PHOSLOCK®

Phoslock Water Solutions Limited

ABN 88 099 555 290

A Revolution in Phosphorous Removal

October 2006

Report No. PS-06

Fouad Haghseresht (Ph.D.)
Technical Manager
Phoslock Water Solutions Ltd
ABN: 92 087 115 295
www.phoslock.com.au
116 Rothschild Avenue, Rosebery, NSW, Australia
Telephone +61 2 317 3390 Fax + 61 2 9317 4437

Table of Content

1. Nutrient in aquatic ecosystems

In the mid 1800s a German agricultural chemist, Justus von Liebig, illustrated a strong relationship between the soil nutrient content and the crop yield. Since his findings, it has been demonstrated that aquatic ecosystems are also responsive to the nutrient level. According to Smith [1], one of the most enduring metaphors in marine ecology that the sea is a farm. Smith further states that this analogy dates back to the work of Brandt, who found a correlation between the abundance of planktons in freshwater lakes and the nitrogen levels in the lake waters in the Holstein region of Germany.

Liebig also demonstrated that the yield of plants can be limited by the nutrient that is present in the environment by the least quantity relative to the plant demand for growth. This theory is known as the Liebig law of minimum. Since this discovery, it is now well understood that among the various minerals required for the plant growth, inorganic nitrogen and phosphorous are two key nutrients that limit the growth of plant life in both terrestrial and aquatic ecosystems.

The same way that the limitation of inorganic nitrogen and phosphorous can reduce plant growth in terrestrial and aquatic ecosystems, profound changes can occur in both ecosystems in presence of excess amounts of these two nutrients. A shift in the nutrient enrichment level of aquatic system, known as a change in the trophic state from oligotrophic (poorly nourished) through to eutrophic and hypertrophic (highly excessive levels of nutrients) conditions is associated with many adverse effects, such as increases in biomass of phytoplankton, and suspended algae; decrease in water transparency; lower dissolved oxygen level; increase in the number of toxin producing algae and taste and odour problems in water supply.

During the last several centuries, the rapid rise in anthropogenic activities has accelerated the eutrophication process significantly, making tremendous changes on the geochemical cycles of carbon, nitrogen and phosphorous. One of its major effects has been the dramatic changes in the flux of growth-limiting nutrients from landscape to the receiving water bodies, resulting from activities, such as intensification of agricultural activities over the last few decades. For example, production of N fertilisers released 10 million metric tones of nitrogen in 1950, but may exceed 135 million tonne by 2030 [2] and in Northern Ireland alone; soil P reserves have accumulated at a rate of 1000 kg P km^{-2} $year^{-1}$ over the past 50 years [3]. Another major cause of nutrient flux into natural water bodies is the use of flowing streams as a convenient method wastewater disposal, which is highly influenced by the population density.

The typical percentages of fresh water bodies that are reported to have problems associated with eutrophication (Table 1) shows that the problems is both widespread and significant [4]. As a result, it has become a focal point of research in water management. A number of researchers have also attempted to describe aquatic ecosystems in terms of their limiting nutrient (N and P) supply. One such model (Table 2) is summarised by Smith [5].

Table 1- Percentage of fresh water bodies with eutrophication problems in various regions of the world

Region	Percentage
Europe	53
North America	48
South America	41
South East Asia	54

Table 2- Average characteristics of lakes, streams and coastal marine waters

	Trophic state	TN (mg m^{-3})	TP (mg m^{-3})	Chl a (mg m^{-3})	SD(m)
Lakes	Oligotrophic	<350	<10	<3.5	<4
	Mesotrophic	350–650	10–30	3.5–9	2–4
	Eutrophic	650–1200	30–100	9–25	1–2
	Hypereutrophic	>1200	>100	>25	<1
				Suspended chl a (mg m^{-3})	**Benthic chl a (mg m^{-2})**
Streams	Oligotrophic	<700	<25	<10	<20
	Mesotrophic	700–1500	25–75	10–30	20–70
	Eutrophic	>1500	>75	>30	>70
				chl a (mg m^{-3})	**SD (m)**
Marine	Oligotrophic	<260	<10	<1	>6
	Mesotrophic	260–350	10–30	1–3	3–6
	Eutrophic	350–400	30–40	3–5	1.5–3
	Hypereutrophic	>400	>40	>5	<1.5

1.1 Effect of excess nutrients on the algae community

Eutrophication not only affects the biomass quantity of water bodies, it also affects their phytoplankton community structure as well. One of its most consistent effects is an increase in the frequency and the intensity of cyanobacteria blooms, as shown by a various researchers [6, 7]. As expected, the level of cyanobacterial activity increases with an increase in the biomass of the water body. A demonstration of this observation is provided by Durate *et al*. [7]. The authors show that there is a gradual change from the dominance of green algae in oligotrophic lakes to dominance by cyanobacteria in eutrophic and hypereutrophic lakes [7]. In addition, they illustrated that in contrast with green algae, there is a clear linear relationship between the increase in the biomass of cyanobacteria (mg L^{-1}) and the total biomass (Figure 1).

There is a general consensus that changes in the nutrient loading can severely affect the phytoplankton community structure, shifting towards the nuisance species. Although the exact nature of the observed shift is not understood, it is expected that the changes in the nutrient ratios could be in part responsible [1]. For example Si limitation is shown to shift the community structure from diatoms to other algae taxa [8].

However, the focal point of most of the eutrophication research is the effect of the inorganic nitrogen and phosphorous. To begin with it is these two nutrients that are highly affected by anthropogenic activities. In addition, many researchers have found that the phytoplankton community composition is highly responsive to the changes in the concentration of these nutrients. For example, Tilman and his co-workers showed that cyanobacteria dominate in nitrogen limiting conditions in fresh water bodies [9]. It is also suggested that in relatively low saline water bodies, low N:P ratio may affect the phytoplankton community structure as well [5].

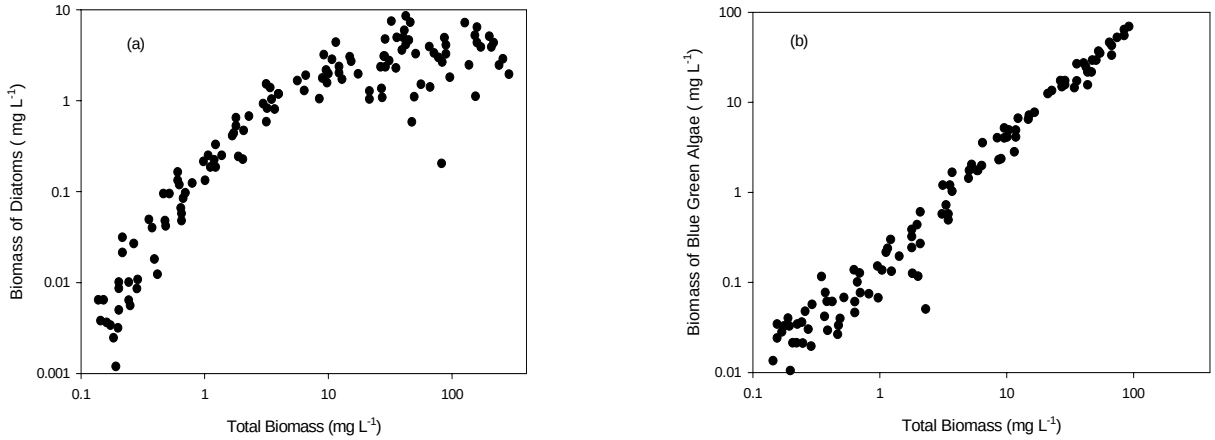

Figure 1- Relationship between the total biomass of the phytoplankton and those of the green algae (a) and cyanobacteria (b)

Due to the significance effect of the N and P on the eutrophication process, there are many models that have been developed to explain the effect of nutrient to the biomass content as well as the phytoplankton community structures in different types of water bodies. According to smith [5], the number of P-loading models is higher than those of N-loading, due to the prevalence of P-limitation in lakes. Other authors, such as Burke *et al.* [10] also agree, and suggest in presence of excess P, cyanobacteria tend to dominate in fresh waters, as they can utilise the atmospheric nitrogen by N fixation. In the case of estuarine waters, however, they suggest that N limitation is more significant. On the other hand, in a review by Hecky and Kilham, some years earlier, it was concluded that the evidence for N-limitation in salt water was fundamentally weaker than in P-limitation in fresh waters [11]. The authors further argue that as the nutrient requirement of the phytoplankton of both fresh and marine is essentially the same and the observed dichotomy in the nutrient requirements is to a degree unexpected.

The significance of the phosphorous in eutrophication has resulted in the development of many remediation plans, based upon phosphorous level management. Not only there is a large body of evidence supporting the significance of phosphorous limitation in many water bodies, it is also accepted that phosphorous control is more achievable than that of nitrogen. Unlike nitrogen, there is no atmospheric source of phosphorous that can is bio-available [12]. In addition, the general equation for photosynthesis (Equation 1) shows that in the organic matter that is created by this process, for every 7 grams of nitrogen 1 gram of phosphorous is needed [13]. This indicates a small reduction is the available phosphorous level can translate into a much larger growth reduction than a similar reduction in the nitrogen level.

$$HPO_4^{2-} + 16NO_3^- + 106CO_2 + 122H_2O + 18H^+ \rightarrow (CH_2O_6)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \quad \textbf{(1)}$$

Due to the significance of phosphorous, both as a limiting nutrient and its ease of control with respect to nitrogen [14], in the next section, a few of key evidence that illustrates its effect on the phytoplankton quantity and composition is summarised.

