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Phoslock Water Solutions Ltd.
ABN 88 099 555 290

Comparison of P-inactivation efficacy and ecotoxicity of Alum and Phoslock®

July 2009

PWS Report Number: IR 015/09

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Executive Summary

Eutrophication occurs when there are increased concentrations of nutrients such as nitrogen and phosphorus in a water body. This causes: visible cyanobacterial (or algal) blooms; surface scums; floating plant mats; benthic macrophyte aggregations; and, death of aquatic life. In addition to external loadings of nutrients from anthropogenic origins, eutrophication can be exacerbated by internal loadings that release nutrients from the lake sediments into the water column over time. Among several other remediation or eutrophication management tools, Alum (Aluminium Sulphate [$Al_2(SO_4)_3.14H_2O$]) has been used in North America and Europe for more than three decades to inactivate phosphate migrating from lake sediments. In contrast to Alum, Phoslock® is a relatively new commercial product that is fast emerging as an effective eutrophication and/or blue-green algae management tool.

Aluminium Sulphate [$Al_2(SO_4)_3.14H_2O$] or Alum is an aluminium based product. Bioavailable Aluminium can liberate from Alum with slight changes of pH and low alkalinity water, and can cause toxic effects to aquatic organisms (e.g. causes fish kills). Therefore, the use of Al based materials for water treatment is restricted in some jurisdictions by Health authorities.

Although Alum appears to be easy to apply, the P-removal action only occurs when it forms a floc. Consequently, it must be buffered when applied to water bodies to initiate the flocking action. Alum floc is easily disturbed by even small lake currents which can dramatically reduce its efficacy as a sediment capping agent.

The successfulness of Alum is affected by several physico-chemical and environmental factors such as the pH, alkalinity and dissolved organic material. The effectiveness of Alum is pH driven; with a maximum efficiency when the pH range is 4 – 6. Efficiency of Alum is reduced significantly with increasing pH. For example, at pH ~7, the P-binding efficiency is only 55% and at a pH 8 (the average pH when there is a moderate algal bloom), the P-binding efficiency falls to 20%. The alkalinity of water (i.e. in low alkalinity water) also increases the toxic effect of the Alum treatment as it reduces the pH and liberates/increases the concentration of toxic soluble aluminium forms, including Al^{3+} and $Al(OH)_2^+$. Therefore, it is often difficult to find a condition where the Alum treatment will be effective without posing any toxic effect to aquatic organisms.

In contrast to Alum, Phoslock® is a lanthanum based product (lanthanum modified bentonite clay). The manufacturing processes of Phoslock® locks lanthanum into the bentonite clay structure and remains within the clay structure reacting with the FRP molecules in the water body. Therefore, the concentration of dissolved lanthanum remains very low in the water body after application of Phoslock®. Physico-chemical or environmental factors have no or minimal impact on the efficacy of Phoslock®. Phoslock® is capable of working over a wide range of pH (~ 4 to 11), with an optimal range of 6 – 9, and binds with phosphate even

under anoxic conditions. Unlike Alum, the addition of Phoslock$^®$ in low alkalinity water does not reduce the pH or produce any toxic residue.

By comparing the toxicity of aluminium to that of lanthanum, lanthanum is used as a beneficial agent to human health and improving agricultural production. Lanthanum does not accumulate in animals and is excreted.

1. Introduction

Increased nutrient concentrations leading to eutrophication in water bodies such as lakes, slow-moving rivers or reservoirs is a major environmental problem worldwide. The consequences of increased nutrients such as phosphorus and nitrogen in a water body are: visible cyanobacterial or algal blooms; surface scums; floating plant mats; benthic macrophyte aggregations; death of fish; and, an increase in sedimentation. The decay of organic matter may lead to oxygen depletion in the water and sediments, which in turn can cause secondary problems such as fish kills, decreasing redox conditions and liberation of toxic substances or phosphates that were previously bound in the oxidized sediment.

