Comparison of efficacy of four P-inactivation agents on Lake Rotorua sediments

NIWA Client Report: HAM2008-105
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Executive Summary

As part of the programme for restoration of the Rotorua lakes, Environment Bay of Plenty has been investigating the use of sediment capping materials to reduce the amount of dissolved reactive phosphorus (DRP) in the lake water column from sediment release. Environment Bay of Plenty commissioned NIWA to conduct laboratory investigations of four P-inactivation agents, (Alum, Phoslock™, a modified Zeolite, and Allophane) for use as sediment capping materials. The objectives of this study were to 1) determine the efficacy of the four P-inactivation agents as capping materials on Lake Rotorua sediments; 2) identify any potentially adverse side effects of these P-inactivation agents on key microbial processes at the sediment-water interface; and 3) evaluate the longevity of these P-inactivation agents through simulated annual cycles of aerobic / anoxic conditions, with the addition of algal biomass to simulate the collapse of seasonal algal blooms.

Experimental treatment dose rates were based on the nominal P-binding capacity[1] of each capping material and these were also used to define P-removal expectations in the longevity experiment. These results include data from subsequent P-saturation testing at different pH values. Further details are summarised in the Technical Summary and full details are provided in the body of the report. The main results of this study related specifically to Lake Rotorua are shown in the following table:-

Capping material	**Alum**	**Modified Zeolite**	**Phoslock ™**	**Allophane**
Material formulation used in tests	Water soluble crystals	Granular (0 - 1 mm)	Amorphous flakes	Granular (relatively fine)
P-binding - Nominal	100	50	20	5
(g P / kg) **- Measured at pH 7.0**	45*	23	12	16
Application comments	Needs buffer to cause flocculation, slow to settle	Settles rapidly	Disperses rapidly, slow to settle	Fine particles slow to settle
Sediment coverage at tested rates	Good at all treatment rates	Poor at 50% and 100%, good at 200%	Good at all treatment rates, formed gel at highest treatment rate	Good at all treatment rates, formed "thick layer"
P-removal at tested rates	Good at all treatment rates	Poor at 50% and 100%, good at 200%	Good at all treatment rates	Good at all treatment rates
P efficacy - dose rate for 100% block (g product / m^2)	80	190	280	220*
Longevity at dose rates	Below expectations	Below expectations	Below expectations	Exceeds expectations
Impact on Nitrification aerobic (% NH_4-N relative to control at 100%)	500	<4	500	100
Impact on Denitrification aerobic (% suppression)	60	40	50	13
Other effects	Floc easily disturbed		Releases La 2 mg m^{-2} d^{-1}	
General comments	Not recommended as capping material for Lake Rotorua.	Needs further work to optimise grain size for best sediment coverage per unit treatment.	Fate of La leachate should be assessed for long-term chronic effects on microbial and benthic biota at the sediment-water interface.	Needs further work to establish the treatment rate required for use as a capping material on Lake Rotorua.

* Best estimate

Longevity results suggest that the undisturbed capping layers should remain effective for at least four years. None of these capping materials should be applied to the permanently aerobic zone of a lake.

[1] The mass of P that can be permanently bound by a unit mass of P-inactivation agent : units g P / kg dry weight.

Technical Summary

In this study, the testing methodology used the continuous-flow incubation system previously applied to Lake Okaro sediments (Gibbs et al. 2007). This technique was applied to sediment collected from below 17 m in Lake Rotorua to evaluate the performance of four P-inactivation agents. Incubation water was Lake Rotorua water, alternately aerobic then anoxic, both at natural DRP and nitrate (NO_3-N) concentrations and then with DRP and NO_3-N amendments to raise the concentrations of these nutrients. The P-inactivation agents were applied as capping materials at dose rates calculated to bind all available P released from the upper 4 cm of sediment (100% treatment), as well as dose rates at half (50% treatment) and double (200% treatment) that rate. Calculation of the amount of material to be applied for each treatment relied on the nominal P-binding capacity data provided from the suppliers of each P-inactivation agent except Alum where a literature value was used. This approach simulated how an end-user might be expected to apply these products. Treatments were in triplicate and compared with four controls (untreated sediments). The experiment was run in the dark, in a ventilated controlled temperature facility set to the lake water temperature (21°C) at the time of sampling. Incubation water pH was maintained within the range 6.8-7.2 consistent with natural lake water in the bottom of Lake Rotorua. Lake Rotorua sediment had a pH of 6.8 and a total available P (TAP) content in the top 4 cm of 3.168 g P m^{-2}, which was being released at the rate of about 27 mg P m^{-2} d^{-1} under anoxic conditions in the control incubation tubes.