1.2 Significance of phosphorous in algal growth

The consequence of nutrient load variation on the total algal mass has been known since the 1930s. In his pioneering work, Pearsall [15] discovered an association between the

cyanobacterial presence and the low nitrogen to phosphorous ratios in English lakes. Since his findings, a strong link between the phosphorous level and the phytoplankton mass activity has been demonstrated by a number of other authors and many models attempting to predict the phytoplankton activity of water bodies, based on the phosphorous levels have been developed. For example, in 1974 Dillon and Rigler [16], developed empirical models for the pioneering studies of Sakamato and Ichimura, showing the increase in the chlorophyll a level with increase in the phosphorous level. Similar observations can also be found by other authors. For example, Heiskary and Markus [17], investigating the relationship between nutrient concentration and phytoplankton abundance in Minnesota, USA rivers, also found a strong correlation between the TP levels of a number of sampling sites and the measured chlorophyll a level over a two year period. Plotting Heiskary's and Dillon's data on the same graph (Figure 2), illustrates the strong dependence of chlorophyll-a on the TP level.

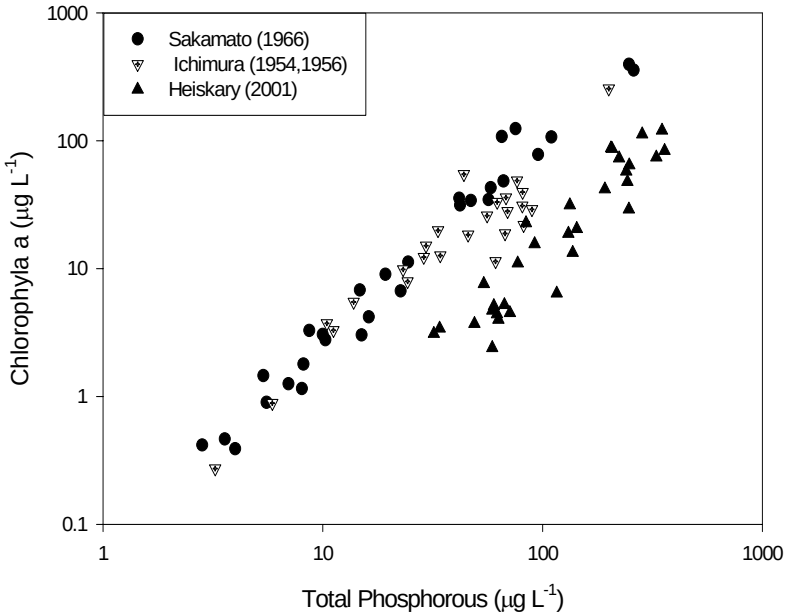

Figure 2- Variation of chlorophyll a level total phosphorous concentration as provided by Dillon and Rigler [16]as well as Heiskary and Markus [17]

The significance of phosphorous in eutrophication control is further illustrated by many phosphorous-based eutrophication classification systems that have been developed worldwide [18]. An example, of the Swedish eutrophication classification system based on the work of Willen [19] is shown in Table 3.

Apart from the effect of phosphorous on the phytoplankton quantity, many authors have demonstrated that the variation of the algal community composition can be described in terms nitrogen to phosphorous mass ratio (N:P). The advocates of this theory believe that in fresh water bodies, the incidence of cyanobacterial blooms is diminished, when the ratio of total inorganic nitrogen to that of phosphorous is increased above the value of 29, as illustrated by Smith in his landmark Science publication in 1983 [20]. On the other hand, many other authors found that this theory does not fit all observations. Examination of the evidence in support as well as against the N:P is reviewed by many authors, such Smith and Bennett [21]. In this review a number of authors attribute their observation of the increases in cyanobacterial blooms to phosphorous availability, rather than to the N:P ratio. For example, Jensen *et al.* [22] in

studying the impact of nutrient load on the algal composition of 32 Danish lakes found that trophic state, measured by the total phosphorous, was a greater predictor of cyanobacterial incidents.

Table 3- Swedish classification system according to the biomass of the planktic algae and phosphorous level

Class	Designation	Biomass ($mm^3 L^{-1}$)		Tropic State	P range ($\mu g L^{-1}$)
		May–October	August		
1a	Particulary small biomass	≤0.1	≤0.1	Ultraoligotrophy	≤6
1b	Very small biomass	0.1–0.5	0.1–0.5	Oligotrophy	6–12.5
2	Small biomass	0.5–1.5	0.5–2	Mesotrophy	12.5–25
3	Moderately large biomass	1.5–2.5	2–4	Eutrophy I	25–50
4	Large biomass	2.5–5	4–8	Eutrophy II	50–100
5	Very large biomass	>5	>8	Hypereutrophy	>100

There are also numerous scientific publications that provide ample evidence of laboratory experimental studies as well as filed data that supports the increase in cyanobacteria with increase in the phosphorous load of water bodies. An example of field evidence is provided by Schindler in as early as 1977 [23], who performed whole lake experiments to show the effects of N:P ratios on the algae community composition. In this work, Schindler investigated the effects of nitrogen and phosphorous limitations by designing whole lake experiments, where various amounts of nitrogen and phosphorous fertilizers were added. He found that lakes that were enriched with nitrogen and phosphorous at ratios above the phytoplankton demands, developed chlorophyte species, while lakes that were enriched with lower ratios developed cyanobacterial blooms. Schindler further explains that lakes that fertilised with excess nitrogen were dominated by the green alga and Scenedesmus and other algae, incapable of N-fixation. On the other hand, lakes that were fertilised with low N:P ratio, were dominated by nitrogen fixing blue green algae.

These trends were also reported in later years by Smith [20], whose work also showed that fraction of cyanobacteria increased at low N:P ratio. His work was based on the results of 17 north temperate lakes. Smith showed that when TN:TP > 29, few proportions of blue-green algae is observed. He then suggested that practical significance of his findings is that N: P ratios of many lakes can be achieved by sewage diversions, phosphorous removal from the waste water or nutrient removal by precipitation within the lakes themselves.

In many instances, the phosphorous levels of water bodies have been used as a predictor of cyanobacterial blooms. For example, Trimbee and Prepas [24] were able to draw quantitative relationship between total phosphorous and the relative biomass of blue-green algae (BG index calculated using Equation 2), using the data from Smith's 1986 article [25]. Figure 3, shows the experimental data together with their model, calculated using Equation 3. The authors found that TP accounted for a greater degree of variance than the TN or TN:TP.

$$BGIndex = \ln\left(\frac{\%BG}{100 - \%BG}\right) \quad \textbf{(2)}$$

$$BGIndex = -5.00 + 2.62 \log TP \quad \textbf{(3)}$$

Where
%BG is the precent of total phytoplankton mass, made up of blue green algae.

The increase in the amount of blue green algae with the total phosphate level is also illustrated more recently by other authors, such as Heiskary and Markus [17] as well. These authors showed a predictable shift in the algae community structure with increase in total phosphorous. Examination of their data shows that cyanobacteria domination increases with increases in the total phosphorous level (Figure 4).

An example of laboratory scale study providing further support to the above-mentioned authors is given by Bulgakov and Levich [26], who investigated the effect of phosphorus amount on the algae community composition of a sample taken from a fish pond. This was achieved through a number of laboratory experiments by adding varying amounts of inorganic nitrogen and phosphorous as NH_4NO_3 and $Ca(H_2PO_4)_2$, respectively. With the initial phytoplankton community of all samples being the same, the flasks were placed in such a way that the pond as well as all samples was subjected to similar lighting and temperature.

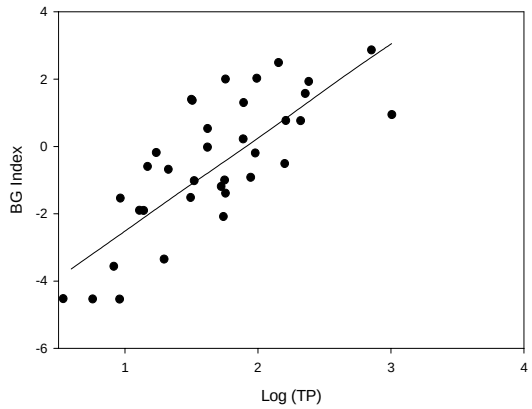

Figure 3- Variation of BG Index with TP

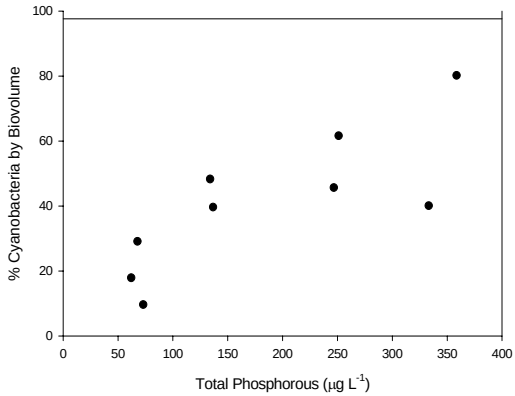

Figure 4- Variation of cyanobacteria with total phosphorous

Figures 5a–d show the domination of the different algae species in different N:P ratio ranges. It can be seen that at N:P>5 the algae community is essentially dominated by chlorophyta, with the maximum reaching at N:P>20. Among the chlorophytes it was found that the mass of the predominant species in their sample, Scenedsmus quadricauda, reached its maximum at N:P=20 and then decreased. However, the biomass of other chlorococcales were increased at N:P range of 50–100. In contrast, it was found that the greatest biomasses of Bcillariophyta and Cyanophyta were achieved at the lower N:P ratios of 2–5. On the other hand, Euglendophytoa decreased at N:P=20 and increased between the N:P ratios of 50–100.

