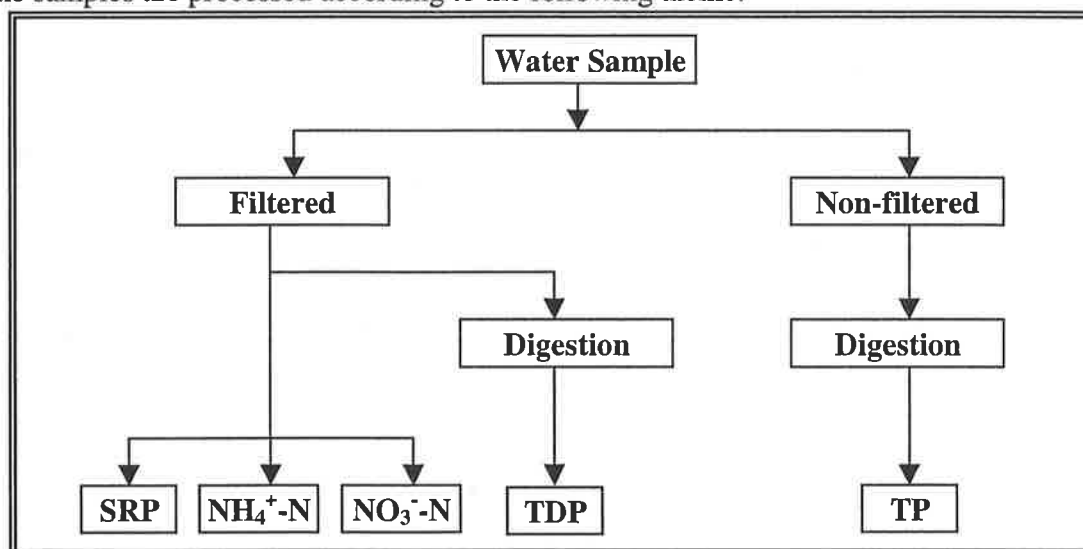
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Appendix A Procedures for Chemical, Biological and Ecological Measurement Methods Used in the Study

I. Procedures for Measuring P in Water Samples

1) Sample Preparation

Samples taken from the field are transferred to the Soil & Water Laboratory in Waite Campus, Adelaide University in icebox. With 48 hours (mostly with 24 hours) of collection, the samples are processed according to the following theme.



B. Digestion (Acid Persulfate Digestion Method):

1. Take 25ml of water sample into 50 ml flasks
2. Add one Potassium Persulfate Power Pillow
3. Add 2.0 ml of 5.25 N sulphuric acid solution
4. Place the flask on a hot plate, gently boil for 30 minutes
5. Cool the sample to room temperature
6. Add 2.0 ml 5.0 N Sodium Hydroxide solution.
7. Make to 25 ml with distilled water.

C. Measurement of P in Water Solution (PhosVer3, Ascorbic Acid Method) Using DR/2000

1. Enter the stored program number (490) for reactive phosphorus
2. Rotate the wavelength dial until the display shows: 890 nm
3. Fill the 25ml cell with sample, and add one PhosVer3 powder pillow. Swirl immediately to mix
4. Allow 2 minutes reaction period by pressing SHILF + TIMER
5. Fill the second cell with sample (the blank)
6. When the timer beeps, place the blank into the cell hold. Close the light shield
7. Press ZERO. When the display shows 0.00 mg/l, replace the blank with the prepared sample. Press READ
8. The Display will show the result in mg/L.

II. Procedures for Determining P Concentration in Plant

A. Preparing dry plant material

- Cut fresh plants into about 5 cm pieces
- Dry plant materials in aluminium containers at 105 °C for 24 hours
- Grind the plant material (0.5 mm) with a mortar

B. Digestion (double acid method)

Reagent: Mix 500ml concentrated nitric acid with 83 ml 70-72% perchloric acid.

Procedure:

- Weigh about 0.25 g of finely ground oven dry plant materials into 50 ml digestion tube
- Add 7 ml of the reagent to the tubes and allow to stand for at least 2 hours (preferably overnight)
- Place the tubes into the digestion block
- Digestion dry plant materials as following:
- 16 hours at 150 °C
- Raise temperature to about 220 °C
- Continue digestion until dense white fumes of perchloric acid appear
- Cool the mixture and add distilled water to obtain a volume of 50 ml, mix content, allow solid material to settle

C. Measure P concentration in digested solution (Molybdovanadate method)

Reagent:

- Mixed Reagent (indication solution)
- 1L concentrated nitric acid
- 1L 0.25% ammonium vanadate (2.5 g NH_4VO_3 in 1 litter RO water)
- 1L 5.0% ammonium molybdate (50.0 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in 1 litter RO water)

Note: Add concentrated nitric acid to ammonium vanadate, mix thoroughly, then add ammonium molybdate, mix well and allow to cool.

Standard Solution

- Stock Solution, 1,000 µg P/ml solution: Dissolve 4.3937 g KH_2PO_4 in distilled water and dilute to 1 L.
- Working Standard, 100µg P/ml solution: Dilute 100 ml stock solution to 1 L with distilled water.

Procedures

- Take an aliquot that contains 0.05-1.0 mg P of the solution (normally 5 ml) into a 50 ml flask
- Dilute to about 35 ml with distilled water.
- Add 4 ml of mixed reagent, and make to volume with distilled water.
- After 10 minutes, read on S. P. meter at 390µu.

D. Convert absorbance to P concentration: $Y = K \times X$

Where Y: P concentration in solution

K: convert coefficient from the standard curve

X: absorbance reading from spectrophotometer

E. Calculate P concentration in plant tissue as follow:

Plant weight: 0.25g

Digest Volume: 50 ml

Aliquot: 5 ml

Dilution = $50\text{ml}/5\text{ml} = 10$

P in aliquot = $50\text{ml} \times kX \mu\text{g/ml}$

P in digested solution = $10 \times 50 \times kX$

P concentration in plant tissue (mg/g) = $500 \times X / 1000 / 0.25 = 2kX$

P concentration in plant tissue (%) = $0.2kX$

III. Procedures for Analysis of Chlorophyll in Phytoplankton

Reagent: 95% EtOH

A. Extract of Chlorophyll

- Filter 100 ml of water sample through 0.45 μm membrane
- Place the membrane in 10 ml plastic tube and add 10 ml 95% EtOH
- Keep the tube in dark for 24 hours
- Centrifuge at 3,000rpm for 15 minutes

B. Measure the optical density using S.P. meter

- Fill a 1 ml cuvette with 95% EtOH
- Fill a 1 ml cuvette with prepared sample
- Place the cuvettes into the S. P. Meter
- Select program by pressing "MODE" and choose the option of "Photometric"
- Enter the relative wavelength and press Zero using blank sample, then read the absorbance of samples
- Read the absorbance at three wavelength: 649, 665, and 750 nm
- (Press "GO TO WL" to change wavelength)

C. Calculate the Chlorophyll Concentration

Calculate the Extinction Coefficient

Path length of cell (PL) = 1 cm

Volume of water sample filtered (VF) = 0.1 L

Volume of ethanol (VE) = 10 ml

Optical density (OD) at 649, 665 and 750 nm = reads from S. P. meter

$$E_{665} = (OD_{665} - OD_{750}) \div PL$$

$$E_{649} = (OD_{649} - OD_{750}) \div PL$$

$$\text{Chl-}a(\mu\text{g/l}) = VE \times (13. \times E_{665} - 5.76 \times E_{649}) \div VF$$

IV. Methods for Estimating Aboveground Biomass (Non-destructive Phenometric Technique)

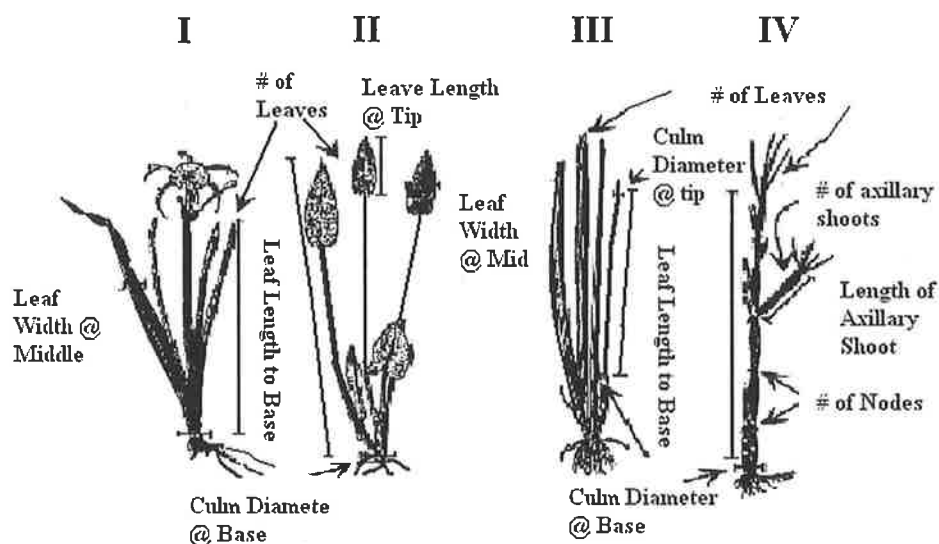
Non-destructive phenometric technique is a well established method for estimating net aboveground primary productivity. Basically, the method involves following individual tagged plants for changes in biomass, which are estimated using regressive phenometric relationships. Shoots biomass are then summed to determine the total aboveground biomass.

Procedures

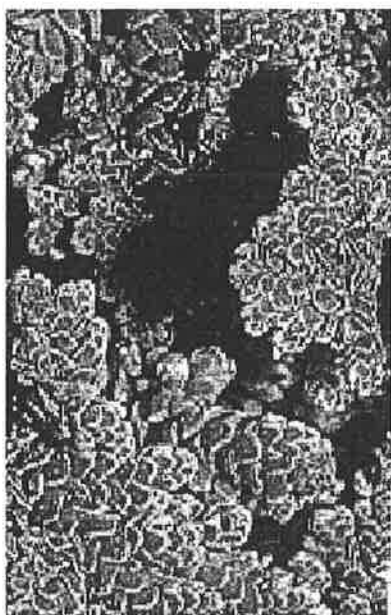
Determining the phenometric parameters for individual species: emergent water plants are divided into 4 basic grouped (illustrated below), for each species, measure a set of parameters.