The initial aerobic-to-anoxic cycle of sediment treated with the capping materials was used to estimate the P-removal efficacy of each P-inactivation agent on Lake Rotorua sediments (Objective 1). Subsequent aerobic-to-anoxic-to-aerobic cycles were used to evaluate the longevity of each P-inactivation agent as a sediment capping material (Objective 3). The results of these experiments were also evaluated for any potentially adverse side effects, especially on the microbial communities associated with nitrification and denitrification (Objective 2).

The results from the first aerobic-to-anoxic cycle showed that three of the four capping materials tested had the capability of blocking all of the DRP released from Lake Rotorua sediment when applied at the 100% treatment dose rate. The modified Zeolite did not achieve complete blocking until the 200% treatment dose rate. This appeared to be a function of the product grain size (0-to-1 mm) which had incomplete sediment coverage at the 50% and 100% treatment dose rates. Complete sediment coverage was achieved with the 200% treatment dose rate. The results from this part of the study coupled with the longevity tests over a 90-day period demonstrated that the actual P-binding capacities of each capping material was substantially different from the nominal P-binding capacities given. The reason for these differences appeared to reflect sediment effects, although the nominal P-binding capacity value given for the Allophane was probably incorrect. For Alum, modified Zeolite, and Phoslock™ the actual P-binding capacities were lower than expected while the actual P-binding capacity of Allophane was much higher than expected.

Subsequent measurement of the P-binding capacities of the three granular products at three different pH values (6.1, 7.0, and 8.9) showed that their ability to adsorb P was strongly influenced by pH. Measured P-binding capacities for Alum, modified Zeolite, and Phoslock™ were about half of the nominal values given while the measured P-binding capacity for Allophane was about 3 times greater than the nominal value given. Using the measured P-binding capacities at the natural lake water pH (7.0), coupled with the P-uptake and the longevity experiment results, provided a P-removal efficacy value[2] for each product, in the formulation as supplied for testing. Based on the P-removal efficacy results, the required dose rates for Lake Rotorua sediment below 15 m are:

- Alum 80 g m^{-2}
- Modified Zeolite 190 g m^{-2}
- Phoslock™ 280 g m^{-2}
- Allophane 220 g m^{-2}

In contrast to the P-removal study, which estimated how much P could be removed by the capping material treatments, the longevity experiment considered how long these treatments would remain effective before a re-treatment was required. In this experiment, the other DRP inputs to the lake sediments from stream inflows and the decomposition of senescing algal blooms and detritus falling to the lake bed, were also considered. In the continuous flow incubation system, the daily mass of P supplied in the lake water (0.08 mg d^{-1}) was similar in magnitude to the efflux of DRP from the sediment (0.10 mg d^{-1}). The longevity experiment was taken through four cycles of anoxic-to-aerobic conditions to simulate seasonal changes over a period of "four years". The results of the 50% Allophane and 200% Phoslock™ treatments, which were closest to their respective P-removal efficacy values, showed that the P bound on these products was not released during the anoxic phase and the capping materials continued to remove P released from the sediment and from the overlying water column and detritus through at least "three years".

This means that if the sediments were treated with any of these materials at application rates based on their respective P-removal efficacy values, the undisturbed capping layer should remain effective for at least four years. Given that the P is permanently bound to the capping layer and not released under anoxic conditions, the lake would essentially be "reset" and re-treatments would only be needed to control P released from sediments that subsequently bury the capping layer. In this evaluation, the operative word is "undisturbed". While the effects of gas ebullition on the integrity of the capping layer would require testing in the lake, there are indications that the Alum floc is very easily disturbed and thus Alum is not suitable for use on a large shallow lake such as Lake Rotorua.

Evaluation of the data for non-target effects (Objective 2) showed that, during the first aerobic and anoxic cycles, there was an apparent dose-rate dependent suppression of the microbial processes of nitrification and denitrification. Suppression of nitrification was seen as an apparent enhancement of

[2] P-removal efficacy value is the optimal amount of capping material required to block 100% of the total available P released from Lake Rotorua sediments.

