

Phosphorus Removal in a Waste Stabilization Pond

Containing Limestone Rock Filters

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Abstract: This study analyzed samples taken along internal transects through a small waste stabilization pond system in New Zealand that had rock filters installed between the final maturation cells. The aim of the study was to determine the respective importance of the ponds and rock filters for phosphorus removal since routine monitoring from the preceding 2 months had indicated effluent P levels below 2 g/m^3 for influent levels around 9 g/m^3 . Despite the filters being constructed from a reactive sorbent (i.e. limestone) it was found that phosphorus removal was mainly occurring in the ponds. A solubility analysis suggested that phosphorus removal may have been due to moderate calcium hardness levels of around 60 g/m^3 as Ca^{2+} , while an analysis of sludge samples in the system suggested that the ratio of calcium to phosphorus in the sludge was consistent with the precipitation of phosphorus as calcium hydroxyapatite.

Key words: Waste Stabilization Ponds, Phosphorus Removal, Limestone Rock Filters.

Introduction

Moeraki is a small town in North Otago, located about 250 km south of Christchurch on the eastern coast of the South Island of New Zealand. It has a large camping ground and a high proportion of holiday homes, so that while the permanent population is only about 150 people, numbers may reach 500 or more over the summer holiday periods. Prior to 1999, all sewage at Moeraki was treated using septic tanks. This was particularly unsatisfactory during busy periods, as septic tank effluent drained onto roads and adjoining properties due to the steeply sloping landscape and the presence of soils with restricted infiltration capacity (Archer and Shirley 1999). To reduce the public health risk, a raw sewage collection scheme and an oxidation pond/wetlands system was constructed and commissioned under the supervision of the Waitaki District Council in late 1999.

The waste stabilization pond (WSP) system consists of a primary oxidation pond (with two maturation cells) followed by two wetland cells in parallel that discharge to a small creek. The treated effluent in the creek flows a short distance through farmland before meeting the sea, not far from a number of shellfish gathering areas and a popular tourist attraction, the Moeraki Boulders. The proximity of the outfall to the shellfish beds and Moeraki Boulders means that a very good effluent quality is required. To achieve this, the primary oxidation pond has two mechanical aerators to assist natural algae/bacterial action when necessary, particularly during peak holiday periods. Secondly; a membrane wall acts as a baffle in the primary pond and there are two gabion walls that divide the tail end of the pond into two maturation cells. The wetlands feature alternating sequences of subsurface flow limestone gravel and open water areas. The

subsurface flow limestone filters have been planted with flax bushes (*Phormium tenax*), and the open water areas with bulrushes (*Schoenoplectus* spp).

During the first two months of operation (February/March), the WSP system achieved significant phosphorus removal with routine monitoring indicating effluent P levels below 2 g/m³ with an influent P level of 9 g/m³. It was unclear however whether the P removal was a result of adsorption on the limestone, assimilation into biological tissue, deposition of mineral phosphorus into the pond sediments or some other mechanism. As a result, in early 2000 the Waitaki District Council undertook to commission the University of Canterbury to investigate the P removal mechanisms at Moeraki.

Phosphorus Removal in WSPs

Removal of phosphorus is one of the most difficult things to achieve in wetland systems with Kadlec and Knight (1996) noting that the area required for significant phosphorus removal being generally the largest of all wetland requirements. In fact, most operating ponds and wetlands remove little phosphorus and there is no established method for designing ponds for phosphorus removal (Mara and Alabaster 1998). Because there are no mechanisms to completely remove phosphorus from a pond or wetland system, any phosphorus removed from the water column has to be stored somewhere. Many plants (eg. bulrushes, flax bushes and duckweed) do store phosphorus; however, Kadlec and Knight (1996) note that phosphorus typically makes up only 0.1-0.4 % of wetland plants on a dry-weight basis. Studies by Mann and Bavor (1993) and Tanner et al. (1999) also conclude that plants have little effect on phosphorus removal. Thus, the remaining mechanisms for removing phosphorus from the water column include chemical precipitation, adsorption to the substratum and biomass (i.e. algae) assimilation. These removal

mechanisms may be somewhat dependent upon the form of phosphorus (i.e. ortho-P, poly-P or organic P).

Chemical precipitation

Chemical precipitation refers to the interaction of dissolved phosphorus with dissolved cations present in the wastewater and has the net result of converting dissolved phosphorus into solid mineral phosphorus that accumulates in the system, typically in the pond sediments. A variety of cations can precipitate phosphorus under certain conditions and Reddy and D'Angelo (1994) suggest the following; (i) under acid conditions, phosphorus is fixed as aluminium and iron phosphates; (ii) under alkaline conditions, phosphorus is fixed by calcium and magnesium; and (iii) phosphorus is least likely to be fixed under slightly acidic to neutral pH conditions.

Subsurface flow wetlands and heavily vegetated free surface wetlands tend to have relatively neutral pH conditions (Kadlec and Knight 1996), while clear water free surface wetlands and ponds tend to be neutral to alkaline, becoming increasingly alkaline under high levels of algal activity due to the removal of CO₂ by photosynthesis (Hartley et al. 1997). The conclusions of Reddy and D'Angelo (1994) therefore suggest that under these conditions phosphorus fixation is governed by the activities of calcium and magnesium.

Precipitation of calcium carbonate/phosphate minerals is common in hardwater lakes, and is thought to be a natural mechanism for the control of eutrophication (Hartley et al. 1997). Similar reactions may also occur in ponds and wetlands and a study by Reddy et al. (1993) found that long-term P accumulation in the Everglades wetlands was linearly correlated with Ca⁺² accumulation. The chemistry of phosphorus precipitation by calcium is quite complex and some of the major mineral phases involved are listed in Table 1. The most thermodynamically stable

calcium phosphate mineral is calcium hydroxyapatite but this does not normally form directly. Generally, other mineral phases form first, such as hydroxycalcium phosphate (Maurer et al. 1999), dicalcium phosphate dihydrate, octacalcium phosphate and amorphous tricalcium phosphate (Van Kemenade and de Bruyn 1987) before being transformed to hydroxyapatite. Whether or not a precipitate forms is related to the supersaturation of these phases and the precipitation is generally induced by increases in pH due to algal activity (Hartley et al. 1997). In addition, phosphorus may be co-precipitated with other minerals, such as calcium carbonate. Co-precipitation occurs because phosphorus ions in solution may be associated with dissolved calcium ions; and, if a calcium ion attaches to a carbonate ion to create a precipitate, adjacent phosphorus ions may be incorporated into the mineral structure (House 1999). The ratio of calcium to phosphorus from theoretical predictions and for co-precipitation are also listed for each of the phases in Table 1.

