



# Options for Addressing P-Enriched Sediments in Lakes: A Literature Review

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TITLE: **Options for Addressing P-Enriched Sediments in Lakes: A Literature Review**

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## Executive Summary

The release of dissolved phosphorus (P) from lake sediments is currently considered to be the primary driver of excessive cyanobacteria growth in Te Roto o Wairewa/Lake Forsyth in Canterbury. The cyanobacteria blooms that routinely occur between spring and autumn each year limit recreational access to the lake, pose a hazard to animals and public health, and adversely affect ecosystems and cultural values.

To Roto o Wairewa (Wairewa) has a highly variable water quality, with rapid shifts in pH, salinity and dissolved oxygen concentrations, all of which can influence the release of sediment-bound P into the water column. The lake is also shallow and well-mixed by the wind, and intermittently opened to the sea. Any successful management option to prevent sediment-bound P release needs to be robust enough to tolerate this dynamic system.

A range of management options exist to prevent or reduce the release of sediment-bound P from sediment. This literature review assesses these options, with particular emphasis on their potential effectiveness in a shallow coastal lake such as Wairewa.

These options include;

- Physical capping of the sediment
- Chemical amendment to bind P more strongly to the sediments
- Removing the existing P-rich lake sediment
- Manipulating lake water chemistry to reduce P release

In each case, the possible advantages and disadvantages or limitations of using different management options in Wairewa are assessed (summarised in Table 1), and case studies from other lake catchments, in NZ and internationally, are described. It is acknowledged that management options will need to be considered in the context of the values associated with the lake by local community and stakeholders.

Finally, other options for reducing P concentrations and algal abundance in the lake are briefly considered.

**Table 1:** Considerations for various in-situ management options for reducing P release from P-enriched sediments in Wairewa. “?” indicates that either the effect is unknown, or that the effect depends on amendment application or other factors.

	<i>Physical barrier to P release</i>	<i>Chemical binding of P</i>	<i>Safe for benthic ecosystem</i>	<i>Safe for phyto-ecosystem</i>	<i>Works in oxic conditions</i>	<i>Works in saline conditions</i>	<i>Works in anoxic conditions</i>	<i>Works in acidic conditions</i>	<i>Works in alkaline conditions</i>	<i>Ongoing removal of incoming P</i>
<b>Physical capping:</b>										
<i>Clay/fine sand</i>	✓	✗	✗	✓	✓	✓	✓	✓	✓	✗
<i>Aquablok</i>	✓	✗	✗	✓	✓	✓	✓	✓	✓	✗
<b>Chemical addition:</b>										
<i>Aluminium</i>	?	✓	?	?	✓	✓	✓	✓	✗	✓
<i>Ferric iron</i>	?	✓	?	✓	✓	✓	✗	?	✗	✓
<i>Lanthanum</i>	?	✓	?	?	✓	✓	✓	✓	✓	✓
<i>Calcium</i>	?	✓	?	✓	✓	✓	✓	✗	✓	✓
<b>Sediment removal:</b>										
<i>Dredging</i>	✗	✗	✗	✗	✓	✓	✓	✓	✓	✗
<i>Flushing the lake</i>	✗	✗	✗	✗	✓	✓	✓	✓	✓	✗
<b>Manipulation of lake chemistry:</b>										
<i>Aeration</i>	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓
<i>pH</i>	✗	✓	✓	✓	✓	✓	✓	✓	?	✓
<i>Salinity</i>	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓

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## Abbreviations

<b>P</b>	Phosphorus
<b>N</b>	Nitrogen
<b>Al</b>	Aluminium
<b>Fe</b>	Iron
<b>yr</b>	Year

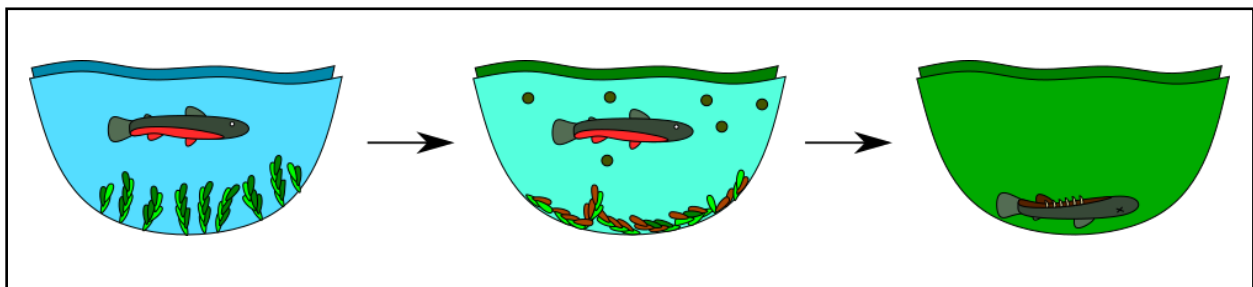
## Terms:

<b>Anoxic</b>	Absence of dissolved oxygen
<b>Benthic</b>	The ecological region at the sediment-water interface
<b>Benthivorous</b>	Eats benthic species, typically macroinvertebrates
<b>Chlorophyll <i>a</i></b>	A pigment found in photosynthetic algae and plants, concentration used as an indicator of algal biomass
<b>Epilimnion</b>	The near-surface layer of water in a thermally stratified lake
<b>Flocculation</b>	The process of producing a floc (particles) from fine or colloidal particles in the water column and sediment pore water.
<b>Hypolimnion</b>	The lowest layer of water in a thermally stratified lake
<b>Microcystins</b>	A class of toxins produced by cyanobacteria
<b>Organic P</b>	Organic compounds containing P
<b>Piscivorous</b>	Eats fish
<b>Planktivorous</b>	Eats plankton
<b>Pore Water</b>	Water present in the spaces between particles in a saturated sediment
<b>Secchi Depth/Disk</b>	A method of measuring the visual clarity of lakes by dropping a black and white disc into water to determine the depth at which it is no longer visible
<b>Suspended Sediment</b>	Inorganic particles that remain suspended in the water column

## Section 1 Introduction

### 1.1 Lake Eutrophication

“Eutrophication” is the process of excess nutrient addition to a body of water, and its effects on the ecosystem. Intense, visible algal blooms are one of the most obvious signs of a eutrophic lake. Algae have a fast reproductive cycle so grow quickly in high nutrient environments, reducing water clarity and biodiversity. Algae biomass also prevents light from penetrating the water column, impeding the growth of macrophytes, and depletes the dissolved oxygen, particularly in the base of the lake. These conditions create a positive feedback loop allowing algae to dominate the lake system (Fig 1).



**Figure 1.** Idealised stages of eutrophication and positive feedback; As nutrients enter the waterways, they are utilised by the algae biomass creating a turbid water column. Macrophytes are unable to grow without light so die back. The organic matter from macrophytes and algae consumes oxygen during decomposition, and releases more nutrients, allowing for more algal growth. Animals unable to live in an oxygen-poor environment will die-off, releasing more nutrients as they decompose.

Phytoplankton requires a specific ratio of nitrogen (N) and phosphorus (P) to reproduce at peak efficiency (Abell et al., 2010). A molar ratio of  $N:P = 16:1$  is a benchmark for optimal algal growth (Redfield et al., 1963) but the exact ratio will vary depending on the species. If one of these nutrients is well below this ratio, then algal growth is considered to be limited by that nutrient, although light, temperature and other micronutrients may also limit growth. In a lake catchment, incoming nutrients may be derived from pasture fertilisers, stormwater, wastewater and sewage outflows, and can be of point source or diffuse origin.

Effective management of just one vital nutrient can be an effective way to reduce algae growth. However, it can be difficult to reduce N input to a lake system as N is the most abundant gas in the atmosphere, and dissolved nitrates, nitrites and ammonia are naturally present in water, biomass and biological waste products. Nitrate is particularly difficult to manage, as it is very soluble and has high mobility through surface and groundwater systems. Additionally, some species of cyanobacteria, including those often present in Wairewa, can fix the N they require from the atmosphere (Schallenberg & Schallenberg, 2013; Schindler et al., 2008). This N-fixing ability allows cyanobacteria to dominate low-N lake systems,

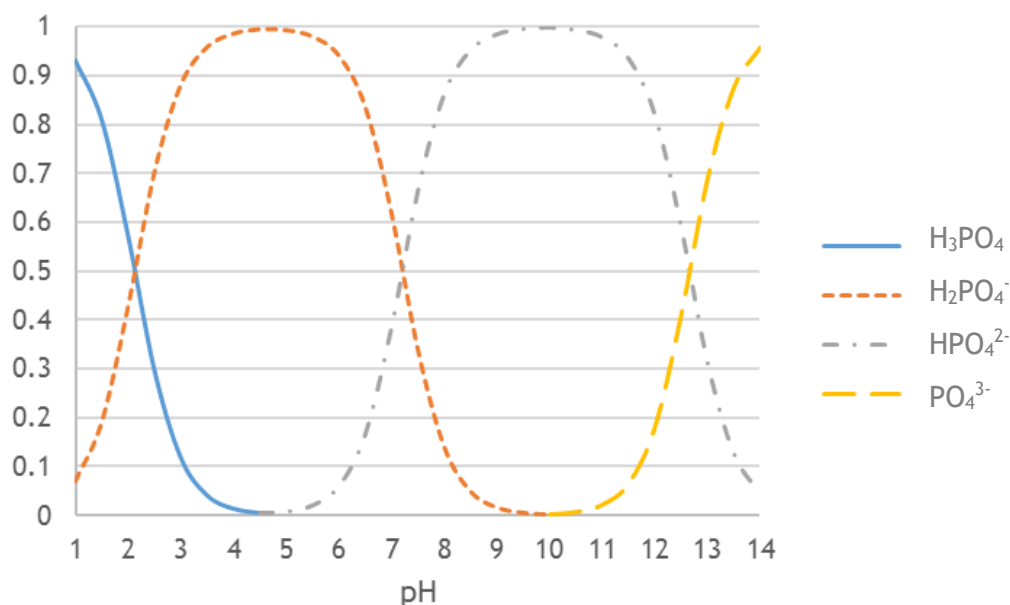


outcompeting other phytoplankton, as long as sufficient P is availability. Therefore P control is considered to be a more effective action to prevent algal blooms in many NZ waterways.

## 1.2 Natural sources and chemical behaviour of P

P is naturally present in unweathered rocks as calcium phosphate minerals (apatite). Apatite is subject to mechanical weathering and can be transported in surface runoff through overland flow as a suspended sediment. Apatite may also be chemically weathered, releasing P under acidic conditions, catalysed by microorganisms (Smits et al., 2012).

P in suspended sediment is absorbed onto the surfaces of reactive minerals such as clays and iron oxides (Ruttenberg, 2003). In a lake water column, P can be present in both the suspended sediment, or in dissolved form as phosphate ion or as organic P. These three different components are collectively referred to “Total P”. Dissolved phosphate ion ( $\text{PO}_4^-$ ) is variously referred to as dissolved inorganic P, dissolved reactive P (DRP), inorganic P, soluble reactive P, free reactive P, filterable reactive P and orthophosphate. Phosphate can take different chemical forms, depending on the pH (Figure 2).