NH_4-N release from the sediments while suppression of denitrification was a reduction in the amount of NO_3-N removed from the overlying water, relative to the concentrations of NH_4-N and NO_3-N, respectively, in the water from the controls.

The suppression effects under aerobic conditions at equivalent P-removal efficacy dose rates were highest with Alum and Phoslock™ which both reduced nitrification (NH_4-N increase to 500%) and suppressed denitrification by 60% and 50%, respectively. The modified Zeolite treatment, reduced the NH_4-N release to <4% of control and suppressed denitrification by around 40%. At its estimated P-removal efficacy dose rate, Allophane would be unlikely to affect nitrification but would probably suppress denitrification by around 13%, the lowest non-target effects of the capping material tested.

These results indicate that there could be a substantial increase in biologically available N in the lake if Alum or Phoslock™ were applied to aerobic sediments. There would also be a substantial decrease in denitrification and thus an increase in N retention in the lake if any of these capping materials were applied to aerobic sediments. Consequently, despite the minimal effects of Allophane, it is recommended that these capping materials should not be used in the permanently aerobic zones such as occur in the littoral zones of a lake, where there are high light levels and the potential for plant and algal stimulation by increased N.

The longevity results demonstrated that nitrification and denitrification suppression through the anoxic cycles was significantly reduced after additions of algal slurry before the 3rd and 4th anoxic cycles. This implies that the denitrification suppression was a surface barrier effect by the capping material rather than a toxicity effect on the microbial denitrifier population.

Experiments with elevated levels of DRP (up to 200 mg m^{-3}) and NO_3-N (up to 2000 mg m^{-3}) showed that P-removal was influenced by the diffusion of DRP into the sediment or capping materials. The results also showed that, although denitrification was suppressed by the capping materials at natural lake water NO_3-N concentrations, the denitrification potential of the sediment was essentially unaffected. The longevity results indicate that burial of the capping material by the thin layer of algal material reinstated the full denitrification potential of the sediment.

Other effects that were noted included:

- The Alum floc is difficult to form and settle, but easily disturbed by even small lake currents which could dramatically reduce its usefulness as a capping material in a large shallow lake.

- The modified Zeolite was the only capping material which reduced the release of NH_4-N from the sediments. This beneficial effect would be rapidly exhausted where sediment N release potential was high.

- Phoslock™ had a persistent release of La (~2 mg La m^{-2} d^{-1}) under aerobic and anoxic conditions, with that release being attributable to pH effects and other interactions with Lake Rotorua sediments, and a lack of DRP to bind with the La as it was released. The concentrations measured (4-7 mg La m^{-3}) were around the no observed effect concentration (NOEC) of 4.3 mg m^{-3} derived from a literature value for the acute and chronic toxicity (48-h EC_{50}) of La to water fleas (*Daphnia carinata*) of 43 mg m^{-3} in soft water. The release of La indicates the potential for food-chain accumulation and elevated tissue levels in trout livers have been measured for previous whole-lake applications (e.g., McIntosh 2007). While clinical studies from the literature have demonstrated that La bioavailability is extremely low and thus safe to use as a phosphate binder in medical treatments of humans, there is limited information on the effects of chronic long term exposure of La on the biota in aquatic ecosystems.

Conclusions from this study are:-

1. The granular products, Allophane, Phoslock™ and the modified Zeolite are likely to be more reliable than Alum when used as a capping material. Disturbance of the very light Alum floc by wind-induced currents in a shallow lake with a large fetch, make Alum unsuitable for use in Lake Rotorua.

2. These three capping materials have comparable P-binding capacities at pH 7.0 and P-removal efficacy estimates indicate that practical dose rates would be similar at around 200 g m^{-2} to block 100% of the TAP released from the top 4 cm of the deeper sediments in Lake Rotorua, under anoxic conditions.

3. The longevity of the capping layer depends on the level of disturbance and the rate of burial. P bound in the capping layer will remain there even under anoxic conditions and, consequently, re-treatment will be required when the P-binding capacity is exhausted or the capping layer is buried beneath new sediment. From this study, the undisturbed capping layers should remain effective for at least four years. Burial and gas ebullition could reduce that time estimate.

4. Non-target effects of these capping materials include significant suppression of nitrification and denitrification under aerobic conditions which could lead to higher dissolved inorganic N concentrations in the littoral zone and enhance N retention in the lake. Although Allophane had the lowest non-target effects, it is recommended that none of these capping materials be applied to the permanently aerated littoral zones of a lake.