The mechanism to explain the cyanobacterial dominance in low N:P ratios is found in the pioneering work of Schindler [23] and it was further supported and advocated by Smith [20]. This explanation links the prevalence of cyanobacteria in waters with low N:P ratios to the excellent ability of these organisms in competing for nitrogen, when it is scarce. In other words, when there is an excess of phosphorous and nitrogen is limited, cyanobacteria are expected to dominate, as they can use the P surplus in the water together with the atmospheric N_2 to dominate the non-N-fixing organism.

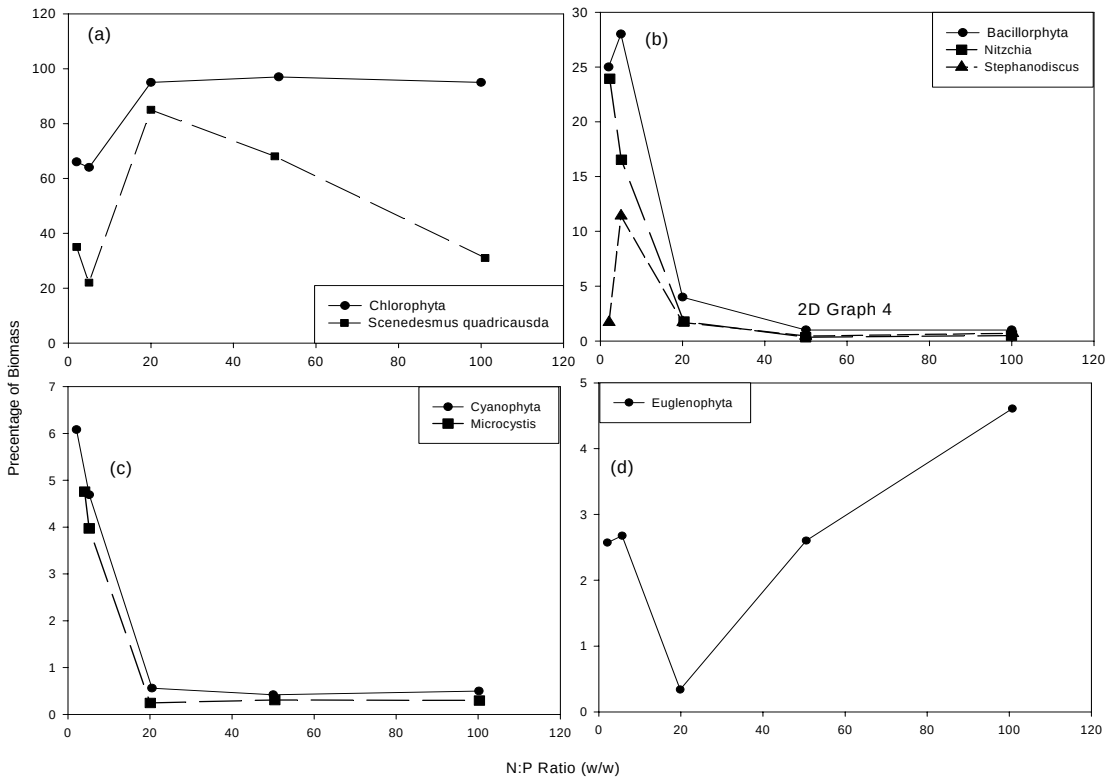

Figure 5- Effect of various N:P on the final biomass composition

As stated earlier, nuisance algae in water bodies leads to undesirable water quality parameters. In a study by Havens [27], where the effect of historical nutrient load changes in Lake Okeechobee in Florida was investigates, it was found that the increase in TP leads to a decrease in Secchi disk (SD) transparency (Figure 6) . This indicates that poor irradiance have negative impacts on the ecological success of N-fixing cyanobacteria.

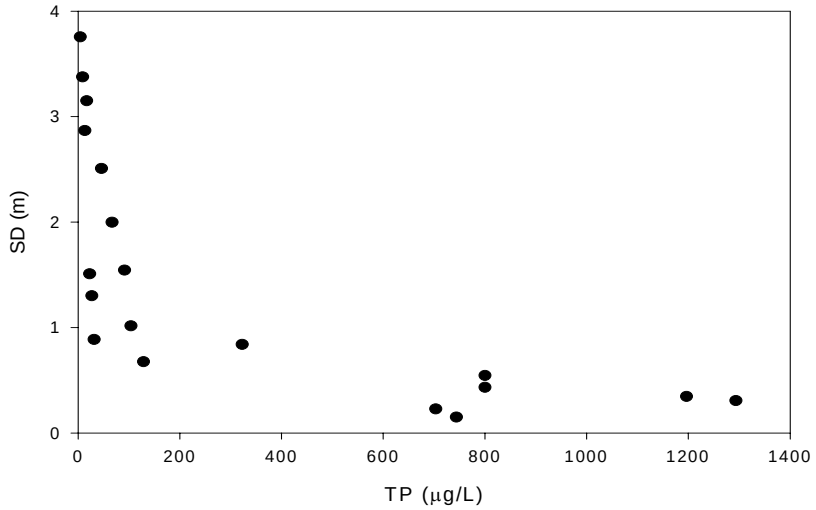

Figure 6- Effect of TP on the Secchi disc transparency

In summary, there is an abundance of evidence supporting the significance of phosphorous control in eutrophication management. One hand, the fundamental photosynthesis equation alone shows that for evert 7 grams of nitrogen; only one gram of phosphorous is required, indicating that a small degree of phosphorous reduction can achieve a much greater degree of

growth reduction of phytoplankton quantity than a reduction of a similar magnitude in the nitrogen level. This fact, together with the plenitude of the gaseous nitrogen availability to N-fixing organisms, makes phosphorous reductions strategies a far more effective alternative in eutrophication management. In addition, there numerous laboratory and field studies demonstrating the effectiveness of phosphorous reduction in managing phytoplankton quantity and inhibition of cyanobacterial growth.

2. Phoslock®: A long lasting solution for Phosphorus reduction

In a recently published review, Douglas *et al.* [28] report that the effectiveness of rare earth elements, especially lanthanum, in removing various forms of phosphate from water bodies has demonstrated since the late 1960s. The authors further explain that the use of lanthanum was demonstrated to be highly efficient with a molar ratio of 1:1 (Equation 4), compared with sodium aluminate ($NaAlO_2$) which is relatively inefficient with a molar ratio of ca 7: 1 to achieve a similar phosphorous uptake. In addition, early researchers showed that the use of lanthanum in secondary treatment of sewage effluent is superior to more conventional iron and aluminium.

$$La^{3+} + PO_4^{3-} \rightarrow LaPO_4 \qquad \textbf{(4)}$$

However, it has also been found that lanthanum is toxic depending on its concentration and application rate [28]. The potential toxicity of lanthanum ions was overcome in the mid 1990s by incorporating it into the structure of minerals of high exchange capacity minerals, such as bentonite. This lanthanum modified bentonite, known as Phoslock®, has been shown that in presence of oxyanions, such orthophosphate forms a stable mineral known as rhabdphane ($LaPO_4.nH_2O$). The stability of rare earth-anion complexes is noted by their low solubility products [29]. Solubility product of lanthanum phosphate salts ranges from -25.8 to -24.5 in fresh water and -28.08 in seawater. As the rare earth element is locked into the clay structure, it can either react with the phosphate anion in the water body or stay within the clay structure under a wide range of physiochemical conditions.

The ability of the incorporation of the lanthanum ions into bentonite is obtained by taking advantage of the cation exchange capacity of clay minerals. This exchange capacity is a result of a charge imbalance on the surface of the clay sheets, which is balanced by surface adsorbed cations, which are exchangeable in aqueous solutions. In preparation of Phoslock®, the lanthanum ions are exchanged with these surface adsorbed exchangeable cations (Figure 7).

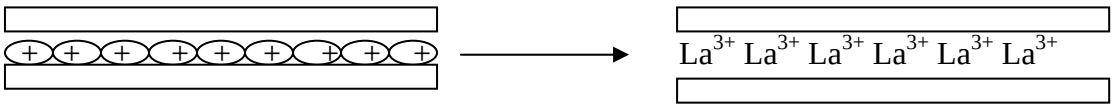

Figure 7- Simplified schematic of lanthanum-modified preparation

2.1 Phoslock® manufacturing process

In manufacturing Phoslock®, Phoslock Water Solutions Ltd (PWS) considers that strict adherence to the following standards to be highly essential.