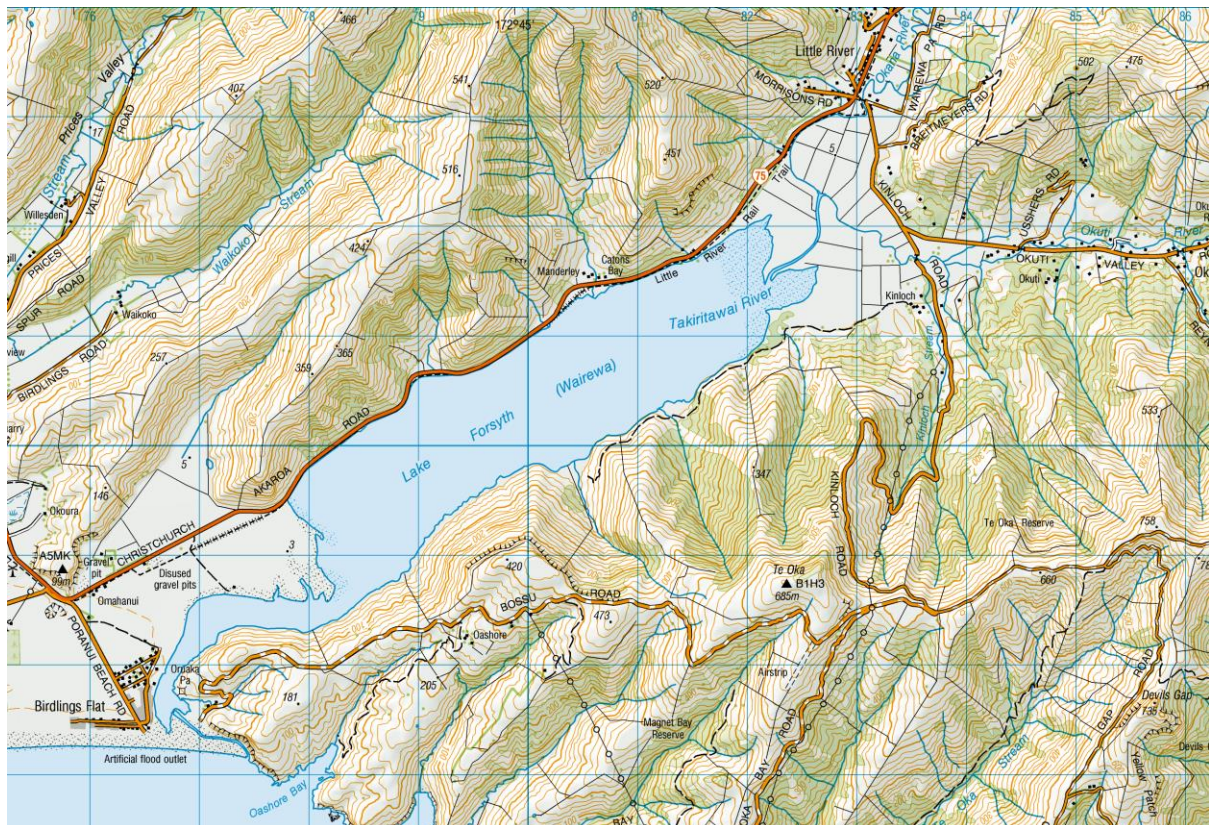


**Figure 2:** Chemical speciation of orthophosphoric acid as a function of pH. Most uncontaminated freshwaters are of near-neutral (pH 6-9) so contain mainly  $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$ . Diagram adapted from (Oliveira et al., 2011).

Organic phosphorous is present in plants and animals, mainly in the form of P-esters (Ruttenberg, 2003). These compounds can be broken down by decomposing bacteria and UV light to form the more bio-available phosphate ions.

### 1.3 Te Roto o Wairewa/Forsyth

Te Roto o Wairewa/Forsyth (Wairewa) is a shallow, coastal lake on the Banks Peninsula, New Zealand (Fig 3). It is at the bottom of a farming catchment with P-rich volcanic soils, and local iwi prize the lake for its mahinga kai (food gathering) values, in particular tuna (eels). It is also a popular recreational area with walking and biking tracks along the northwest side of the lake. The catchment has a relatively small population of approximately 1,000 people, mainly in the Little River township at the north end of the lake, and in a small community at Birdling's Flat, at the coastal end of the lake.



**Figure 3.** Topographical map showing Wairewa and nearby communities (source map from LINZ, 2014).

The lake has experienced frequent, natural and anthropomorphic eutrophication-induced algal blooms since the early 1900's (Schallenberg & Schallenberg, 2013), and has historically flipped between macrophyte-dominated and algae-dominated (Schallenberg & Sorrell, 2009). In recent years the algal blooms have become increasingly problematic, due to the presence of toxin-producing cyanobacteria, which limits recreational activities, water use and traditional fisheries (Davie, 2005).

**Table 2:** The average and range for physical and chemical parameters in Wairewa, from 1993 to 2017, for “n” data collected by Environment Canterbury at their monitoring station (ID SQ33147) on the northwest side of the lake (Environment Canterbury, 2017). The macrophyte coverage estimate is from Waters (2016).

	Average	Range	n
<b>Water Level</b>	1.7m	0-15.5m	513
<b>Salinity</b>	4‰	1-14‰	700
<b>Temperature</b>	13.6°C	2.40-25.1 °C	895
<b>Dissolved oxygen</b>	10.2 mg L <sup>-1</sup>	16.6-4.3 mg L <sup>-1</sup>	405
<b>pH</b>	7.9 (median)	6.5-9.9	667
<b>Electrical conductivity</b>	9.22 mS cm <sup>-1</sup>	0.29-36.0 mS cm <sup>-1</sup>	749
<b>Turbidity</b>	28.9 NTU	1.10-450 NTU	690
<b>Total P</b>	0.238 mg L <sup>-1</sup>	0.004-2.80 mg L <sup>-1</sup>	597
<b>Dissolved reactive phosphorous</b>	0.019 mg L <sup>-1</sup>	0.001-0.61 mg L <sup>-1</sup>	593
<b>Total N</b>	2.13 mg L <sup>-1</sup>	0.12-200 mg L <sup>-1</sup>	597
<b>Nitrate and nitrite (as N)</b>	0.078 mg L <sup>-1</sup>	0.002-1.1 mg L <sup>-1</sup>	599
<b>Ammonia (as N)</b>	0.059 mg L <sup>-1</sup>	0.005-2 mg L <sup>-1</sup>	600
<b>Chlorophyll <i>a</i></b>	96.9 ug L <sup>-1</sup>	0.100-6790 ug L <sup>-1</sup>	860
<b>E coli</b>	46 MPN/100ml	1-1700 MPN/100ml	136
<b>Macrophyte coverage</b>		0-33%	

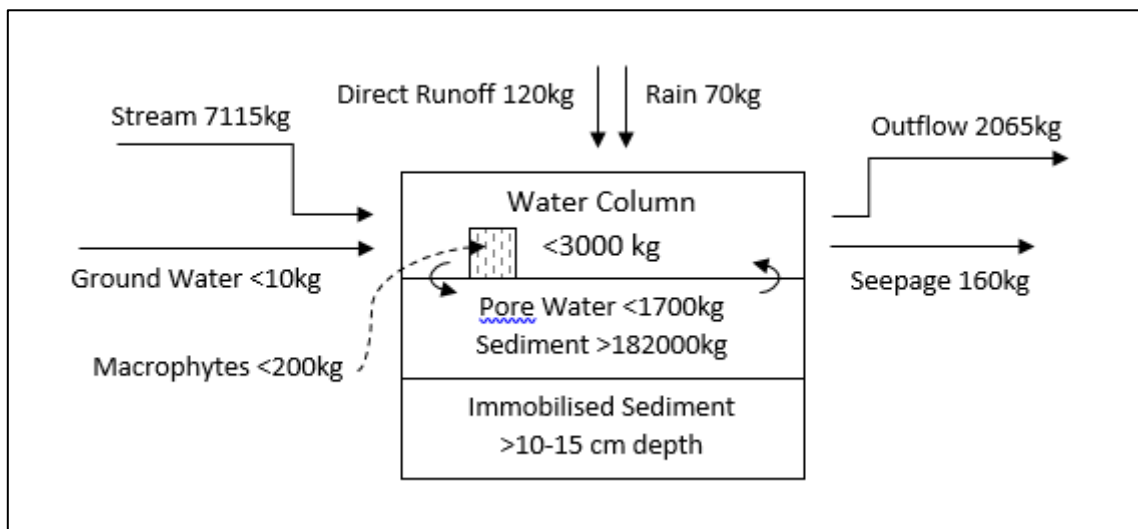
**Table 3:** Key biological species identified in Wairewa (Schallenberg & Schallenberg, 2013; Wairewa Rūnanga Incorporated & Christchurch City Council, 2013; Waters, 2016).

<b>Phytoplankton and Cyanobacteria</b>	<i>Nodularia spumigens</i> , <i>Anabaena</i> spp., <i>Merismopedia</i> , <i>Nodularia spumigena</i> , <i>Aphanizomenon</i> sp.
<b>Protozoan</b>	<i>Pfisteria shumwayae</i>
<b>Macroalgae</b>	<i>Enteromorpha intestinalis</i>
<b>Macrophytes</b>	<i>Myriophyllum triphyllum</i> , <i>Ruppia</i> sp., <i>Potamogeton pectinatus</i> and <i>Tolypella nidifica</i>
<b>Ocean plants</b>	<i>Eryngium variculosum</i>
<b>Benthic invertebrates</b>	<i>Potamopyrgus</i> sp., caddisfly larva ( <i>Oecetis unicolor</i> ), chironomids, mysid ( <i>Tenagomysis chiltoni</i> ), amphipod ( <i>Paracalliope fluviatilis</i> ), ostracods, leeches, dragonfly larva ( <i>Procordulia</i> sp.), moth larva ( <i>Hygraula nitens</i> ), oligochaetes
<b>Zooplankton</b>	<i>Gladioferens pectinatus</i> (estuarine copepod), cyclopoid & harpacticoid copepods
<b>Fish</b>	Longfin eel, shortfin eel, common bully, black flounder, smelt ( <i>Retropinna retropinna</i> ), inanga, lamprey ( <i>Geotria australis</i> ), perch
<b>Water birds</b>	Crested grebe, New Zealand scaup, egrets, swans, herons
<b>Ocean birds</b>	Oystercatchers, white-fronted terns, spotted shags, pied cormorants, white-flippered penguins

Lake chemistry is highly variable (Table 2). Nutrient, ammonia and chlorophyll *a* concentrations, pH and dissolved oxygen vary in response to extremes in algae photosynthesis and respiration. The lake is periodically manually opened to the sea via a canal across Birdlings Flat, which enables accumulated dissolved nutrients to be flushed to the ocean. However, these openings often cause a substantial increase in lake salinity, when the seawater flows back through the canal. Fluctuating lake physical and chemical conditions stress biota in the lake, limiting the diversity of species present (Schallenberg et al., 2003), as shown in Table 3.

### 1.3.1 The P Budget in Wairewa

Most of the P input to Wairewa occurs when sediment-bound P is carried in surface runoff from the catchment during heavy rainfall events (Waters & Webster-Brown, 2016). A single such event accounted for over 60% of the P load entering the lake over a 15-month period in 2014/15. The accumulated P-rich sediment now forms a large P reservoir in the base of the lake (Fig 4). Waters & Webster-Brown (2016) determined a P budget for the lake, and reported that over 5000 kg of P accumulates in the lake each year, predominantly held within the lake sediment. Other P reservoirs (macrophytes, dissolved P, porewater, etc.) had a relatively minor role, as shown in Figure 4.



**Figure 4:** P reservoirs and annual fluxes in Wairewa (Waters & Webster-Brown, 2016).

## Section 2 Sediment Capping

The sediment reservoir of Wairewa is the principle source of dissolved, bioavailable P to the water column. One option for preventing this internal P cycling is to cap the sediment, preventing further release of P.

With all capping methods, there is the possibility of smothering existing benthic communities in the lake. The effect on benthic macrophytes and micro- and macro-invertebrates will be dependent on the thickness of the material and mobility of the biota. Much of the literature on benthic smothering is related to ocean deposition of clays from dredging and terrestrial sources (Alf et al., 2002; Cabaço et al., 2008; Thrush et al., 2004). The effect of burial on seagrass species has been extensively reviewed by Cabaço et al. (2008) and offers insight into the possible effects of smothering of macrophytes. Sediment burial was found to be most detrimental to smaller species of seagrass, with vulnerable species demonstrating 100% mortality at a burial depth of 2cm. Larger more tolerant species withstood up to 30cm of sediment deposition. If the capping material does not release ecotoxic chemicals, then most benthic communities would be expected to re-establish after the cap has been applied.

### 2.1 Physical Capping Methods

#### 2.1.1 Natural clay/fine sand

Applying a layer of low permeability material to the top of contaminated sediment can prevent the release of all undesirable chemicals into the water column. An inert cap serves as a physical barrier to interaction between the sediments and lake water. Materials with a permeability of less than  $10^{-8} \text{ ms}^{-1}$  (clay to fine sand, Table 4) are best suited to this application (Merritt et al., 2010).