Formation of magnesium/phosphate precipitates does not seem to be as common as calcium/phosphate precipitates in natural systems and Maurer et al. (1999) suggest the formation of magnesium precipitates is improbable in domestic wastewater. However, Reddy et al. (1993) found that magnesium accumulation followed a similar pattern to calcium accumulation (which correlated well with phosphorus accumulation), although at a smaller molar ratio. The main magnesium/phosphate precipitate is struvite, which has equal quantities of magnesium, ammonium and phosphate as shown in Table 1. Much of the published literature on struvite relates to the anaerobic digestion of sludges from biological phosphorus removal plants (Battistoni et al 2000; Munch and Barr 2001). These sludges tend to have extremely high ammonium and phosphate concentrations and under these conditions any magnesium ions

present readily precipitate the re-released phosphate out as struvite. Magnesium can also be co-precipitated with calcium carbonate, in a similar fashion to phosphorus (Hartley et al. 1997).

Precipitation is only possible if it is thermodynamically favorable, and this can be predicted from solubility equilibria. Consider the dissociation reaction for calcium hydroxyapatite as extracted from Table 1.



Table 1 Mineral reactions and equilibrium constants

Mineral Phase	Dissociation Reaction	Theoretical Calcium:Phosphorus Molar Ratio	Equilibrium Constant (20-25°C)
Hydroxycalcium Phosphate^a	$\text{Ca}_2\text{HPO}_4(\text{OH})_{2(\text{s})} \equiv 2\text{Ca}^{+2} + \text{HPO}_4^{-2} + 2\text{OH}^-$	2	$1 \times 10^{-22.6}$ mole ⁵ /litre ⁵
Octacalcium Phosphate^b	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}(\text{s}) \equiv 4\text{Ca}^{+2} + 3\text{PO}_4^{-3} + \text{H}^+ + 3\text{H}_2\text{O}$	1.33	1×10^{-48} mole ⁸ /litre ⁸
Amorphous Tricalcium Phosphate^c	$\text{Ca}_3(\text{PO}_4)_{2(\text{s})} \equiv 3\text{Ca}^{+2} + 2\text{PO}_4^{-3}$	1.5	$1 \times 10^{-25.2}$ mole ⁵ /litre ⁵
Dicalcium Phosphate Dihydrate^c	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}(\text{s}) \equiv \text{Ca}^{+2} + \text{HPO}_4^{-2} + 2\text{H}_2\text{O}$	1	$1 \times 10^{-25.2}$ mole ² /litre ²
Calcium Hydroxyapatite^c	$\text{Ca}_5(\text{OH})(\text{PO}_4)_3(\text{s}) \equiv 5\text{Ca}^{+2} + 3\text{PO}_4^{-3} + \text{OH}^-$	1.67	$1 \times 10^{-58.5}$ mole ⁹ /litre ⁹
Calcite with Co-Precipitated P^c	$\text{CaCO}_3(\text{s}) \equiv \text{Ca}^{+2} + \text{HPO}_4^{-2} + 2\text{OH}^-$	60-250 ^e	$1 \times 10^{-8.47}$ mole ² /litre ²

Struvite^d	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \equiv \text{Mg}^{+2} + \text{NH}_4^+ + \text{PO}_4^{-3} + 6\text{H}_2\text{O}$	1	$1 \times 10^{-12.6}$ mole ³ /litre ³
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^aEquilibrium constant and Ca:P ratio from Maurer et al., (1999)

^bEquilibrium constant and Ca:P ratio from Christoffersen et al., (1989)

^cEquilibrium constant and Ca:P ratio from Hartley et al., (1997)

^dEquilibrium constant and Mg:P ratio from Battistoni et al., (2000)

^eCa:P from House (1999)

The equilibrium expression for this reaction is shown below with the solubility equilibrium constant.

$$[2] \quad K_{sp} = \{\text{Ca}^{+2}\}^5 \{\text{PO}_4^{-3}\}^3 \{\text{OH}^-\} = 1 \times 10^{-58.5} \text{ mole}^9/\text{litre}^9 \text{ (@ } 20^\circ\text{C)}$$

The concentrations are expressed as ion activities which are the product of the molar concentration of the ion and the ion activity coefficients. These latter coefficients usually vary from 0 to 1 and are calculated using the Debye-Hückel limiting law for the ionic strength and the Güntelburg approximation for the activity coefficient (Snoeyink and Jenkins 1980).

If the right hand side of the equation exceeds K_{sp} , then precipitation is possible. This is reflected in the saturation index, calculated for calcium hydroxyapatite as ...

$$[3] \quad \text{Saturation Index} = \log \left(\frac{(\gamma_i [\text{Ca}^{+2}])^5 (\gamma_i [\text{PO}_4^{-3}])^3 (\gamma_i [\text{OH}^-])}{1 \times 10^{-58.5} \frac{\text{mole}^9}{\text{litre}^9}} \right)$$

and which gives a measure of how thermodynamically favorable a precipitation reaction is. If the saturation index is positive, the direction of spontaneous change will be towards precipitation; if negative the direction of spontaneous change will be towards dissolution. Note that the saturation index provides no information about whether a kinetically viable pathway exists for the change to occur or for the equilibrium to be reached (Atkins 1994).

Biomass assimilation

The removal of phosphorus by biomass assimilation suggests a small proportion of the phosphorus is incorporated into non-biodegradable tissues which settle out in the sediments. It is difficult to remove significant amounts of phosphorus by this mechanism since most tissues are biodegradable and decomposition releases the nutrients back into the water column. In addition, the phosphorus component of algae (which make up the majority of biomass in maturation ponds and clear free water surface wetlands) is quite low, with a typical formula being $C_{106}H_{181}O_{45}N_{16}P$ (Green et al. 1996). Considering that for a raw wastewater with a typical concentration of $30 \text{ g/m}^3 \text{ NH}_4\text{-N}$ and $10 \text{ g/m}^3 \text{ P}$ the molar ratio of N:P is about 6:1, therefore it would be impossible to remove more than about 50 % of phosphorus in the water through algal uptake. This is consistent with the performance of algae-harvesting systems where approximately 50% of influent phosphorus is removed by assimilation (Nurdogan and Oswald 1995). The upper limit to the performance means that phosphorus removal by harvesting biomass has not proven feasible in normal pond or wetland systems (Kadlec and Knight 1996).

Adsorption

Adsorption of phosphorus refers to physical (physisorption) or chemical (chemisorption) bonding of phosphorus to substrata such as rocks, gravel or sand. For treatment systems with a large amount of substrata such as subsurface flow wetlands, adsorption has been suggested as one of the most important removal mechanisms (Kadlec and Knight 1996). A study by Mann and Bavor (1993) monitored the performance of a full scale subsurface flow gravel wetland over 2 years and demonstrated that non-reactive sorbents can remove significant amounts of phosphorus, but that sorption sites for removal quickly become saturated. The wetland studied

had around 20 m³ of gravel per m³ of flow and removed 10-40 % of applied phosphorus in the first year, but released large amounts of phosphorus in the second year. Recently laboratory studies have been carried out to help select the best reactive sorbents for full-scale use (Mann and Bavor 1993; Drizo et al. 1999, Sakadevan and Bavor 1998; Johansson 1999). The term 'reactive' implies that these substrates have phosphorus assimilative capacities over and above pure physical sorption processes.