The product must be able to remove the maximum possible amount of the filterable reactive phosphorous (FRP) in the shortest time.

1. The environmental toxicity — resulting from the application of Phoslock®— must be negligible. Possible sources of toxicity include any chemical that is introduced during the manufacturing process or inherent ones leached out of the bentonite or the lanthanum chloride (such as loosely bound lanthanum ions, trace metals and radionuclides).
2. The dispersed particles should settle within reasonable time periods after the application and become part of the natural sediment.

In order to adhere to these essential principles vigilantly, by enforcing a strict quality control regime, PWS ensures that the chemical properties of its raw materials and the finished product meet the performance requirement for Phoslock®, as well as regulatory standards, such as the sediment quality Guidelines by The Australian and New Zealand Environment Conservation Council (ANZECC).

As the lanthanum exchange process is carried out in solution, Phoslock® is initially prepared as slurry. In fact, until 2004, it was the only available form of Phoslock®. However, a number of disadvantages were associated with the production and the application of Phoslock® slurry. These included transportation of excess water and the presence of excess residual lanthanum ions from the manufacturing process. These issues were resolved with the advent of the granular form of Phoslock®. The key basic physiochemical properties of this Phoslock® form are summarized in Table 4. By manufacturing granular Phoslock®, the transportation and the application of Phoslock® have become significantly more economical and convenient. In addition, the low dust level and the acceptable degree of packaging stability of the Phoslock® granules make the transportation and the application of the product convenient as well as minimizing any possible health risk associated with dust levels to the personnel involved in these processes.

Table 4- Summary of properties of Phoslock® granules

Physical/Chemical Property	Description
Phoslock® Content	>90%
Dispersing agent	Precipitated silica 5%
Water content	5%
Appearance	Brown free flowing granules
Packaging stability	No deterioration of the packaging or physical appearance of the product
Size of the granules	2–4 mm × 1 –3 mm
Bulk density	910–960 kg m^{-3}
pH	6.8–7.5
Dust content	<1% weight 50 μm

2.2 Application of Phoslock®

Granular Phoslock® is required to be dispersed into fine particles, with a particle-size distribution that is similar to that of the parent slurry (Figure 8). Such particle size distribution allows the maximum phosphate uptake, without any adverse effects on the settling rate of

Phoslock. In fact, laboratory trials have shown that 90 % of the resulting turbidity is reduced with hours of the application (Figure 9).

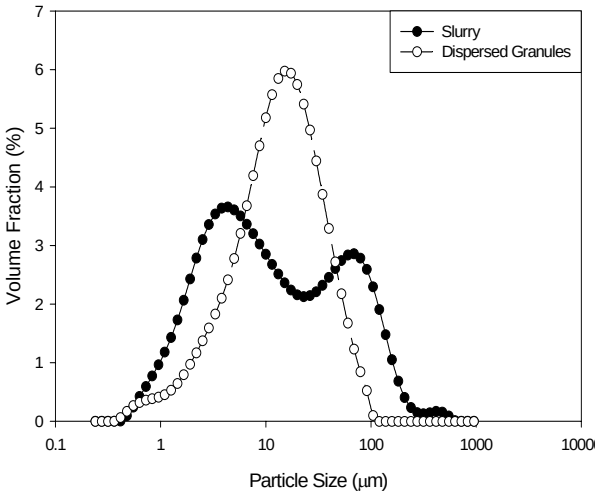

Figure 8- Particle size distributions of the parent slurry and the dispersed granule

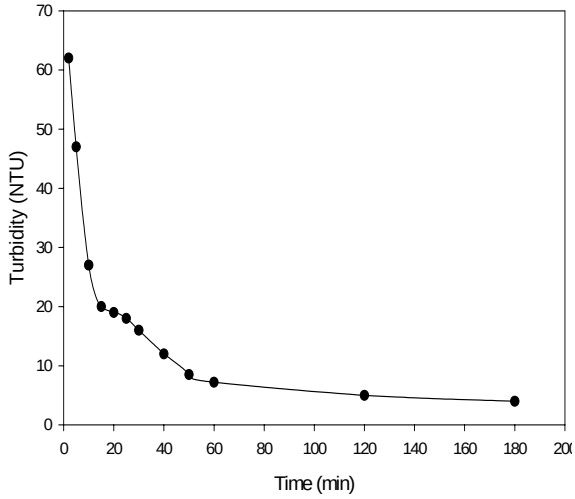

Figure 9- Decline of turbidity after the initial Phoslock® addition

In field applications, granular Phoslock® is mixed with the in situ water, and applied either from the shoreline or a boat, depending on the size of the water body (Figure 10a and b), using specially designed applicators. As a result of the inclusion of a dispersing agent, together with appropriate amount of mixing, supplied by the applicator, the granular Phoslock® is then dispersed into fine particles.

Figure 10a- Application of Phoslock® from shoreline

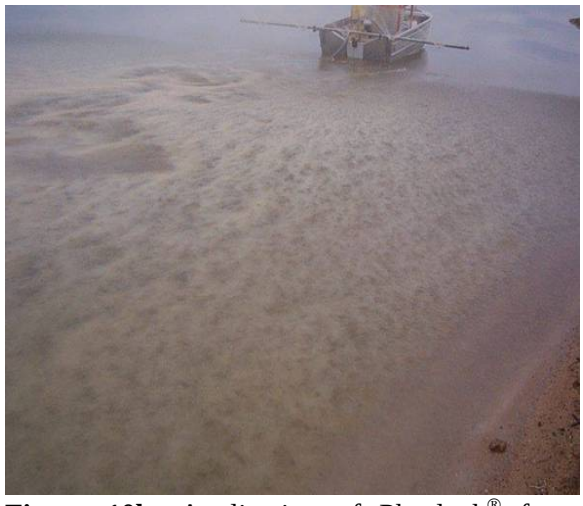

Figure 10b- Application of Phoslock® from boat

2.3 Factors affecting the performance of Phoslock®

To assess the performance of Phoslock® under various environmental conditions, numerous laboratory investigations have been carried out by CSIRO during its early developmental stages [30] as well as by PWS.

Among the various physiochemical and biological parameters, pH and presence of anaerobic conditions are understood to be key factors affecting the uptake and the stability of the adsorbed phosphorus. In addition, the presence of the native bacteria population can also affect the nature of the adsorbed phosphorus as well. In fact, it is well understood that both iron and aluminium-based adsorbents are highly sensitive to solution pH and redox potential. In contrast to other chemical methods, the performance of Phoslock® is shown to be robust under a wide range of pH and anaerobic conditions and presence bacteria, as demonstrated below.

2.3.1 Equilibrium uptake capacity of Phoslock®: Effects of pH

As in the case of most adsorption in the aqueous phase, any changes in the solution chemistry would lead to other changes in other equilibria in the system, including changes in the lanthanum and phosphate species. For example, with an increase in pH not only the concentration of the different orthophosphate species change, lanthanum ions, the active sites of Phoslock®, are hydroxylated in three steps (Eq. 5–7), with the $La(OH)_3$ being the only insoluble species, formed at pH=7.58 [31].

$$La^{3+} + OH^- \rightarrow La(OH)^{2+} \quad \textbf{(5)}$$

$$La(OH)^{2+} + OH^- \rightarrow La(OH)_2^+ \quad \textbf{(6)}$$

$$La(OH)_2^+ + OH^- \rightarrow La(OH)_3 \quad \textbf{(7)}$$

The effect of pH on the maximum adsorption capacity of Phoslock® was investigated by obtaining its adsorption isotherms at pH 5–9. Each isotherm was obtained by adding different amount of Phoslock® to a number of flasks, containing 200 mL of 10 mg/L of FRP solution, with a given pH. All flasks were then placed in water shaking batch, set at 25 °C for 5 hrs to reach equilibrium.

All adsorption isotherms were then fitted by the Langmuir equation by plotting C_e/Q vs. C_e (Equation 8) to obtain the corresponding equilibrium adsorption capacity, Q, and the Langmuir constant, b, a measure of the affinity of the solute for the adsorbent (Table 5). The determined Langmuir parameters were then used to plot the calculated isotherms. These isotherms, tother with the corresponding experimental ones are shown in Figure 11. The correlation coefficient values, R^2, shown in Table 5, together with the calculated isotherms (Figure 11), demonstrated that the Langmuir Equation fitted the data well. Figure 11 also demonstrates that the equilibrium adsorption capacities of clay changed very little within the pH range of 5–7. However, it decreased in solutions with higher pH values. In addition, in most cases the equilibrium adsorption capacity of the clay was achieved when the corresponding solution equilibrium concentration was approximately 1 mg P/L.

The calculated parameters (Table 5) showed that the maximum adsorption capacity, Q, decreased slightly, when pH=7. However, when the solution pH was increased to higher pH values, further decreases in Q were observed, with a maximum reduction of 29 % occurring when pH=9.