5. All three granular capping materials require further study to resolve issues identified in the is report:
    - Modified Zeolite should be tested in a finer grain size range which gives a better sediment coverage per unit dose rate.
    - Allophane should be tested at lower dose rates to define the minimum dose rate.
    - The fate of La leaching from the Phoslock™ treatment on natural Lake Rotorua sediments should be assessed with specific reference to long-term chronic effects on microbial and benthic biota at the sediment-water interface.

Glossary

Capping material	Material that can form a continuous layer on top of the sediment.
P-inactivation agent	Material that actively adsorbs DRP under specified conditions.
P-binding capacity (PBC)	The total amount of DRP that can be adsorbed irreversibly by a P-inactivation agent. Units: g P / kg P-inactivation agent.
Nominal PBC	The P-binding capacity given by the supplier of the P-inactivation agent.
Measured PBC	The P-binding capacity determined from a P-saturation test over at least 50 hours as the total mass of P adsorbed per unit mass of P-inactivation agent.
P-removal efficacy	The theoretical amount of P-inactivation agent required to remove 100% of the available P in the top 4 cm of sediment determined under field conditions for a specific lake. (g P-inactivation agent / m^2).
Break-through	P break-through occurs when the P-binding capacity of the capping material becomes exhausted and can not adsorb any more P, and free DRP appears in solution.
ERMA explanation	Environmental Risk Management Authority: this authority provides guidelines for products – in this report Phoslock^{TM} – not the active ingredient of the product – for Phoslock^{TM} the active ingredient is Lanthanum (La). The ERMA guideline for a product can be related to the active ingredient in that product from the product formulation data. For example, Phoslock^{TM} has 45 mg La g^{-1}, thus the ERMA chronic ecotoxic guideline of 1 g Phoslock^{TM} m^{-3} is equivalent to a La guideline of 45 mg La m^{-3}.
Chronic (toxicity)	Involving a stimulus that lingers or continues for a relatively long time (often one-tenth of the life span or more). Chronic should be considered a relative term depending on the life span of an organism. A chronic effect can be lethality, growth, reduced reproduction, or some other parameter. Chronic means long. Frequently applied to non-lethal effects.
Acute (toxicity)	Involving a stimulus severe enough to induce a rapid response. In toxicity tests, a response observed in 96 hours, or less, is typically considered to be acute. An acute effect is not always measured in terms of lethality; it can measure a variety of effects. Note that acute means short, not mortality.
EC_{50}, EC_{25}	The effective toxicant concentration resulting in a 50% or 25% response (respectively) of a given parameter at a specific time of exposure (e.g., reduced growth or reproduction). Effective concentration (EC) refers to a range of effect measures (e.g., mortality, growth reduction) and thus the terminology may include lethal concentration (LC) values.
LOEC	Lowest observed effect concentration: The lowest measured concentration of an effluent or a toxicant that causes a significant observed effect on a test organism. The effect measured may differ between tests (e.g., lethality, growth reduction).
NOEC	No Observed Effect Concentration: The highest measured concentration of an effluent or a toxicant that causes no observed effect on a test organism. May be estimated as 10% of the EC_{50} (ANZECC 2000).
TEC	Threshold effect concentration: Calculated as the geometric mean of the NOEC and LOEC.
Trigger value (TV)	A term applied to a chemical guideline calculated using a risk-based assessment procedure as used in the ANZECC (2000) water quality guidelines.

1. Introduction

As part of the programme for restoration of the Rotorua lakes, Environment Bay of Plenty has been investigating measures to reduce the amount of dissolved reactive phosphorus (DRP) in the lake water column. This action is required to reduce algal biomass, by enhancing phosphorus (P) limitation to algal growth, and to shift the algal species assemblage away from potentially toxic cyanobacteria, which can become a dominant, scum-forming, nuisance species when there is an excess of DRP. One of the options to achieve this is the treatment of the lake with P-inactivation agents, either as flocculants to precipitate P from the water column or as a sediment capping material to block the release of DRP when the lakes stratify and the bottom waters (hypolimnion) become anoxic (Burger et al. 2007). Preliminary trials with several P-inactivation agents on Rotorua lakes and in the laboratory - Alum (Lake Okaro: Paul et al. 2008), Phoslock™ (Lake Okareka: McIntosh 2007), and a modified Zeolite (Lake Okaro: unpub. data; laboratory incubations: Gibbs et al. 2007) – have shown that these products can reduce the amount of DRP in the lake water column. The laboratory study demonstrated that these products could be tested under a range of simulated lake conditions to provide an estimate of their P-inactivation efficacy and any potential adverse effects from their use on a lake.