There are few examples of full-scale use of reactive substrates and those studies seldom appear to have compared predictions of reactive sorbent performance by laboratory investigations to actual performance under full-scale conditions. However, the study by Mann and Bavor (1993) did compare Langmuir adsorption isotherms from a laboratory study to full-scale performance, and concluded that the lifetime predicted by the laboratory study (about 100 days at 100% removal) was approximately the observed lifetime (about 300 days at 30% P removal). A laboratory column study was also carried out by Drizo et al. (1999) who compared predictions of maximum P retention capacity from laboratory isotherms for shale and bauxite to performance in laboratory columns (which more closely resemble field conditions). While the maximum P retention capacities were similar for shale (730 mgP/kg under column conditions as opposed to 610 mgP/kg from the Langmuir model), they were markedly different for bauxite (350 mgP/kg as opposed to 650 mgP/kg). These studies highlight the difficulty in trying to predict full-scale performance from laboratory measurements.

Research Objectives

This study attempts to (i) document the phosphorus removal of the Moeraki system by taking both water and sludge samples and analyzing them for a range of phosphorus components; (ii) determine the respective importance of the clear water and rock filter sections of the system for phosphorus removal; and (iii) clarify the mechanisms and processes for phosphorus removal in WSPs containing limestone rock filters, in order to make an assessment as to whether the current performance will be continued long-term.

Methodology

Sampling Methodology and Analytical Methods

The dimensions of the Moeraki wetland cells are given in Figure 1a and the profile of the rock filters is shown in Figure 1b. Liquid grab samples were taken in 500 mL plastic containers from a number of different locations as shown in Figure 1a. Temperature, pH and dissolved oxygen were measured insitu before the samples were preserved, placed in an ice cooler and transported to the University of Canterbury, Christchurch for analysis within 7 days of sampling. The flow rate out of the final pond was also measured using a 10 liter bucket and a stopwatch, first thing in the morning and then approximately every 3-4 hours afterwards. Rock filters in Wetland Cell A containing sampling points 4, 5, 8 and 9 had tubes installed (150 mm diameter plastic pipes perforated by 12 mm drilled holes in the sides) to allow samples to be taken internally from the filters. When sampling from the tubes, approximately 20 liters was pumped out before samples were taken to avoid sampling stagnant water. Points 4, 5, 8 and 9 from Wetland Cell B did not have sampling tubes and so a shallow hole was dug each time a sample needed to be obtained. Time and expense limited a comprehensive sampling regime, as well as the number of sampling expeditions; thus samples were taken in a one-off fashion with three

sample periods characterized as being from winter conditions (May, June and July), one sample period being from the spring (November) while the final sample period representing early summer conditions (December). On return to the laboratory, tests were performed for COD, NH₄-N, NO_x-N, TN, TP, total and calcium hardness and suspended solids according to Standard Methods (APHA 1998). During the first sampling expedition, liquid samples were taken at different water depths, however little difference in values were observed; thus, in general, all subsequent measurements were taken approximately 0.1 m below the surface. More detail is presented in Strang (2001) however, in the main, only the hardness and phosphorus results are presented in this paper in keeping with its focus.

Composite sludge samples were also taken from Moeraki at the end of the study period (December). This involved wading into the ponds and the approximate location of sampling points are also shown on Figure 1a. A 50 mm diameter clear Perspex tube was used to lift the sludge off the bottom. The tube was pushed into the sludge until clay on the bottom of the ponds formed a plug at the base and the top of the tube was below water level. A rubber bung was then inserted into the top of the tube to reduce the pressure of the water on the clay plug and the sample was lifted from the bottom. The clear Perspex tube allowed the depth of sludge to be estimated before the rubber bung was removed, water decanted off and sludge scooped out. The sludge samples were removed with a plastic spatula to avoid mixing pieces of the clay liner in with the sample. Each composite sample was made up of at least 5 individual sludge samples taken from the grid pattern from the floor of the pond. The composite sample was placed in a cooler and couriered to a commercial laboratory for testing of total kjeldahl nitrogen (TKN) and

total phosphorus (TP). Selected samples were also analyzed for calcium and magnesium using atomic absorption spectrophotometry by the same commercial lab.