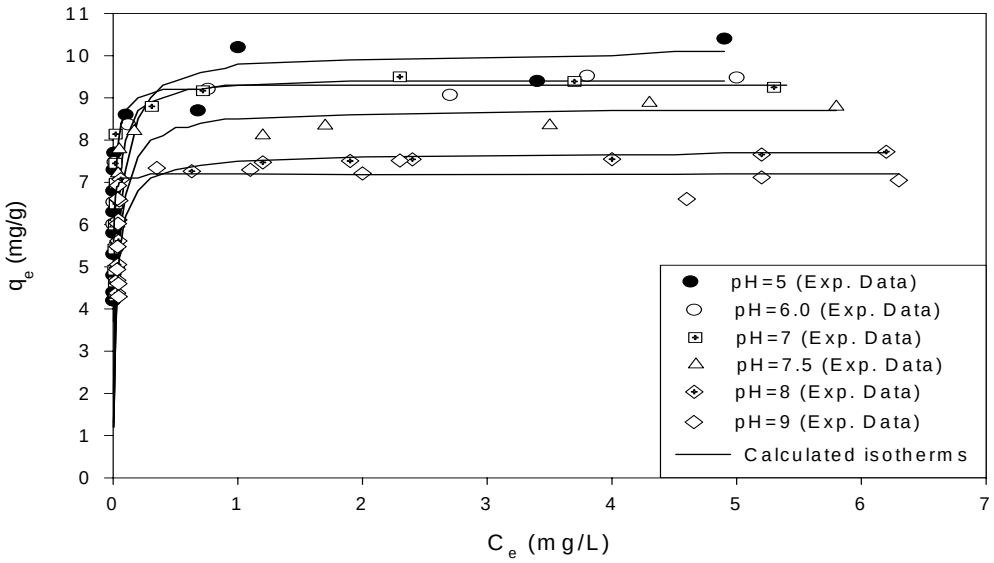

Figure 11- Phosphate adsorption isotherms for the modified clay with pH 5–9

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \qquad \textbf{(8)}$$

Where
q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium solution concentration (mg L^{-1}) and b is the Langmuir constant, which is energy constant, describing the adsorptivity of the solute onto the adsorbent.

Solution pH	Modified Langmuir parameters		
	Q (mg/g)	b (L/mg)	R^2
5.00	10.14	26	0.9963
6.0 (a)	10.19	19	0.994
6.0 (b)	9.47	53	0.9995
7.00	9.34	134	0.9999
7.50	8.76	33	0.9992
8.00	7.69	40.6	0.9999
9.00	7.19	696	0.9994

Table 5- Parameters of the modified Langmuir equation for the isotherms at various pH values (6.0(a) and 60(b) are duplicates)

2.3.2 Equilibrium uptake capacity of Phoslock®: Effects of anaerobic conditions

Douglas and his co-workers [32] also investigated the FRP uptake of Phoslock® under anaerobic conditions by combining 0.1 g of Phoslock® with a 1.0 g of bottom sediment from Swan River in 50 mL centrifuge tubes. After autoclaving and cooling of the samples, 30 mL of autoclaved water (0, 5 and 30 ppt salinity, prepared by dilution with sea water) was then added to each tube. Samples were then places in an anaerobic chamber for 96 hrs.

Table 6 shows the resulting FRP concentrations of the water samples in absence of Phoslock®. By comparing these FRP concentrations with the residual concentrations in Figure 12, it can be

seen that the addition of Phoslock® assisted in reducing the FRP concentrations of all samples significantly. Moreover, Figure 12 shows that the FRP uptake of Phoslock® under aerobic conditions is very close to the corresponding values under aerobic conditions for all salinities except for when the salinity was 30 ppt. This moderately higher residual phosphate concentration was attributed by the authors to the colloidal matter that was below 0.45 µm, brought about as a result of the coagulation of organic matter at high salinities. The phosphate that would have been adsorbed onto the colloids could easily be desorbed during the analytical procedure of FRP determinations.

Table 6- FRP release of the sediment samples with no Phoslock®

salinity	FRP Concentration (µg/L)
0	114
5	108
30	136

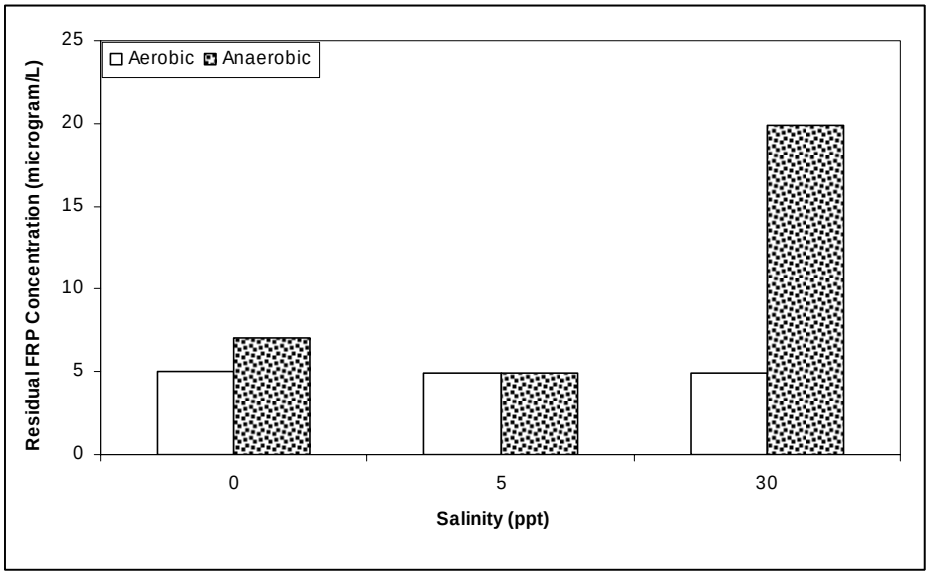

Figure 12- Residual FRP remaining after 96 hrs of Phoslock® exposure to phosphate ions

In another work by PWS's Technical Division, the performance of Phoslock® under anaerobic conditions was examined in large scale laboratory trials. In this work, two Perspex reactors (1m high with I.D of 0.16 m) were filled with water from a local lake. With both reactors surrounded by three day light spectrum light tubes (connected to a timer to simulate the diurnal lighting cycle) and an IKA overhead stirrer, one of them was used or the Phoslock® treatment and the other one was left without any treatment.

The water samples in both reactors were subjected to the simulated diurnal lighting cycle for several days until the FRP content of both reactors was utilised by their algal population, resulting in a significant increase in algal growth. To one reactor, Phoslock® then applied at a rate 250 g per sqm and the lights, surrounding the reactors, were turned off to encourage anaerobic conditions in the reactors. The first Phoslock® application led to a drastic decrease of the FRP concentration of the treated column to 0.1 mg/L. Its FRP concentration was then monitored for a few days, before a second Phoslock® application to reduce the remaining FRP to close to the detection level.

The effect of anaerobic conditions on the dissolved oxygen concentration (DO), redox potential (E_h) and the FRP concentrations (monitored at the water surface and 50 cm below the surface) of both the treated and untreated reactors are shown in figures 13a–c. Examination of these figures reveal the followings:

- The DO level of both reactors remained below 0.25 mg/L, indicating anaerobic conditions.
- The redox potential of both reactors was well below -50 mV for most of the trial, indicating the presence of highly reducing conditions.
- Regardless of the extreme anaerobic and reducing conditions, the FRP of the treated column remained steady after both Phoslock® applications, while the FRP of the untreated column increased with time.

