Recent studies of sediment capping and flocculation for nutrient stabilisation

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Executive Summary

Water quality in the Rotorua Lakes has declined in the past 30 to 40 years due to increasing nutrient loads, specifically nitrogen and phosphorus. *In situ* restoration techniques, including sediment capping and flocculation, have been developed to attempt to reduce internal nutrient loads, which can be comparable in magnitude to external loads in eutrophic lakes. The aim of this report is to summarise the current state of knowledge, and to documents some recent studies of sediment capping and flocculation techniques designed to remove nutrients from the water column by retaining them permanently within the bottom sediments. Experimental set-ups for testing the efficacy of different materials range from conventional batch adsorption studies to sediment reactor experiments. Natural ecosystems have also been simulated with mesocosms in Lake Okaro. A full scale application of aluminium sulphate (alum) in Lake Okaro has also been intensively monitored. The different studies have provided information on the restoration potential of some sediment capping agents and flocculants, but many questions still remain. Given the current state of knowledge it is not possible to confirm *a priori* the circumstances under which a whole lake trial would be successful. Future research should be carried out on the following foci:

- Establishment of chronic or acute toxic effects of the adsorbent materials.
- Effect of treatment applications on benthic biota, particularly capping materials that may alter physical characteristics of the sediments.
- Application of computer models for the purpose of both hindcasting and better understanding effects of application of an adsorbent to a lake, and for the purpose of predicting the changes in trophic status.
- Application techniques and costs, particularly in view of potential for quite radical changes in source of adsorbent materials, grain sizes and methods of application for a single adsorbent.

1. Introduction

Water quality in several of the Rotorua Lakes has declined in the past 30 to 40 years due to increasing nutrient loads, specifically nitrogen and phosphorus (Environment Bay of Plenty, 2005). The resulting eutrophication and increasing occurrence of harmful algal blooms in some lakes are of particular concern. Eutrophication of freshwater ecosystems has become a global problem (Smith, 2003). The management of lake eutrophication primarily involves exerting controls on loads of nitrogen and phosphorus from diffuse and point sources in lake catchments (Cooke *et al.* 1993).

There is a large pool of nitrogen and phosphorus in the bottom sediments of lakes. These sediments can play an important role in the nutrient dynamics of the water column because internal nutrient loads, i.e., transfers of nutrients from the sediments to the water column, can represent a large fraction of the total nutrient load of a lake. For example, the internal nutrient load in Lakes Rotorua and Rotoiti are at least comparable to the external load for each of these lakes (Hamilton *et al.* 2004). In addition, internal loads can delay the improvement of water quality after restoration measures (Jeppesen *et al.* 2005).

Until the 1970s it was generally believed that sediments acted as a net sink for phosphorus, and that phosphate is released to the hypolimnion almost exclusively in periods of water column anoxia (Mortimer, 1971). In recent years a much more complicated picture has developed. Phosphorus release from sediments depends on a variety of physical, chemical and biological processes. Gächter (1988) and Sinke *et al.* (1990) showed that sediment microorganisms can rapidly take up and release inorganic phosphorus. Holdren and Armstrong (1980) demonstrated that phosphorus-release rates increase with increasing temperature. There is also evidence that bioturbation from benthic invertebrates enhances phosphorus release rates, particularly where sediments have low concentrations of total iron (Phillips *et al.* 1994). Resuspension by wind-wave action also has a significant effect on total phosphorus concentrations in the water column (Hamilton and Mitchell, 1997). Remobilisation of phosphorus from the sediments is furthermore controlled by its speciation (Selig and Schlungbaum, 2003). Therefore, knowing the total phosphorus content of the sediment is not sufficient to define the amount of phosphorus that is exchanged with the water column (see Nürnberg, 1988). Phosphorus speciation in sediments can be resolved using a technique of sequential chemical extraction (Golterman, 1982), which can assist in predictions to determine how sediments influence lake water concentrations (Pettersson *et al.* 1988; Spivakov *et al.* 1999). Calcium-bound phosphorus is generally released at low rates, while phosphorus bound to iron and aluminium is easily released anaerobically and at high pH levels (Pettersson *et al*. 1988). Aerobic release of phosphorus from sediments has been explained in part by high phosphate-ferrous and phosphate-calcium molar ratios in porewaters (Jensen and Andersen, 1992). However, the exclusive use of the chemical extractions to infer release rates based on phosphorus to metal cation ratios has also been criticised (Barbanti *et al*. 1994; Ruban *et al*.1999).