**Table 4:** General permeability of sediments, where K is the permeability coefficient and represents the average speed water will move through the material in  $\text{m s}^{-1}$  (Powrie, 2014). Mobility is a general class, with physical caps requiring “low” mobility materials.

K ( $\text{ms}^{-1}$ )	Aggregate Type	Mobility
10	Gravels	Rapid
1		
$10^{-2}$	Sands	
$10^{-3}$		
$10^{-4}$		
$10^{-5}$	Very fine sand	Moderate
$10^{-6}$	Silts	
$10^{-7}$	Some clays	
$10^{-8}$	Homogeneous clay, Polymers	Low
$10^{-9}$		
$10^{-10}$		
$10^{-11}$		

The integrity of such a cap is critical, as holes or cracks in the barrier will allow contaminants to leach through. Uneven coverage, macrophyte growth and physical disturbance after application can all result in breaks in the cap (Alf et al., 2002; Merritt et al., 2010).

The material used for a physical cap is preferably chemically and ecologically inert, which allows for the rapid recolonization of benthic species after application. It will, of course, smother any benthic animals and plants present in the lake sediment at the time of application.

Case studies utilising physical capping techniques to manage nutrient release are rare. Most are related to preventing mobility of heavy metals and hydrocarbons from industrially contaminated soils and sediments (USEPA, 2007). However, a physical barrier should be effective, irrespective of the contaminant of interest.

**Case Study: Benthic smothering in an estuary environment, Okura Estuary, New Zealand**

A study was conducted in Okura Estuary, New Zealand, on the effect of a non-toxic sediment layer on benthic ecosystems (Alf et al., 2002). Alf et al. deposited 3, 6 and 9 cm of silt/clay in 2m diameter circular mesocosms separated by 15m, repeated in triplicate. There were also three control sites, and the experiment was repeated at an exposed and a sheltered location, to observe the effects of wave disruption.

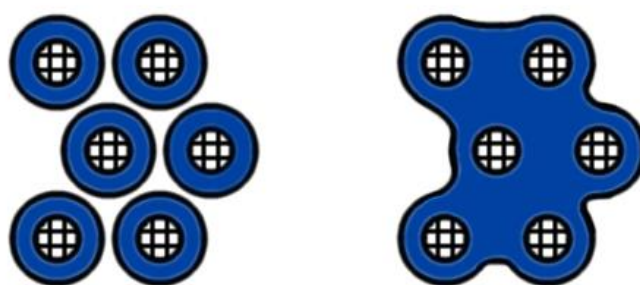
The results showed a clear negative impact on the benthic biota as a result of smothering. Species from the taxa *Mollusca*, *Annelida* (worms), *Crustacea* and *Cnidaria* (sea anemones) were monitored. Near identical responses were seen at all sites, for all levels of deposition. Macro-fauna abundance had dropped by 57-71%, by the third day after application and continued to fall for up to 10 days to <10% initial abundance. A storm event at day 28 removed the overlying material from the exposed site, allowing for rapid recovery. However, the distribution of species was altered, with the deep burrowing adult individuals being largely absent. At the sheltered site where the sedimentary layer remained intact, recovery was still incomplete 13 months' after sediment application.

When these findings are applied to a whole lake, with the geoengineering required as part of a capping program, these effects on benthic communities could be intensified.



### 2.1.2 Aquablok®

Aquablok® is a bentonite clay-polymer composite used non-specifically as a capping material. It consists of an aggregate core, coated in a clay and polymer mixture which can be modified depending on the application (USEPA, 2007). The particles hydrolyze in water with the external clay layer expanding to form a continuous structure supported by the polymer. In its hydrolysed form the Aquablok® layer has a very low permeability, in the order of  $10^{-11} \text{ ms}^{-1}$ , and transmission of aqueous chemicals is therefore very limited (USEPA, 2007). This technology has been used in United States Super Fund sites to control a broad range of organic and metal contaminants in lake sediments (Merritt et al., 2010; USEPA, 2007).



**Figure 5:** Aquablok® consists of spherical particles with an aggregate core (■) coated with a clay/polymer (■). The coating hydrolyses in water, expanding and forming a continuous structure.

#### **Case Study: Aquablok® pilot study, Anacostia River, Washington DC, United States**

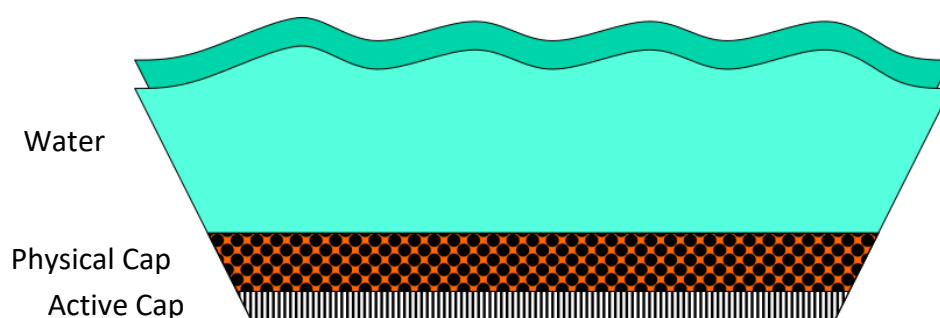
A 2004 pilot study into the effectiveness of Aquablok® was conducted in a coastal river environment on the Anacostia River (Merritt et al., 2010). The sediments contained a spectrum of organic and inorganic compounds. A 15cm layer of Aquablok®, covered with clean sand, was applied to 930m<sup>2</sup> of river bed next to naval yards in Washington DC. The 30-month study confirmed no structural change in the deposited sediment layer (USEPA, 2007). Aquablok® was shown to be highly impermeable to contaminants. There was no detectable detrimental effect on benthic ecological communities, which quickly recolonised the sand layer. One concern raised in the final report was that, in time, gas could become trapped below the Aquablok® layer and with sufficient build-up could breach the layer.

## 2.2 Active Capping Methods

Active capping is the process of adding a reactive chemical substrate layer on top of a sediment. The chemical binds P, locking it into an insoluble form and preventing P dissolution and bioavailability. Such chemicals can also remove dissolved P from the water column as they settle to form a layer of reactive material over the sediment.

Physical caps have been used in combination with active caps to provide a protective layer that can withstand both natural and anthropomorphic forces (Zhang et al., 2016). The physical cap separates the active capping material from the water column, preventing the release of

active, possibly toxic, reagents from the active layer (Figure 6). This process can allow a thinner layer of active capping material to be applied to the sediment (Zhang et al., 2016).



**Figure 6:** Physical (■) and active chemical caps (▨) used together to improve effectiveness. The physical cap prevents the release of chemicals to the water column, and limits disturbance. The active chemical layer impedes P release from the underlying sediment (Zhang et al., 2016).

Many active capping materials rely on the *in situ* formation of fresh hydroxide and oxide minerals (“(hydr)oxides”), which have a high capacity for adsorbing phosphate ion. Phosphate adsorption to the surface of (hydr)oxide minerals is a surface complexation reaction with P forming inner-sphere complexes at hydroxyl sites (Li et al., 2013). This fast adsorption surface reaction (minutes-hours) is followed by a slower (days-months) diffusion process, whereby P is incorporated into the interior of particles (Philip, 1988). Surface adsorption reactions are reversible, so changes in water chemistry can release P from adsorbent capping agents. Also, due to the rapid nature of adsorption reactions, a low particle surface area can be an immediate limitation on P binding (de Vicente et al., 2008).

### 2.2.1 Aluminium-based treatments

Aluminium-based amendments most commonly involve the addition of an aluminium (Al) compound that will react in water to form fresh Al (hydr)oxide minerals. Active capping reagents using P adsorption onto Al hydroxide have been used in more than 200 lakes worldwide (Welch (2005) cited in Jensen et al., 2015).

Al (hydr)oxides are capable of absorbing phosphates in the pH range of 2-9, with the highest absorbance occurring around pH 4 (Tanada et al., 2003). Phosphate adsorption can be affected by a variety of other chemical conditions such as high humic acid, silica and magnesium concentrations, all of which will decrease P adsorption (de Vicente et al., 2008). Magnesium ions are particularly relevant in coastal lakes, as magnesium is a major ion present in seawater. Other major ions in seawater such as sodium, chloride, carbonate and sulphate do not significantly influence phosphate removal by Al (hydr)oxide (de Vicente et al., 2008; Tanada et al., 2003).



### **Alum (Al sulphate)**

Alum<sup>1</sup> addition is the most common method for removing dissolved reactive P from lake waters (Hickey & Gibbs, 2009). It can be applied as a slurry or powder to the lake surface or injected into the epilimnion (top layer of the lake). Alum removes P via two mechanisms depending primarily on pH and phosphate concentrations;

- a) At acidic pH and inorganic P concentrations greater than 1 mg L<sup>-1</sup>, direct precipitation of Al phosphates is favoured;  $Al_2(SO_4)_3 \cdot xH_2O + 2PO_4^{3-} \rightarrow 2AlPO_4(s) + 3SO_4^{2-} + xH_2O$  (Cooke & Kennedy, 1981)
- b) At near-neutral pH (6-8) in moderately hard waters, maximum Al (hydr)oxide flocculation occurs producing an adsorption surface capable of binding P. Al floc forms by reaction with carbonate:  $Al_2(SO_4)_3 \cdot xH_2O(s) + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3(s) + 3CaSO_4(s) + xH_2O + 6CO_2$  (Cooke & Kennedy, 1981). This floc also traps algae and other suspended solids as it settles, thereby clarifying the water column as well as depositing sediment-bound P

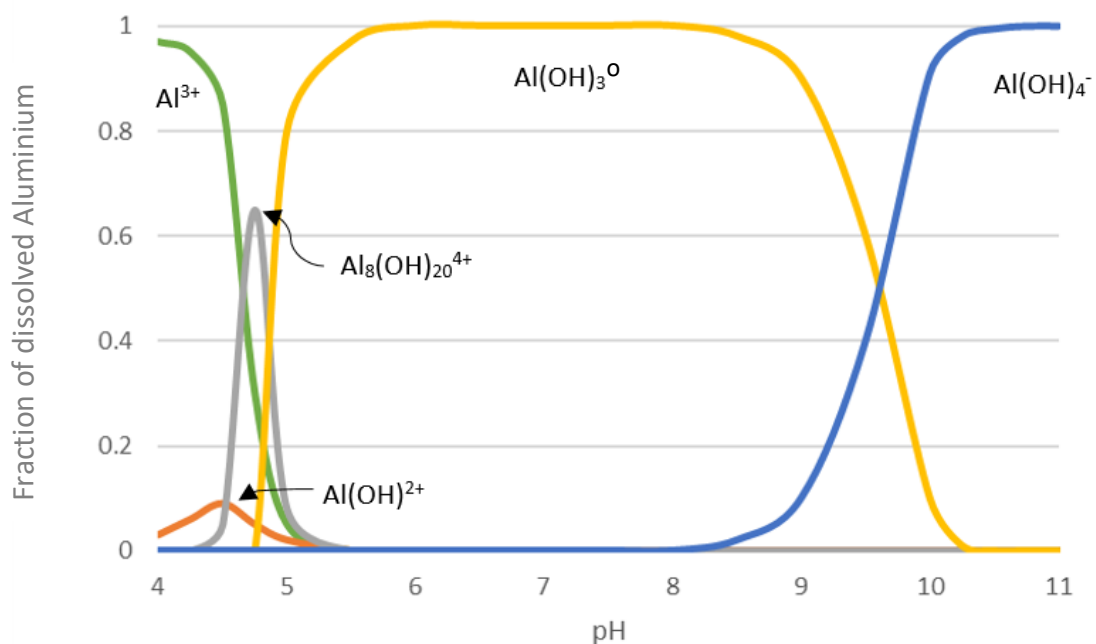
Under high pH conditions, alum is converted to soluble aluminate ion  $Al(OH)_4^-$  (Cooke & Kennedy, 1981) and will not act to remove dissolved P.

Addition of alum creates acidic conditions, which can be mitigated by the use of pH buffers such as sodium aluminate (Hickey & Gibbs, 2009). One significant disadvantage of creating acidic conditions (pH <5) is that alum can undergo disassociation, releasing toxic free Al ion (Al<sup>3+</sup>) into the environment (Cooke et al., 1993). Applying alum too rapidly or in large quantities without buffering will acidify the lake, increasing the potential for releasing dissolved Al free ion.