Determining the Phenometric relationships

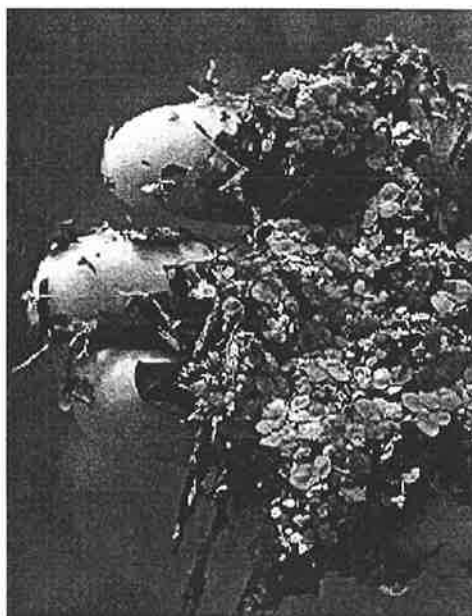
- Harvest at least ten individual plants by clipping shoots above the sediment surface;
- Measure the related parameters;
- Label individual plants and dry at 106°C for 24 hours;
- Measure the weight of individual plant;
- Determine the regressive phenometric relationship between measured parameters and dry biomass by standard multivariate stepwise regression.
- Randomly select plots (normally 0.25 m² in area) along a transection, measure the set of parameters for each group of plants;
- Calculate biomass for each group using the phenometric relationship determined by above method.



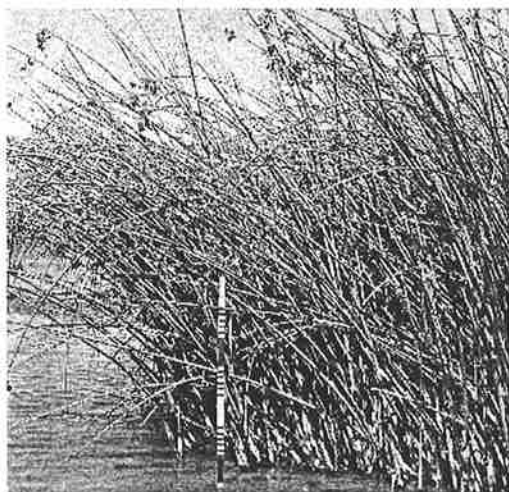
Appendixes B. Pictures of the Water Plants Tested in the Study



Azolla



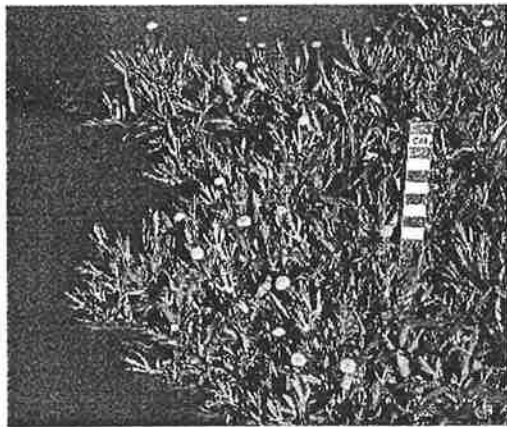
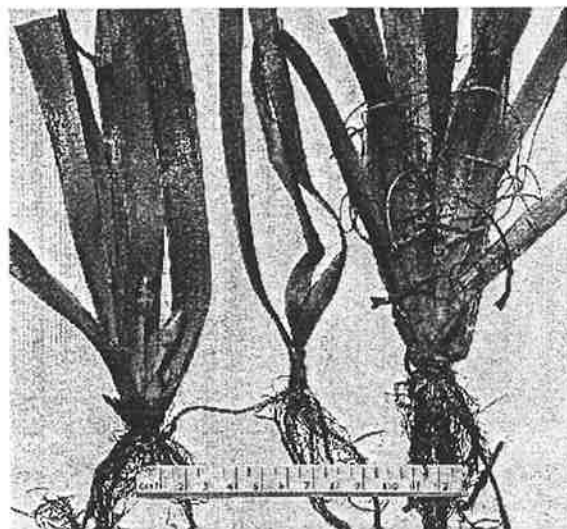
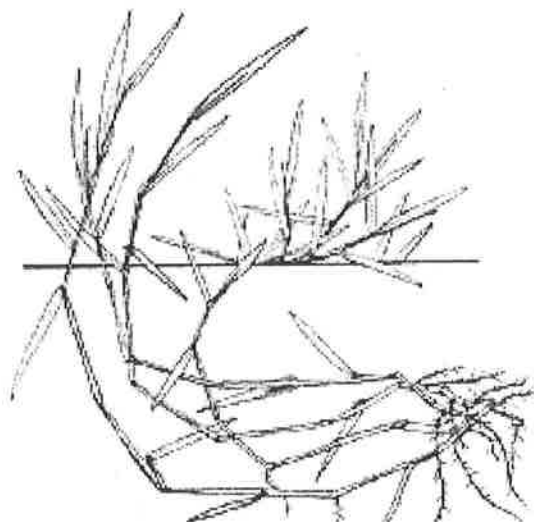
Duckweeds (*Lamna* spp.)



Bulrushes (*Juncus* spp)



Common Reed (*Phragmites australis*)

Cattail (*Typha spp*)Parrot feather (*Myriophyllum aquaticum*)Waterbuttons (*Cotula coronopifolia*)Water primrose ((*Ludwigia peploides*)River Ribbon (*Triglochin procerum*)Water couch (*Paspalum paspalodes*)

Appendix C. Procedures for P fractionation, P adsorption/release Experiment

I. P fractionation

Reagents:

1. Formaldehyde solution
2. NH_4Cl (1M)
3. NaOH (0.1N)
4. Hydrochloric acid (HCl) 0.5N
5. NaCl (1M)

Procedure:

1. Weigh 0.5g (dry weight equivalent) of wet sample (<2mm) into 50-ml centrifuge tubes.
2. Add 25 ml of NH_4Cl solution.
3. Add 1 ml formaldehyde solution.
4. Shaking (over-turn) at room temperature for 2 hrs.
5. Centrifuge tubes for 15 min at 2,400 rpm.
6. Decant solution to another tube (Solution I).
7. Repeat the step 2-5.
8. Wash the soil residue twice with 25 ml 1M NaCl by stirring and centrifuging. Save the two extracts and combine them with Solution I.
9. Add 25 ml of 0.3N NaOH solution to the soil residue, shaking at room temperature for 17 hrs.
10. Centrifuge the suspension, and decant the solution into another flask (Solution II)
11. Wash the soil residue with 25 ml 1M NaCl by stirring and centrifuging. Save the two extracts and combine them with Solution I.
12. Add 25 ml of 0.5N HCl solution to the soil residue. Shaking at room temperature for 24 hours. Centrifuge the suspension, and decant the solution into another flask (solution III).
13. Wash the soil residue once with 25 ml 1M NaCl solution, centrifuge and decant the supernatant to solution III.
14. Filter solution I, II, III through 0.45 μm membrane.
15. Measure the P concentration in solution I, II, III by APAH method, resulting in loosely sorbed P, Ca/Mg-P and Fe/Al-P.
16. Digest portion of solution III, P in the digested solution is the NaOH-total P.
17. Digest the soil residues from step 12, P in digestion represent the residue P.

II. P adsorption/release

Reagent

1. 0.01 M CaCl_2 solution
2. Formaldehyde solution
3. 100 mg/l P solution as HK_2PO_4
4. 1000 mg/l P solution as HK_2PO_4

Procedures

1. Weigh 0.5g (dry weight equivalent) of wet soil/sediment sample (<2mm) into 50-ml centrifuge tubes. A total of 27 samples are needed (three replicants).
2. Add required amount of P solution to CaCl_2 solution resulting dissolved inorganic P concentrations of: 0, 0.2, 0.5, 1, 2, 5, 10, 50, 80 mg/l (Solution I).
3. Add 25 ml of solution I into the centrifuge tubes.
4. Add 1 ml formaldehyde solution.
5. Shaking (end-over-end) at room temperature for 24 hrs.
6. Centrifuge tubes for 15 min at 3,000 rpm.
7. Decant solution to another tube.
8. Filter through 0.2 μm filter (Solution II).
9. Measure the SRP concentration in solution II.

Appendix D

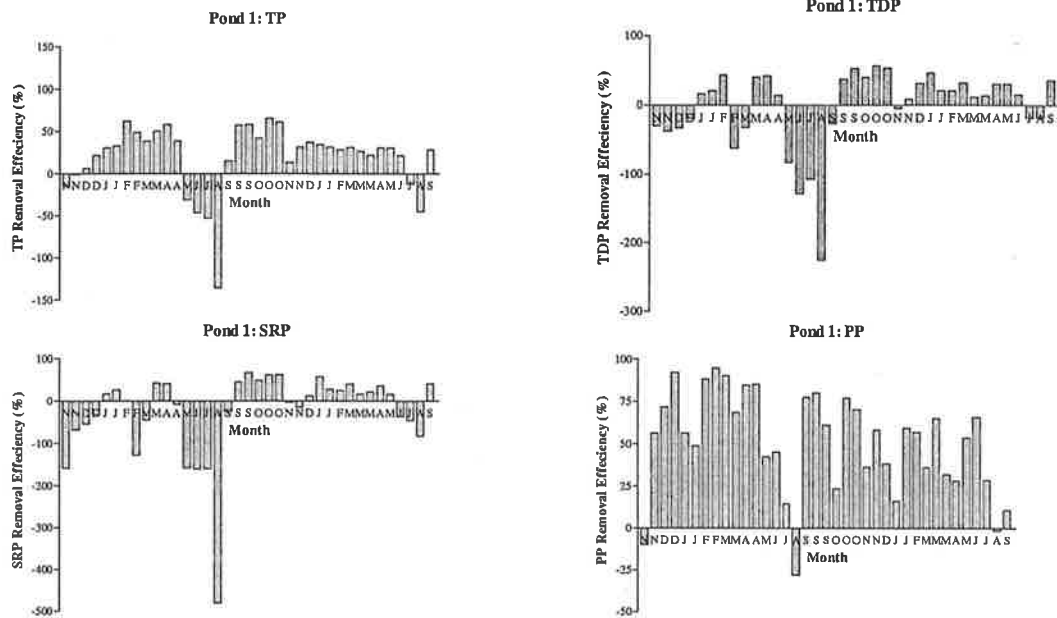
Figures for P Removal Efficiency (%) and Rate ($\text{g/m}^2/\text{day}$) in Experimental Ponds