Many *in situ* restoration techniques have been developed over the last three decades to reduce internal nutrient loads (Klapper, 2003). Within-lake restoration can involve physical modification of the lake environment (e.g. Ruley and Rusch 2002), biological modifications (e.g. Bontes *et al.* 2005) and chemical restoration (e.g. Cooke *et al.*1993). Chemical restoration of lakes includes a series of reactions generally dominated by flocculation or physical sealing of the sediment. The removal of harmful algae blooms using clay minerals has also been reported by Pierce *et al*. (2004) and Beaulieu *et al*. (2005).

Flocculation or phosphorus precipitation with iron or aluminium salts is the most common method to decrease concentrations of bioavailable phosphorus in the water of lakes with long retention times (Klapper, 2003). The formation of hydroxides from these salts predominates in the competitive process of phosphate uptake. The metal-phosphate complex is either occluded within the flocs or deposited on the outside (Cooke *et al.*1993). In addition, under certain pH or other environmental conditions, insoluble hydroxide complexes may be formed which, upon precipitating, link together to form long chains or meshes, physically trapping small particles into larger flocs. Aluminium is more commonly used than iron, because iron is redox-sensitive and there may therefore be redissolution of phosphate under anoxic conditions. The surplus aluminium settles on the lake bed where it can form an aluminium hydroxide layer that may reduce the release of phosphorus from the sediment. However, during formation of the flocs following alum application, there may be considerable consumption of alkalinity resulting in poor buffering capacity for hydrogen ions (H^+) that may potentially result in an ecologically unacceptable decrease in pH. The aluminium salts are either applied from the surface or directly into the hypolimnion, depending on the application target.

Sediment capping is a method of preventing phosphorus release from the sediments through the formation of a diffusion barrier (Klapper, 2003). Sand, mineral soils and clay minerals are used to physically seal areas of the lake bottom sediment (Miller, 2005). In the case of sediment capping, clay may not only seal the lake bed to prevent phosphorus release, but also precipitate phosphorus and algae from the water column while sinking through it. The efficacy of such materials for nutrient uptake depends predominantly on the adsorption capacity and the ion exchange capacity. Adsorption is a process that occurs when a liquid or solute accumulates on the surface of a solid, or more rarely when a liquid forms a molecular or atomic film. Ion exchange is a process in which ions are exchanged between a solution and an ion exchanger, producing an insoluble solid. Ion exchangers are either cation exchangers for positively charged cations or anion exchangers for negatively charged anions. The sorption capacity and ion exchange capacity of these materials can be enhanced by modification.

The objective of this report is to document some recent studies on sediment capping and flocculation for nutrient stabilisation. Although experiments described herein were conducted at different temporal and spatial scales, the results of all studies are compared in order to provide an overview of the current state of knowledge. Furthermore, suggestions for additional research are made, specifically in relation to evaluation of the efficiency of restoration approaches and to prevent precipitous decisions with regard to full scale applications.

2. Materials

Miller (2005) examined a number of New Zealand sourced inorganic and organic materials with a view to determining their actual or potential usefulness for reducing or removing nutrients from lakes, streams or groundwater in the Rotorua District. The major properties and nutrient removal potential of the various materials were examined. Several researchers have recently examined a number of materials with a view to examining their capacity for *in situ* lake restoration. Table 1 shows researchers and materials used for each study. Miller (2005) is excluded from this table, as his study was a summary of the characteristics of several potential remediation materials rather than a quantitative analysis of their efficacy.

Table 1: Authors and materials used in each study.

	Alum	Allophane	Baraclear	Carbon	Iron slag	Lime	Phoslock™	Pumice	Zeolite
Faithfull *et al.* 2005				✓	✓		✓		✓
Özkundakci, 2006	✓	✓			✓	✓	✓		✓
Paul, 2006	✓								
Yang *et al.*2004			✓				✓	✓	✓
Zheng, 2006	✓				✓		✓		✓

Modified zeolite is in an ongoing development phase with Scion (Rotorua) with a view that a full-scale application may be made in Lake Okaro in 2007. It cannot be assumed that the results of the zeolite studies have used an identical product or that this product is the same as what might be applied for lake restoration in the future, and there may potentially be differences associated with different batches of this product. Similarly, other materials listed in Table 1 may also be modified in terms of their particle size and composition, in order to improve efficacy of phosphorus uptake for specific purposes.