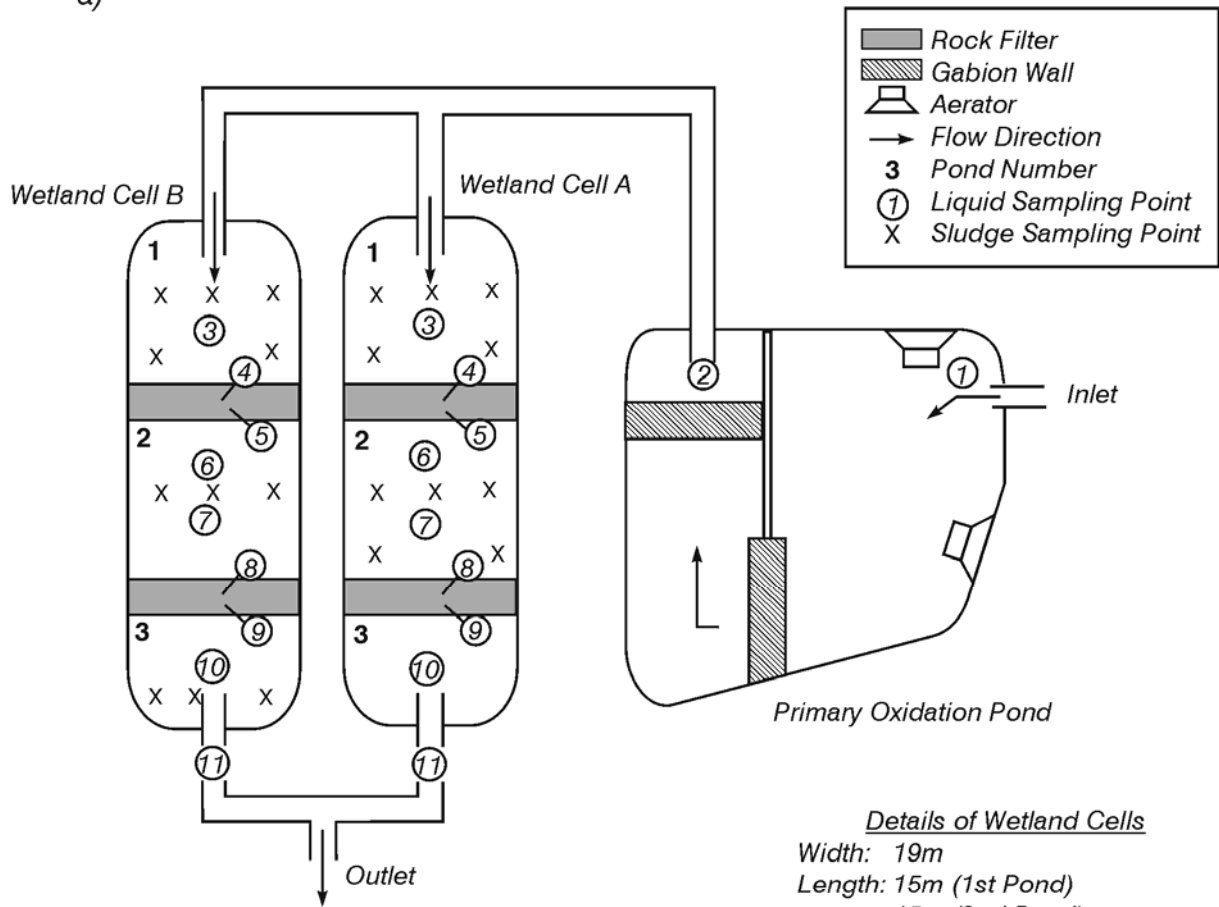
Results

Hardness Data, Phosphorus and pH Profiles

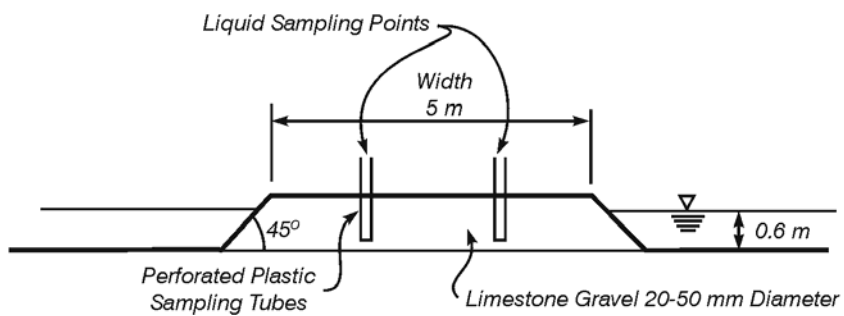
The Moeraki water supply is piped from an area with a large amount of limestone and therefore would be expected to have a reasonably large amount of calcium. Hardness measurements taken during November at Moeraki indicate an average total hardness of 190 g/m^3 as CaCO_3 with an average calcium hardness value of 60 g/m^3 as Ca^{+2} (150 g/m^3 as CaCO_3). Assuming that total hardness is due only to Mg^{+2} and Ca^{+2} hardness, this implies a magnesium hardness of 9.6 g/m^3 as Mg^{+2} (40 g/m^3 as CaCO_3).

Fig. 1. a) Schematic of Moeraki sewage treatment system and b) Cross-section of limestone rock filters

a)



b)



The Moeraki phosphorus profiles from Wetland Cell A (shown in Figures 2a, 2b and 3a) indicate good phosphorus reduction occurred throughout the system during the months of May, June and July. The reduction in November and December (Figure 3b (Wetland Cell B)) however was poor, occurring mainly in the final pond. Figure 4 shows the pH profiles for all the sampling periods and indicates that for May the pH was around neutral throughout the system, in June and July averages were higher than neutral rising through the last pond, while November/December, the pH was quite high in the initial phases dropping to around neutral for the rest of the system.

Sludge Sampling Results

As mentioned, composite sludge samples were taken and the results were used to compute the total phosphorus, calcium and magnesium in the sludge as shown in Table 2. A sample calculation is shown below assuming a sludge density of $1 \times 10^3 \text{ kg/m}^3$ (i.e. the sludge was not dried or thickened and therefore the solids content was likely to be less than 10%, meaning the density was unlikely to deviate significantly from water). Note that unfortunately, sludge samples were not taken from Wetland Cell A, Pond 3.

Sample calculation for Pond 1, Wetland cell A:

$$[4] \quad \text{TP in sludge} = \text{Volume of Sludge} \times \text{Density of Sludge} \times \text{Composition as TP}$$

$$[5] \quad \text{TP in Pond 1} = ((15 \text{ m} \times 19 \text{ m}) \times (0.032 \text{ m}) \times (1 \times 10^3 \frac{\text{kg}}{\text{m}^3}) \times \frac{0.07}{100}) = 6.38 \text{ kg}$$

Discussion

Location of Phosphorus Reduction

As mentioned, the phosphorus profiles indicate strong phosphorus reduction (particularly for May, June and July) with the profiles showing most phosphorus being lost in the ponds

(primarily pond 1) rather than the rock filters. While admittedly there was no control wetland cell without rock filters, it appears that although reduction did occur in the filters during those 3 months; it comprised only about 20 % of the total reduction achieved in the system. The low removal through the limestone rock filters was surprising since the effectiveness of the phosphorus removal had been assumed to be caused by their presence. Phosphorus removal through the system was poor over November and December, meaning that the system performed best over winter, the least critical season for eutrophication.

Table 2. Chemical composition of sludge

	Wetland Cell A	Wetland Cell A	Wetland Cell B	Wetland Cell B	Wetland Cell B
	Pond 1	Pond 2	Pond 1	Pond 2	Pond 3
Sample Depth (m)	0.032	0.018	0.027	0.010	0.013
TKN^a (%)	0.13	0.08	0.19	0.07	0.11
Total P^a (%)	0.07	0.06	0.12	0.06	0.11
Ca^a (%)	-----	-----	0.20	0.14	0.19
Mg^a (%)	-----	-----	0.16	0.08	0.13
TKN (kg)	11.86	4.10	14.62	2.00	2.72
Total P (kg)	6.38	3.08	9.23	1.71	2.72
Calcium (kg)	-----	-----	15.39	3.99	4.69
Magnesium (kg)	-----	-----	12.31	2.28	3.21