For the restoration of Lake Rotorua, Environment Bay of Plenty commissioned NIWA to conduct laboratory investigations of four P-inactivation agents, (Alum, Phoslock™, Modified Zeolite, and Allophane) for use as sediment capping materials. The objectives of this study were to:

1. determine the efficacy of the four P-inactivation agents as sediment capping materials on Lake Rotorua sediments;
2. identify any potentially adverse side effects of these P-inactivation agents on key microbial processes at the sediment-water interface;
3. evaluate the longevity of these P-inactivation agents through repeated cycles of aerobic / anaerobic conditions.

During the review process for this report, in addition to the normal peer review comments, input comments were sought from the capping agent suppliers. The responses indicated some issues of clarity and more importantly, a need to measure the actual characteristics of each product rather than just use the data provided by the suppliers. As these tests were conducted after the laboratory study, this report presents the results of the laboratory study together with the supplementary study to interpret the results. P-inactivation efficacies are derived for each agent when used as a sediment capping material on Lake Rotorua sediments. These data provide an

indication of the dose rates required to block the DRP release from the sediment, and provide an indication of how the efficacy of each sediment capping material is likely to be affected by burial with algal detritus following the collapse of seasonal algal blooms. This report also shows the non-target effects these capping materials may have on the sediment-water nutrient and trace metal effluxes in Lake Rotorua.

1.1 Background

A laboratory study of the efficacy of the sediment capping material Z2G1, a modified Zeolite, prior to its use on Lake Okaro (Gibbs et al. 2007), demonstrated that this capping material had a high uptake or binding capacity for both phosphate (DRP) and ammoniacal nitrogen (NH_4-N) from lake sediment cores. Based on triplicate results from 14-day incubations, the DRP efflux from Lake Okaro sediments was estimated to be about 40 mg m^{-2} d^{-1} and the NH_4-N efflux was about 150 mg m^{-2} d^{-1}. The laboratory experiments showed that Z2G1 at dose rates of 350 and 700 g m^{-2} completely blocked the release of these nutrients. These experiments also indicated that there was only a minimal effect on the nitrification-denitrification sediment microbial processes under anoxic conditions over the 14 day period of the study.

Based on sediment analyses, Lake Okaro sediments had 1.56 g P m^{-2} in the surface 20 mm. At an efflux of about 40 mg m^{-2} d^{-1}, all of the P in the surficial sediments would be released in about 40-50 days with the overlying water beneath the thermocline reaching DRP concentrations of around 160 mg m^{-3} which is consistent with lake water quality measurements during summer stratification.

The nominal uptake capacity of Z2G1 was 50 g P kg^{-1} (Scion data). NIWA laboratory saturation experiments at pH 7 measured an uptake capacity of around 20 g P kg^{-1} Z2G1 with most of that uptake occurring in the first few hours. At the nominal uptake capacity, the proposed nominal application rate of 500 g Z2G1 m^{-2} across Lake Okaro, the P uptake capacity was 25 g P m^{-2}, or 16 times the measured P load in the surface sediments.

In 2006, effluxes of DRP from the sediments of Lake Rotorua measured by Mark McCarthy (unpublished data) ranged from <10 µmol P m^{-2} h^{-1} (<7.5 mg P m^{-2} d^{-1}) in the inshore waters up to 60 µmol P m^{-2} h^{-1} (45 mg P m^{-2} d^{-1}) below 20 m under anoxic conditions. These values are consistent with the seasonal mean P efflux rates of 8-44 mg P m^{-2} d^{-1} estimated by Burger et al. (2007) measured *in situ* over the same depth range. At first the similarity of the deep water anoxic sediment effluxes of DRP with the Lake Okaro efflux was surprising given that analyses showed Lake Rotorua had about 2.9 g P m^{-2} in the surficial sediments, almost twice the amount in the Lake

Okaro sediments. The laboratory efflux estimations for both lakes were made using continuous flow incubations of surficial sediment cores under controlled conditions. The similarity of these effluxes under very different conditions and from different lake sediments, indicates that the P efflux is limited by the rate of supply of DRP to the porewater from mineralisation of organic material in the sediments, as suggested in the Lake Okaro study report (Gibbs et al. 2007).