Figure D-1. P removal efficiency in pond 1

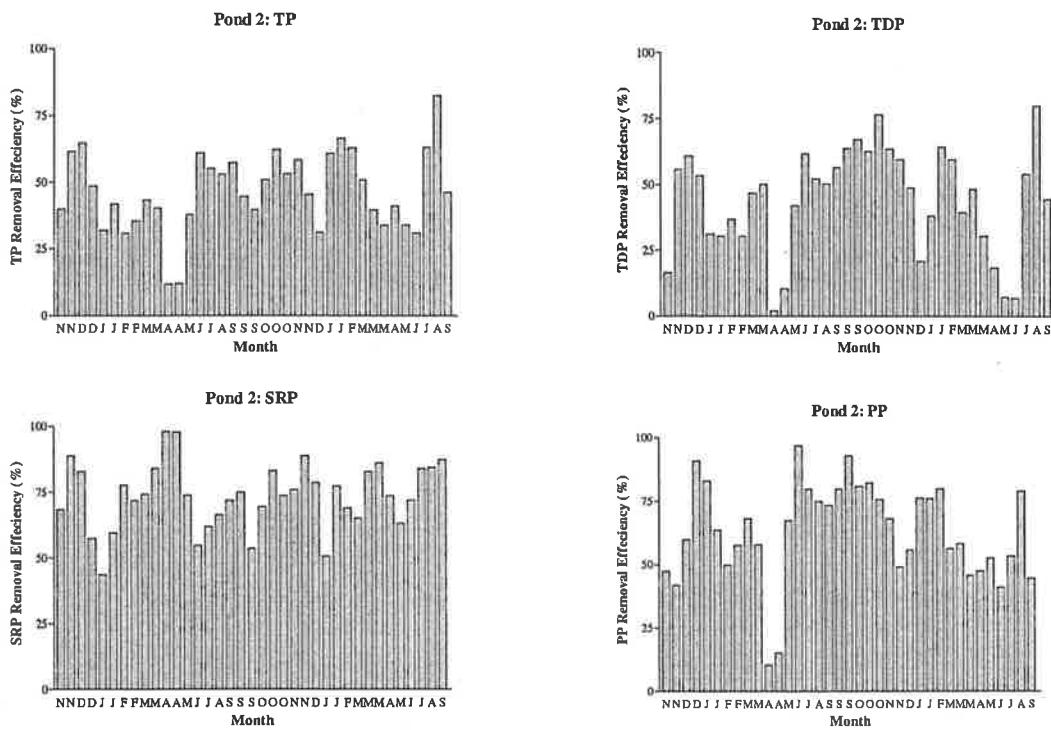


Figure D-2. P removal efficiency in pond 2

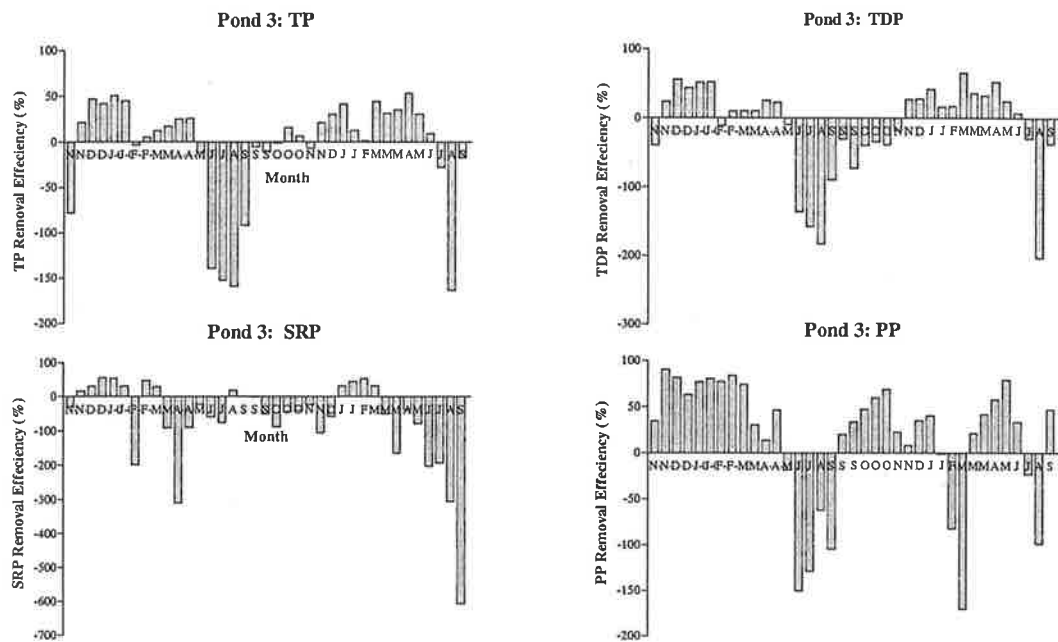


Figure D-3. P removal efficiency in pond 3

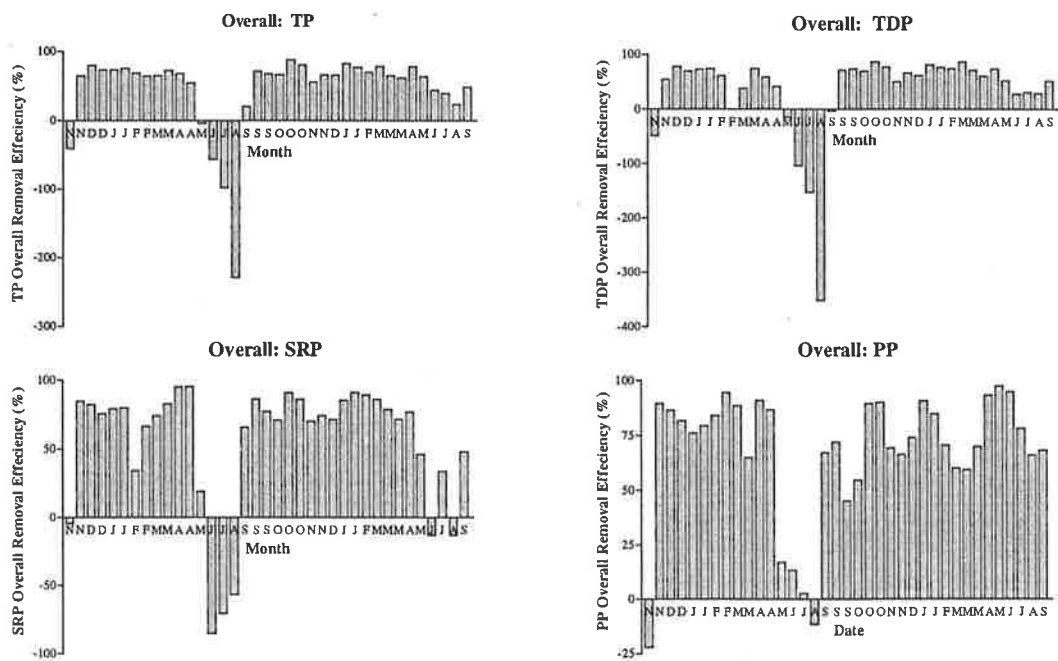


Figure D-4. P removal efficiency in the 3-pond system

Fig