In most cases, excess nutrient input in a water body results from anthropogenic origins such as: municipal and industrial sewage discharges; runoff from fertilisers and manure applied to agricultural land; or, from diffuse sources in catchment areas. In addition to external loadings and even after their reduction, eutrophication can continue to be a problem in water bodies due to internal loadings that release nutrients from the lake sediments into the water column over time. Sediments play an important role in the overall cycling of nutrients in lakes and reservoirs (Nürnberg, 1987). Molecular diffusion and the convective transfer process through the sediment-water interface control internal loadings of bio-available P and N in the overlying water (Ignatieva, 1996). This makes a significant contribution to the total nutrient budget in the reservoirs, plays a critical role in the overall nutrient cycling and supports the production of blue-green algae (Chowdhury & Bakri, 2006). Bottom sediment acts both as a source and a sink for P and N (Chowdhury & Bakri, 2006). Nutrient regeneration from sediments or benthic efflux of inorganic nutrients could supply up to 55 – 100% of the estimated nitrogen demand, and 30 – 70% of the phosphorus requirements for the initial growth of algae (Sundback *et al.*, 2003).

Nutrient limitation or nutrient precipitation is one of the practical means of reducing eutrophication. Removing nutrients (e.g. phosphorus) from the water column and controlling its release from sediments can control the growth of algae. The chemical inactivation of phosphorus by aluminium sulphate (Alum) addition is a common chemical treatment of eutrophication (Klapper, 1991; Barroin, 1999). Alum has been used in North America and Europe for more than three decades to inactivate phosphate migrating from lake sediments, regardless of the redox status. However, the longevity of an Alum treatment is highly variable (Welch & Cooke, 1999); there is a lack of data on the P-retention capacity of Al in situ (Cooke et al., 1993b; Welch & Cooke, 1999); and, data on strong adsorbents that permanently bind P, are also very limited (Boers et al. 1993). A recent study on the P-inactivation efficacies of four agents suggests that Alum was effective as a short-term removal strategy for phosphorus, however, as a long-term capping agent it demonstrated the poorest performance (Gibbs et al. 2008). Moreover, the P binding capacity of Alum is pH sensitive; Alum addition produces a decline in pH at low to moderate Alum doses, leading to the

appearance of, and increasing concentration of, toxic soluble aluminium forms, including Al^{3+} and $Al(OH)_2^+$ (Kennedy & Cooke, 1982; Driscoll & Schecher, 1990).

In contrast to Alum as a P-inactivation agent, the use of Phoslock[®] is fast emerging as an effective eutrophication or blue-green algae management tool. This technology involves the use of a lanthanum-modified clay product, capable of removing the Filterable Reactive Phosphorus (FRP) or Soluble Reactive Phosphorus (SRP) efficiently as it descends through a water column. As Phoslock[®] settles, it forms a permeable cap on the bottom sediment, preventing any further release of FRP into the water column. The use of lanthanum chloride salt in water treatment was discussed a number of decades ago. Early researchers (e.g. Melnyk et al., 1974) showed that lanthanum can precipitate a number of different species of phosphorous. However, dissolved or free forms of the rare earth element, lanthanum, was suggested to be toxic to aquatic organisms depending on its concentration and application rate (Peterson et al., 1974). The toxicity problem of lanthanum limited its use significantly, until an appropriate carrier that could lock the lanthanum ions into its structure was discovered in the mid 1990s by the CSIRO, Australia. Lanthanum toxicity and the availability of it's free form was dramatically reduced by incorporating the lanthanum ions into the structure of a high exchange capacity mineral, such as bentonite - hence an innovative product "Phoslock[®]" was developed.

This report summarises the short-term and long-term phosphate removal by Alum and Phoslock[®] and makes a comparison on how various external factors affect the use of these products. The possibilities and potential release of bioavailable Al^{3+} and La^{3+} (the active ingredients of these products) and their toxic effects to aquatic ecosystems are also discussed.

2. The products

2.1. Alum

Aluminium Sulphate [$Al_2(SO_4)_3.14H_2O$] is commonly known as Alum. Historically it has been used in water treatment plants to clarify drinking water and in lakes to reduce the amount of phosphorus in the water column. It is also used to prevent the influx of phosphorus from sediments. Alum is generally supplied in bulk as a liquid, but it can also be supplied in a granular form.