This means that accumulation rates of DRP in the hypolimnion of Lake Rotorua should be similar to those in Lake Okaro but with the potential to reach twice the DRP concentrations. This would happen if Lake Rotorua were monomictic. However, because Lake Rotorua is polymictic, the bottom water accumulations are dispersed throughout the lake by wind mixing events on several occasions during each year. It is now known that these weak stratification events can occur during each calm period even in winter (Lake Rotorua monitoring buoy data, D. Hamilton, pers comm.). These short term pulses of nutrients from sediment release are effectively pumping the nutrients into the water column thus sustaining the growth of nuisance algal blooms which would otherwise sediment out of the water column in monomictic lakes.

Blocking the release of DRP from the sediments by the application of a P-inactivation agent used as a sediment capping material offers a possible remedy to the semi-continuous injection of DRP into the water column of the lake. However, before such an undertaking, it is important to determine the likely effects the application of a capping material to the Lake Rotorua sediments and to assess the efficacy of different capping materials and their P-removal efficacy application rates. This is the purpose of this study.

2. Methods

2.1 Sampling

Sediment cores were collected from a depth of about 17 m in Lake Rotorua on 14 February 2008 at a general location (Fig.1) where high sediment P concentrations had been found (Pearson 2007). At the time of sampling, the lake was calm and thermally stratified. The sediment surface below 17 m was coated with a layer of pale sulphur bacteria, *Beggiatoa* (Fig. 2). *Beggiatoa* was not found on sediment cores taken at depths shallower than 15 m.

Intact, undisturbed sediment cores (40) were collected using a Jenkins Corer (Fig. 3A) and the upper 10 cm of sediment from each was transferred into an incubation tube (Fig. 3B) complete with the overlying water. Each incubation core was sealed with a 40-mm thick high-density foam plug in the top and bottom, and stored upright in a plastic crate in a water bath for transport to the laboratory.

The top 10 cm of one additional core were extruded and sectioned into 2-cm thick slices which were placed in pre-weighed 100-ml polyethylene screw-cap pottles and sealed for chemical analyses.

Raw lake water was collected in six 120-litre wide-neck black alkathene drums fitted with two 50-micron plastic bag liners, one inside the other. The water was pumped from near the edge of the lake with the pump intake inside an upright submerged 20-litre plastic bucket to reduce the amount of detritus in the water. When each drum was full, the individual plastic liners were tied tightly with plastic cable ties and the drum lid was fitted to prevent spillage during transport.