Benchtop experiments have been used to determine dose rates of alum to achieve the desired level of phosphate reduction. A full procedure for determining dose rates is documented by Cooke & Kennedy (1981). Optimal wastewater treatment of sludge required 2.3kg (as Al) of alum to remove 1kg P (Linstedt et al., 1974). In the least efficient systems, 525kg of Al per kg of P was only able to remove 90% of P in Lake Mendota waters (Eisenreich et al., 1977, as cited in Cooke & Kennedy, 1981). Benchtop experiments have also been used to determine the rates of P release from sediments after alum application (Gibbs et al., 2008).

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<sup>1</sup> In geology and mineralogy “alum” can refer to a class of compounds of the general formula  $AM(SO_4)_2 \cdot 12H_2O$ , where A is a monovalent (+1) cation such as potassium, and M is a trivalent (+3) metal ion such as Al. In lake remediation and in this report, “alum” refers to specifically to Al sulphate:  $Al_2(SO_4)_3 \cdot xH_2O$ .



**Figure 7:** Dissolved species of Al as a function of pH (for Al =  $5.0 \times 10^{-4}$  M). Redrawn from Rubin (1976).

**Case Study: Whole lake alum application, Lake Okaro, Bay of Plenty, New Zealand**

Alum application in Lake Okaro, Bay of Plenty in 2003 and its short term effects were documented by Paul et al. (2008) and Özkundakci et al. (2010). In this case, a boat applied a 47%  $\text{Al}_2\text{SO}_3 \cdot 14\text{H}_2\text{O}$  solution, at a dosage rate of  $0.6\text{g(Al)} \cdot \text{m}^{-3}$ , to the whole lake and no pH buffer was used. At the time, the lake was thermally stratified, with an anoxic hypolimnion.

After application there was no apparent change in the trophic state of the lake; including chlorophyll *a* and total P concentrations. There was no statistically significant reduction in the total P of the surface waters, when compared to those present the year before treatment.

Dissolved Al levels were  $<0.09\text{g m}^{-3}$  before application. After treatment, Al concentrations increased at all depths, with a maximum of  $0.6\text{g m}^{-3}$  near the surface. The Al concentrations exceeded ANZECC (2000) guidelines for the protection of 95% freshwater species, for at least three months after application. However, the authors reported no fish kills during the study, and in time, Al concentrations dropped slowly as Al (hydr)oxide precipitated into the bottom of the lake. There was also an increase in ammonium after treatment, which was attributed to increased mortality of phyto- and zooplankton in the presence of toxic Al.

Notably, the condition of the lake was not optimal for phosphate removal at the time. Temperature, dissolved oxygen and redox potential, pH and dosing rate were all identified as factors that could have affected P binding.

**Case Study: Novel tributary dosing with alum, Lake Rotorua, New Zealand**

Tributary application of alum has been trialed in Rotorua; dosing Utuhina Stream in 2006 and Puarenga Stream in 2010 (Smith et al., 2016). Between 2006 and June 2015, 496 tonnes of Al was added to these tributaries, as alum, at a variable dosage rate up to 600kg day<sup>-1</sup>. This technique was effective at reducing P loads going into Lake Rotorua, and the lake achieved its target TLI of 4.2 in 2012. Modelling of the lake system predicted that the effects of tributary dosing would continue for up to 2-3 years after dosing ceased (Hamilton et al., 2015). There has been little impact on local biota due to the low rate of application (Tempero, 2015). The resource consent for this project expires in 2017 (Hamilton et al., 2015).

**Case Study: Whole lake application of alum, Lake Courtille, Limousin, France**

Alum was applied at 1.5g Al m<sup>-3</sup> as Al<sub>2</sub>SO<sub>3</sub>·18H<sub>2</sub>O in Lake Courtille, also known as Etang de Courtille (van Hullebusch et al., 2002). The dosage rate was determined by benchtop laboratory experiments, designed to ensure that the pH remained above 6. The lake contained high levels of organic matter that can act as a pH buffer and this restored baseline pH within two weeks of alum application.

Low levels of dissolved Al were reported post application, with maximum toxic free Al ion concentrations of 73 µg L<sup>-1</sup>. This concentration decreased rapidly and returned to near pre-treatment levels within a week. At the maximum Al concentration, ecological toxicity was expected based on toxic effects observed for vulnerable species at and below this concentration, under experimental conditions.

The effects of the treatment were relatively short term. The P increased after 60 days, returning to pre-treatment concentrations. Turbidity decreased through flocculation, but improved clarity resulted in the growth of benthic algae, which liberated nutrients from the sediment, increasing dissolved nutrient concentrations for 100 days after treatment.

However, it was noted that the treatment occurred at a period of high biological activity. It is therefore likely that the decrease in dissolved P may have been due to uptake by biomass, rather than P being removed by the alum.

**A Review: 21 alum-treated lakes in the United States**

A review of alum-treated lakes in the United States was conducted by Welch and Cooke (1999). The review included an assessment of the effectiveness and longevity of alum treatment on total P and chlorophyll *a* concentrations for 9 unstratified and 12 stratified lakes. The authors reported a range of application conditions, including dose rates of 2.6-30g Al m<sup>-3</sup>, in buffered and non-buffered systems, and via different injection depths.

The analysis of unstratified lakes determined that 6 of the 9 lakes responded positively to treatment showing decreased total P concentrations. Successful treatments resulted in an average 51% decrease in P in the water column and an average 73% reduction in P released from the sediment. These average values dropped slightly to 48% and 68% in the longer-term

(4-11 years), but some treatments were still effective eight years after application. Chlorophyll *a* responded similarly to P, where treatment was successful. Analysis of blue-green algae content in three of the lakes showed a significant decrease in these species post application, with toxic *Aphanizomenon* no longer present in two lakes after treatment.

Lakes with unsuccessful treatments and the poorest performing successful treatments also had higher macrophyte coverage. Macrophytes may have prevented an even alum application, but the relationship remains unclear. One hypothesis proposed by the authors was that the clarity of the water after treatment might have caused an increase of macrophyte biomass. Their decay led to an increase in dissolved P in subsequent years.

Stratified lakes had a lower response to treatment, showing only 37% initial and 42% long-term reductions in average dissolved P concentrations. The reduction in sediment P release rate averaged 80% reduction. However, the external P loading persisted so that algal blooms continued to occur, even with reduced internal cycling.

### ***Al chlorohydrates***

*(Poly) Al chloride, (Poly) Al chlorohydrate, Poly Al silicate chloride*

Al chlorohydrates are a class of compounds that use similar chemical pathways to those of Al sulphate to achieve *in-situ* flocculation of a Al (hydr)oxide adsorbing surface for P: i.e.,  $2Al_2(OH)_5Cl + Ca(HCO_3)_2 \rightarrow 4Al(OH)_3(s) + CaCl_2 + 2CO_2$ . The major chemicals in this group are (poly) Al chloride ( $Al_2(OH)_3Cl_3$ ), and (poly) Al chlorohydrate ( $Al_2(OH)_5Cl$ ). Al chlorohydrates have some advantages over alum, as they require less carbonate to flocculate and cause less acidification (Gebbie, 2001).

The latest compounds to be added to this family are the polyAl silicate chlorides. These chemicals have silica substituted into the polyAl chloride polymer at a given ratio, depending on the application. These compounds are more effective at removing turbidity from wastewater, but less effective at removing phosphate (Zouboulis & Tzoupanos, 2009).

#### ***Review: Al chlorohydrate treatment of six Danish lakes***

Jensen et al. (2015) evaluated the effectiveness of Al chlorohydrate treatments on six Danish lakes between 2001 and 2009, and their long-term (4-11 year) effectiveness. There was an immediate reduction in both the total dissolved P, and in P release from sediment in all 6 lakes. In all but one lake, there was a decreased total dissolved P for the entire study period. The one unsuccessful treatment returned to pre-treatment dissolved P concentrations within 3 years, perhaps because the external P loading had been underestimated. All lake treatments decreased in effectiveness over the 4-11 year study period.

There was little change in clarity and algal bloom density. Secchi depth measurements showed long-term (>2-3 year) improvements in only two of the lakes. One possible explanation is that the change in total dissolved P concentration was not enough to cause a regime change. In one case, where Al treatment was coupled with biomanipulation to increase the mussel population, there was a long-term improvement in Secchi depth. The

reduction of total dissolved P was therefore likely to be a contributing factor in effective treatment through bioremediation.

### ***Al (hydr)oxide***

As well as forming from other Al chemicals, Al hydr(oxide) can be added directly to a water body. Allophane, a poorly crystalline hydrous Al oxide-silicate clay, can also be used in this capacity. Acidification is not a consequence of the addition of these Al-amendments.

### **2.2.2 Modified zeolite and pumice**

Zeolite and pumice are porous crystalline hydrated aluminosilicates. The highly porous nature of these rocks creates a large reaction surface area and a high capacity for chemical doping with other reactants.

New Zealand manufacturer, Blue Pacific Minerals Ltd., produces Z2G1, a modified zeolite which now trades as Aqual-P® (Gibbs & Özkundakci, 2011). This product combines the natural phosphate absorbing properties of zeolites with Al-doping, to promote P precipitation and Al (hydr)oxide adsorption reactions. Dissolved Al is not released, which reduces potential toxicity, and acidification issues. Zeolite also absorbs other potentially problematic nutrients such as nitrate and ammonium (Wen et al., 2006; Yang et al., 2004).

Works Filter Systems Ltd produces pumice modified for water clarification in Matangi, New Zealand. In benchtop experiments, it was shown to remove P from water, but at lower rates than modified zeolites (Yang et al., 2004).

#### ***Case Study: Application of modified zeolite to Lake Okaro, New Zealand***

A trial of Z2G1 was conducted in Lake Okaro in Rotorua Lakes District (Gibbs & Özkundakci, 2011). The lake is a 33ha, low-alkalinity, hypertrophic crater lake. It has a mean depth 12.1m (maximum depth 18.0m) and stratifies annually. In September 2007, 110 metric tonnes of 1–3 mm grain size Z2G1 was applied to the whole lake at a dose rate of 350 g m<sup>-2</sup> (Özkundakci et al., 2010). There was an immediate reduction in the concentrations of phosphate in the hypolimnion, to less than 50% of the values recorded for the previous five years.

However, other restoration projects were undertaken concurrently and may have contributed to this result (Özkundakci et al., 2010). These projects included the construction of a wetland on the two major lake tributaries, riparian protection and better farm nutrient management implemented during and before the study. It is therefore not possible to isolate the effects of modified zeolite addition.

### 2.2.3 Ferric iron

Iron (Fe) is present in the environment as both ferrous ion ( $\text{Fe}^{\text{II}}$ ) and the more oxidised ferric ion ( $\text{Fe}^{\text{III}}$ ). Ferric iron is relatively insoluble, forming (hydr)oxides of iron ( “rust” and related Fe oxidation products) under natural and alkaline pH conditions, whenever oxygen is present. Like Al (hydr)oxide, Fe (hydr)oxide has a high capacity to adsorb other ions and it is the dominant phase binding P in the sediment in most oxygenated water environments. Also like Al (hydr)oxide, Fe hydr(oxide) surfaces are most reactive, and capable of adsorbing P and other ions most effectively, when freshly formed. Therefore the use of Fe (hydr)oxides in waste and other water treatment systems works best when the (hydr)oxides are formed *in situ* through the addition of a precursor Fe chemical.