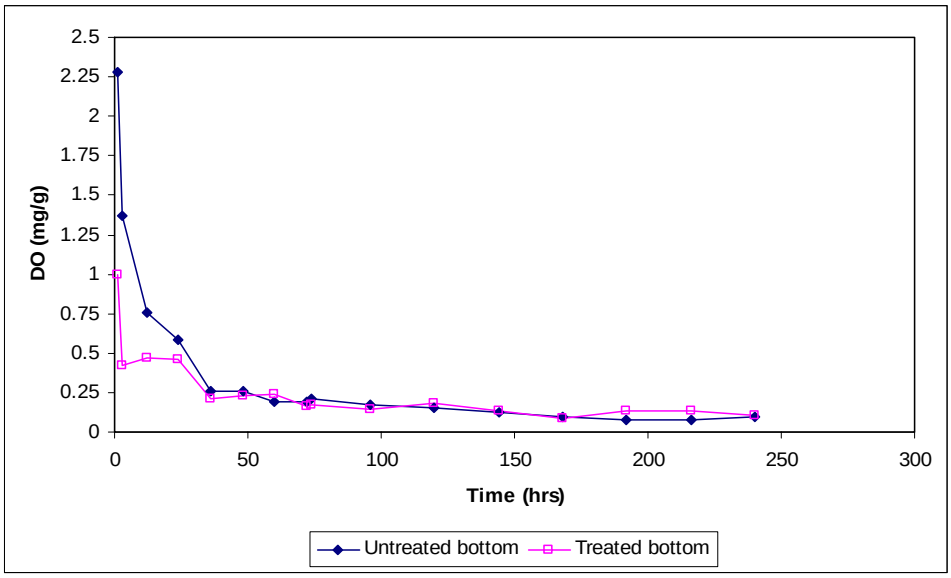

Figure 13a- Variation of the dissolved oxygen concentration throughout the trial

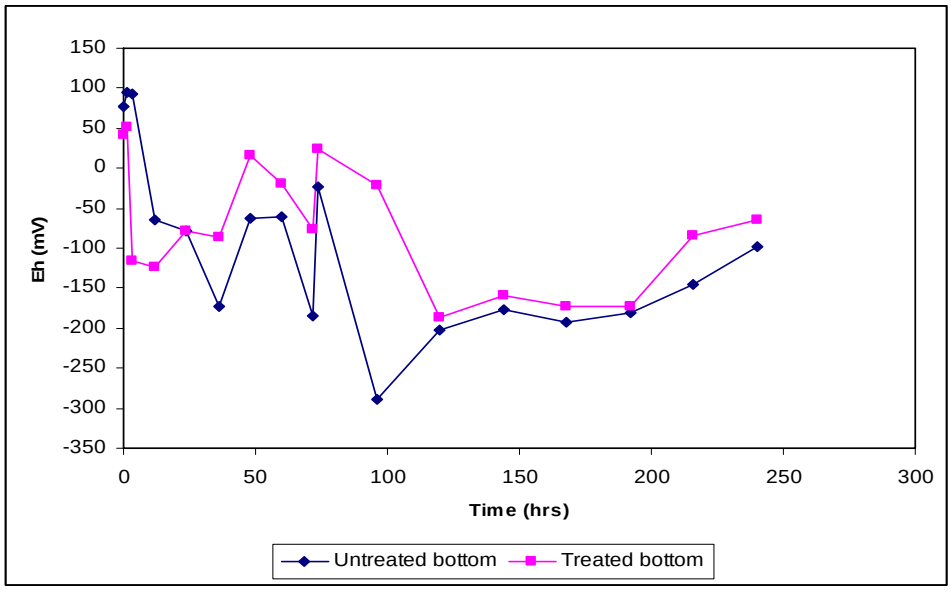

Figure 13b- Variation of the redox potential, E_h, throughout the trial

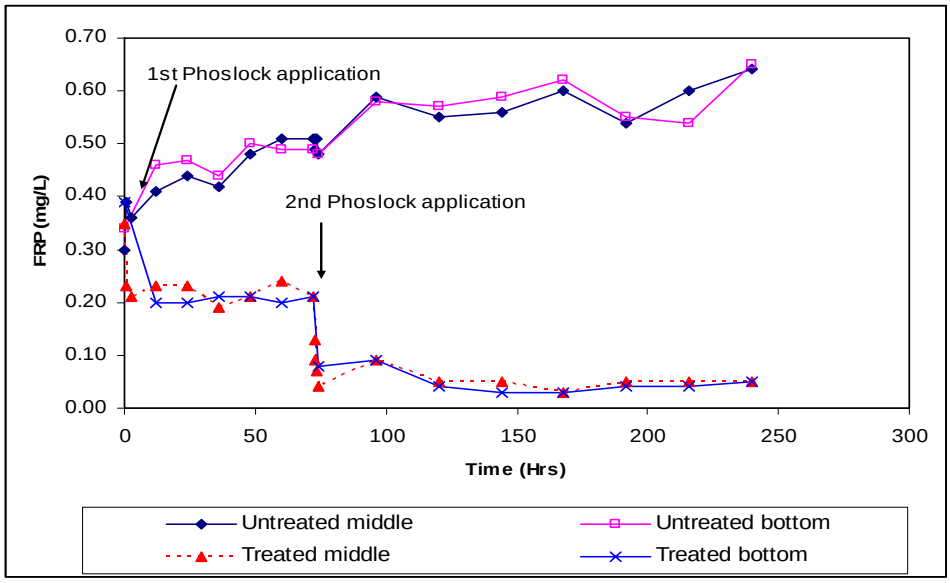

Figure 13b- Variation of the FRP concentrations after two different Phoslock® applications, throughout the trial

2.3.3 Effect of microbial activity on the performance of Phoslock®

One of the factors that affect the long term stability of Phoslock® is the resistance of the bound phosphate to microbial attack and any possible inhibitory effect of Phoslock® on the growth of micro-organisms. In an earlier study, Douglas *et al.* [32] found that the adsorbed FRP was not solubilised by microbial activity. In an extension to this study, the authors designed a series of other experiments that assessed the robustness of Phoslock® in presence of phosphorous limited facultative anaerobes [33]. The growth of the organisms was measured from the biological oxygen demand (BOD) measurements, obtained over five days.

The bacteria in their work were collected from the bottom sediment of the Swan River and gown anaerobically in the laboratory. The resultant bacteria that were used in the nutrient limitation experiments were then washed with distilled water to remove the excess phosphate and minimise any possible contaminations. During this study, Douglas and co-workers used four different treatments to examine the availability of the phosphate bound to the clay. They were as follows:

A. *Media+ bacteria:* This was to see there was any phosphate carried over into the BOD experiments.
B. *Media+ bacteria + excess KH_2PO_4 (50 ppm):* This was to examine the viability of the organism in presence of excess phosphate.
C. *Media+ bacteria + Phoslock® (dialysed)***:** This was to investigate the availability of the bound phosphate to Phoslock® for microbial growth.
D. *Media+ bacteria + Phoslock® (dialysed)+ excess KH_2PO_4(50 ppm)***:** This was to examine the inhibitory effect of Phoslock® on the growth of the organisms.

BOD measurements in Table 7, illustrate that in absence of phosphorous no growth occurred (treatment A). On the other hand, when excess phosphorous was available, substantial growth

occurred. In presence of Phoslock®, however, very little growth occurred. In fact, the authors report that only in three plates out the total of eight replicates growth was observed. Considering that the process involved washing off the excess FRP, prior to the BOD experiments, there was a higher chance of contamination, in treatment C, where the number of replicates was higher than the other treatments. Finally, the highest degree of growth was observed in treatment D, where there was a great excess of FRP. This experiment shows that Phoslock® did not have any inhibitory effects on bacterial growth. In fact, its high surface area may have provided support for further growth.

Table 7- Results of the BOD experiments to assess the availability of Phoslock® bound phosphorous

Treatment	A (n=2)	B (n=4)	C (n=8)	D (n=3)
BOD (ppm)	0.0±0.0	58±33	8±11	263±196

2.4 Performance of Phoslock®

2.4.1 Laboratory scale evaluation of Phoslock® performance

Performance of Phoslock® in reducing FRP levels was investigated since the early developmental stages of this product. A compilation of the FRP reduction data that were obtained through a diverse number of laboratory trials, conducted by CSIRO [30] and PWS are shown in Table 8. This table shows that in most cases, Phoslock® removed more than 97% of the FRP content of the water samples.

In the case of the wastewater samples, 0.1 gram of Phoslock® was added to 50 mL of the filtered water samples in a Nalgene centrifuge tube. The Nalgene tubes were then placed on a horizontal roller for 24 hrs before removing a sample for the final FRP measurement [30]. In the case of the natural water samples, however, for every 1 mg of FRP in solution, 220–230 mg of Phoslock® granules was added into a beaker, containing 2 L of the test solution. The mixture was then left unstirred fro 24 hrs, before taking a sub-sample for the final FRP measurement.

Table 8- Summary of the small scale laboratory trials

Water Type	FRP Concentration (mg/L)		Fraction Removed (%)
Natural waters:	**Initial**	**Final**	
Reverse osmosis treated Water	1.00	0.005	>99
Golf Course Pond (QLD)	0.65	0.01	98.5
Stanwell Dam (QLD)	0.655	0.048	93
Wastewaters:			
Subjaco STP	1.13	<0.005	>99
Denmark STP	3.49	<0.005	>99
Northam STP	2.41	0.005	>99
Piggery abattoir	5.32	0.008	>99
Cooling tower	0.907	<0.005	>99
Constructed wetland	0.092	<0.005	97
Winery effluent	1.18	0.021	98
Aquaculture	0.087	<0.005	97
Cheese effluent	35.9	0.068	89

2.4.2 Core experiments

Another significant aspect of the performance of Phoslock® is its ability in capping sediment to prevent the re-release of phosphate ions into the water column. In a study that was performed by Douglas *et al.* [32], the authors investigated this by capping sediment core samples that were obtained from the bottom sediment of Swan River. The Phoslock® sample that was used in study was a lanthanum-modified saponite sample. In order to test its ability in sediment capping, the sediment remediation material was added at a rate of 226 g m^{-2} at the surface of the water after the transfer and the equilibration of the core and water samples in the laboratory. At the last stage of the experiment, anoxic conditions were induced by bubbling N_2.

Figure 14 shows that application of Phoslock® led to the reduction of the FRP level to below detection limit, which was sustained for 150 hrs. The robustness of Phoslock® under anoxic conditions is also highlighted during the last stage of the experiment, as there is no significant FRP re-release evident.