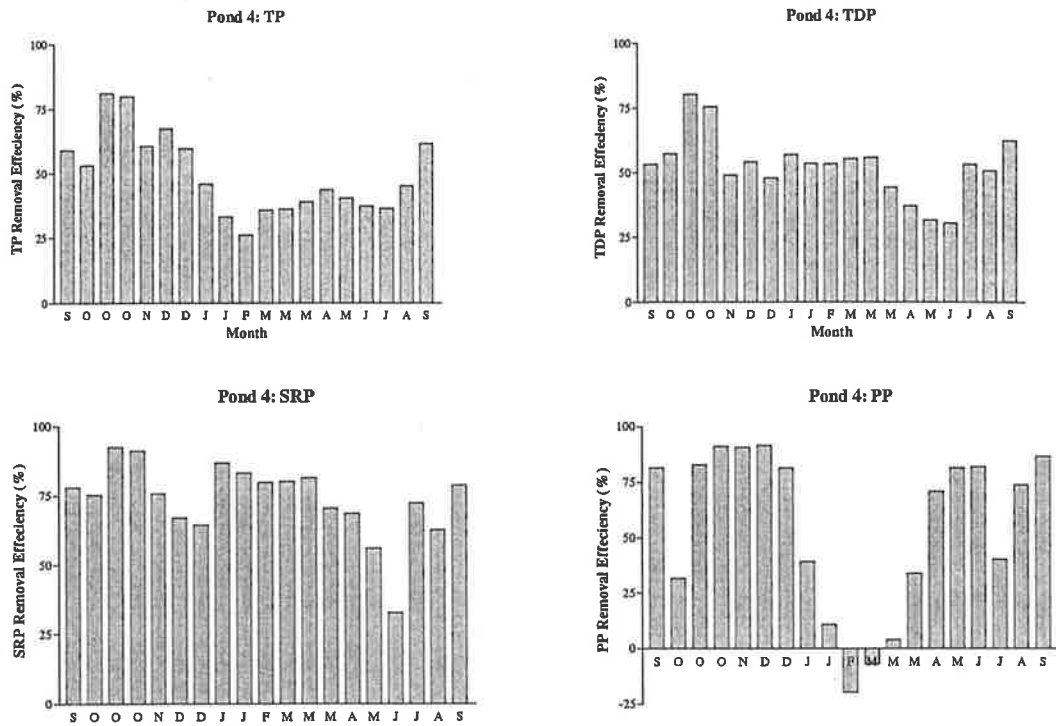


Figure D-5. P removal efficiency in Pond 4

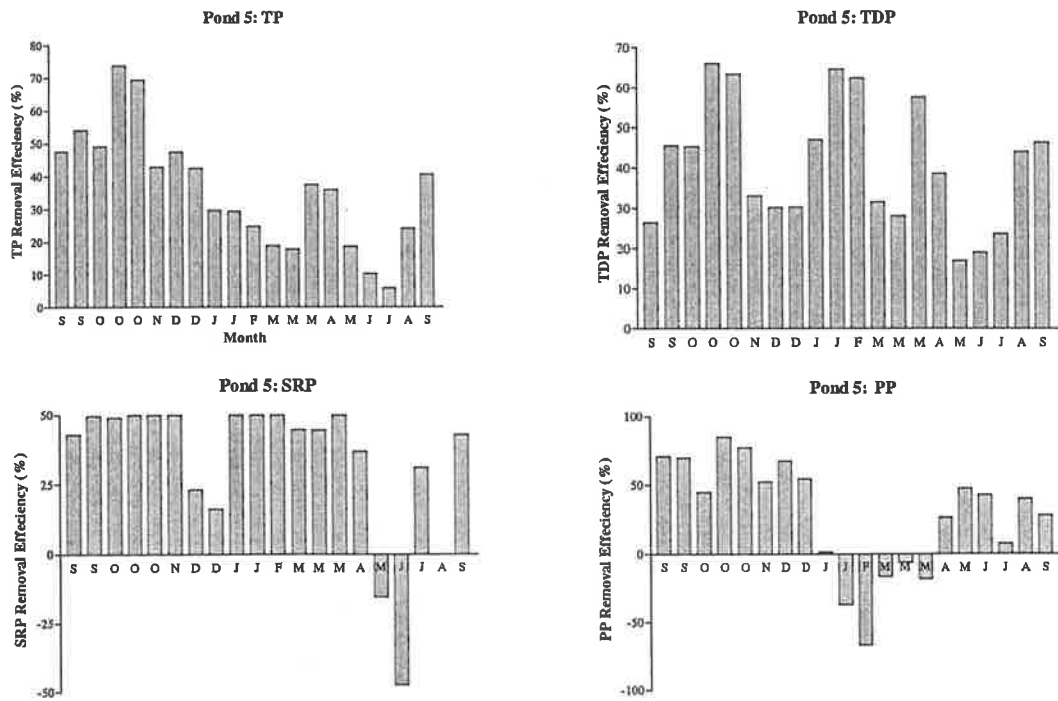


Figure D-6. P removal efficiency in Pond 5

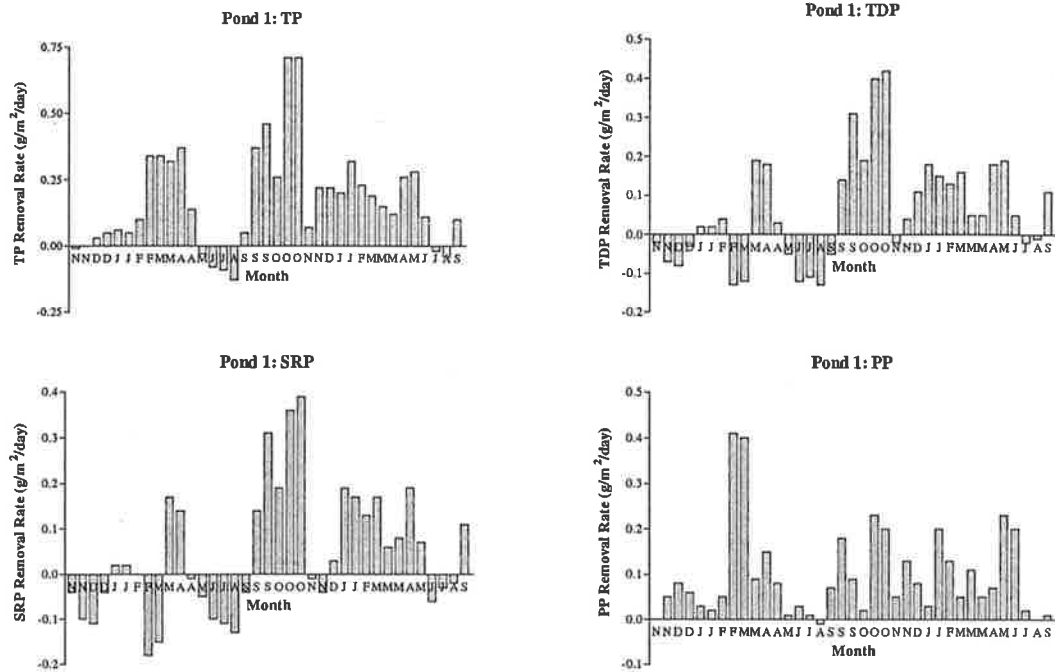
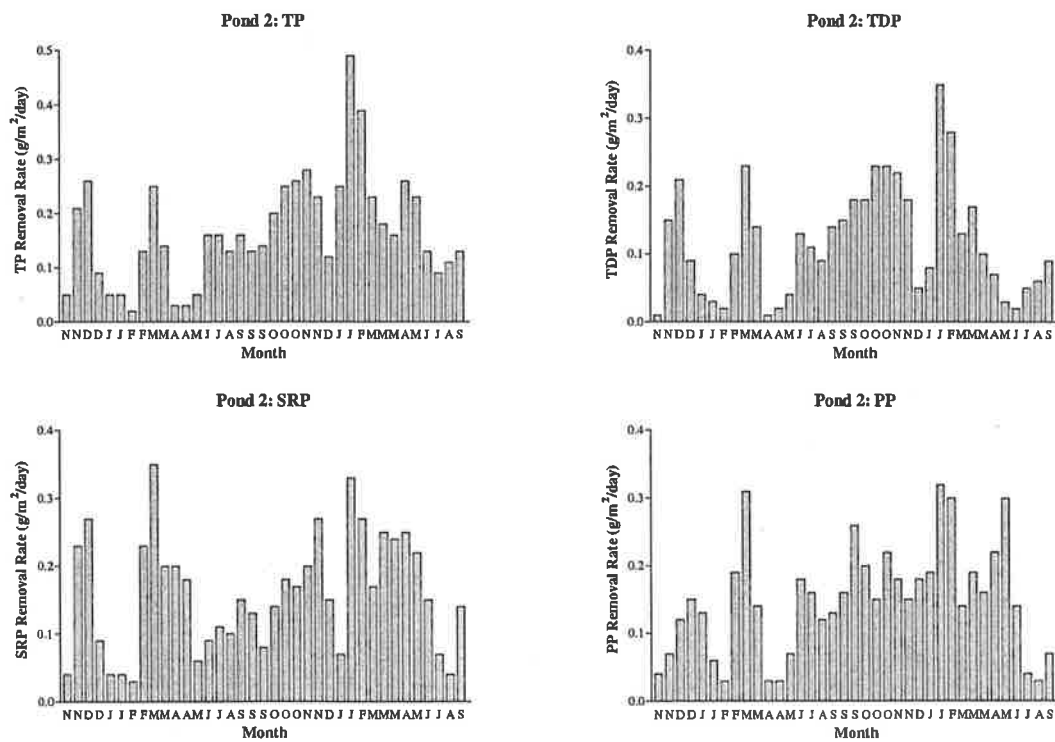
Figure D-7. P removal rate ($\text{g/m}^2/\text{day}$) in pond 1