2.2. Phoslock[®]

Phoslock[®] is a bentonite clay product (modified with the active ingredient Lanthanum), developed by the Land and Water Division of Australia's CSIRO (Commonwealth Scientific and Industrial Research Organisation) to significantly reduce the amount of FRP present in the water column and in the sediment pore

water of a water body. Phoslock[®] is generally supplied in a granular form (in 25kg bags) and can be applied to the water body both as a slurry and as granules.

3. The mechanisms of action of Alum and Phoslock[®]

3.1. Alum

When Alum is applied to lake water with a circumneutral pH, the Alum ion hydrolyses, forming a fluffy aluminium hydroxide precipitate called a floc. Aluminium hydroxide binds with phosphorus to form an aluminium phosphate (Al-P) compound. This compound is insoluble in water under most conditions, so the phosphorus can no longer be used as food by phytoplankton. As the floc slowly settles, some phosphorus is removed from the water. On the bottom of the lake the floc forms a layer that acts as a phosphorus barrier and combines with phosphorus as it is released from the sediments (US EPA 1982; Cooke et al., 1982; Welch & Cooke, 1999).

However, the FRP (or SRP) removal mechanism of Alum is not as simple as described above. After application, Alum dissociates, and the dissolved Al undergoes a series of hydrolysis reactions that result in the generation of acidity and a decrease in water pH. The magnitude of the pH shift is related to the initial lake alkalinity and corresponding Alum dosage (Nordstrom & May, 1989; Stumm & Morgan, 1981). Therefore, the effectiveness of Alum is pH driven; with a maximum efficiency when the pH range is 4 - 6 (Peterson et al., 1976). It is also well established that the concentration of the dominant species of aluminium in a water body is dependant upon water pH (Cooke et al., 1993a). Al toxicity problems are possible unless pH is maintained in the 6 – 8 range (Cooke et al., 1993a). At the pH of 6 − 8 (normal pH of most lakes), the concentration of the hydrated and soluble Al^{3+} is low, the dominant species is the polymeric $Al(OH)_3$. This is insoluble and is observed as a precipitate or floc form. As the floc precipitates, phosphorous is removed from the water by an adsorption process, entangling the various phosphate species within the floc. This leads to the formation of numerous complexes of aluminium phosphate. A large number of aluminium phosphate solid phases have been identified by x-ray diffraction of natural samples, although only a few of them have been reproduced in the laboratory (Goldshmid & Rubin, 1988).

3.2. Phoslock[®]

In contrast to Alum, the removal of FRP (or SRP) by Phoslock[®] is very straight forward as shown in Equation 1. Moreover, the effectiveness of Phoslock[®] is not driven by water pH as is with Alum. The removal of FRP (or SRP) by Phoslock[®] is attributed to the lanthanum that adsorbs phosphate molecules, forming a highly stable mineral known as Rhabdophane ($LaPO_4.nH_2O$).

$$La^{3+} + PO_4{}^{3-} = LaPO_4 \qquad\qquad (1)$$

When Phoslock® is applied to a water body as a slurry or in a granular form, it moves down through the water column and up to 95% of the FRP is rapidly removed and adsorbed onto the surface of Phoslock®. This forms an insoluble complex within the clay structure. As the Phoslock® settles at the sediment-water interface, it forms a layer. This layer of Phoslock® is capable of adsorbing FRP from the sediment layer on its available binding sites. Once the FRP is bound to Phoslock®, it is no longer bioavailabile for use by algae for assimilation and growth. Phoslock® operates over a wide range of pH (~ 4 to 11), with an optimal range of 6 – 9, and binds with phosphate even under anoxic conditions. As the lanthanum is locked into the clay structure, it can either react with the FRP molecules in the water body or remain within the clay structure. Therefore, the concentration of dissolved lanthanum remains very low in the water body.

4. Effects of pH on the performance of Alum and Phoslock®

4.1. Alum

Surface water pH plays an important role in Alum treatment effectiveness and the environmental impacts of Alum on the aquatic environment. The P-binding capacity of Alum is pH sensitive with maximum efficiency over the pH range of 4 - 6 (Peterson et al. 1976). At a lower pH, there is a significant risk of free Al^{3+} ions being released into the water column. At pH ~7, the P-binding efficiency is only 55% and at a pH 8 (the average pH when there is a moderate algal bloom), the P-binding efficiency falls to 20% (Gibbs et al., 2008).