^a Results are given as a percentage on a wet weight basis

Fig. 2. Phosphorus profiles from Moeraki a) May b) June

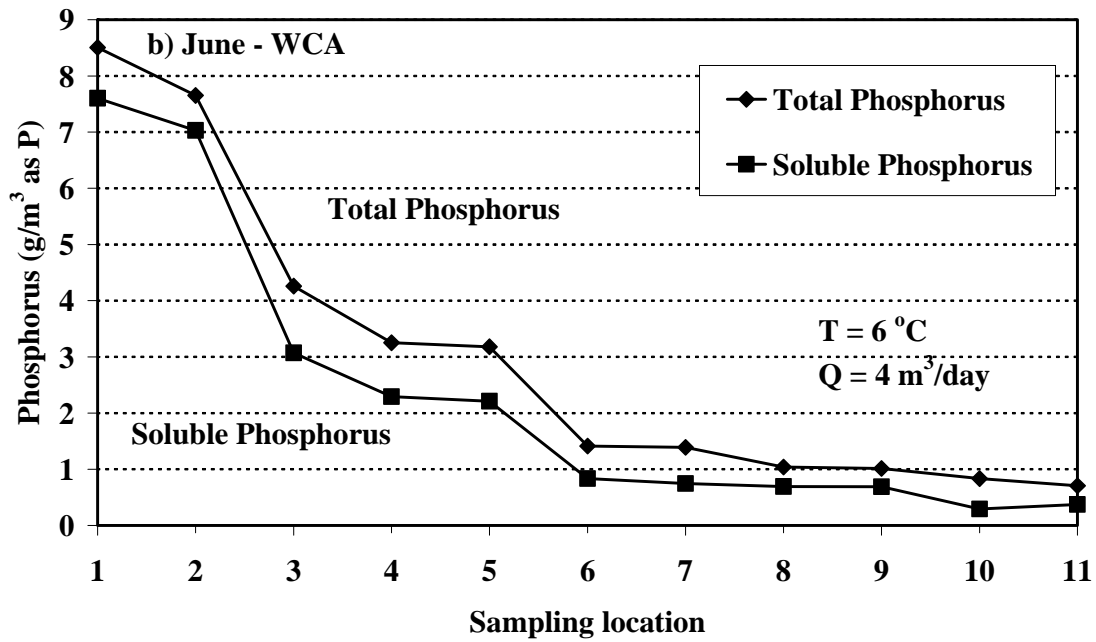
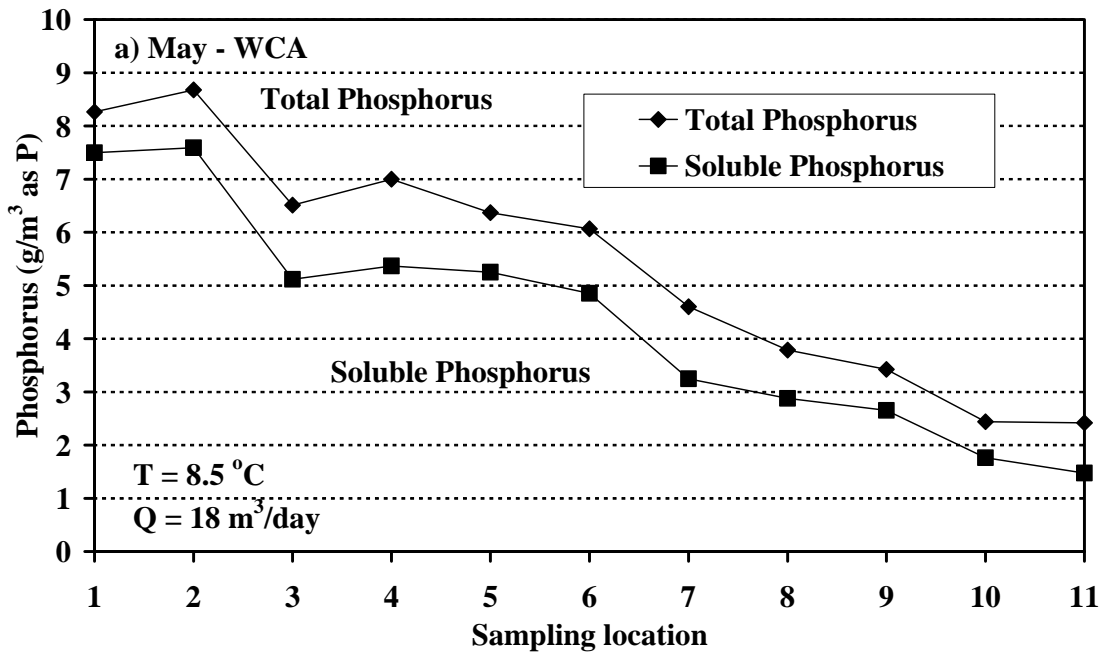
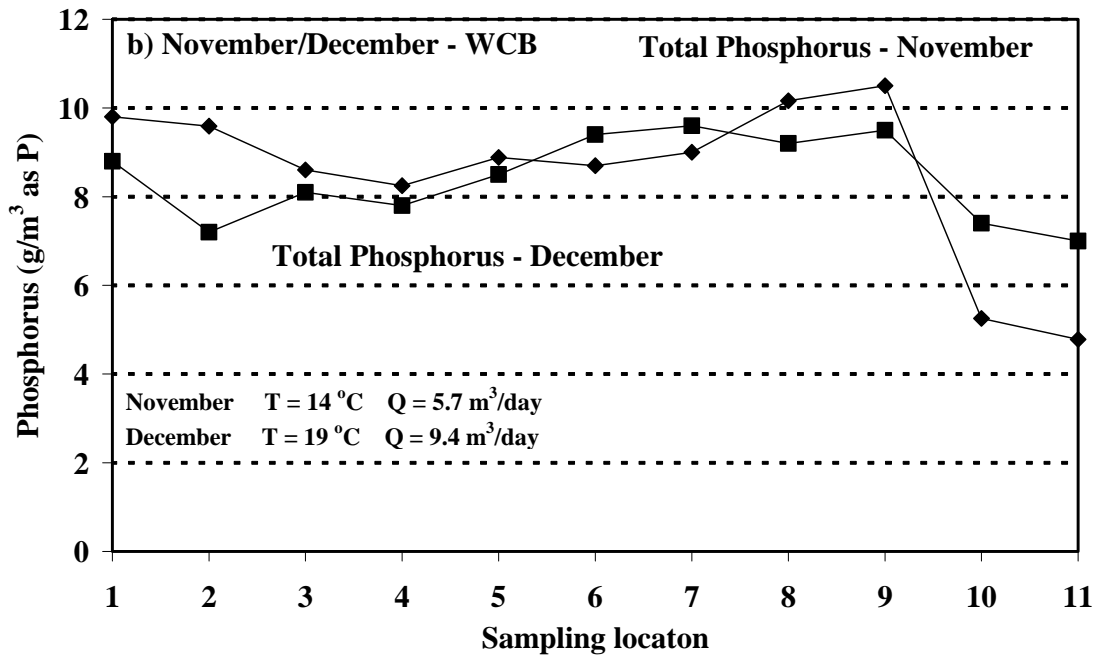
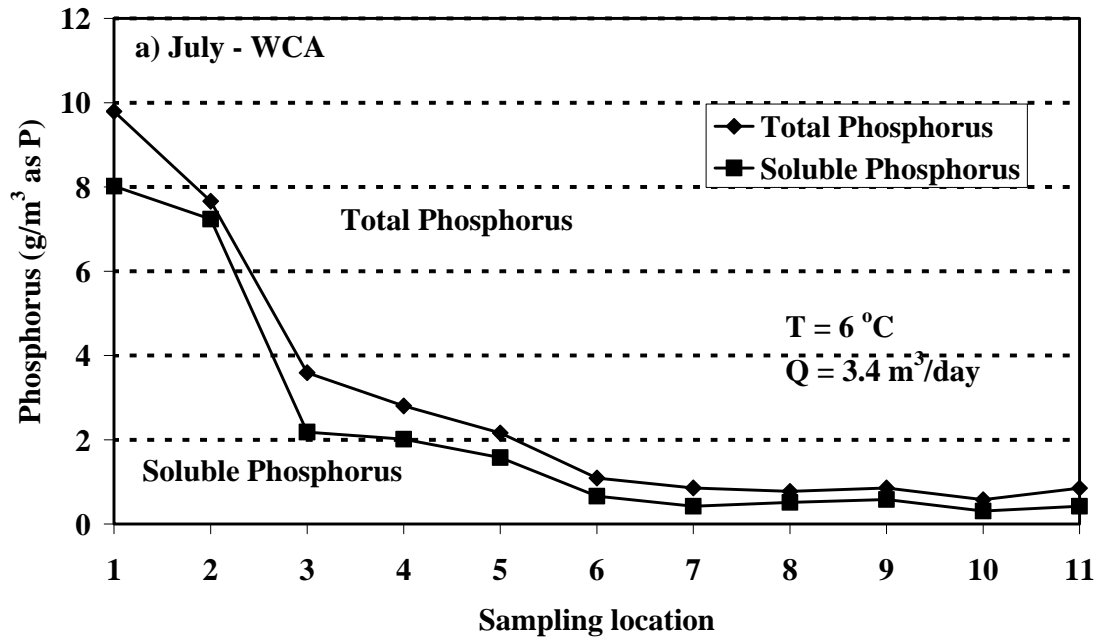