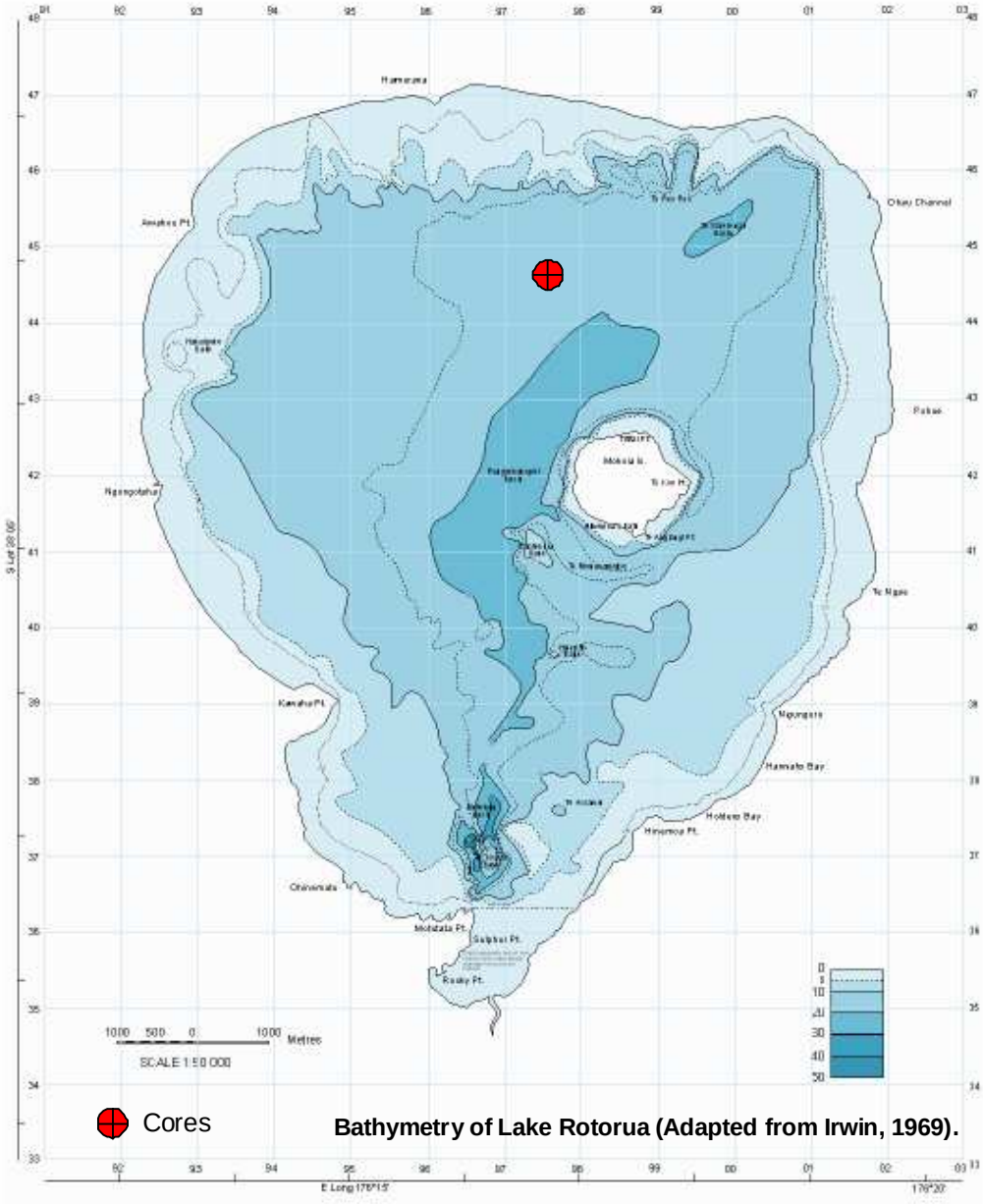

Figure 1. Site map of Lake Rotorua relative to the lake bathymetry. Sediment cores were collected in a depth of about 17 m in the northern part of the lake (red symbol).