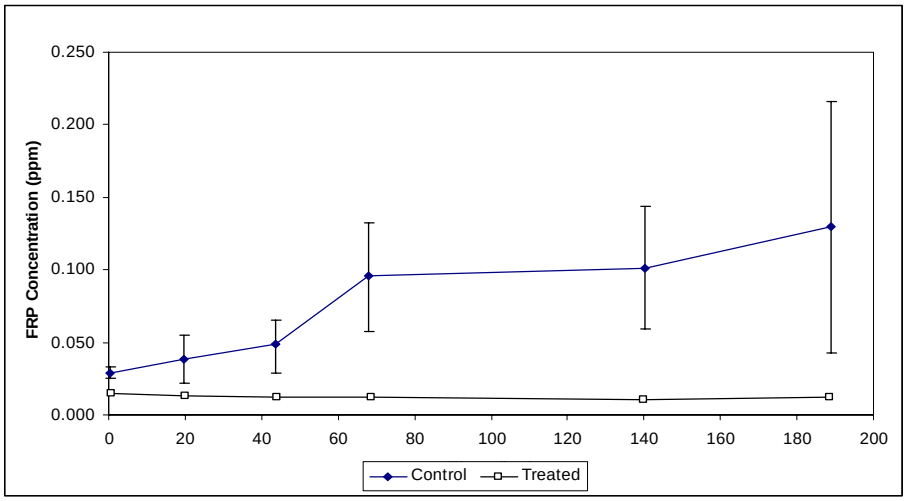

Figure 14- The effects of Phoslock® in inhibiting the re-release of FRP from the sediment

2.4.3 Consequences of Phoslock® application

The effects of Phoslock® application on the water quality was studied in a preliminary large scale laboratory trial, where the variation of a few physiochemical parameters of an estuarine water sample was measured with time. A summary of the initial physiochemical characteristics of the water, determined in the laboratory prior to the addition of Phoslock®, is given in Table 9. Following the initial determinations, Phoslock® was added at the rate 200 g m^{-2}, similar to a typical commercial application rate.

Figures 15 shows the effect of Phoslock® application on the FRP level of the treated sample throughout the trial, while Figure 16 shows the reduction of the total P content of the treated water after one day. It can be seen that the FRP concentration of the treated water was reduced to below 0.01 ppm after the first 24 hrs. In addition, Figure 16 shows an 83% reduction in the total phosphorous level during the same time period.

The effect of the FRP reduction on the biomass content of the water was monitored by measuring the chlorophyll-a level of the untreated and treated water samples throughout the trial

(Figure 17). This Figure shows that the chlorophyll-a level of the treated water increased to approximately 60 µg/L 48 hrs after the application. It then decreased to below detection levels. The observed increase could have been due to the presence of residual P in the biomass and the increase in water clarity and hence an improved light penetration after Phoslock® application. On the other hand, the chlorophyll-a level of the untreated water sample increased to well above 125 µg L^{-1} within the same period. It then decreased before another further increase to a value of 75µg L^{-1} by the end of the trial.

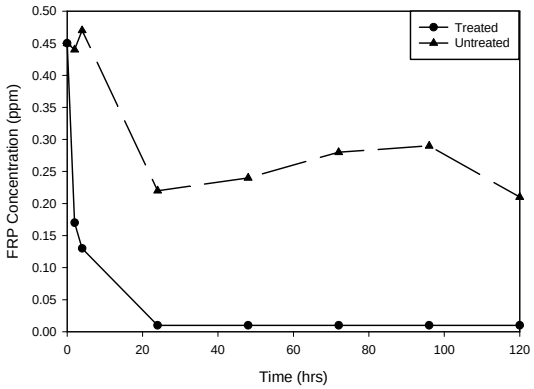

Figure 15. Variation of the FRP in untreated and treated water samples

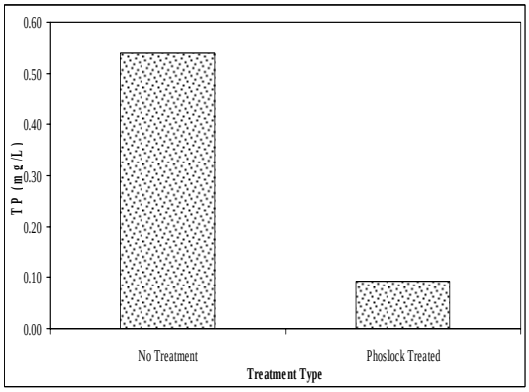

Figure 16. TP concentrations of the untreated and treated water samples

Table 9- Summary of the physiochemical characteristics of the water sample

Chemical Characteristics	Value
pH	7.50
Conductivity (mS/cm)	27.6
Salinity (g L^{-1})	12.6
Total organic carbon (ppm)	8.6

Comparison of the variation of chlorophyll-a and pH with time in figures 17 and 18 shows that as the phytoplankton activity of the treated water increased in the first 48 hrs, its pH also increased as well. However, with a drop in the phytoplankton activity, the pH also dropped to near neutral values rapidly. A similar trend is also observed in the untreated sample, except that the pH remained high, as the phytoplankton activity of untreated water also remained high as well.

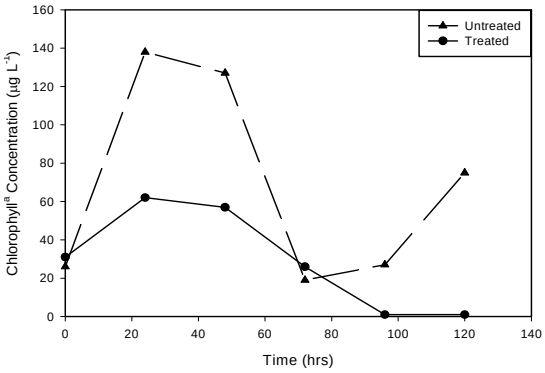

Figure 17- Variation of chlorophyll-a levels in untreated and treated reactors

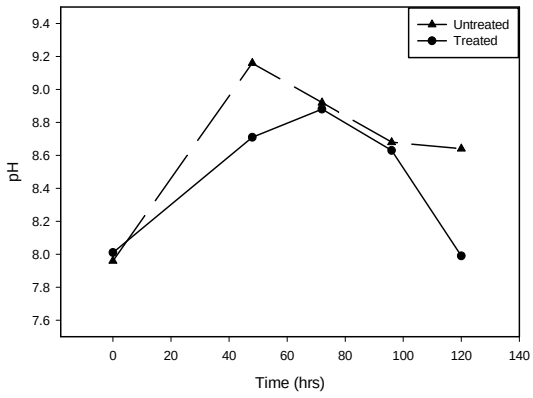

Figure 18- Variation of pH in the untreated and treated reactors

The effect of lowering the biomass level was apparent in the comparison of the visual appearances of the untreated and treated water samples. This was done by comparing the absorbance spectra of the filtered water samples, five days after the application of Phoslock® (Figure 19). This figure shows that throughout the spectral range, the absorbance of the untreated water is approximately 0.05 units higher than the treated sample. In addition, the absorbance of the treated water fell to about zero in between the 450–900 nm range, indicating a distinct improvement in the transparency of the treated water.

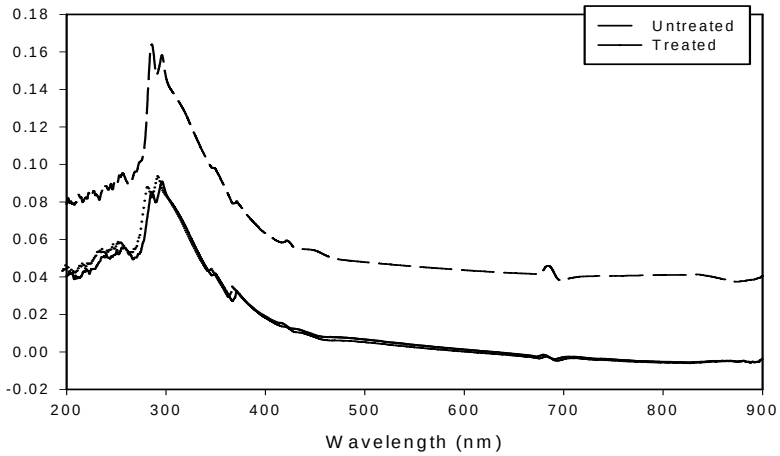

Figure 19- The absorbance spectra of the treated and the untreated water samples

2.4.4 Effect of Phoslock® application on fish growth

The effect of Phoslock application and its consequence on the fish life was examined in aqua trials by Douglas *et al.* [30]. In this work, the authors constructed eight aquaria (four controls & four experimental). Each aquarium, containing 40 L of water and 2.5 kg of washed sand. All aquaria were allowed to reach equilibrium for 5 days, before the addition of the common gold fish (Carassius Autautus). A further 5 days period was then allowed for further equilibration, before the start of the experiments. All fish were fed per every second day (0.01g per fish).

Variation of the FRP concentrations of the treated and control tanks are shown in Figure 20. It shows that both the control and the treated aquaria had similar FRP concentrations. However, after the addition of Phoslock®, the mean FRP concentrations of the treated ones decrease significantly. On the other hand the mean FRP concentration of the control tanks increase throughout the trial. In addition, the authors explain that in contrast to natural and wastewaters, Figure 20 shows that the FRP reductions to below detection limit was not achieved in the experimental aquaria. The authors attribute this observation to the dynamic nature of aquaria. Due to ingestion of food and generation of excrement, there is a continual turn over of nutrients, such as FRP. Nevertheless, Figure 19 shows that in comparison with the trend in the FRP concentrations of the experimental aquaria, the upward trend in the FRP concentration of the control aquaria is very significant.

Douglas and co-workers also found a strong relationship between the extent of FRP removal and fish growth. The effect of FRP removal, expressed as the difference between the mean control and treated FRP concentrations ($Control_{(FRP)}$-$Treated_{(FRP)}$), illustrates that reduction of FRP led to positive growth rates. Clearly, if the pattern that is shown in Figure 21 can be replicated in commercial aquaculture, this would represent a substantial increase in production efficiency.