#### ***Fe chloride***

Experimental and field studies have trialled a wide range of ferric Fe chemicals for the removal of phosphate from waterways, by either direct precipitation of Fe phosphate minerals;  $\text{Fe}^{3+} + \text{PO}_4^{3-} \rightarrow \text{FePO}_{4(s)}$ , or absorption of phosphate onto a freshly-formed Fe (hydr)oxide surface. Ferric chloride is the most commonly used Fe-based chemical used in wastewater treatment to remove P (Caravelli et al., 2010). Ferric chloride has been demonstrated to readily form Fe (hydr)oxide surfaces over a wide range of pH, between 5 and 9, but causes a pH decrease when added to water, due to the production of hydrochloric acid. Therefore, addition to either high carbonate environments or with the simultaneous addition of pH buffers (e.g., sodium bicarbonate) is required to maintain natural pH levels and effective phosphate removal rates (Caravelli et al., 2010). The key reactions are;  $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_{3(s)} + 9\text{Cl}^- + 3\text{H}^+$  and  $2\text{FeCl}_3 + 3\text{Ca}(\text{HCO}_3)_2 \rightarrow 2\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}_{(s)} + 3\text{CaCl}_{2(s)} + 6\text{CO}_2$ .

#### ***Case Study: Ferric chloride addition to lake mesocosms, Nakamun Lake, Canada***

Lake Nakamun is a naturally productive, hypertrophic lake with both residential and agricultural development in the catchment (Orihel et al., 2016). 15 large enclosures were installed in the lake to examine the effects of different concentrations of ferric chloride, made up as a 13.7% solution, on dissolved P.

Ferric chloride both reduced the P load in the water column and effectively prevented P release from the sediment. The lower levels of phosphorous resulted in a lower algae growth. However, at the low application rate of  $<18 \text{ mg} \cdot \text{L}^{-1}$ , there was an increase in algal biomass. The authors attributed this to the treatment acting as a micronutrient in an Fe-poor lake.

The study also showed a suppression of the microcystin toxin produced by cyanobacteria, compared to control conditions. This effect is further discussed in Section 5.6 .

### ***Fe oxide tailings***

Fe (ferric) oxide tailings, a by-product of Fe mining, has been trialled as a potential low-cost phosphate adsorption agent (Zeng et al., 2004). The slurry was dried and applied as a brown fine-grained powder with Fe as the major constituent (33.1 wt%). The oxide absorbed 8.6-4.6 gP.kg<sup>-1</sup> from a 10 gP.kg<sup>-1</sup> test solution. The highest levels of absorption occurred at the lowest pH 3.2, but significant absorption was observed up to pH 9.5. Impurities in the tailings were moderately high, but the experiment showed no significant release of toxic heavy metals to the solution.

### ***Fe-rich microbial mats***

Microbial organisms can produce Fe-rich mats with abundant Fe (hydr)oxide sheaths surrounding microbial cells and in the mucilaginous matrix of a biofilm (Rentz et al., 2009). These mats have demonstrated excellent P removal characteristics. The biogenic nature of the Fe oxides did not affect their removal capabilities, which were similar to other Fe oxide substrates. Wastewater treatment techniques have utilised Fe-oxidising bacteria for ferrous Fe removal, demonstrating that, if needed, they could be produced industrially. This source of Fe oxides could act as a dual action phosphate removal system as the bacteria would remove phosphorous to increase their biomass, as well as provide a substrate for P adsorption onto biogenic Fe (hydr)oxide.

### ***Fe-doped clays***

Bentonite clay doped with ferric Fe ions is a possible alternative to lanthanum-doped (see section 2.2.5). In benchtop experiments, Fe-doped clays were shown to have comparable phosphate absorbing capacity to their lanthanum-doped clay counterparts, but were of less environmental concern (Zamparas et al., 2012). The Fe-doped clays performed well over a wide range of naturally occurring temperatures, pH and salinity levels, with a slight increase in phosphate absorption observed in high salinity environments.

## **2.2.4 Ferrous iron**

### ***Fe sulfate***

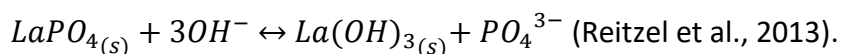
In natural systems, Fe present in a reduced, ferrous oxidation state does not react with, or form a solid to absorb, phosphate ions. It therefore does little to limit P mobility in lake and river systems. Instead phosphate will actually be released if ferric (hydr)oxides or ferric phosphate minerals are reduced under anoxic conditions to form ferrous ions; e.g.,  $Fe(III)PO_{4(s)} + e^- \rightarrow Fe^{2+}_{(aq)} + PO_4^{3-}_{(aq)}$ . Oxidic conditions are therefore usually a requirement for Fe-based sediment amendment.

However, ferrous sulphate is commonly used in wastewater treatment (Caravelli et al., 2010) where oxygen levels can be readily manipulated to oxidise ferrous sulphate to ferric ion, which then forms Fe (hydr)oxide. In natural water systems, this reaction will decrease dissolved oxygen, with obvious adverse effects on biota;  $12FeSO_4 + 3O_2 \rightarrow 4Fe_2(SO_4)_3(s) + 2Fe_2O_3(s)$  (Caravelli et al., 2010). Consequently ferrous sulphate would only be considered for lake remediation if it was the only viable Fe-rich source material, and would need to be used in combination with active aeration or other oxidation of the water column.

### 2.2.5 Lanthanum-doped clay

Phoslock® is a lanthanum-doped bentonite clay developed by CSIRO in Australia for phosphate removal from waterways. It has been extensively used and investigated with around 200 environments treated worldwide (Copetti et al., 2016). Lanthanum (La) is a rare earth metal found naturally in its La<sup>III</sup> oxidation state, and not readily influenced by redox reactions. The lanthanum ions react with phosphate to precipitate a lanthanum phosphate mineral on the clay surface;  $La^{3+} + PO_4^{3-} \rightarrow LaPO_4(s)$ .

The recommended application rate by the manufacturer is 100:1, Phoslock: P by mass (Reitzel et al., 2013). Maximum efficiency in P removal is achieved at pH 5-7, as above pH 7.58 lanthanum starts to form fully hydrolyzed, insoluble lanthanum hydroxide (Haghseresht et al., 2009), with the release of any lanthanum-bound P;



The effectiveness also decreases markedly above pH 9 (Ross et al., 2008), as higher pH levels increase the particle size of Phoslock®, reducing reactive surface area (Ross et al., 2008).

Phoslock® is not classified as a dangerous material or toxic material, based on its low human toxicity hazard rating (SePRO Corporation, 2012). A report on the toxicity of Phoslock® and lanthanum, produced by Phoslock® Water Solutions Limited in 2009, primarily focussed on the risk to human health (Afsar & Groves, 2009). They based their analysis mainly on the effects of lanthanum carbonate (Fosrenol®), used to inactivate phosphate in the treatment of hyperphosphatemia. Reviews of this drug found it to be safe. Therefore, lanthanum concentrations in the water after application, at the rates noted above, would not pose a risk to human health. Lanthanum bio-accumulates in fish, but this occurs primarily in the liver, rather than in the fish flesh. Consequently, exposure to lanthanum via this pathway is also not considered to be a human health risk (Landman & Ling, 2006).

However, lanthanum is a possible ecological/environmental toxin. The Phoslock® Material Safety Data Sheet advises: "DO NOT discharge into sewer or waterways" (SePRO Corporation, 2012). Lanthanum has been reported to adversely affect zooplankton and fish fry in laboratory and field trials, and increased toxicity was observed at lower alkalinity, and lower dissolved organic carbon concentrations (Department of Health, 2014). Lanthanum concentrations shortly after field scale application in water systems were higher than an



estimated ecotoxicological threshold (Copetti et al., 2016). Although there seem to be no published reports of long-term ecotoxic effects as a result of lanthanum treatment of a natural waterway, the potential for bioaccumulation of lanthanum in the aquatic food web justifies a level of concern and the need for future investigation (Copetti et al., 2016).

Lanthanum is more readily released from the bentonite clay matrix under saline conditions (Douglas et al., 2000 as cited in Copetti et al., 2016). In a personal communication, Douglas advised that “The results of this experimentation indicated that the application of the LMB [lanthanum modified bentonite] in even moderately saline environments (>0.5‰ salinity) is to be avoided”.

Many naturally occurring chemicals in the water have been shown to adversely affect the binding capacity of Phoslock®. Humic acids appear to react with lanthanum reducing the amount available to bond with phosphate (Lüring et al., 2014). Experiments showed an increased concentration of dissolved free lanthanum ions in solutions that contained high humic concentrations. Phoslock® binding efficiency has also been shown to be reduced in the presence of oxyanions such as carbonate (Reitzel et al., 2013). Carbonate ions can also bind to the lanthanum, reducing its phosphate binding capacity. P binding is also reduced by high calcium concentrations (Reitzel et al., 2013) which causes clays to flocculate by changing their surface charge, reducing the reaction surface for the lanthanum.

**A Review: 18 lakes treated with Phoslock®**

A systematic review of the effect of Phoslock® on 18 lakes throughout Europe and Canada treated with Phoslock® was compiled by Spears et al. (2016). Overall Phoslock® use reduced total P, soluble reactive P and chlorophyll *a*, and increased Secchi disk depth (indicating increased water clarity).

The dosage rates for the lakes varied between 1.6 and 6.8 tonnes ha<sup>-1</sup> with no significant positive correlation between decreased P concentration and dosage rates. There was a correlation with dissolved organic carbon in the lake; higher dissolved organic carbon concentrations reduced P removal, consistent with previous laboratory experiments (Lüring et al., 2014).

The review also showed an increased quantity and growing depth of macrophyte species after Phoslock® treatment, for the sites with data available.

**Case Study: Effect of Phoslock® Application on Lake Okareka, New Zealand**

Environment Bay of Plenty applied Phoslock® to the surface of Lake Okareka on three occasions between August 2005 and March 2007 (McIntosh, 2007). There was a significant decrease in P leaching from the sediments for at least six months after application. Phoslock® had no effect on the pH of lake waters which was generally between 6.5 and 8. However, dissolved oxygen levels in the hypolimnion improved during the three-year monitoring program, with shorter and later periods of anoxia each year compared to pre-application. There was no significant decrease in dissolved P levels in the lake as a direct result of the

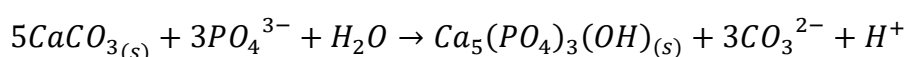
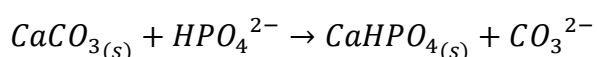
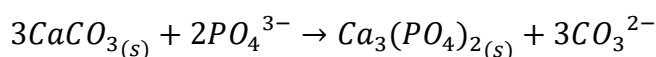
Phoslock, likely because concentrations of P in the lake were more strongly influenced by rainfall events and sewage flows than sediment leaching.

Lanthanum concentrations in the lake were highest just after application, at 0.1g/m<sup>3</sup>, but reduced over 2-3 months. Within 5 months of use, the lanthanum concentrations had returned to pre-treatment levels. There was no significant effect on fish health as a result of the Phoslock® application during the 2006 monitoring period (Landman & Ling, 2006).

## 2.2.6 Calcium

*Calcite (limestone, SoCal®, EScal®, calcium hydroxide)*

In natural systems, phosphate can be regulated by calcium carbonate in sediments, particularly in high alkalinity and hard water lakes. Under these conditions, calcium and phosphate form a range of calcium phosphate precipitates (Lopez & Morgui, 1992), depending on salinity and pH, e.g.;



Calcium carbonate can be added directly or precipitated *in situ* by the reaction between calcium hydroxide and dissolved carbon dioxide gas. The fresh precipitate will remove organic P and suspended sediments from the water column as it flocculates and settles. It has been proposed that carbon dioxide could be artificially pumped into a lake to ensure flocculation in low carbon dioxide environments;  $\text{Ca}(\text{OH})_2(s) + \text{CO}_{2(g)} \rightarrow \text{CaCO}_{3(s)} + \text{H}_2\text{O}$  (Hart et al., 2003).

Various products exist for direct calcium carbonate application including natural crushed limestone and other calcium carbonate derivatives. Structurally altered derivatives such as SoCal® and EScal® that have been dissolved and recrystallized to increase their surface area and phosphate removal capacity, are available but are more expensive.

The performance of crushed limestone and the derivatives, SoCal® and EScal®, have been compared under laboratory conditions, using sediment cores were taken from Lake Carramar in Victoria, Australia (Hart et al., 2003). An active barrier of calcium carbonate was applied to the surface, and the level of P release was measured and compared to that of a sand layer. A 2% SoCal®, 98% sand layer was shown to reduce P flux from the sediment to <1% of the control's P flux. 2% EScal® in 98% sand was not as effective but still reduced P release to <7% of the control's P flux. The crushed limestone product was ineffective at reducing P release, suggesting that a high surface area greatly enhances the reactivity of the amendment; SoCal® had the smallest particle size and the highest surface area.