Figure D-8. P removal rate in pond 2

Fig

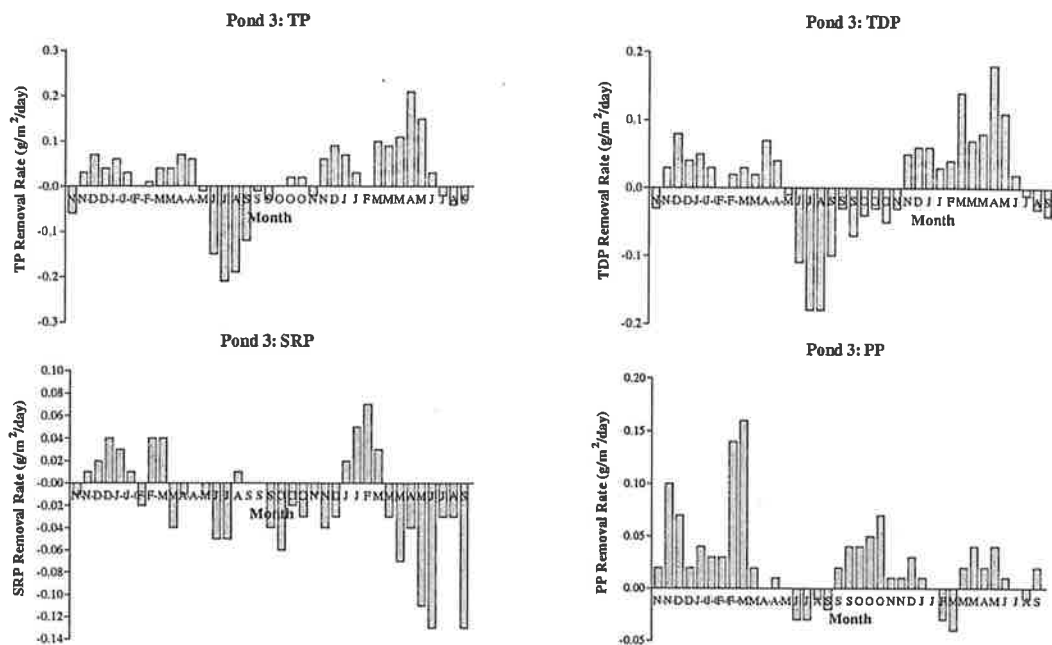


Figure D-9. P removal rate in pond 3

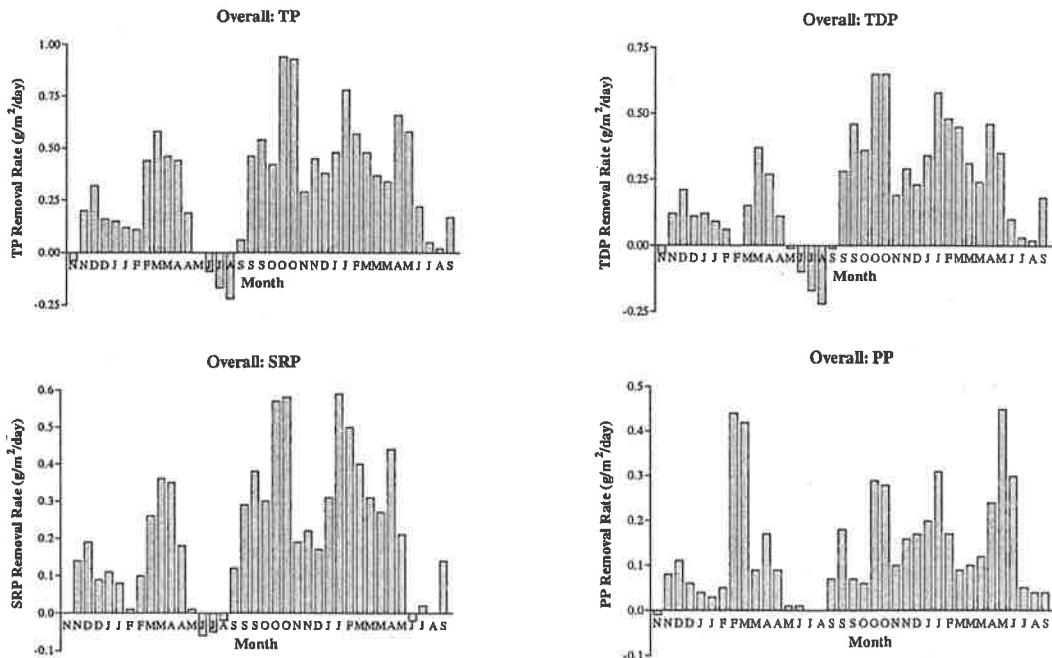


Figure D-10. P removal rate in the 3-pond system

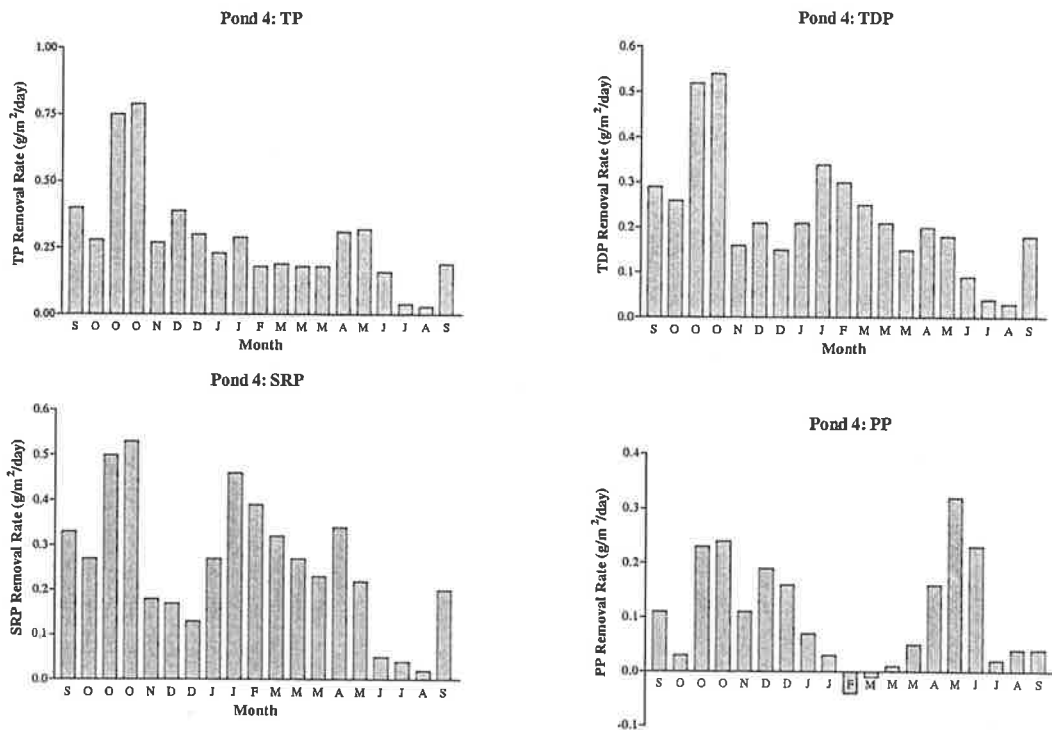


Figure D-11. P removal rate in pond 4

Fig

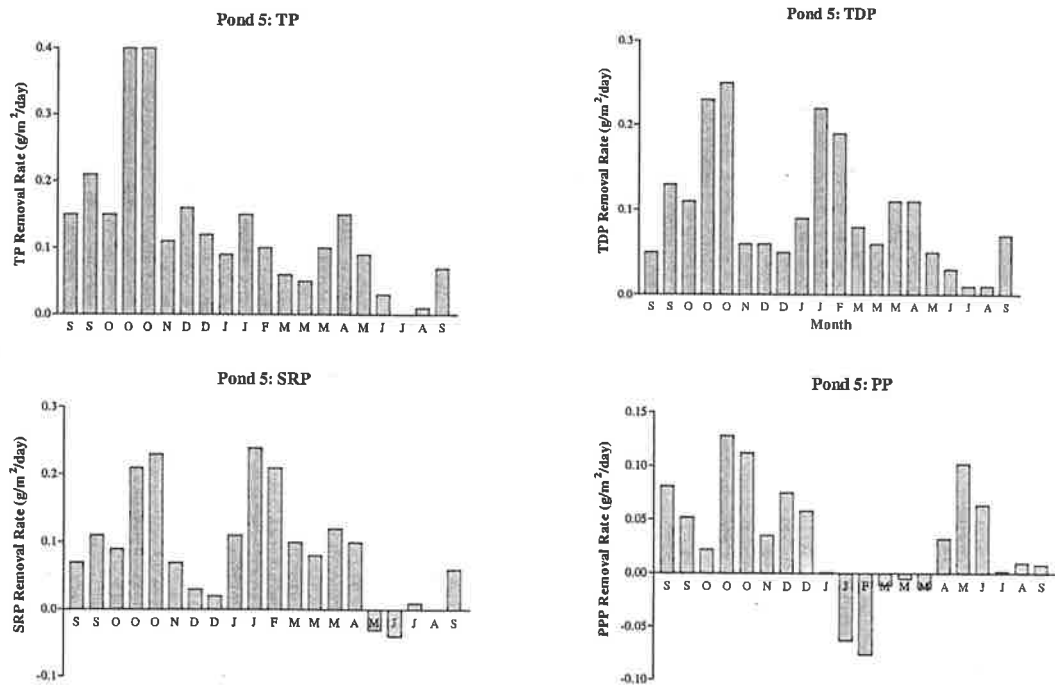


Figure D-12. P removal rate in pond 5

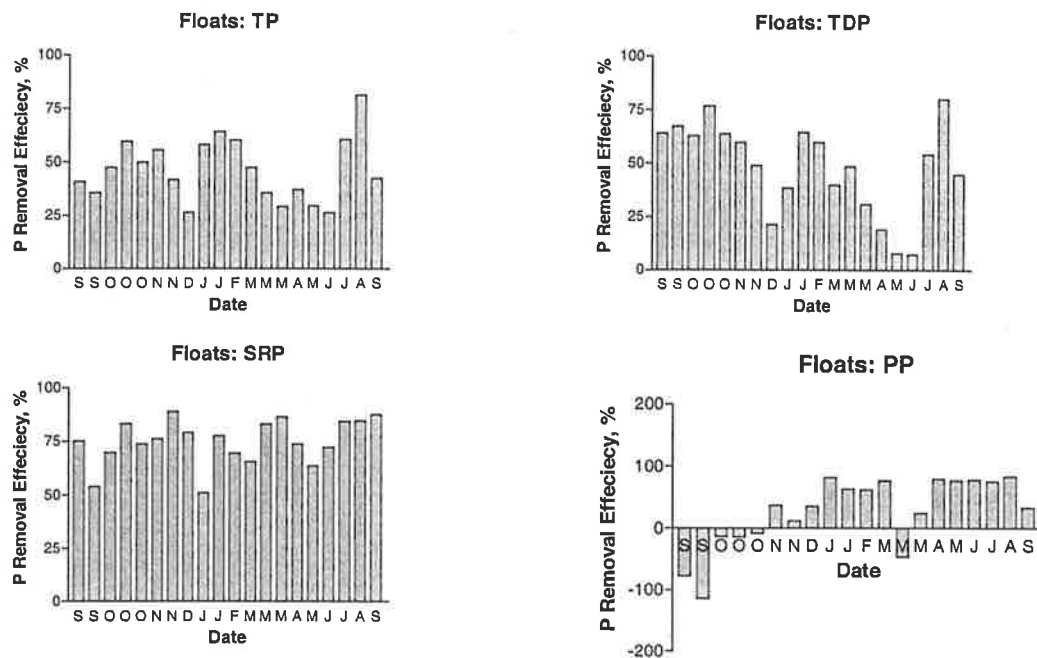


Figure D-13. P removal rate in floating ponds during the implementation of planted floats

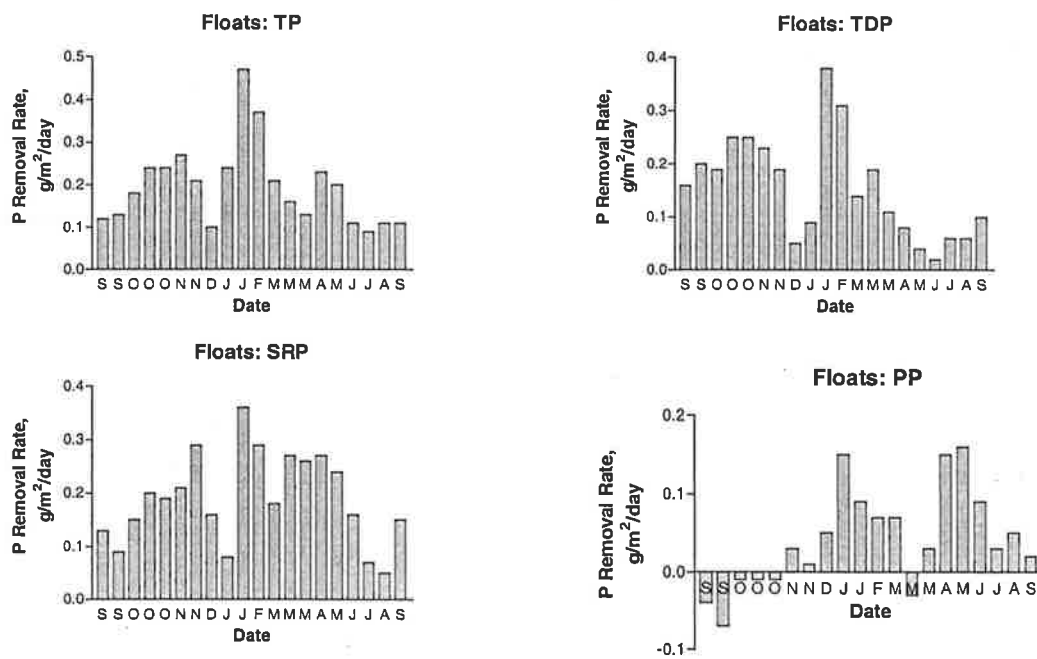


Figure D-14. P removal rate in floating ponds during the implementation of planted floats