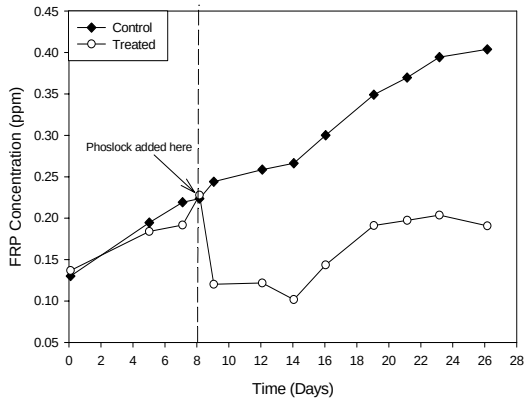

Figure 20- Variation of the FRP in aquaria trial

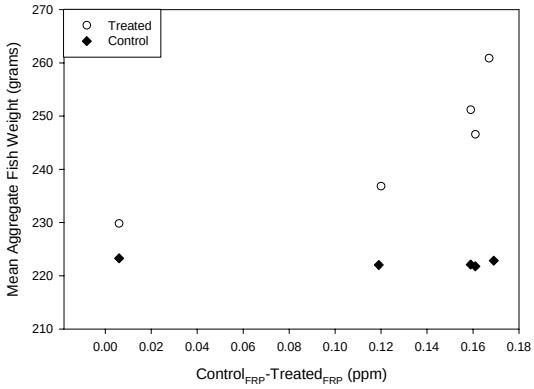

Figure 21- Variation of fish weight with the mean difference in FRP concentrations of the treated and the control aquaria

References

1. Smith, V.H., *Cultural Eutrophication of Inland, Estuarine and Coastal Waters*, in *Successes, Limitations, and Frontiers in Ecosystem Science*, M.L. Pace and P.M. Groffman, Editors. 1998, Springer-Verleg New York Inc.: New York. p. 7-49.
2. Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman, *Human alteration of the global nitrogen cycle: Sources and consequences.* Ecological Applications, (1997). **7**(3): 737-750.
3. Foy, R.H., R.V. Smith, C. Jordan, and S.D. Lennox, *Upward Trend in Soluble Phosphorus Loadings to Lough-Neagh Despite Phosphorus Reduction at Sewage-Treatment Works.* Water Research, (1995). **29**(4): 1051-1063.
4. Farmer, A.M., *Phospahe Solution: A Global View of the Problem*, in *Phosphorous in Environmental Technology:Principles and Applications*, E. Valsami-Jones, Editor. 2004, IWA. p. 174-191.
5. Smith, V.H., G.D. Tilman, and J.C. Nekola, *Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems.* Environmental Pollution, (1999). **100**(1-3): 179-196.
6. Pick, F.R. and D.R.S. Lean, *The role of macronutrients (carbon, nitrogen, phosphorus) in controlling cyanobacterial dominance in temperate lakes.* New Zealand Journal of Marine and Freshwater Research, (1987). **21**(3): 425-34.
7. Duarte, C.M. and D.E. Canfield, *Patterns in Phytoplankton Community Structure in Florida Lakes.* Limnology and Oceanography, (1992). **37**(1): 155-161.
8. Officer, C.B. and J.H. Ryther, *The Possible Importance of Silicon in Marine Eutrophication.* Marine Ecology-Progress Series, (1980). **3**(1): 83-91.
9. Tilman, D., S.S. Kilham, and P. Kilham, *Phytoplankton Community Ecology - the Role of Limiting Nutrients.* Annual Review of Ecology and Systematics, (1982). **13**: 349-372.
10. Burke, S., L. Heathwaite, and N. Rreedy, *Transfer of Phosphorous to Surface Waters; Eutrophication*, in *Phosphorous in Environmental Technology:Principles and Applications*, E. Valsami-Jones, Editor. 2004, IWA. p. 120-146.
11. Hecky, R.E. and P. Kilham, *Nutrient Limitation of Phytoplankton in Fresh-Water and Marine Environments - a Review of Recent-Evidence on the Effects of Enrichment.* Limnology and Oceanography, (1988). **33**(4): 796-822.

12. Cook, D.G., E.B. Welch, S.A. Peterson, and P.R. Newroth, *Limnology, Lake Diagnosis and Selection of Restoration Methods*, in *Restoration and Management of lakes and Reservoirs*. 1993. p. 9-51.
13. Hereve, S., *Chemical Variables in Lake Monitoring*, in *Hydrological and limnological aspects of lake monitoring*, G.Z. Pertti Heinonen, André Van der Beken, Editor. 2000, John Wiley and Sons Ltd: New York. p. 42-54.
14. Smith, V.H., *The nitrogen and phosphorus dependence of algal biomass in lakes: an empirical and theoretical analysis.* Limnology and Oceanography, (1982). **27**(6): 1101-12.
15. Pearsall, W.H., *Phytoplankton in the English lakes. II. The composition of the phytoplankton in relation to dissolved substances.* Journal of Ecology, (1932). **20**: 241-62.
16. Dillon, P.J. and F.H. Rigler, *Phosphorus-Chlorophyll Relationship in Lakes.* Limnology and Oceanography, (1974). **19**(5): 767-773.
17. Heiskary, S.M., Howard, *Establishing relationships among nutrient concentrations, phytoplankton abundance, and biochemical oxygen demand in Minnesota, USA, rivers.* Lake and Reservoir Management, (2001). **17**(4): 251-262.
18. Smith, V.H., *Eutrophication of freshwater and coastal marine ecosystems. A global problem.* Environmental Science and Pollution Research International, (2003). **10**(2): 126-139.
19. Willen, E., *Phytoplankton in Water Quality Assesment-An Indicator*, in *Hydrological and limnological aspects of lake monitoring*, G.Z. Pertti Heinonen, André Van der Beken, Editor. 2000, John Wiley and Sons Ltd: New York. p. 57-80.
20. Smith, V.H., *Low Nitrogen to Phosphorus Ratios Favor Dominance by Blue-Green-Algae in Lake Phytoplankton.* Science, (1983). **221**(4611): 669-671.
21. Smith, V.H. and S.J. Bennett, *Nitrogen : phosphorus supply ratios and phytoplankton community structure in lakes.* Archiv Fur Hydrobiologie, (1999). **146**(1): 37-53.
22. Jensen, J.P., E. Jeppesen, K. Olrik, and P. Kristensen, *Impact of Nutrients and Physical Factors on the Shift from Cyanobacterial to Chlorophyte Dominance in Shallow Danish Lakes.* Canadian Journal of Fisheries and Aquatic Sciences, (1994). **51**(8): 1692-1699.
23. Schindler, D.W., *Evolution of Phosphorus Limitation in Lakes.* Science, (1977). **195**(4275): 260-262.
24. Trimbee, A.M. and E.E. Prepas, *Evaluation of Total Phosphorus as a Predictor of the Relative Biomass of Blue-Green-Algae with Emphasis on Alberta Lakes.* Canadian Journal of Fisheries and Aquatic Sciences, (1987). **44**(7): 1337-1342.
25. Smith, V.H., *Light and Nutrient Effects on the Relative Biomass of Blue-Green-Algae in Lake Phytoplankton.* Canadian Journal of Fisheries and Aquatic Sciences, (1986). **43**(1): 148-153.
26. Bulgakov, N.G. and A.P. Levich, *The nitrogen:phosphorus ratio as a factor regulating phytoplankton community structure.* Archiv fuer Hydrobiologie, (1999). **146**(1): 3-22.
27. Havens, K.E., R.T. James, T.E. East, and V.H. Smith, *N:P ratios, light limitation, and cyanobacterial dominance in a subtropical lake impacted by non-point source nutrient pollution.* Environmental pollution, (2003). **122**(33): 379-90.
28. Douglas, G.B., M.S. Robb, D.N. Coad, and P.W. Ford, *A Review of Solid Phase Adsorbents for the Removal of Phosphorous from Natural and Wastewaters*, in *Phosphorous in Environmental Technology:Principles and Applications*, E. Valsami-Jones, Editor. 2004, WA. p. 291-320.
29. Firsching, F.H., *Solubility Products of the Trivalent Rare-Earth Arsenates.* Journal of Chemical and Engineering Data, (1992). **37**(4): 497-499.

30. Douglas, G.D., J.A. Adeney, and L.R. Zappia, *Sediment Remediation Project: 1998/9 Laboratory Trial Report, CSIRO Land and Water*. Report No. 6/00 (2000): CSIRO.
31. Suzuki, Y., H. Saitoh, Y. Kamata, Y. Aihara, and Y. Tateyama, *Precipitation incidence of the lanthanoid(III) hydroxides: II. Precipitation from chloride and perchlorate solutions.* urnal of the Less-Common Metals, (1989). **149**: 179-84.
32. Douglas, G.D., D.N. Coad, and J.A. Adeney, *Sediment Remediation Project: Laboratory and Field Trials, Report to the Rivers Commission*. Report No. 97-58 (1997): CSIRO.
33. Douglas, G.D., J.A. Adeney, and D.N. Coad, *Sediment Remediation Project: 1997/98 Laboratory Trials: Final Report*. Report No. 98-60 (1998): CSIRO Land and Water.