Calcium carbonate is strongly alkaline, so when it dissolves in waterways will cause pH to increase;  $H_2O + CaCO_{3(s)} \rightarrow CO_{2(g)} + 2OH^- + Ca^{2+}$ .

**Case Study: Calcium carbonate application to stormwater lakes in Edmonton, Alberta**

Calcium hydroxide and calcium carbonate treatments were applied to three stormwater lakes in the City of Edmonton, Alberta, Canada (Babin et al., 1989). A fourth control lake on the other side of the city did not receive treatment.

When only calcium carbonate was applied, there was no significant change in either total P or chlorophyll *a*. However, at application rates at 50mg/L or more, calcium hydroxide significantly decreased P in all three lakes. Chlorophyll *a* usually decreased but increased at two of the eight trial sites, possibly due to seeding of algae from another pond. Notably the pH and calcium concentrations increased after each treatment.

**Case Study: Calcium hydroxide application in Frisken Lake in British Columbia, Canada**

One tonne ha<sup>-1</sup> of calcium hydroxide was applied as a slurry to Frisken Lake, an 11m deep, 33.8 ha lake rich in apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,Cl,OH)) (Murphy et al., 1988). The application consisted of 4 treatments between June 1983 and May 1984.

Flocculation and sedimentation of algae occurred as a result of the treatment, with 85-95% of the chlorophyll *a* removed from the epilimnion, increasing clarity in the water column. There was a long-term reduction in algae biomass. P bound to the calcium and precipitated in the epilimnion, but dissolved P concentrations in the water column remained high. More than 95% of bound P had redissolved within a year and dissolved P concentrations were again similar to those pre-treatment.

The results of the 1984 application, which was the largest at 16.0 tonnes, were the best documented. There was a drop in the dissolved reactive P post application, primarily in the shallowest lake waters. There was also a sharp increase in the pH, especially in the top 5m of the lake, from 8.2 to 9 which lasted two weeks.

There were no apparent adverse effects on the ecosystem from the three smaller treatments in 1983. However, during the higher dose treatment in 1984, chlorophyll *a* concentration dropped by 20µg L<sup>-1</sup> in 24 hours. Bacteria feeding on the decaying algae doubled in concentrations 18 days after treatment. Zooplankton and macroinvertebrates showed a range of responses; *Daphnia pulex* and *Keratella quadrata* populations growing rapidly up to 18 days after application, while *Polyarthra* and *Keratella cochlearis* populations decreased to <10% of the pre-treatment populations over the same time-period.

### 2.2.7 A Comparison of four P-inactivation agents in Lake Rotorua

Gibbs et al. (2008) compared the effectiveness of alum, modified zeolite, Phoslock® and allophane in a simulated Rotorua lake system. The study used a continuous flow incubator to

determine the effect of active capping materials, in a vessel containing lake sediment. Lake water was pumped over the sample under both aerobic and anoxic conditions. Each agent was initially applied at a rate predicted to be sufficient to bind all available P from the top 4cm of sediment, and then repeated at half and double this concentration.

The initial application rate resulted in complete control of P for all treatments except zeolite, possibly due to incomplete coverage of the sediment as a consequence of the larger particle size of the zeolite. In all cases, the P-binding capacities were significantly different from those given by the supplier; alum, modified zeolite and Phoslock® were only half as effective at removing P as expected, and allophane was around three times more effective. The authors attributed this to the effects of sedimentation.

All four P capping methods were predicted to remain effective for at least three years. However, alum and Phoslock® both reduced nitrification in the system, resulting in a 500% increase in the ammonia concentrations. Zeolite caused less ammonia production, while allophane had no effect on ammonia concentrations. The authors recommended that all four treatments be used only in aerobic sediments.

Due to the low density of alum floc, it was easily disturbed and this promoted nutrient re-release. Phoslock® persistently released potentially toxic lanthanum at rates that could bioaccumulate in culturally valuable species such as trout.

### 2.2.8 Summary information for active capping agents

**Table 5.** A summary of the main advantages and disadvantages of active capping agents capable of reducing P concentrations in the water column. Note that the possibility of benthic smothering is common to all active (and physical) capping methods.

		Commercial products	Advantages	Disadvantages
Aluminium	Alum	US\$200/tonne	History of use in waste and water treatment systems Improved clarity of water column Assimilates into sediment Not affected by salinity Active over a wide range of pH Effective under anoxic conditions	Ecotoxic effects if free Al ion released Acidifies water column if not buffered Requires moderately hard water to flocculate Can result in higher levels of dissolved P due to algal dieback Less effective in the presence of organic acids and some ions Reversible binding reaction Light weight floc so easily disturbed May increase ammonia
	(Poly)Al chlorohydrate		As above	As above but does not acidify water column
	Al (Hydr)oxide	Allophane	As above	As above but does not acidify water column
Iron	Ferric Chloride		History of use in waste and water treatment systems Low environmental toxicity Assimilates into sediment Active at near-neutral pH May assist in degradation of cyanobacterial toxins	Acidifies water column in carbonate-poor environments Reversible binding reaction May be less effective in saline conditions Ineffective under strongly acidic, or alkaline conditions Ineffective under anoxic conditions
	Ferric (Hydr)oxide		As above	As above but does not acidify water column
	Ferrous Sulphate		As above	As above, and also reduces dissolve oxygen levels in water column

Lanthanum	Lanthanum	Phoslock®	History of use in water treatment No human health impacts	Possible La bioaccumulation and ecotoxicity Not recommended for use in saline environments Less effective in presence of humic acid or oxyanions Less effective in high Ca (e.g., hard waters) Ineffective at pH > 9 May increase ammonia
Calcium	Calcium Carbonate	Crushed limestone SoCal®(US\$3800/tonne) ESCal®(US\$2000/tonne)	Low environmental toxicity	Requires hard water Increase in pH of water column Reversible binding (P released at low pH)
	Calcium Hydroxide		Low environmental toxicity Relative inexpensive	Requires hard water Requires high levels of dissolved carbon dioxide to ensure sedimentation Significant increase in pH during application Reversible binding under low pH conditions
Modified Zeolite & Pumice		Aqual-P® (Z2G1)	Highly doseable (e.g., with Al) while preventing toxic Al-release May also bind nitrate and ammonium	Performance not well studied in lakes

## Section 3 Sediment or Water Removal

### 3.1 Dredging

Dredging has been used as a lake restoration technique, removing the legacy of contaminated sediment from the lakebed. Dredging reduces the internal loading of nutrients by removing the P-rich upper sediment layer. This process has been successfully trailed on peat lakes sediments in the Netherlands (Van der Does et al., 1992). It has also been successfully used in Sweden, with lakes showing reduced cyanobacteria biomass in the years following sediment removal (Cronberg 1982, as cited in Lüring & Faassen, 2012).

**Table 6:** Van der Does et al. (1992) suggests the following criteria to assess whether a peat-rich lake is suitable for dredging.

Characteristic	Criteria
<b>External P-loading</b>	Low relative to internal loading
<b>P-Lake</b>	$>0.08 \text{ mg P L}^{-1}$
<b>TP- Upper sediment</b>	$>0.08 \text{ mg P g}^{-1}$
<b>Bio-available P in upper sediment</b>	$>25\%$
<b>P release rate in upper sediment</b>	$>2.5 \text{ mg P m}^{-2} \text{ day}^{-1}$
<b>TP Lower layer</b>	$<0.70 \text{ mg P g}^{-1}$
<b>Bio-available P in lower sediment</b>	$<20\%$

Dredging works best when reductions in external P (& sediment) loading have not resulted in a proportional decrease in total P in the lake (Table 6, Van der Does et al., 1992), indicating that internal P loading is a major contributor to the lake P. Ideally dredging targets P-rich sediment, while retaining the deeper nutrient-poor sediment layer that can evolve into a new benthic layer. The effects of improper sediment selection are evident in a series of laboratory experiments by Reddy et al. (2007). In these experiments, a 30cm deep simulated dredge event significantly reduced internal loading, reducing equilibrium P concentrations from 0.033 to 0.008  $\text{mg.L}^{-1}$  after 1.2 years. However, when the top 55cm was dredged a thick P-rich peat layer was exposed, and the P leaching rate increased. Overlying water P concentrations were as high as 0.037  $\text{mg.L}^{-1}$ , higher than control conditions.

**Case Study: Phoslock® and Dredging in De Ploeg, Netherlands**

A small urban pond in De Ploeg in Heesch, Netherlands, was subjected to a dredging and Phoslock remediation experiment (Lürting & Faassen, 2012). Multiple cylinders were driven into the lake bottom and either dredged or treated with Phoslock®, or both, in triplicate and with three controls. An excavator was used to remove the top 30cm of sediment, then some of the mesocosms were treated with 312.5g of Phoslock®; enough to bind the P in the water column and the top 5cm of sediment.

The combination of dredging and Phoslock® consistently reduced soluble reactive P, total P, total N, chlorophyll *a* and microcystin toxin concentrations relative to the control ponds. Treatments involving only dredging may have reduced P but the results were somewhat inconclusive. Notably the controls did deviate from typical lake conditions, developing low oxygen conditions which increased P release.

### **3.2 Flushing or draining the lake**

If not occurring naturally with high flow events, manual flushing of a lake with clean water can potentially dilute P concentrations, remove algal biomass and, if extreme flows are available, physically remove P-rich surface bed sediments (Hosper & Meyer, 1986; Jagtman et al., 1992).

Draining water from a lake can also be used to mobilise nutrients and remove contaminated water and sediments. However, low lake levels can also lead to increased water temperature, unintended backflow from a connected waterway, such as an estuary, and increased turbidity (Wairewa Rūnanga Incorporated & Christchurch City Council, 2013). Increased temperature can affect algae speciation and biomass. An analysis of 143 lakes in Europe and South America showed that warmer climates did not result in higher overall phytoplankton biomass but did increase the proportion of cyanobacteria (Kosten et al., 2012). In coastal lakes, backflow can result in increased levels of salinity (refer Section 4.3 ). Increasing turbidity in the water will decrease the light availability for all benthic and phyto organisms (Dzialowski et al., 2011).

In Wairewa, the history of manually opening the lake to the sea and the drainage and flushing that this causes, may be able to provide useful evidence of whether this type of action could improve water quality (in the absence of backflow, refer Section 4.3).



## Section 4 Manipulating Water Conditions to Reduce P Release

### 4.1 Increasing Aeration

P is more readily released from sediment under anoxic environmental conditions (Mortimer, 1941) as anoxic conditions create reducing environments ( $Eh < -250\text{mV}$ ) in hypolimnetic water and in sediment (Boyd, 2000). Wairewa sediments and basal waters are periodically anoxic (Waters, 2016) and this results in a significant increase in P release from the sediments. More persistent anoxic conditions occur in stratified, deep lakes where the water does not circulate for at least part of the year.

Lake water can be oxygenated by pumping atmospheric air or pure oxygen into the hypolimnion. This serves to both mix the lake water column and to oxygenate it (Gächter & Wehrli, 1998). Mixing of the water column enables water from the bottom of the lake to move to the surface, and be exposed to the atmosphere. Alternatively, pumping pure oxygen into the lake as microbubbles, oxygenates without mixing the water column, allowing stratification to be maintained. Stratification prevents nutrient transfer from the bottom of the lake, to the surface where it can be consumed by surface algae.

Due to the cost of the initial setup and operation, aeration is predominantly used in small lakes, where the least amount of piping needs to be installed.

#### ***Case Study: 10 years of mixing and oxygenation in two lakes in Switzerland***

Aeration and mixing were used continuously for ten years in Lake Baldegg (5.2 km<sup>2</sup>, 66m deep) and Sempach (14.5 km<sup>2</sup>, 87m deep) in Switzerland (Gächter & Wehrli, 1998). The lakes were mixed using pressurised air during winter, and microbubbles of pure oxygen during summer to prevent nutrient transfer into the epilimnion, thus preventing eutrophication of the surface water.