Fig. 3. Phosphorus profiles from Moeraki a) July b) November/December

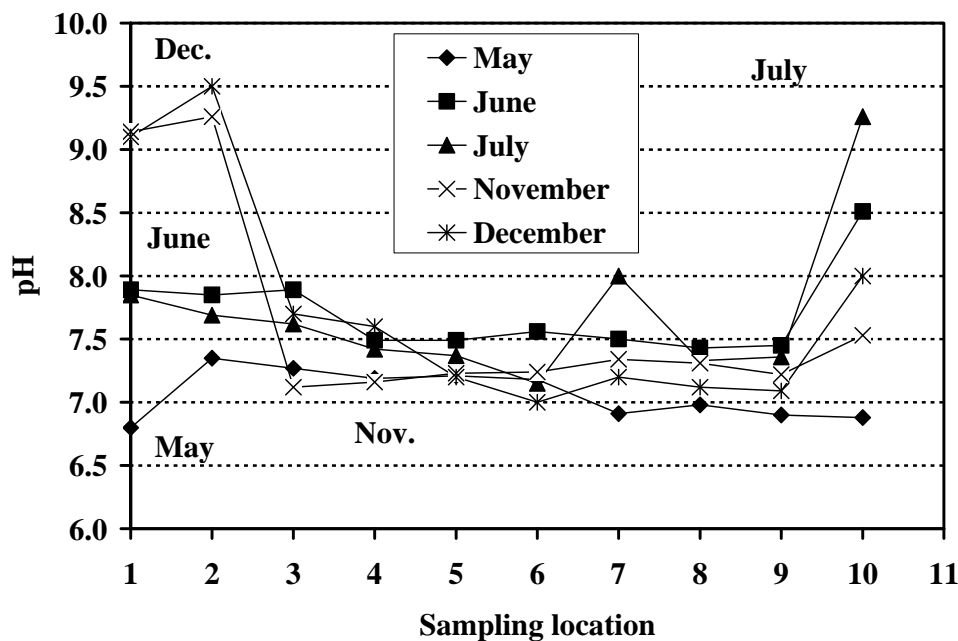


An approximate mass balance was performed to see if the loss of phosphorus from the water column over the 10 months of operation could be roughly accounted for by the weight of phosphorus accumulated in the sludge. For calculation purposes, the total phosphorus (TP) removal of a pond was taken as the difference between TP at the downstream end of the pond and the sampling tube or point immediately preceding that pond. That is,

[6] $TP \text{ reduction in pond 1} = TP \text{ at sample point 3} - TP \text{ at sample point 2}$

[7] $TP \text{ reduction in pond 2} = TP \text{ at sample point 7} - TP \text{ at sample point 5}$

Fig. 4. pH profiles from Moeraki



[8] $TP \text{ reduction in pond 3} = TP \text{ at sample point 11} - TP \text{ at sample point 9}$

These reduction values were multiplied by the respective flow rate for the corresponding month as shown below for the month of May.

$$[9] \quad \text{TP Removal in Pond 1} = (8.7 - 6.5) \frac{\text{g}}{\text{m}^3} \times 18 \frac{\text{m}^3}{\text{d}} = 39.6 \text{ g/day}$$

The TP removed from the water column over the 10 months of operation was estimated from a time-weighted average of the five sampling periods. Each sampling period was weighted to provide an estimate of the full 10 months. That is, the May results were weighted for 3 months; the June results for 1 month; the July results for 2 months; the November results for 3.5 months; and the December results for 0.5 months.

For ponds 1,2 and 3 respectively (only wetland cell A had complete liquid data), the TP reductions were estimated to be 5.0 kg, 2.6 kg and 4.7 kg, giving an overall TP reduction of 12.4 kg for the first 10 months of operation. There were not enough samples to estimate the average TP reduction in the water column of Wetland Cell B; however, it is assumed that it would be similar to Wetland Cell A and also be between 12 and 13 kg of TP removed for the 10 months of operation.

Table 3 compares the calculated values of TP removed from the water column with the actual TP amount measured in the sludge (Table 2) and it suggests that the amount of phosphorus removed from the water column is roughly equivalent to the amount of phosphorus accumulated in the sludge.

Mechanism of Phosphorus Reduction

To construct a graph showing the saturation index of each phosphorus mineral phase as a function of pH, the Debye-Hückel limiting law and the Güntelberg approximation was combined with the dissociation reactions and equilibrium constants listed in Tables 1. Equilibrium conditions were calculated by iteration, for representative steady state maturation pond concentrations of 4 g/m³ total inorganic phosphorus concentration (as P), 20 g/m³ ammonia

concentration (as N), 12 g/m³ magnesium concentration (as Mg⁺²) and a hardness of 60 g/m³ calcium concentration (as Ca⁺²). Solubility lines for supersaturated calcium phosphate phases at this calcium concentration (Figure 5) confirms the thesis by Maurer et al. (1999) that formation of struvite is improbable at domestic wastewater concentrations, since the saturation index for struvite remains negative over the pH range considered. It is noted however that because the Moeraki water temperatures were low (around 6°C in winter) this may shift the supersaturation lines slightly since the solubility data was obtained at 20-25°C. Notwithstanding, the saturation index for calcium hydroxyapatite is very high, and there are a number of intermediate calcium precipitates (for example hydroxydicalcium phosphate or octacalcium phosphate) that are also supersaturated. For pH values above 7.0, the solution is also saturated with respect to CaCO₃, and therefore co-precipitation of phosphorus is possible. These considerations suggest that precipitation of calcium phosphates may be a significant removal mechanism, while co-precipitation of phosphorus is also possible.