To facilitate flocculation of Alum in water, a buffer solution (sodium bicarbonate) is added prior to dosing the Alum. After application the resultant distribution of Al phases and floc quality are pH dependent, with the aluminate anion $[Al(OH)_4]$ dominating at high pH, solid $Al(OH)_3$ forming and flocculating between 6 and 8, and free $Al(H_2O)_6{}^{3+}$, $Al(OH)^{2+}$ and $Al(OH)_2{}^+$ cations prevailing below normal pH ranges (Kennedy & Cooke, 1982; Stevenson & Vance, 1989). Thus, pH values above and below neutrality (pH 7) support higher dissolved Al concentrations, therefore lowering the amount of the solid phase capable of binding P. Moreover, increased dissolved concentrations of Al and hydro-complexes can lead to aquatic toxicity.

The objectives of an Alum application are best achieved by maintaining the pH of the water body between 6 and 8. The strict required adherence to the pH range of 6 - 8 has led to a number of issues. One of them is that a surface application of the slurry is not recommended, as the surface biota could be exposed to toxic concentrations of aluminium ions.

The effectiveness of an Alum application at high pH (the characteristics of eutrophic lakes) is also low. Van Hullebusch et al. (2003) have shown that high pH and intensive re-suspension can increase the risk of phosphorous release from the sediment significantly. This was demonstrated in an Alum treatment of a number of shallow lakes (~2 m depth) in Washington State (Cooke et al., 1993a). Cooke et al. (1993a) explains that the poor outcome for Lake Wapto was mainly due to the dramatic rise of water pH to 10.1, and the subsequent release of the adsorbed P. The decreased performance of aluminium floc in increased water pH was also suggested in a long term study of the effects of P reduction by Alum in Lake Süsser See in Germany (Lewandowski et al., 2003). It is important to note that any future pH changes of the water or at the sediment-water interface, can propagate the release of both aluminium and phosphate from Alum into the aquatic environment.

4.2. Phoslock®

In contrast to Alum, the effect of water column pH on the efficacy of Phoslock® is negligible. Phoslock® is effective in removing FRP (or SRP) in a broad range of pH (~ 4 to 11). Laboratory investigations have shown that Phoslock® removed >99% of the FRP over the range of pH 6 – 8 (Douglas et al. 2000). However, when the solution pH is raised above 9, the FRP removal rate of Phoslock® was slowed; with only 40% of the FRP is removed after first hour and after 24 hrs 60% is removed (Douglas et al., 2000). The observed decline is due to the formation of the hydroxyl species of the lanthanum ions. Douglas et al. (2000) further comments that if the observed rate of the P uptake at pH 9 were to continue, 99% of the phosphorous load could be removed in less than 4 days. Unlike Alum, any future fluctuations in pH will not release La or phosphate into the aquatic environment.

5. Effects of alkalinity on the performance of Alum and Phoslock®

5.1. Alum

Alkalinity of water affects the effectiveness of an Alum treatment and may cause the release of soluble Al which can be toxic to aquatic life. The dose rate of Alum is therefore determined based on phosphorus content and alkalinity of water. In lakes with low to moderate alkalinity (<100 mg/L of $CaCO_3$), the Alum addition produces a decline in pH at low to moderate Alum doses, leading to the appearance of and increasing concentration of toxic soluble aluminium forms, including Al^{3+} and $Al(OH)_2^+$ (Kennedy & Cooke, 1982; Driscoll & Schecher, 1990). Aluminium treatment has to therefore be low, which limits the effectiveness of phosphorus uptake (Lund & Chester, 1991).