3. Methods

3.1. *Overview of experiments*

Several methods have been used to examine the efficacy of different treatment materials. Experimental set-ups range from conventional batch adsorption studies (Yang *et al.* 2004; Özkundakci, 2006) to sediment reactor experiments (Faithfull *et al.* 2005). Natural ecosystems have also been simulated with mesocosms in Lake Okaro (Özkundakci, 2006; Zheng, 2006). A full scale application of aluminium sulphate (alum) in Lake Okaro has also been intensively monitored by Paul (2006).

The variables that were monitored were not consistent across the different experiments. Physical, biological and chemical variables were more intensively monitored during the full scale application of alum (Paul, 2006) and the mesocosm experiments in Lake Okaro (Özkundakci, 2006; Zheng, 2006). However, several nutrient species were analysed during all studies, making it possible to make comparisons of materials across the different studies.

3.2. *Experimental designs*

3.21 Batch adsorption studies

Yang *et al.* (2004) conducted a series of batch adsorption studies to compare the performance of commercially available nutrient removal media with that of modified zeolite (designed by SCION) and pumice. The most important variables selected for monitoring were soluble reactive phosphorus (SRP) and nitrate (NO_3). Adsorption isotherms, adsorption equilibria, adsorption kinetics, and sensitivity to pH of different materials were examined in artificial nutrient solutions and in surface waters of Lake Okaro. Artificial nutrient solutions contained very high nutrient concentrations, with up to 100 mg L^{-1} NO_x and 500 mg L^{-1} SRP in order to test the nutrient uptake capacity at low levels of media application. The pH was adjusted in all experiments, except for those in which the pH sensitivity was investigated specifically. All experiments were conducted at an ambient temperature of 25 °C. For a Lake Okaro case study, lake water was collected from the inlet and contained nutrient concentrations of 0.185 mg L^{-1} SRP and 1.52 mg L^{-1} NO_x.

Özkundakci (2006) carried out a batch adsorption study using Lake Okaro water. Three different nutrient concentrations were used in the batches. Lake Okaro water was used in the first trial and two different modified Lake Okaro water samples enriched with artificial nutrient solutions were used as an intermediate and a high nutrient concentration case. No adjustment of pH was carried out in order to examine the effect of treatments on pH and conductivity. Experiments were conducted at an ambient room temperature of 20 °C. Nutrient adsorption properties were described for each individual case but adsorption isotherms, adsorption equilibria, adsorption kinetics, and pH sensitivity of the different materials were not described. However, nutrient adsorption characteristics were examined for SRP, NO_3, NH_4, TP and TN.

3.22 Sediment reactor study

Faithfull *et al*. (2006) conducted a sediment reactor experiment with intact sediment cores from Lake Ngaroto, a Waikato peat lake. In the laboratory the cores were incubated for 8 days with oxygenated whole lake water sourced from Lake Ngaroto, which was pumped through each core to prevent anoxia, with small stirrer bars inside the top of the core to prevent stratification. Anoxia in the sediment cores occurred after approximately four days and enabled nutrient adsorption characteristics to be examined under the anoxic conditions. Nutrients analysed included SRP, NO_3, NH_4, TP and TN.

3.23 Mesocosm field studies

Both, Zheng (2006) and Özkundakci (2006) conducted separate mesocosm field studies in Lake Okaro. For each study, 15 mesocosms were deployed in the lake and treated with different materials. Experimental durations were 51 days and 30 days for Zheng (2006) and Özkundakci (2006), respectively. Nutrient analyses for both experiments included SRP, NO_3, NH_4, TP and TN. Physical, chemical and biological variables were recorded by both investigators at discrete depths, and included water temperature, dissolved oxygen concentration, conductivity, pH, and chlorophyll *a* concentrations.