Dissolved oxygen levels in both lakes increased significantly during aeration. Lake Sempach rarely dropped below 4mg L<sup>-1</sup> dissolved oxygen at the bottom of the lake during the full ten-year study period. Lake Baldegg was not as aerated during summer, but oxygen levels were significantly improved, with several years of fully oxic conditions in the water column.

However, increased oxygenation did not increase sedimentation rates of P in the lakes or reduce P release from the sediment. P continued to leach from the deeper layers of sediment that remained anoxic and reducing. Gächter and Wehrli (1998) concluded that oxygenation had little to no effect on the trophic state of a lake.

### 4.2 pH Manipulation

Waters (2016) showed a significant increase in P release from the sediment in Wairewa at pH >8.6; conditions which are frequently present as a result of photosynthesis during the summer months. Similar results have been demonstrated for other lake systems (e.g., Koski-Vähälä et al., 2001). Consequently, maintaining a near-neutral pH may be beneficial for reducing P release and therefore reducing algal biomass.

Leavitt et al. (1999) described pH manipulation in lake systems using HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, concluding that algal abundance did not decline until lake conditions were below pH 4.5, conditions unlikely to support lake ecosystems or other values. Also, because biologically active lakes are able to buffer pH, any manipulation of pH is likely to be short term. Case studies demonstrating the effects of biological buffering in highly productive lakes include Murphy et al. (1988) and van Hullebusch et al. (2002).

### **4.3 Salinity Management**

The periodic opening of Wairewa to the ocean creates a salinity gradient along the lake, with the most saline water at the southern end (Waters, 2016). Increased salinity correlated with increased dissolved P, and decreased dissolved Fe, in the sediment pore-waters. Waters (2016) attributed this to the increased sulphate concentrations in more saline waters, which forms hydrogen sulphide when reduced. Fe reacts with hydrogen sulphide to form Fe sulphide (e.g., pyrite), and this does not adsorb or otherwise bind P. Increased salinity can also promote stratification, and associated low dissolved oxygen in basal lake waters, as fresh and sea-water influxes both induce salinity stratification. Increased salinity correlated with winter cyanobacterial blooms, with salinity accounting for 60% of the variability of chlorophyll *a* concentration (Waters, 2016). Some of the P released from sediment in more saline conditions may also be a result of sulphate out-competing phosphate ion for adsorption sites on the sediment (Gardolinski et al., 2004).

Salinity has been shown to have a broad range of effects on freshwater ecosystems (Nielsen et al., 2003). Freshwater algae, aquatic plants and macroinvertebrates, are intolerant of salinity above 1‰, while some types of cyanobacteria do tolerate higher salinity conditions (Paerl et al., 2001) and can thrive in an environment with lower competition for nutrients. Increased salinity has been shown to have an adverse impact on zooplankton diversity and abundance in New Zealand, with species richness at a minimum at 5-7 ‰ salinity (Hall & Burns, 2003), less than the salinity maxima recorded in Wairewa.

Consequently, maintaining a low salinity in a coastal lake such as Wairewa would help reduce P release from sediments, and the abundance of cyanobacteria in the algal blooms.

## Section 5 Discussion: Other options for lake management

Although the focus of this literature review has been on ways to prevent the release of P from existing lake sediments, there are a number of other actions that could be taken in the lake and in the wider catchment to reduce P input to the lake and to manage the effect of P bioavailability in the lake water.

### 5.1 Soil Stabilisation

Most P input to lake systems occurs via surface runoff during rainfall events, in which P is transported, at least partially, on suspended sediments (Ruttenberg, 2003). Globally, this input has been increased through the use of P fertilisers on agricultural land, particularly during the latter half of the 20<sup>th</sup> century. Forest clearing and agricultural development also increased the erosion of soils over this time.

Preventing P bound to soils from entering waterways is difficult, as it is diffuse source and a storm-related phenomenon. However, source control may include the addition of soil stabilising polymers (Lentz et al., 1998), conservative tilling of agricultural land and the use of riparian planting to preventing soil from entering waterways. Excluding livestock from waterways will also help to prevent bank erosion (Prepas, 2003).

### 5.2 Wetlands on Lake Tributaries

Wetlands on tributaries can reduce external P loading to lakes, by filtering and settling out the suspended sediment, promoting phosphate uptake into wetland plants and providing fine sediment surfaces that facilitate adsorption processes. Recycling lake water through a natural or constructed wetland system has been trialled (e.g., Coveney et al. 2002). Nutrient-rich wetlands are biodiversity-rich habitats (Hansson et al., 2005), but it is often difficult to find enough space in a developed catchment to create an effective wetland. The use of “floating wetlands” on the lake surface is an idea which has been put forward to help address this issue, but there appears to be little published literature on their use. Notably, natural wetlands can perform poorly during high flow events, which is when most of the sediment and P is transported into a lake.

***Case study: Construction of external artificial wetland for Lake Apopka, Florida, USA.***

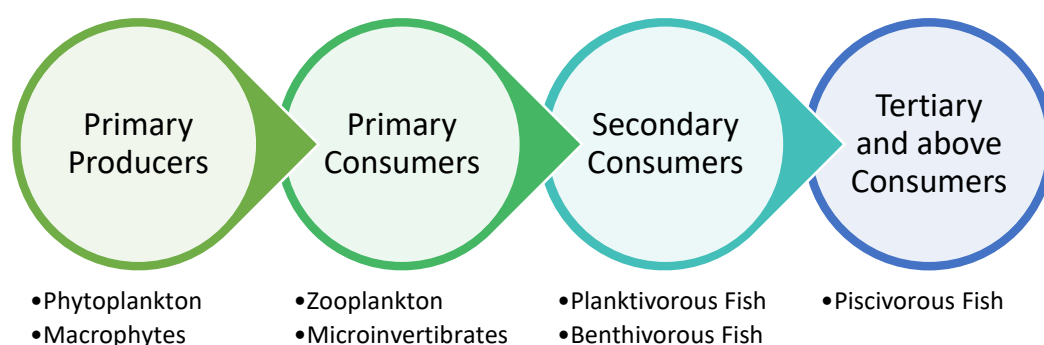
A 2km<sup>2</sup> artificial wetland was constructed next to Lake Apopka in Florida, USA (Coveney et al., 2002). Water was pumped out of the lake into the treatment area before slowly returning to the lake through a series of channels. This wetland project was undertaken in conjunction with other remediation programs including farm nutrient management plans and removal of fish.

The naturally regenerated wetland consisted of two cells with a combined area of 213ha. The first 73 ha cell removed 350kg.yr<sup>-1</sup> of P during the 10-month study period. This first cell deposited >90% of suspended solid, which accounted for most of the P removed. The authors suggested that the system could have supported twice this P removal, by increasing the flow of water. Long term use increased the efficiency of the system; Whereas there had been a significant release of P from the wetland during its first high rainfall inundation, this type of release had almost ceased after the first year. The estimated maximum P removal rate was 3 g.m<sup>-2</sup>.yr<sup>-1</sup>, for a total of 2180 kg.yr<sup>-1</sup>. The wetland construction cost approximately US\$1million.

### 5.3 Biomanipulation

Biomanipulation can be used to deliberately alter the species in an existing ecosystem to improve ecosystem quality. Two methods for reducing algal abundance are increasing the abundance of algae-consuming organisms, and creating more competition for resources such as nutrients.

This management approach needs to take two competing ecological hypotheses in account; “trophic cascade” and “bottom up: top down”. The trophic cascade hypothesis is that a change in predator (consumer) biomass will result in a change of biomass down the food web, right down to the primary producers (Carpenter et al., 1985). The competing hypothesis is that top-down effects of grazing and predation are not as powerful as bottom-up effects of resource abundance (McQueen et al., 1986). Both models have been shown to work in different whole lake environment (Reynolds, 1994, as cited in Benndorf et al., 2002). Benndorf et al. (2002) concluded that bottom-up interactions dominated shallow lakes with a mean depth <3 meters. The strongest influence on primary producers is therefore nutrient abundance, although primary producers may still be influenced by top-down effects, especially in environments where macrophytes were present.



**Figure 8:** A simplified food chain in a typical lake environment. Changes in biomass in one layer will affect the biomass of layers directly above and below.

### 5.3.1 Modifying predator/consumer populations

#### ***Fish removal***

A reduction in planktivorous fish should result in a rise in zooplankton, which would increase pressure on phytoplankton (Perrow et al., 1997). Notably planktivorous fish cannot consume cyanobacteria, so may not be present in a lake dominated by this type of algae (Hosper & Meijer, 1993).

A reduction in benthivorous fish should reduce the degree to which bed sediment is resuspended as they forage, thereby reducing the release of nutrients (Perrow et al., 1997). Several factors can affect the success of this type of bioremediation. For example, if the removal of algae produces a more transparent water column, the resulting increase in macrophyte biomass will ensure long-term effectiveness. However, if it does not, because the turbidity is mainly due to suspended sediment, there may be no change in macrophyte abundance (Hosper & Meijer, 1993).

Removal of particular species can be achieved by targeted fishing, perhaps supplemented with stocking piscivorous fish. A removal rate of >75% is required for significant beneficial effects (Meijer et al., 1999; Perrow et al., 1997) and large fish catches over a short period improve cost effectiveness and chances of success. The timing of the fish removal is also important, in order to prevent spawning replenishment. It is usually best achieved in winter, which is also when fish may be less active and more abundant.

#### ***A Review: Biomanipulation of fish in 18 lakes in the Netherlands***

Biomanipulation has been practised in the Netherlands since 1986. Hosper and Meijer (1993) composed a questionnaire to determine the likelihood of biomanipulation success, based on their experiences in the Netherlands. The effectiveness of biomanipulation in 18 lakes has been assessed, and the factors contributing to success identified (Meijer et al., 1999).

In all successful biomanipulations, the algae dropped to very low levels and this led to a dramatic increase in macrophyte abundance. This success was achieved, in most cases, by a 75% reduction in target fish species. Successfully manipulated lakes retained significantly better clarity for up to 9 years. Fish biomass remained low in most cases with most lakes stabilising at half of the pre-manipulation biomass.

### 5.3.2 Creating competition for resources

Nutrient availability primarily drives algae biomass. Cyanobacteria is well placed to compete successfully, given the ability of some species to fix N from the atmosphere. Biomanipulation to create competition for macronutrients can be achieved by adding supplements to encourage more desirable species to grow.

## ***Diatoms***

### ***(Diatomix)***

Diatoms are a type of phytoplankton that has a silica cell wall. Silica availability is often the limiting factor for these plankton species, and a ratio of <4:1 for N:Si was found to cause changes in phytoplankton assemblages in laboratory environments (Gilpin et al., 2004). Diatomix by AlgaEnviro is a 100-900nm nanoparticle silica suspension, which also contains micronutrients to promote diatom growth (AlgaEnviro, 2017).

## ***Archaea***

### ***(The Water Cleanser)***

Archaea are a type of microorganisms, distinct from Bacteria and Eukaryota organisms. Although this domain is commonly defined by its extremophiles, they are present in a wide range of environments (DeLong, 1998) and can compete effectively with cyanobacteria if they have the right nutrients. “The Water Cleanser” is a system of paraffin wax blocks containing a semi-soluble component of 5-20% w/w diesel engine oil, paraffin oil or crude paraffin oil in a paraffin wax matrix (Morgan, 2007). This product seeks to promote archaea growth in lakes, by adding oils that are inedible to most other organisms.

## ***Macrophyte Management***

Harvesting macrophyte beds may reduce the internal load of P released from decaying organic material, as well as preventing the stratification and pH elevation noted in the macrophyte beds in Wairewa (Waters, 2016). Harvested material could be valuable as a fertiliser or animal feed, given its high nutrient value. The sale of the harvest could offset some of the costs associated with macrophyte management (Quilliam et al., 2015). However, this type of intervention may also disrupt the macrophyte/algae balance, as they compete for the same nutrients.

To extract the most nutrient from the lake in a harvest, timing will be important. In a study of Lake Wingra, Wisconsin, seasonal differences in nutrient content of the macrophytes and its biomass were found to be substantial (Carpenter & Adams, 1977). The possible harvestable value doubled from 300 to 600kg P in just one month, due to variations in biomass and nutrient concentrations in the plant matter. Nitrogen and potassium concentrations in the plants continued to increase throughout the growing season, whereas P decreased rapidly at the end of the season.