Appendix E. Linear relationship between influent/effluent P in experimental ponds

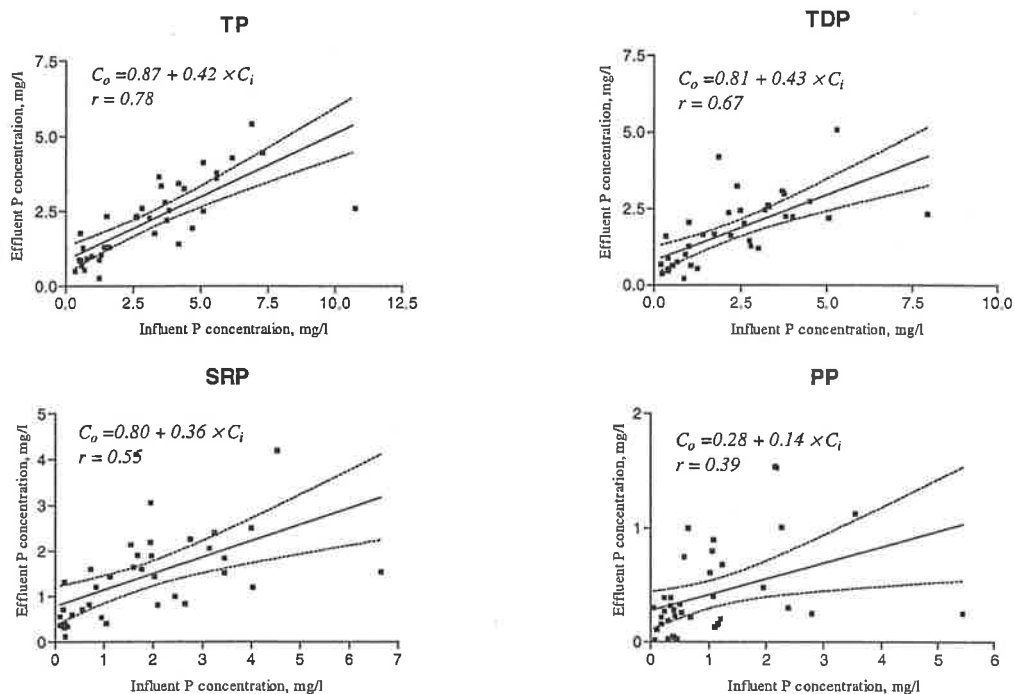


Figure E-1. Relationships of in/out P (concentration) in pond 1. Dots represent measured data; solid lines are fitted models; dashed lines show the $\pm 5\%$ prediction limits. C_i and C_o are influent and effluent P concentrations.