3.24 Full scale application

Alum was applied to Lake Okaro on 16 and 17 December, 2003. Over these two days, 13 m^3 of alum solution was applied to the surface of the lake (Paul, 2006). Sampling took place over a period of 43 days at several depths. Nutrients that were analysed included SRP, NO_3, NO_2, NH_4, TP and TKN. Physical, chemical and biological variables were recorded at certain depths and included water temperature, dissolved oxygen concentration, conductivity, pH, chlorophyll *a* concentration, and Secchi depth. Additionally, phytoplankton was collected at a depth of 1.5 m, and samples were also taken by Environment Bay of Plenty for analysis of dissolved and total aluminium at several depths. Sedimentation rates of particulate Al were measured with three replicate sediment traps position at three discrete depths in the water column.

3.3. Dose rates of materials

The dose rates of treatment materials varied across the studies. The dose rate of alum for the full scale application in Lake Okaro was equivalent to 0.6 g Al^{3+} m^{-3} (Paul, 2006). This dose rate was calculated by McIntosh (2002) and took into consideration the very low alkalinity of Lake Okaro (22.2 g m^{-3} as $CaCO_3$; Paul (2006)). Dosage is sometimes also estimated by considering the rate of internal P loading from the sediment or the mass of redox-sensitive P in the upper layers of the sediment (Rydin and Welch 1998). Alum dose rate of the mesocosm studies was equivalent to 0.43 g Al^{3+} m^{-3} (Zheng, 2006) and 0.86 g Al^{3+} m^{-3} (Özkundakci, 2006).

Dose rates for the mesocosm study of Zheng (2006) for all of the adsorbent test materials used was equivalent to 159 g m^{-2}. The dose rates for all the adsorption materials used in Özkundakci (2006) were two-fold higher while Faithfull *et al.* (2006) used 200 g m^{-2}.

In the batch adsorption case study using Lake Okaro water (Yang *et al.* 2004), different dose rates of the tested materials were used, equivalent to 1, 4, 10 and 20 g L^{-1}. These dose rates are surprisingly high and, scaling up to a whole lake application, may be logistically difficult to achieve. In the batch adsorption study of Özkundakci (2006) a dose rate for all materials equivalent to 0.05 g L^{-1} was chosen, which he considered to be more realistic of what might be used for *in situ* applications. The batch adsorption study of Yang *et al.* (2004) with artificial nutrient solutions gives no indication of a dose rate of treatment materials. However, based on their results, an attempt was made to calculate an optimal dosage for 95 % removal of SRP. For two different zeolites an optimal dose rate was calculated to be 17.4 and 30.4 g L^{-1}. For Phoslock™ and Baraclear the optimal dose rates were established at 40 and 27.6 g L^{-1}, respectively.

4. Results

The success of nutrient uptake by the materials in the different studies varied with spatial and temporal scale of experiments even though some of the materials were identical in the different studies. However, results from the studies are compared in this paper and presented in alphabetical order of materials, not necessarily in order of efficacy.

4.1. Alum

Paul (2006) reported a decrease in SRP in the epilimnion after alum dosing. No other nutrient species showed a significant difference in concentration before or after dosing. A general increase was reported for ammonium ions (NH_4^+) at all depths for the sampling period. Of particular note was a four-fold increase at 1.5 m depth almost immediately following the alum application. This is noteworthy, given that Özkundakci (2006) observed a rapid increase of ammonium at 1 m depth in mesocosms immediately following alum application. It is suggested that alum may have induced death of bacteria or zooplankton that may then have released ammonium into the water column. Without specific investigation of this phenomenon, it is mostly speculation as to why ammonium might increase rapidly with alum applications, but it could play an important role in supplying nitrogen to phytoplankton that are potentially nitrogen-limited, possibly leading to bloom formation soon after treatment (Paul, 2006). The study by Özkundakci (2006) also showed a reduction of TN and TP at 1 m depth following alum application, suggesting flocculation took place and resulted in sedimentation of bound particulate material. Paul (2006) did not record a reduction of TN and TP, but found evidence of flocculation supported by increases in particulate Al content throughout the water column. The more obvious evidence for flocculation reported by Özkundakci (2006) is probably due to the high dose rate of alum, since the additional alum may form long chains or meshes to physically trap small particles into the larger floc. Zheng (2006) did not report any significant reduction of any nutrient species following an alum application, and suggested that this was due to low dose rates. Longevity of nutrient reduction by alum was short-lived in all studies compared with international literature.

Welch and Cooke (1999) report successful reduction in lake TP for periods up to 21 years after alum application.