5.2. Phoslock®

The dose rate of Phoslock® is also determined based on phosphorus content and alkalinity of water. Lanthanum associated with bentonite clay preferentially binds with PO_4, but it also binds with CO_3. Therefore, in low alkalinity water, Phoslock® dose rate should be based on available phosphate only. Unlike Alum, the addition of Phoslock® in low alkalinity water does not reduce pH and does not produce any toxic residue. However, if a higher dose rate of Phoslock® is applied to low alkalinity water, there is the potential for dissolved La to be present in the water column which could possibly (depending on the concentration) be taken up by aquatic organisms. However, toxicity of La to aquatic organisms (e.g. fish) is negligible. Fish health monitoring reports from the Lake Okareka after Phoslock application® (Landman et al., 2007) showed that La that was initially found in the fish after the Phoslock application was excreted over time and the concentrations returned to prior application levels.

6. Effects physical factors on the performance of Alum and Phoslock®

6.1. Alum

The P-removal effectiveness and Al-speciation associated with an Alum treatment are also affected by physical factors including floc size and distribution. As the aluminum octahedral bundles are mixed, they grow in size and the surface area decreases with an increase in the settling rate. This leads to a decrease in the contact time and less P-removal from water column with depth (Kennedy & Cooke, 1982). Moreover, the Alum easily disturbed by even small lake currents which can dramatically reduce its efficacy as a sediment capping material.

6.2. Phoslock®

Phoslock® is relatively quick to settle when applied as a slurry or as granules. As the slurry moves down through the water column, up to 95% of the FRP is rapidly removed and adsorbed onto the Phoslock® surface. When Phoslock® settles at the sediment-water interface it forms a reactive layer and prevents further release of FRP from the underlying sediment. For faster settlement of the Phoslock® and to target sediment containing high phosphate, the product can be applied as granules to the water column or released as granules close to the sediment.

7. Effects of dissolved organic matter (DOC) on the performance of Alum and Phoslock®

7.1. Alum

The effect of dissolved organic matter on the P-removal capacity of Alum was investigated by Omoike and Vanloon (1999). They chose tannic acid as a model compound. The P-removing capacity of Alum in a number of solutions containing different amounts of tannic acid was measured (using Al:P ratio of 1:1). The results demonstrated that the performance of Alum is reduced dramatically as a result of the presence of tannic acid (only 7 ppm tannic acid reduced Alum performance by >50%). The authors attributed the observed results to the increase in the solubilisation of aluminium in the presence of organic matter.

7.2. Phoslock®

The effect of dissolved organic matter on the P-removal capacity of Phoslock® was investigated in solutions containing humic acid with the concentration of 100 ppm (Douglas et al, 2000). The molar ratio of the active ingredient (moles of La) to the available quantity of P was 0.7:1. The results demonstrated that in the presence of 100 ppm humic acid, the performance of Phoslock® was not reduced significantly up to pH 7. However, at pH 9, performance was reduced. Douglas et al. (2000) also mentioned that the kinetic study of the P uptake at pH 9 appeared to continue after 24 hrs. The authors suggested that if the study was to continue, quantitative removal would have occurred after 9 days.

8. Dose determination of Alum and Phoslock®

8.1. Alum

The process of dose determination for Alum appears to be somewhat more complicated than Phoslock®. As a number factors such as organic matter content of the water can affect the $Al(OH)_3$ floc formation, the required Al:P can vary from one application to another. This is further complicated by the possible number of different aluminium phosphate species and molar ratios. Lewandowski et al. (2003) investigated Alum treatment in Lake Süsser See in Germany for 15 years and showed that the molar ratio of added aluminium to additionally bound phosphorous was 2.1:1. However, the Alum application in Lake Süsser See was reported to be unsuccessful. Another study conducted by Rydin et al. (2000) in Washington Lake showed that the ratio of the added Al to Al-P was 11:1 by weight, which would translate into 12.7:1 by molar ratio. Another factor that is known to affect the amount of aluminium available for floc formation is the presence of fluoride ions. Increased fluoride ions in low alkalinity water could increase the concentration of filterable Al and lead to aluminium toxicity.