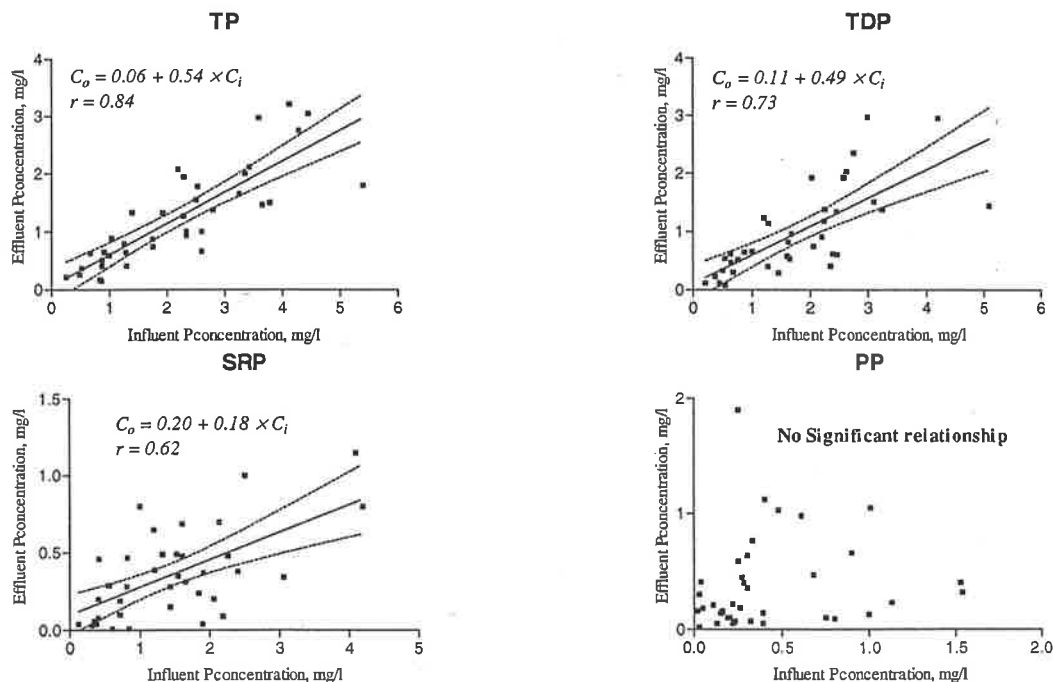


Figure E-2. Relationships of in/out P (concentration) in pond 2

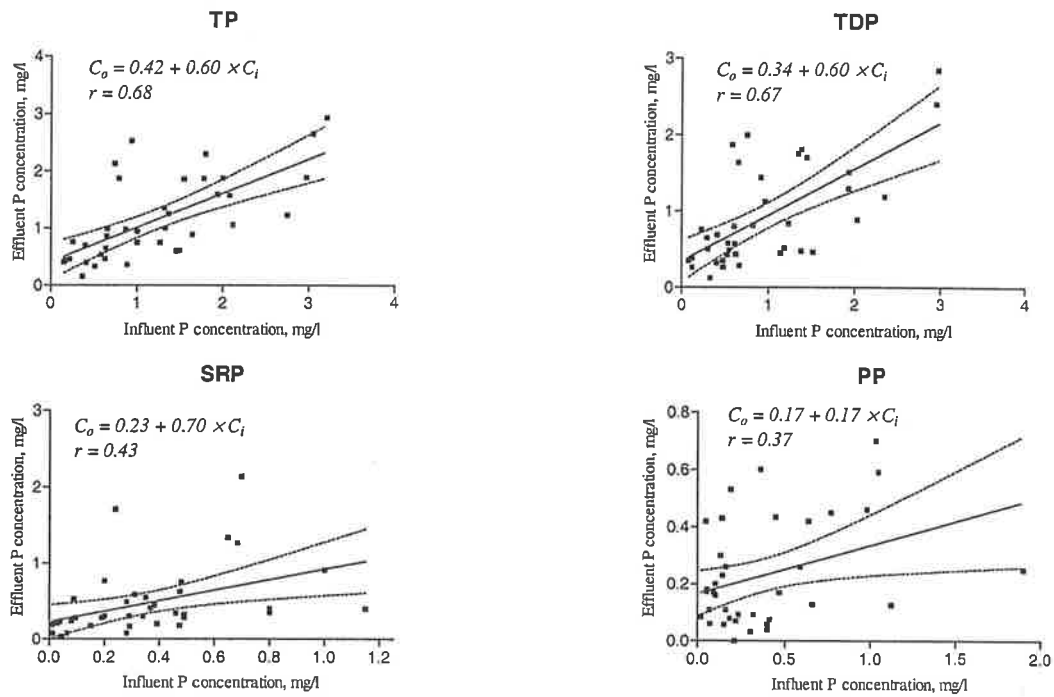


Figure E-3. Relationships of in/out P (concentration) in pond 3

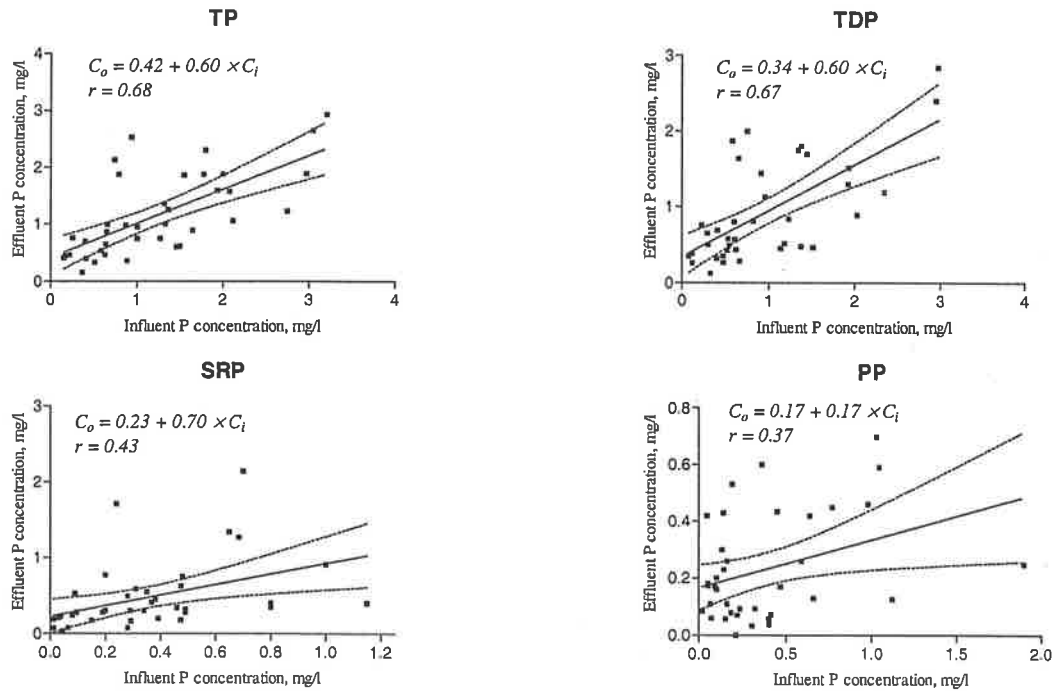


Figure E-4. Relationships of in/out P (concentration) for the 3-pond system

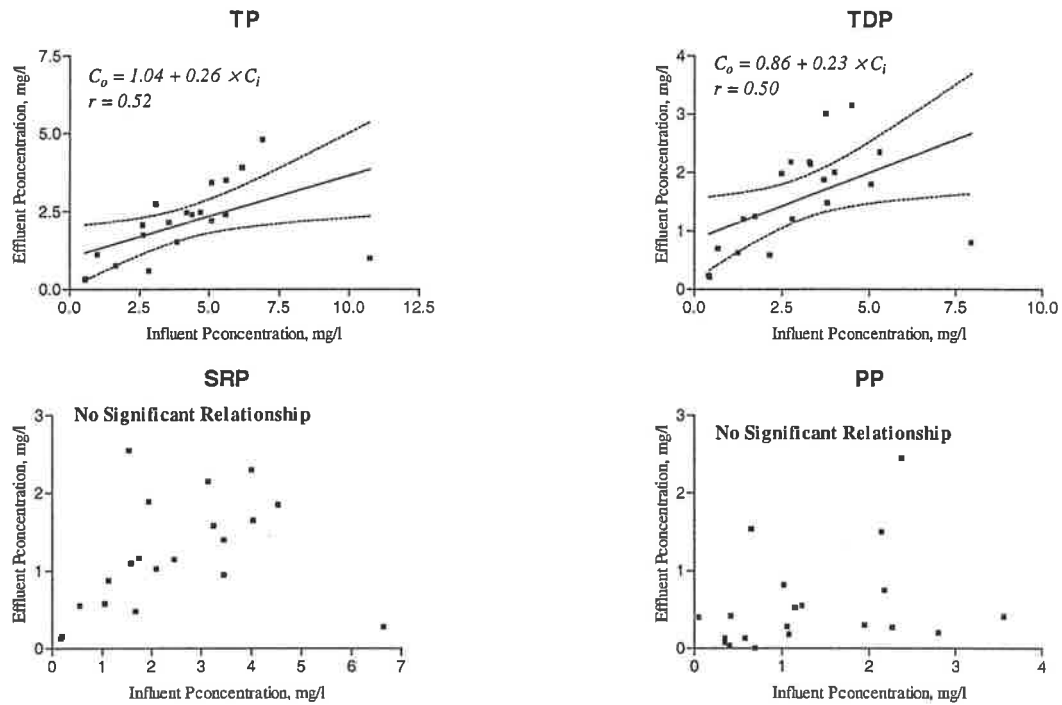


Figure E-5. Relationships of in/out P (concentration) in pond 4

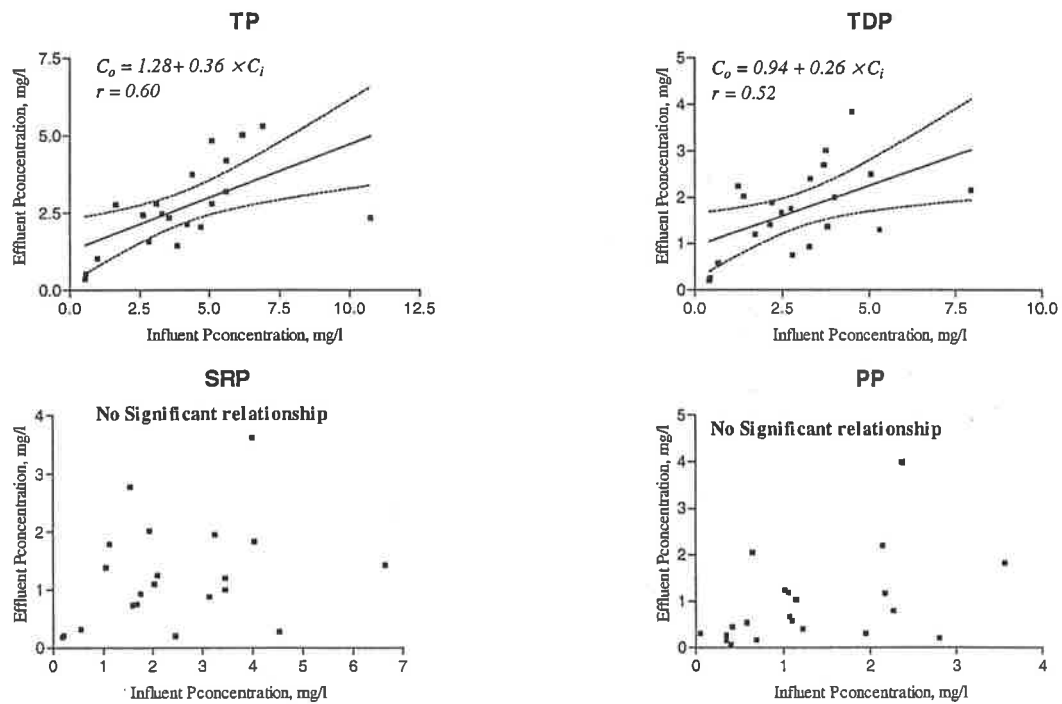


Figure E-6. Relationships of in/out P (concentration) in Pond 5

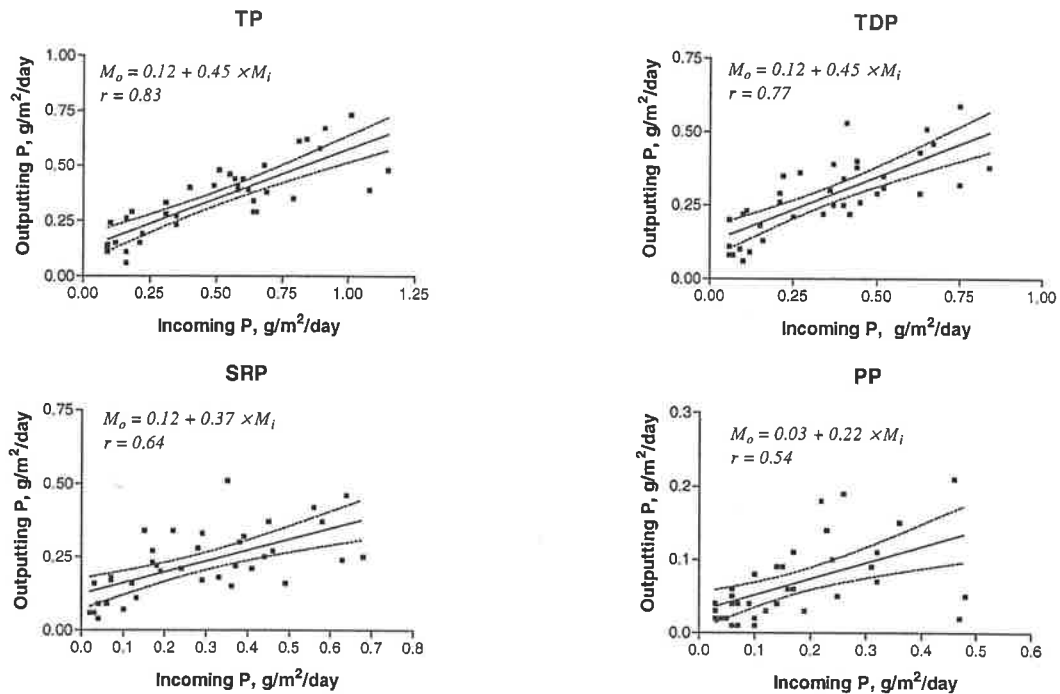


Figure E-7. Relationships of in/out P (mass) in pond 1. Dots represent measured data; solid lines are fitted models; dashed lines show the +/- 5% prediction limits. M_i and M_o are influent and effluent P (g/m²/day).