4.2. Allophane

Allophane as allophane-rich soil was used only by Özkundakci (2006) in both a mesocosm field study and a batch adsorption study. No significant reduction of any nutrient species was observed in his study and he concluded that an impure allophane material might have caused the ineffectiveness of this material. Miller (2005) provided a rank of potential adsorbent materials in order of potential usefulness, where allophane was the highest in the ranking list.

4.3. Baraclear and Pumice

Pumice showed very high uptake capacity for phosphate in the batch adsorption study of Yang *et al.* (2004), but at a high dose rate of 30 mg L^{-1}. Baraclear demonstrated high efficiency for removal of soluble reactive phosphorus from Lake Okaro water, with removal capacity exceeding 90 %. Only Yang *et al.* (2004) has used these materials and it is difficult to make direct comparisons of their results with other studies.

4.4. Iron slag

Iron slag from SteelServ Ltd. was used by Faithfull *et al.* (2005), Özkundakci (2006) and Zheng (2006), allowing for direct comparison of experimental results at different spatial scales. Iron slag was the least effective of the treatments trialled by Faithfull *et al.* (2005), and nutrient concentrations remained within the range observed in controls. Özkundakci (2006) reported a reduction of only NH_4 in the intermediate nutrient concentration case for his batch adsorption study. Zheng (2006) also reported no significant differences between control and iron slag treatments for any nutrient species. Shilton *et al.* (2006) used a very similar slag material from the same provider (SteelServ Ltd.) in an active slag filter of a wastewater treatment plant (Waiuku Wastewater Treatment Plant, Waiuku, New Zealand), to upgrade the plant for phosphorus removal. They reported 77 % reduction of TP by the slag material with a hydraulic retention time of effluent in the beds of approximately 3 days. Mann (1997) found in an equilibrium study (contact time ranging from 30-300 hrs and phosphorus concentrations ranging from 5-100 mg L^{-1}) that phosphorus adsorption by iron slag varied with contact time and with initial phosphorus concentration. It is possible that the contact time of iron slag with the water was insufficient in the lake studies examined here, perhaps due to rapid sedimentation of the relatively dense material, while the dosages were insufficient to produce a continuous surficial lining of the sediment bed with iron slag. An increase in pH in the mesocosms treated with iron slag would be expected immediately after treatment due to the specific chemical composition of iron slag. Mann (1997) found that elevated pH at slag-water interfaces was correlated with high calcium content of the material. This alkalinity at the slag-water interface was expected to encourage precipitation of calcium compounds, which in turn would result in increases in pH. Özkundakci (2006) and Zheng (2006) found pH did not change distinctly after treatment. This finding further supports the concept that the iron slag was not applied in sufficient quantities to affect pH, or else that the rate of sedimentation was too fast for it to have a significant impact on water column pH.

4.5. Lime

Lime was used only by Özkundakci (2006) in the batch adsorption study. Phosphate was only reduced in the high nutrient concentration case where initial SRP concentration was 0.35 mg L^{-1}. It remained unclear why a 97 % reduction of phosphate concentration occurred only for the high nutrient concentration case. Lime demonstrated moderate levels of ammonium removal, however, in all of the treatment cases. This effect may have been due to formation of ammonia (NH_3) after pH increased above 9 following the lime application.

4.6. Carbon

Additions of carbon in the form of molasses reduced nitrate most effectively of any of the treatments used by Faithfull *et al.* (2006). Although carbon compounds have the ability to bind nitrogen ions, low concentrations of nitrate were considered to be due to the rapid decline of oxygen within the carbon treatment cores, and subsequent denitrification. The rapid decline of oxygen recorded in the carbon treatment was probably due to the stimulation of bacterial activity by the carbon source (molasses) and concomitant oxygen consumption, as carbon is a major energy source for bacteria.