8.2. Phoslock[®]

The P-removal capacity of Phoslock[®] does not change drastically under different chemical or environmental conditions. Laboratory studies using both lanthanum chloride and Phoslock[®] showed that the molar ratio of lanthanum to the reacted phosphorus was 1:1 (Haghseresht, 2004). Therefore, the determination of the required quantity of Phoslock[®] for both P precipitation (reduction of the phosphorus concentration from the water column) and P-inactivation (long term control of release of the sediment phosphorus) has become a very simple process. The recommended dose of Phoslock[®] normally considered two components, namely the amount of Phoslock[®] that is needed to precipitate the dissolved soluble species of phosphorous in the water column and the amount required to create adequate capping for the bottom sediment. As a general rule, Phoslock applied at the rate of 100:1, i.e. 100 g Phoslock required to remove 1 g of bioavailable phosphorus (FRP).

8.3. Comparison of the required dosages of Alum and Phoslock[®] (case studies)

Unlike Alum, the advantage of a Phoslock[®] application is that the active ingredient (i.e. lanthanum) is introduced into the water body by a carrier (the bentonite clay). This ensures that the lanthanum ions only react with the available oxyanions and remain unavailable to the biota. In addition, the molar reactivity of La with P is 1:1, which simplifies the dosage determination process. Moreover, by comparing the dose rate of Alum and Phoslock[®], as well as the application of Al and La in water body, the addition of lanthanum should be lower than the amount of aluminium needed for P-removal. Table 1 summarises the required dosage of Alum with Phoslock[®] as well as the amount of aluminium that was used in case studies and the amount of lanthanum needed for those applications.

Case Study	Initial TP content	Added Al (kg)	La Required (kg)
Mirror Lake: Dimensions: 5 ha with a D_{max} of 13.1 m and D_{min} of 7.8 m (Cooke et al., 1993a).	0.15 ppm Total P = 78.34 kg	6.6 mg/L **Total Al = 3449 kg**	**Total La = 391.7 kg**
Shadow Lake: Dimensions: 17 ha with a D_{max} of 11.6 m and D_{min} of 5.3 m (Cooke et al., 1993a).	0.065 ppm Total P = 93.4 kg	5.7 mg/L **Total Al = 8188 kg**	**Total La = 467 kg**
Lake Süsser See: Volume: 1.16×10^{10} L (Lewandowski et al., 2003)	0.20 ppm Total P = 2320 kg	2 mg/L/yr **Total Al = 23,200 kg**	**Total La = 11,600 kg**

Table 1: Comparison of the aluminium and lanthanum requirements for three lakes treated with Alum (case studies). La requirement was calculated based on the dose rate of Phoslock[®] (100:1) and ~5% of lanthanum in the Phoslock[®].

Table 1 shows that, in all cases, the added amount of aluminium was higher than the corresponding required amount of lanthanum. This is without taking into account the amount of the aluminium contribution from the sodium aluminate that is commonly used as a buffering agent. In terms of the effect of the Alum on the reduction of the phosphorus content of the lakes, the first two cases were highly successful. The SRP as well as TP remained low for 12 years. However, no ecological impact studies were reported. On the other hand, the Alum application in Lake Süsser See was reported to be unsuccessful. This lake had received Alum treatments annually and biannually from 1977 to 1992, receiving 7000 tonnes of Alum during this time period. The authors that examined the long term effect of P precipitation with Alum, concluded that the lack of improvement in the trophic state of the lake was due to underestimating the required Alum dose for adequate P reduction, as well as possible re-suspension of the precipitated floc and the high concentration of phosphorus in the inflows (Lewandowski et al., 2003). Similar problems with under-dosing of Alum are also reported by other researchers (Van Hullebusch et al., 2003).

9. Application method of Alum and Phoslock[®]

Both Alum and Phoslock[®] can be applied using similar equipment. While the application of Phoslock[®] is a straight forward and robust process, the application of Alum is affected by a number of physical factors. The most important among these factors are the significant reduction of the P uptake capacity of Alum at low temperatures, the need to apply a buffering agent to the water before application

(and therefore rapidly changing the pH of the water body that may in turn have negative affects on aquatic organisms), and the adverse affect of windy weather on its application process. Furthermore, effects of weathering on the Alum floc in a number situations, such as in shallow lakes applications can not ensure a successful outcome (Cooke et al., 1993a).