As seen in Table 2, the level of calcium in the sludge was measured for the ponds in Wetland Cell B. This allows the molar ratio of Ca:P to be calculated as being 1.3, 1.8 and 1.3 respectively for Ponds 1, 2 and 3. An example calculation for Pond 1 in Wetland Cell B is presented below.

$$[10] \quad \text{Ca:P (molar ratio)} = \frac{15.39 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mole}}{40 \text{ g}}}{9.23 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mole}}{31 \text{ g}}} = \frac{384.8 \text{ moles of Ca}}{297.7 \text{ moles of P}} = 1.3$$

As seen, the Ca:P ratios at Moeraki are in the range of 1.3 to 1.8, and these ratios can be compared to those in Table 1 showing theoretical Ca:P ratios for calcium hydroxyapatite, hydroxydicalcium phosphate and octacalcium phosphate (i.e. the phases shown to be

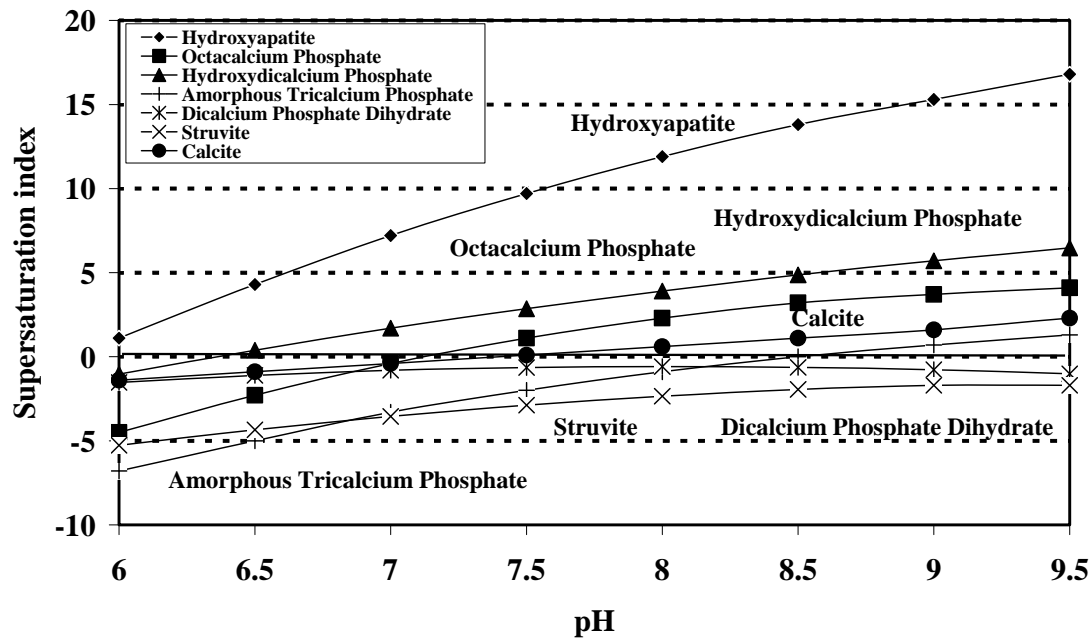
supersaturated in Figure 5). It appears then that there is some support for precipitation of phosphorus as one or more of these phases. It is clear however that the ratio of Ca:P is much lower than would be expected for co-precipitation with calcite, suggesting that that is unlikely to be a dominant removal mechanism.

It is conceivable that a portion of the phosphorus in the sludge may be attributed to biomass assimilation. One way to account for this proportion is to measure the amount of nitrogen in the sludge and assume a N:P ratio for the biomass. The N:P ratio is 16:1 using the formula for algae as $C_{106}H_{181}O_{45}N_{16}P$ (Green et al. 1996).

Table 3. Approximate mass balance for total phosphorus at Moeraki

Pond	Wetland Weighted TP Reduction (kg/10 months)	Cell A TP in Sludge (kg)	Wetland Cell B TP in Sludge (kg)
1	5.0	6.4	9.2
2	2.6	3.1	1.7
3	4.7	----	2.7
Total System	12.4	----	13.6

Fig. 5. Solubility lines for calcium and magnesium phosphorus phases: calcium hardness = 60 g/m³ as Ca⁺², PO₄⁻³ = 4 g/m³ as P, NH₄⁺ = 20 g/m³ as N, Mg⁺² = 12 g/m³



Note that this assumes all nitrogen in the sludge is in the form of algal biomass and that nitrogen and phosphorus are released at similar rates under biodegradation. Assuming that 1/16 of the nitrogen molecules in the sludge are phosphorus molecules associated with biological uptake, the resulting Ca:P can be recalculated as shown below using an adjusted (and consequently lower) value for phosphorus. As can be seen this has the effect of increasing the Ca:P ratio.

$$[11] \quad \text{Adjusted P} = 297.7 - \frac{1}{16} \left[14.62 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mole}}{14 \text{ g}} \right] = 232.4 \text{ moles of P}$$

$$[12] \quad \text{Ca : P (molar ratio)} = \frac{384.8 \text{ moles of Ca}}{232.4 \text{ moles of P}} = 1.7$$

The recalculated Ca:P ratios for Ponds 1, 2 and 3 of Wetland Cell B are 1.7, 2.2 and 1.6 respectively. Real precipitates may differ in their molar ratios from theoretical predictions and Maurer et al. (1999) notes that it is possible to create pure crystals of calcium hydroxyapatite with Ca:P ratios ranging from 1.3 to 2. Assuming that other phases could also exist at a similarly

large range of molar ratios leads to the suggestion that the Ca:P ratio at Moeraki would be consistent with precipitation as any of the calcium phases listed in Table 1, except for calcite. However, House (1999) suggests octacalcium phosphate is an unstable precursor phase that will rapidly transform to hydroxyapatite while Maurer et al. (1999) suggest that hydroxydicalcium phosphate slowly transforms to hydroxyapatite. In the latter case however, this transformation is within the context of the normal residence time of a biological phosphorus removal plant; and, as such, it is even more likely in the 10 month case considered here that these transformations would be further along. It seems therefore that much of the phosphorus in the sludge would be in the form of hydroxyapatite, although, it acknowledged that true equilibrium might not be reached for months (or even years) since some transformations take considerable time to reach equilibrium.

Effect of pH

Although it is suggested that the most likely mechanism for phosphorus reduction at Moeraki is phosphorus precipitation with dissolved calcium ions; as Figure 5 shows, conditions for precipitation become more favorable as the pH rises. Precipitation would be expected to be influenced by the activity of algae which raise the pH of pond water due to the removal of CO₂ by photosynthesis (Hartley et al. 1997). Figure 3b is inconsistent with this hypothesis however, since the majority of the phosphorus reduction occurs in the final wetland cell pond where the bulk water pH is about 7.5, rather than the primary pond where the pH is above 9.0 (Figure 4).

The first possible explanation for these results is that the limestone may contribute additional calcium to the water, therefore making conditions more favorable to precipitation after

the final limestone rock filter. However, at the calcium concentration of 60 g/m^3 measured for Moeraki in November, the wastewater is already supersaturated with respect to CaCO_3 (Figure 5) and therefore it seems unlikely that the limestone would contribute additional calcium.