4.7. Phoslock™

Faithfull *et al.* (2006), Özkundakci (2006) and Yang *et al.* (2004) have reported significant reductions in phosphate in various applications laboratory and field applications. Faithfull *et al.* (2006) and Özkundakci (2006) indicated that Phoslock™ adsorbed the most phosphorus, although the longevity of applications was rather short; eight days in the mesocosm field study by Özkundakci (2006) and c. 89 h in the sediment reactor study by Faithfull *et al.* (2006). By comparison, the full-scale application of Robb *et al.* (2003), where two Phoslock™ applications were used in the Vasse River (Western Australia), showed that phosphate concentrations were still lower in the treated area than in the untreated area after a period of 194 days. Yang *et al.* (2004) showed in a batch adsorption study, that Phoslock™ was effective in removing phosphate from solution and that the phosphorus appeared to be irreversibly bound. A collation of the Phoslock™ results suggests that Phoslock™ is effective in binding phosphate, but in the field-oriented studies more phosphate can become available from other phosphorus fractions in the water column, the bottom sediments or via inflows, potentially overwhelming the capacity of Phoslock™ for phosphorus removal. This suggests that Phoslock™ application rates need to be considered carefully, both in terms of quantity and requirements for ongoing application, in order to achieve sustained phosphorus removal. Testing the uptake capacity under *in situ* conditions would reveal more insight into the P uptake behaviour of Phoslock™. A valuable evaluation of the efficiency of Phoslock™ should arise from an analysis of the monitoring data of two Phoslock™ applications in Lake Okareka in 2005 and 2006, with possibly a third application in 2007. These data could provide a valuable indication of whether the lanthanum modified clay, Phoslock™, is an effective product for sustained internal phosphorus load management.

4.8. Modified zeolite

Modified zeolite performed well for adsorbing phosphorus in different batch adsorption tests in the study of Yang *et al.* (2004). Faithfull *et al.* (2005) also found significant reductions in phosphate concentrations in the water overlying treated sediment cores. This result is interesting when compared with Özkundakci (2006) and Zheng (2006), who found no significant differences in phosphate concentration compared with controls. It is possible that the zeolite material differed in composition between the different experiments, as different batches and treatment techniques have been used over the duration of these studies.

5. Discussion

The effectiveness and longevity of management of internal nutrient loads using the sediment capping or flocculation is usually judged in terms of reduction in total phosphorus in the water column and concomitant decreases in chlorophyll *a* concentration (Welch and Cooke, 1999; Klapper, 2003; Berg *et al*. 2004), both of which are both indicators of the trophic state of a lake. Due to the large number of possible measures of success and the complexity of lake ecosystems, a clear application target for a successful restoration has to be set *a priori*. Waterbody managers, scientists and the community could collectively participate in setting goals for treatments. A reliance on remediation of a water body by using chemicals alone is likely to be expensive in the long term and should not be used without having made every effort to reduce external loads of nutrients arising from the catchment. Both scientists and managers have a clear role in managing the goals and expectations of a community may wish to have instantaneous improvements in lake water quality. Often it is only possible to achieve a compromise between expectations and actual accomplishment of lake restoration (Klapper, 2003).

Dose rates and timing of treatment are crucial for a successful application. Depending on the application target, an optimal dosing time would be after a harmful algal bloom has just occurred or before nutrient release from the sediment can be expected, e.g., before the hypolimnion becomes anoxic. To our knowledge, guidelines for favourable dosing times have not been stipulated for different materials. Dose rates, for alum in particular, estimated by considering the rate of internal phosphorus loading from the sediment or the mass of redox-sensitive phosphorus in the upper layers of the sediment, may be severely underestimated (Welch and Cooke, 1999). It has been difficult so far to establish general relationships between phosphorus forms and the intensity and duration of internal loading (Søndergaard *et al.* 2003). Furthermore, there is little information concerning the reactivity of various organic phosphorus species in the sediments, at what rates they are transformed and made available again for biological uptake, and which forms can be considered as refractory and thus will be buried in deeper sediment layers (Ahlgren *et al.* 2005). Phosphorus release from sediments can be calculated using different methods. Measured pore water gradients have been used to calculate diffusive fluxes of phosphate towards the sediment surface using Fick's first law of diffusion (Sinke *et al.* 1990). Knowing adsorption potential of phosphate for a potential capping material could help in the calculation of an effective dose rate to counteract the diffusion from the sediment into the water column.

Care must be taken, when considering full-scale applications in shallow lakes, since wind-generated waves can disturb the sediment capping material (Stüben *et al.*2002). Therefore the critical shear stress of potential treatment materials will be a valuable parameter, to determine the physical stability of the material in shallow lakes in particular. This may also be relevant to the 'nepheloid layer' in Lake Rotorua; the very mobile layer of fine sediment that appears to either remain suspended just above the sediment-water interface, or which settles to the sediments only temporarily under extremely calm conditions. Bioturbation may also decrease the long-term efficiency of a diffusion barrier with regard to phosphorus stabilisation (Stüben *et al.* 2002; Berg *et al*. 2004).