### ***Case Study: Macrophyte harvesting and algae in Lake Mendota, Madison, United States***

An experiment was conducted in Lake Mendota in Madison, USA, to determine the relationship between algae biomass and macrophyte harvesting (Nichols, 1973). There was no significant correlation between algae biomass and macrophyte harvesting during the first year. However, there was an increase in algae biomass in harvested areas in the second year.

A deeper treatment site had a weaker relationship, but the reduction in macrophytes led to a decrease in algae.

## 5.4 Algaecide

### 5.4.1 Copper-based algaecides

*Copper Sulphate, Clearigate<sup>®</sup>, Cutrine-Plus<sup>®</sup>*

Copper-based compounds are the most used algaecide, with the most common being copper sulphate (Jančula & Maršálek, 2011). Copper sulphate is very cheap and has been used since 1904 to control algae blooms. Clearigate<sup>®</sup>, Cutrine-Plus<sup>®</sup> are both copper-ethanolamine complexes that release dissolved free copper ion in water (Murray-Gulde et al., 2002).

Dissolved free copper<sup>II</sup> is toxic to algae, as it interferes with membrane proteins and/or enters cells where it substitutes for magnesium in the chlorophyll heme (De Schamphelaere & Janssen, 2006; Jančula & Maršálek, 2011). Water hardness or dissolved organic carbon does not significantly change the toxicity of copper to algae, but high pH caused increased toxicity to four different algal species in laboratory experiments (De Schamphelaere & Janssen, 2006). Toxicity is also inversely related to algal cell density, with exponentially higher application rates required to control higher concentrations of algae biomass (Murray-Gulde et al., 2002).

Copper is very toxic to non-invertebrates and fish species, with adverse effects reported at the concentrations required to control algae (Murray-Gulde et al., 2002). Copper sulphate application has also been linked to human health problems. For example, an epidemic of hepatitis-like symptoms occurred in Palm Island, Australia, during 1979 which may have been related to copper treatment of drinking water (Prociv, 2004). Chelated copper compounds were shown to have the highest margin of safety for non-target species.

Copper needs to be repeatedly applied due to its rapid removal by ecosystems and sedimentation (Table 7, Haughey et al., 2000; Murray-Gulde et al., 2002). Copper has been observed precipitating rapidly immediately after the application of copper sulphate, only to later be re-released from the sediment (Haughey et al., 2000). There have been instances of this kind of treatment regime leading to toxicity resistance in algae communities, under laboratory conditions (García-Villada et al., 2004).

**Table 7:** Half-life of effective copper application (in days) for algae under laboratory conditions (Murray-Gulde et al., 2002).

	Low hardness Low alkalinity	Moderate hardness Low alkalinity	High hardness High alkalinity
Copper sulphate	3.5	Approx. 3	2.6 < x < 4.4
Clearigate <sup>®</sup>	5.5	Approx. 3	2.6
Cutrine-Plus <sup>®</sup>	5.7	Approx. 3	4.4

**Case Study: Copper sulphate treatment of Lake Cazenovia, New York, USA**

A study was conducted into the low-level application of copper sulphate in a regularly treated, hard water, alkaline lake - Lake Cazenovia, New York (Effler et al., 1980). Three treatments of 455kg of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , applied as a 10% solution, were undertaken approximately a month apart between July to September 1977. Detectable levels of dissolved copper ( $>2\mu\text{g} \cdot \text{L}^{-1}$ ) were observed for 2-5 days. There was a small but detectable decrease in chlorophyll *a* after each treatment, but these recovered to pre-treatment levels in less than a week. There was also a change in phytoplankton communities with cyanobacteria, particularly *Anabaena flos-aquae*, dominating after application.

At these low-level applications, few effects on non-target species such as zooplankton or macrophytes were observed. However, water-borne bacteria abundance decreased immediately after each treatment.

#### 5.4.2 Photosensitizers

*Hydrogen peroxide, Phthalocyanines, titanium dioxide*

Photosensitizers are a class of compounds that create reactive oxidising chemicals under ultraviolet light, and include hydrogen peroxide, e.g.,  $\text{H}_2\text{O}_2 \rightarrow 2 \cdot\text{OH}$ . These oxidising species undergo a range of destructive reactions with organic molecules, so are toxic to bacteria, fungi and plant cells (Jančula & Maršálek, 2011). The major advantage of these compounds is that they are highly biodegradable. They have also been shown to react with microcystin toxins removing them from the waterways after the cyanobacteria have been destroyed (Matthijs et al., 2012).

**Case Study: Application of Hydrogen Peroxide to Lake Koetshuis, the Netherlands**

A whole lake treatment using hydrogen peroxide at a rate of  $2\text{mg L}^{-1}$  in Lake Koetshuis, in the Netherlands, was undertaken to control cyanobacteria (Matthijs et al., 2012). Laboratory experiments determined the rate of application as the minimum concentration required to remove cyanobacteria, while not harming zooplankton. After application the levels of hydrogen peroxide dropped from  $2\text{mg L}^{-1}$  to  $0.7\text{mg L}^{-1}$  after 24 hrs, and were below detection after two days.

There was an immediate decrease in cyanobacteria, with a 18-30% reduction within 3 hours and a 99% reduction within 10 days. Cyanobacterial biomass remained low for 7 weeks after treatment, only increasing after 7 weeks due to an infusion of water from another lake with the same species of cyanobacteria. Green algae and zooplankton species were not significantly affected by hydrogen peroxide addition.

Applications were repeated in the following two years with similar results.



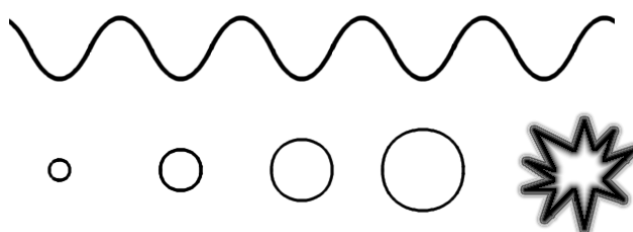
### 5.4.3 Herbicides

*Diuron*®, *Endothal*®, *Atrazine*®, *Simazine*® (etc)

Organic herbicides can be used for controlling algal biomass via a range of actions including photosynthesis disruption (e.g., *Diuron*®) (Jančula & Maršálek, 2011). Many organic herbicides have low biodegradability and can accumulate in the environment. Herbicides such as *Diuron* and *Endothal* are nonspecific and are toxic to macrophytes, fish and zooplankton as well as algae (Jančula & Maršálek, 2011). Resistance to repeated treatments also has been shown in various studies. A 90% increase in detectable microcystin toxins was reported after application of a Paraquat herbicide to kill cyanobacteria (Ross et al., 2006).

## 5.5 Ultrasonic Systems

Ultrasonic systems are the latest technology to be considered for cyanobacteria control. This approach has been seriously investigated since 2000, but its effectiveness at a lake scale is still a matter of debate (Rajasekhar et al., 2012b). Sonication of water bodies causes a series of high and low-pressure cycles, generating cavitation bubbles which create a temperature spike, as well as a pressure wave, when they collapse. Ultrasonic systems emit a frequency above 20kHz which can lead to structural and functional disruption of cyanobacterial cells due to the disruption of gas vacuoles, photosynthetic centres, and cell walls/membranes (Rajasekhar et al., 2012b).



**Figure 9:** Bubble formation and expansion during the relaxation of the pressure waves. Large bubbles implode generating locally high temperatures and pressures, in the range of 5000°C and 500 bar.

Cyanobacteria often contain a structure called a gas vacuole, which gives the algae the buoyancy to stay near the lake surface and absorb light. Ultrasound can collapse these structures, causing the algae to sink to a depth at which they are unable to get enough light to photosynthesize (Lee et al., 2001). However, gas vacuoles have been shown to rapidly regenerate under laboratory conditions, with full recovery within 24 hours (Lee et al., 2000).

Sonication can also lead to disruption of the photosynthetic centres of algae. This is a species-specific response that changes depending on the relative abundance of phycocyanin and chlorophyll *a* and associated structures (Lee et al., 2001; Tang et al., 2003). Unlike the experiments that caused vacuole damage, the colonies that showed signs of impacted photosynthetic centres did not return to normal levels again after the 7 day experimental

period (Tang et al., 2003). There is also some evidence that cell walls and membranes may be damaged by the free radicals produced by sonication (Rajasekhar et al., 2012b). However, this effect appears to be small (Zhang et al., 2006).

The effectiveness of sonication is very dependent on its power and frequency, and currently there is no recommended combination (Rajasekhar et al., 2012b). Lower frequencies are preferred as they require lower energy consumption and create more intense cavitation events. However, a review of studies indicates a better effectiveness at higher frequencies (Rajasekhar et al., 2012b) when resonance peaks are able to be produced closer to the vulnerable gas vacuoles. However, higher intensities may lead to the release of toxic compounds from damaged cells (Zhang et al., 2006). At very high frequencies this effect may be reversed, as microcystin toxins have been shown to be degraded through sonochemical reactions (Ma et al., 2005). Ideally, the perfect combination of power and frequency would result in gas vacuole collapse, damage to the external cell structure (without releasing toxins) and photosynthesis inhibition, while remaining energy efficient.

Sonication has been shown to be highly selective, removing only those species with gas vacuoles. This selectivity was observed between *M. aeruginosa* (with gas vacuole) and *Synechococcus* PCC 7942 (without gas vacuole) when tested by Tang et al. (2004). *M. aeruginosa* exhibited the associated drop in cell viability, as shown in other studies investigating vacuole collapse, whereas there was no change in the concentration of *Synechococcus*. Another study also demonstrated this selectivity, comparing the sonication effects on *M. aeruginosa* and *A. circinalis*, both with gas vacuoles, compared to green algae *Chlorella sp* without gas vacuoles (Rajasekhar et al., 2012a). Again, both the cyanobacteria showed significant growth inhibition, compared to the green algae. A possible correlation between the filamentous nature and susceptibility to sonication was also identified (Purcell, 2009; Rajasekhar et al., 2012a).

## 5.6 Iron oxides to regulate microcystin

There is evidence of a link between Fe abundance and the production of microcystin toxins by cyanobacteria (Orihel et al., 2016). There appears to be a small but significant increase in the levels of microcystin-LR in Fe-deprived cultures, when compared to the controls (Sevilla et al., 2008). This conclusion is not consistent for *all* model strains used in benchtop experiments, but some certainly show that greater Fe availability reduces microcystin production (Alexova et al., 2011; H. Li et al., 2009).

Fe may also be involved in the decomposition of microcystins, as Fe chloride has been shown to rapidly detoxify both microcystin-RR and -LR, with a 50% decrease in concentration within 10 minutes and full removal in 16 hours (Takenaka & Tanaka, 1995). This finding has been repeated at a range of pH values.

## **Section 6 Recommendations for further investigation**

The purpose of this report was to review the literature pertaining to methods to reduce P release from sediments in a shallow coastal lake such as Wairewa. There are therefore no conclusions to be drawn from this review, other than to note that there do appear to be potentially feasible in-lake management options which could be further investigated.

In the authors' opinion, further investigations should include bench top and mesocosm studies to establish;

1. Optimal application rates for physical capping materials, and commercially available Al- and Fe-based amendments (including doped clays, zeolites and pumice etc), to Wairewa sediment to prevent P release.
2. The "side effects" of their use on water quality and ecology.
3. Optimal applications rates for Phoslok® and commercially available calcium-based treatments, and identification of "side effects" as above.
4. The potential for short term (weeks to months) control of cyanobacteria with hydrogen peroxide. This algaecide has been shown to be highly species specific and may allow for the targeted removal of cyanobacteria and enable the establishment of non-toxic algae species.
5. The likely consequences of macrophytes harvest on algae and phosphate.

Other management options requiring large scale engineering or lake chemistry/biology manipulation do not lend themselves as well to laboratory- or mesocosm-scale investigation. We defer to the experience of those actively involved in the environmental management of this catchment when it comes to assessing the feasibility or otherwise of these options.

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