10. Toxicity of Alum and Phoslock

10.1. Alum

Aluminium Sulphate [$Al_2(SO_4)_3.14H_2O$] is commonly known as Alum which contains a potential toxic metal Al. Aluminium toxicity to living organisms (e.g. plants, fishes etc) has been demonstrated in many instances (Yokel & Golub, 1997). The toxicity of aluminium is governed by its bioavailability (Bérubé & Brûlé, 1999). Aluminium, as opposed to other toxic metalloids or metals (e.g. As, Pb, Hg), exists in a unique oxidation state and does not form stable alkylation compounds in natural environments (Bérubé & Brûlé, 1999). Aluminium has the capability to take hazardous routes or to form more hazardous species, such as the well known, more bioavailable, low molecular weight organic complexes (Bérubé & Brûlé, 1999). Aluminium is more toxic when water is acidic (i.e. pH is low). Therefore, Australian guidelines for Al in drinking water are 1 µg/L at pH <6.5 and 55 µg/L at pH >6.5 (ANZECC and ARMCANZ, 2000).

The toxicity of aluminium to fish in acidic waters has been well documented. Al becomes more soluble, hence, potentially more toxic to freshwater biota as the pH decreases below 6 (Gensemer & Playle, 1999). Aluminium acts as a gill toxicant to fish, causing both ionoregulatory and respiratory effects (Neville & Campbell, 1988), and has been reported to be a major factor contributing to fish kills in acidic freshwater systems (Dillon et al., 1984; Schindler, 1988; Charles, 1991). Aluminium has been observed to cause acute toxicity to fish in mixing zones (pH 4.8 – 6.5) below acidic tributaries (Rosseland et al., 1992; Henry et al., 1999; Gensemer & Playle, 1999) and to alter snail behaviour when ingested (Elangoven et al., 1997; Campbell et al., 2000). Alum sludge extracts prepared from natural receiving waters were shown to inhibit the growth of freshwater green alga (*S. capricornutum*) at pH 5, but were toxic in all extracts if the receiving water had a hardness of less than 35 mg $CaCO_3$/L (George et al., 1995).

10.2. Phoslock

Phoslock[®] is a modified bentonite clay product that contains the rare earth element, lanthanum. In contrast to the toxicity of Alum or aluminium, lanthanum has been used in the medical industry. Lanthanum carbonate (Fosrenol[®]) is an effective non-aluminium, non-calcium oral phosphate binder for treatment of hyperphosphatemia in patients with chronic kidney disease who are undergoing

dialysis. Tablets of 500, 750 and 1,000 mg are available for use in end stage renal disease patients (ESRD) with a mean C_{max} of lanthanum 1,000 ng/L plasma (Behets *et al.*, 2004). The FDA (US Food and Drug Administration) approved human dose rate for Fosrenol[®] (as appears on the Fosrenol[®] website - http://www.fosrenol.com/) is 750 – 3,000 mg per day. Moreover, Fosrenol[®] has also just been approved for inclusion on the Australian Public Benefits Scheme (Pharmaceutical Benefits Advisory Committee (PBAC) meeting notes, 2008; http://www.health.gov.au/pbs).

Trace quantities of rare earth elements (including lanthanum) are routinely applied to at least 40 different crop species in the People's Republic of China, where reports indicate that applications can increase crop production between 8% and 50%, but are typically in the range of 8 – 10% (Guo, 1987; Zhang et al., 1988; Tribe et al., 1990). Rare earth elements (including lanthanum) have been reported to increased physiological responses of crops including greener foliage, faster development, larger roots, stronger tillering and better fruit colour (Brown et al., 1990). The effects of rare earth elements on crop growth in Australian soils also demonstrated promising results under conditions of water-stress (Buckingham et al., 1995).

In contrast to published work on Alum, only a small amount of literature is available on the toxicity of lanthanum to aquatic organisms. However, since the development of Phoslock in mid 1990s, a large number of toxicity studies and assessment of Phoslock and Lanthanum were conducted by several independent organisations. None of the experiments have shown that Phoslock is toxic to aquatic life or aquatic ecosystems at dose rates suggested by Phoslock Water Solutions Ltd. These ecotoxicity reports can be found on the Phoslock web site (www.phoslock.com.au). Lanthanum does not accumulate in animals and humans and is excreted. Reports from the Lake Okareka Phoslock[®] application (Landman et al., 2007) also reiterate that the lanthanum that was initially found in the fish after the Phoslock application was excreted over time and the concentrations returned to prior application levels.