Whether a clay mineral is applied as a natural material or as a modified product, theoretically there is potential for clay minerals in binding certain nutrient species (Muljadi *et al*. 1966; Edzwald *et al*. 1976; Violante and Pigna, 2002). However, adsorption and ion exchange are reversible (Gaines and Thomas, 2004) and therefore the longevity is questionable. Modification of the mineral in certain ways could enhance the longevity and also the selectivity for certain nutrient species. Nevertheless, the diversity of results among the studies with identical materials suggests that more processes than adsorption and ion exchange are involved following clay mineral addition to natural waters, such as unwanted flocculation of small algae which could cause clogging of pores and prevent further uptake of phosphorus into the clay matrix.

Addition of any material, whether it occurs naturally or is manufactured, to natural ecosystems, is likely to have some adverse ecological consequences. Alum, for example, is known to cause a decrease in pH which can potentially result in ecologically unacceptable consequences to aquatic invertebrates and some other fauna (Cooke *et al.* 1993). Disturbance of the benthic flora and fauna to some degree seems unavoidable in use of sediment capping materials, particularly if there is a rapid deposition of sediment following a flocculant application (Klapper, 2003).

6. Prospects for future work

Our recent studies on sediment capping and flocculation for nutrient stabilisation, and our review of recent literature on this topic have provided information on the restoration potential of some sediment capping agents and flocculants, but many questions still remain. Given the current state of knowledge it is not possible to confirm *a priori* the circumstances under which a whole lake trial would be successful. Thus, whole-lake applications carry the risk of a financial burden, depending on the size of the application, with potential for limited success; dosing more of the adsorbent media is not necessarily better in an environmental setting where dose rates may influence biota health. A more comprehensive understanding of the effect of Phoslock™ applications in Lake Okareka may be possible by further analysis of the data collected by Environment Bay of Plenty as part of their regular monitoring programme and as part of the specific requirements for monitoring Phoslock™.

Future research should be carried out on the following foci:

- Establishment of chronic or acute toxic effects of the adsorbent materials.
- Effect of treatment applications on benthic biota, particularly capping materials that may alter physical characteristics of the sediments. Simple sediment environmental indices (e.g. pH, redox etc.) should also be examined closely as they may provide useful rapid assessment tools for assessing wider environmental effects of adsorbent media applications.
- Application of computer models for the purposes of both hindcasting application of an adsorbent to a lake and, with increasing confidence in these results, for the purpose of predicting the effects.
- Application techniques and costs, particularly in view of potential for quite radical changes in source of adsorbent materials, grain sizes and methods of application for a single adsorbent.

Where phosphorus in the bottom sediments is the application target, it will also be necessary to obtain a good understanding of the phosphorus species in the sediment and which species are transformed and made available again for biological uptake. Sediment porewater concentrations and their gradients have to be known in order to develop relationships for exchange processes at the sediment-water interface. Considerable knowledge has been built up in relation to the temporal and spatial variability of nutrients in the bottom sediments of Lake Rotorua over the past year through M.Sc. studies supported by Environment Bay of Plenty, but less so for Lake Rotoiti where less emphasis has so far been placed on sediment remediation compared with Lake Rotorua. Research by Özkundakci as part of a Ph.D. study at the University of Waikato (in progress) involves the use of nuclear magnetic resonance (NMR) to characterise phosphorus species in the sediments of key Rotorua lakes and is likely to improve understanding of how different adsorbent media may 'capture' phosphorus.

The scientific quandary that has emerged to date is how to accurately predict the long-term results of whole-lake treatment, without effectively engaging in a whole lake treatment. The methods used so far, including mesocosms in the form of limnocorrals and reactor studies in the laboratory, have weaknesses that detract from their usefulness in making predictions about whole lake treatment. There is scope for development of novel experimental techniques that improve upon the presently available methods. Numerical simulation relies on the quality of the input data and will be most effective when reliable data from long-term studies of treatment of whole lakes is available. At some stage, results from theory, simulations, small scale models and partial treatments must be compared with the results obtained from a whole lake treatment.

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