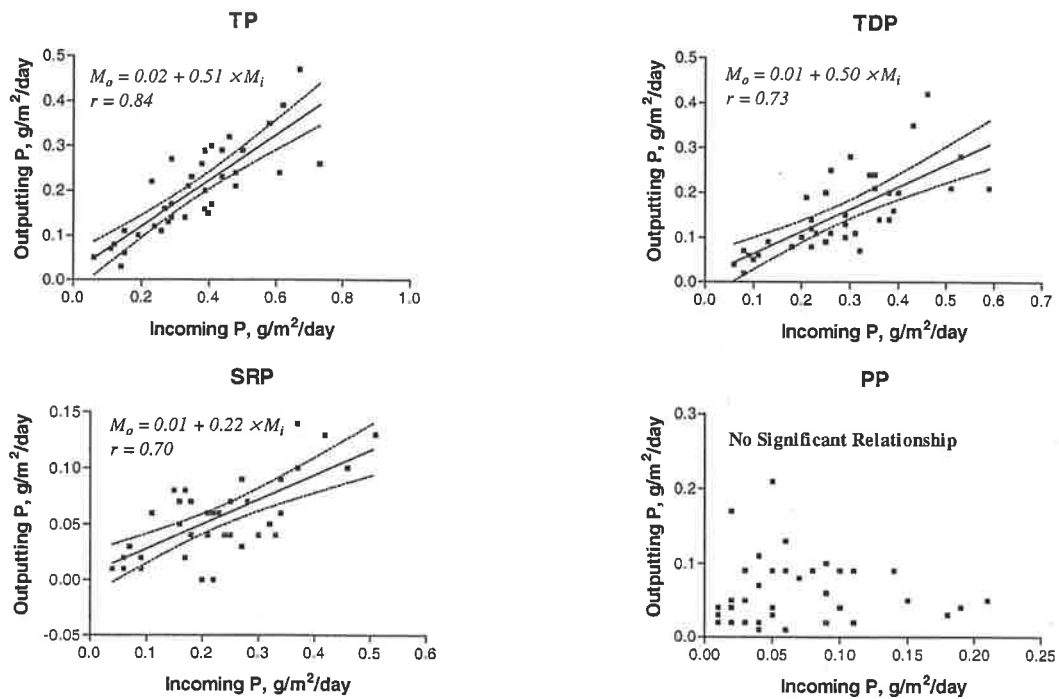


Figure E-8. Relationships of in/out P (mass) in pond 2

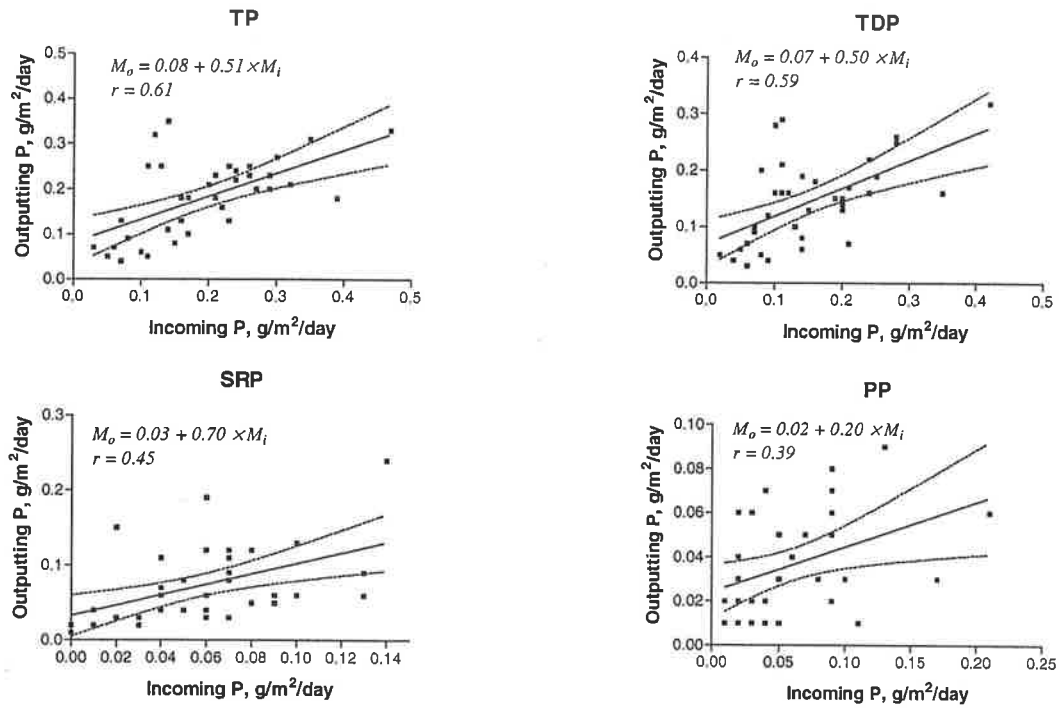


Figure E-9. Relationships of in/out P (mass) in pond 3

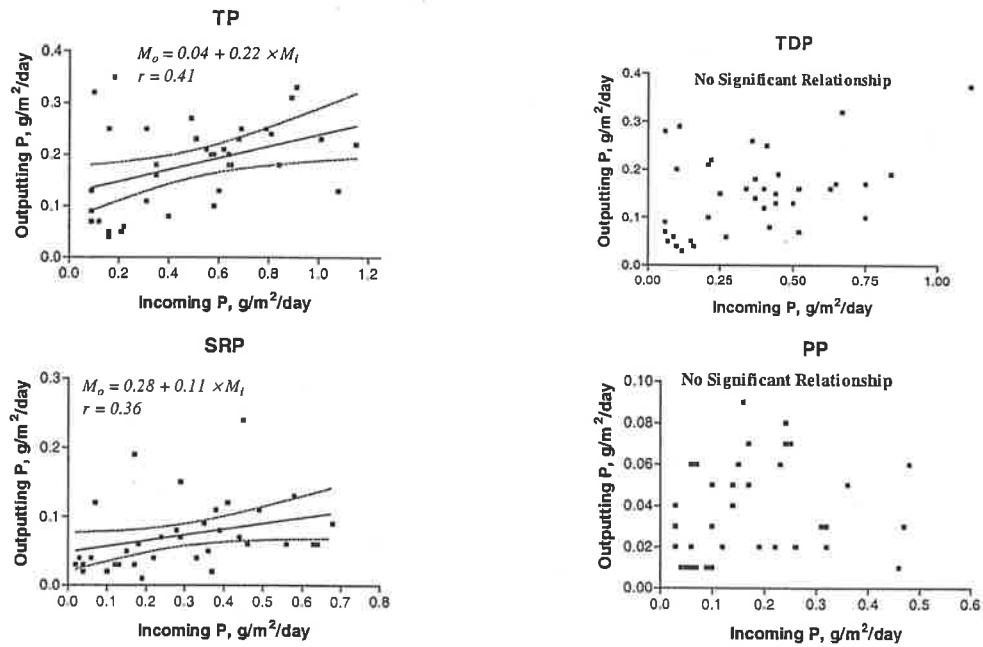


Figure E-10. Relationships of in/out P (mass) in 3-pond system

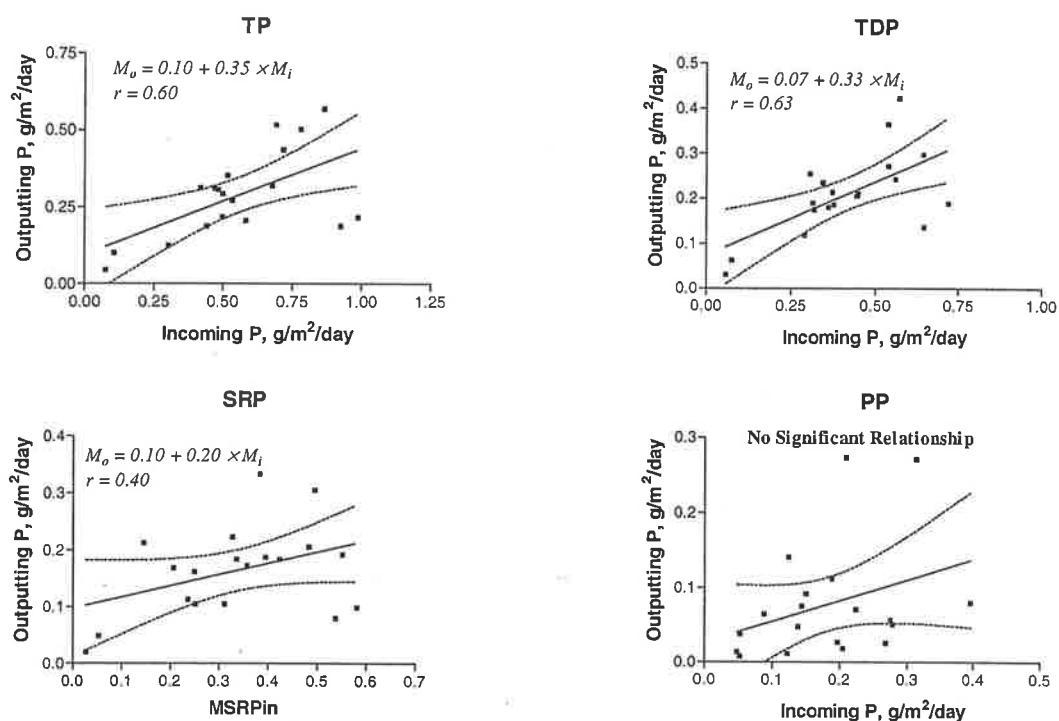


Figure E-11. Relationships of in/out P (mass) for Pond 4

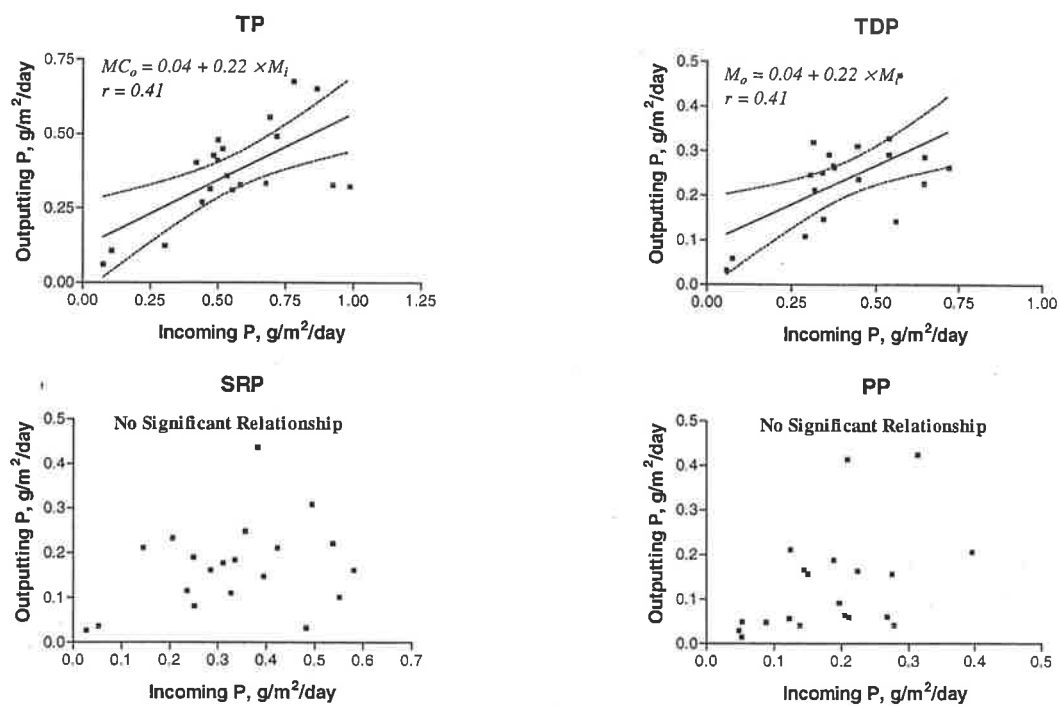


Figure E-12. Relationships of in/out P (mass) in Pond 5