A second possible explanation is that the precipitation may have been governed by localized pH conditions rather than bulk water conditions. House (1999) suggests the presence of algae and algal biofilms may lead to localised conditions that are more favorable to precipitation than conditions in the bulk water and cites studies recording pH changes of up to 1.6 over distances of 800 mm above a photosynthetically active biofilm (Hartley et al. 1997). It is therefore possible that conditions in the third wetland cell pond were more suitable for the development of localized pH conditions than the primary pond (which was mixed by the aerators). It should also be noted that the precipitation of phosphorus as hydroxyapatite consumes OH^- ions (Hartley et al. 1997) and hence this would lower the bulk water pH in the pond where the precipitation is occurring.

Phosphorus Adsorption by Reactive Sorbents

As the profiles indicate, the limestone rock filters at Moeraki do not remove the majority of phosphorus lost in the system. In addition, any capacity for phosphorus adsorption attributed to the losses observed in the May, June and July profiles appeared to have been saturated by the November and December profiles, which both show a release of phosphorus from the filters. This may have been a seasonal effect caused by the amount of phosphorus being released by degradation of organic matter being greater than the absorptive capacity of the filters, but the results do not lend support for the use of limestone as a reactive sorbent. Phosphorus adsorption isotherms were not measured for the Moeraki limestone, however the performance of the

Moeraki system can be compared to isotherms in the literature, in an attempt to suggest why the performance of the limestone has been so poor.

Table 4. Bonding capacities and $P_{\text{adsorption}}$ maxima^a

Substrate	Bonding Capacity (k)	$P_{\text{adsorption}}$ Maximum (S_{max}) (g P/kg substrate)
Bauxite	0.26 ± 0.01	0.61 ± 0.08
Shale	0.61 ± 0.02	0.65 ± 0.07
Limestone	0.10 ± 0.02	0.68 ± 0.09
Zeolite	0.03 ± 0.01	0.46 ± 0.08

^aAdapted from Drizo et al, (1999)

Both Johansson (1999) and Drizo et al. (1999) compared phosphorus adsorption isotherms for limestone to other reactive sorbents. Drizo et al. (1999) used the Langmuir model to calculate bonding capacity and adsorption maxima and selected values have been presented in Table 4. Their study used the phosphorus adsorption maxima to estimate the expected life of constructed wetland systems made from some of the substrates. Some of these expected lifetimes were very impressive, therefore a similar calculation was carried out for Moeraki below, to determine what sort of lifetime laboratory studies would predict. The value of 0.68 gP/kg substrate from Table 4 was used for the $P_{\text{adsorption}}$ maximum and a porosity of 0.4 and a density of $2.65 \times 10^3 \text{ kg/m}^3$ for the solid material was assumed (Craig 1992).

$$[13] \quad (5 \text{ m} \times 19 \text{ m} \times 0.6 \text{ m}) \times 0.6 \times \frac{2.65 \times 10^3 \text{ kg}}{\text{m}^3} = 90,630 \text{ kg / filter}$$

Using this value for the amount of limestone in each rock filter, the expected adsorption capacity of the limestone based on 0.68 g P /kg substrate can then be calculated for the two filters as ...

$$[14] \quad 2 \text{ filters} \times 90,630 \frac{\text{kg}}{\text{filter}} \times \frac{0.68 \text{ g P}}{\text{kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 123 \text{ kg}$$

This capacity can be compared to the average phosphorus inflow for the May, June and July profiles:

$$[15] \quad \frac{1}{3} \left[8.3 \frac{\text{g}}{\text{m}^3} \times 18 \frac{\text{m}^3}{\text{day}} + 8.5 \frac{\text{g}}{\text{m}^3} \times 4 \frac{\text{m}^3}{\text{day}} + 9.8 \frac{\text{g}}{\text{m}^3} \times 3.4 \frac{\text{m}^3}{\text{day}} \right] \times \frac{365 \text{ days}}{\text{year}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 26.4 \frac{\text{kg}}{\text{year}}$$

These calculations suggest the limestone should have the capacity to adsorb all the phosphorus in the wastewater for about:

$$[16] \quad \frac{123 \text{ kg}}{26.4 \frac{\text{kg}}{\text{year}}} = 4.7 \text{ years}$$

Approximately 5 years could be a reasonable design life and so on paper limestone appears to have enormous potential for cheaply and effectively removing phosphorus. However, in fact the phosphorus-removing performance of the filters has been poor while the November and December results seem to suggest that the adsorptive capacity may already be saturated.

One possible reason for the low performance of the Moeraki filters (as compared to predictions by the Langmuir model) is that the Langmuir model may not be appropriate for use with limestone (and hence the expected lifetime calculated may be unrealistic). The Langmuir model was developed to describe the adsorption of gases, and is based on the assumption that the binding energy remains constant up until saturation (Sakadevan and Bavor 1998). Results from adsorption studies by Johansson (1999) however suggest that phosphorus adsorption by limestone may be highly dependant on the phosphorus concentration. His experiments showed that the behavior of limestone was radically different to any other material, and while the limestone absorbed only 30 % of the P after equilibration at an initial concentration of 10 g/m³, it absorbed about 80 % of the P at an initial concentration of 25 g/m³. This suggest that there may

be a number of energetically different sites for sorption on limestone, and that more sites become available for sorption as the phosphorus concentration increases (Mann and Bavor 1993). Therefore, the maximum capacity of limestone for absorbing phosphorus may vary with each different initial concentration, behavior that does not seem to be consistent with the Langmuir model theory.

Conclusions

The major aim of this study was to investigate the ability of limestone rock filters at Moeraki to act as a reactive sorbent for removing phosphorus. However, rather than showing significant phosphorus reduction through the filters, analysis of water samples taken throughout the Moeraki system indicated that most phosphorus reduction occurred in the wetland cell ponds rather than the limestone filters. While the filters removed small amounts of phosphorus over the winter months, this became a net phosphorus release over spring and summer.

An analysis of sludge samples taken from the Moeraki system suggested that the molar ratios of calcium to phosphorus in the sludge were consistent with the precipitation of phosphorus as calcium hydroxyapatite. The hardness concentration at Moeraki was 60 g/m^3 as Ca^{+2} therefore it was concluded that it was possible to obtain significant phosphorus reductions through chemical precipitation in waste stabilisation ponds if calcium levels are high. It should be noted, however, that the precise conditions for chemical precipitation were not identified and that at times precipitation did not occur where precipitation theory would suggest that conditions were most favorable.

It is beyond the scope of this study to prove the long-term consistency of the phosphorus removal in the Moeraki system, or to provide quantitative predictions of performance. However,

this study does suggest that removal is dependent upon the physical conditions that prevail in the wetland cell ponds, rather than the sorptive capacity of the limestone rock filters. It is therefore feasible to suggest that the current performance will be continued long-term, provided that the physical conditions in the ponds remain similar. It should be noted that the performance of the system was poor during summer, which is the most critical season for eutrophication.

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