11. Conclusion

Both Alum and Phoslock[®] are used as P-inactivation agents in eutrophic lakes and reservoirs throughout the world. Alum has been used in North America and Europe for more than three decades. In contrast to Alum, the use of Phoslock[®] is new, however it is a fast emerging as an effective eutrophication or blue-green algae management tool. Phoslock[®] is an innovative product, developed by the CSIRO (Commonwealth Scientific and Industrial Research Organisation), Land & Water, Australia over 15 years of research and development. Phoslock[®] has been applied to water bodies (including aquaculture) in over 20 countries and has been proven as a sustainable, environmentally friendly tool for eutrophication control as well as management of blue-green algae.

Alum is an aluminium based product. Aluminium toxicity to living organisms (e.g. plants, fishes etc.) has been well documented. There are several physico-chemical and environmental factors that influence the efficacy of Alum, and restrict it's use in the water bodies. For example, the effectiveness of Alum is pH driven; with a maximum efficiency when the pH range is 4 – 6 (i.e. in slightly acidic condition). However, at the lower pH there is a significant risk of the toxic Al^{3+} ions being released into the water column. At pH ~7, the P-binding efficiency is only 55% and at a pH 8 (the average pH when there is a moderate algal bloom), the P-binding efficiency falls to 20%. Alkalinity of the water affects the effectiveness of an Alum treatment and may cause the release of soluble Al. In lakes with low to moderate alkalinity, an Alum addition produces a decline in the pH at low to moderate alum doses, leading to the appearance of and increasing concentration of toxic soluble aluminium forms, including Al^{3+} and $Al(OH)_2^+$. The P-removal effectiveness and Al-speciation associated with an Alum treatment are also affected by physical factors including floc size and distribution. Alum floc is easily disturbed by even small lake currents which can dramatically reduce its efficacy as a sediment capping material.

Phoslock® is a lanthanum based product (lanthanum modified bentonite clay). The manufacturing processes of Phoslock® were designed to incorporate the lanthanum ions into the structure of a high exchange capacity mineral, such as bentonite. As the lanthanum is locked into the clay structure, it can either react with the FRP molecules in the water body or remain within the clay structure. Therefore, the concentration of dissolved lanthanum remains very low in the water body. The effectiveness of Phoslock® is not driven by water pH as is with Alum. The removal of FRP (or SRP) by Phoslock® is attributed to the lanthanum that adsorbs phosphate molecules, forming a highly stable mineral known as Rhabdophane ($LaPO_4.nH_2O$). Phoslock® operates over a wide range of pH (~ 4 to 11), with an optimal range of 6 – 9, and binds with phosphate even under anoxic conditions. The alkalinity of water partially affects the effectiveness of Phoslock® treatment. In low alkalinity water, the Phoslock® dose rate should be based on the available phosphate only because lanthanum also binds with CO_3. Unlike Alum, the addition of Phoslock® in low alkalinity water does not reduce the pH and dose not produce any toxic residue. Moreover, the P-removal capacity of Phoslock® does not change drastically under different chemical or environmental conditions.

By comparing the toxicity of Alum (aluminium) and Phoslock (lanthanum), it can be concluded that Al poses more threat to aquatic life than that of lanthanum. In contrast, lanthanum has been used as a beneficial agent to human (e.g. Fosrenol® drug) and agriculture (growth promoter). Lanthanum does not accumulate in animals and is excreted. Comprehensive reports published after the Lake Okareka application in New Zealand (written by the Environment Bay of Plenty and found on the EBOP and Phoslock web sites) also reiterate that the La that was initially found in the fish after the Phoslock application was excreted

over time and the concentrations returned to prior application levels. Therefore, application of Phoslock to water bodies (including drinking water reservoir and aquaculture) is fast emerging as an effective, safe and environmentally friendly tool for P-inactivation or eutrophication management.

12. References

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