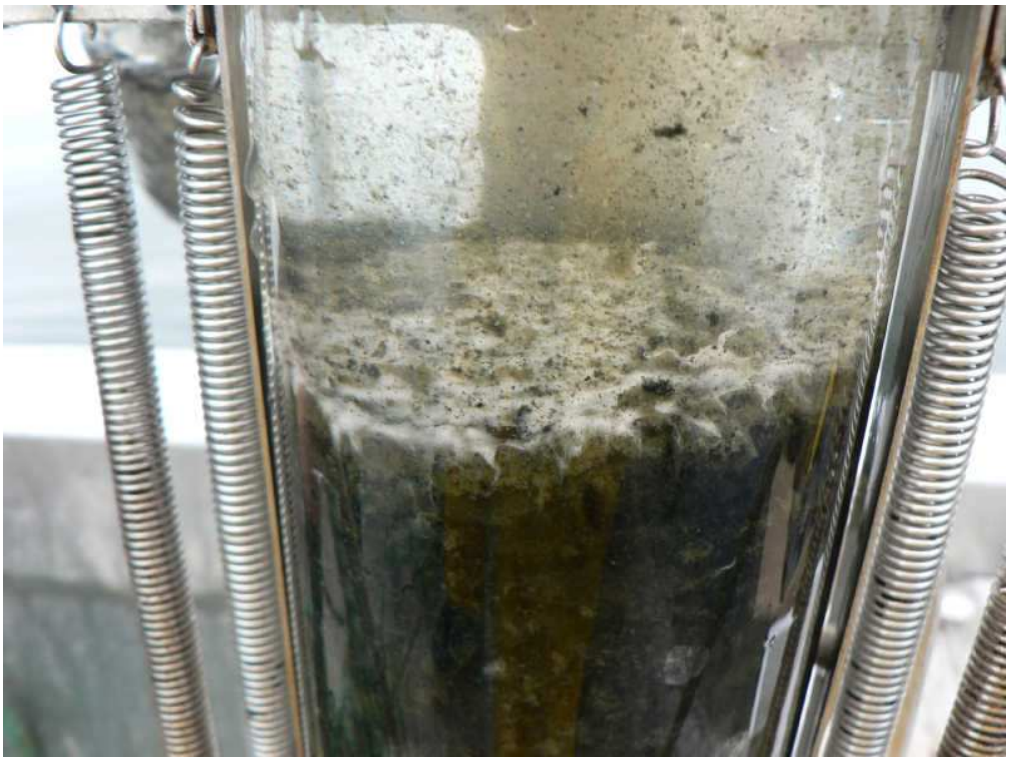

Figure 2. ***Beggiatoa*** sulphur bacteria on Lake Rotorua sediment from a depth of 17 m.

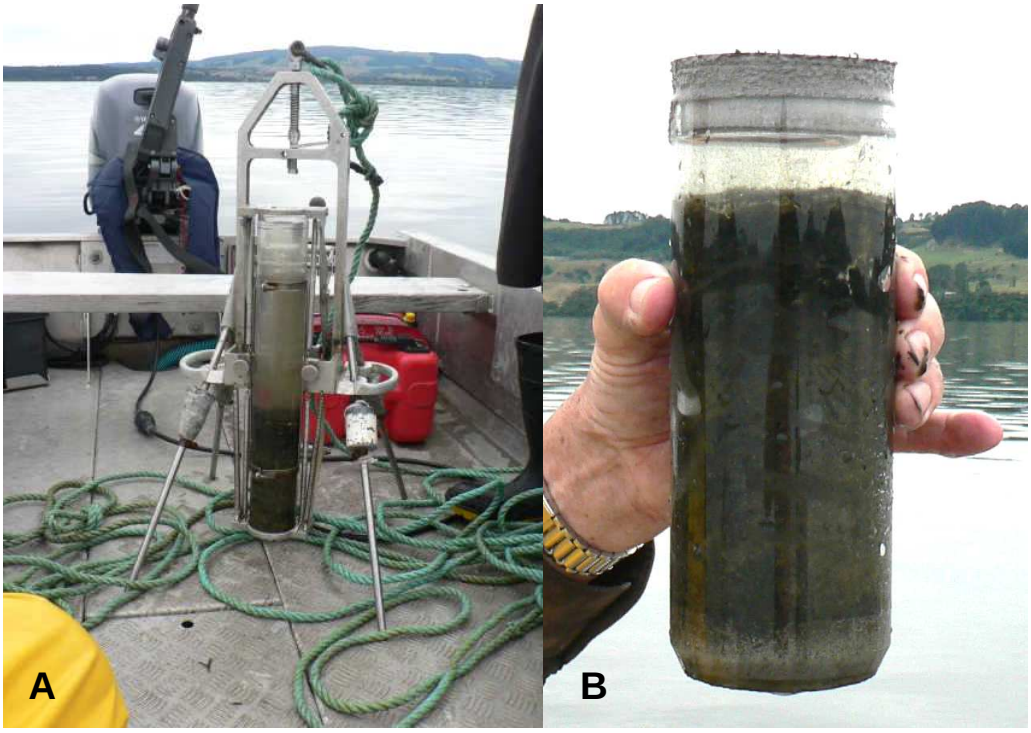

Figure 3. **A**) Jenkins corer**; B**) Sediment after transfer to the incubation tube.

2.2 Set up

On return to the laboratory, the sediment incubation cores and water drums were transferred to a ventilated controlled temperature room set to a temperature of 21°C, the surface temperature of the lake at the time of sampling. The sediment incubation tubes were opened and the sediment mixed to remove methane gas pockets. The level of the sediment in each incubation tube was adjusted, by moving the bottom plug, until there was a volume of about 100 ml between the sediment surface and the top plug when it was inserted. With the top plugs removed, the incubation cores were placed in plastic crates in a water bath of aerated lake water, submerged, and allowed to equilibrate for four days to let the sediment surface become aerobic.

On the first day of the experimental run, the four capping materials, Alum, Allophane, Phoslock™, and the Modified Zeolite, were applied to the sediment surface either as a liquid (Alum), or as a slurry so that the sediment surface was coated as evenly as possible (Fig. 4). Control sediments were left untreated. To facilitate flocculation of the Alum treatments, the water in those incubation tubes was buffered with sodium bicarbonate solution (2 ml of 0.9% stock solution) prior to adding the Alum.

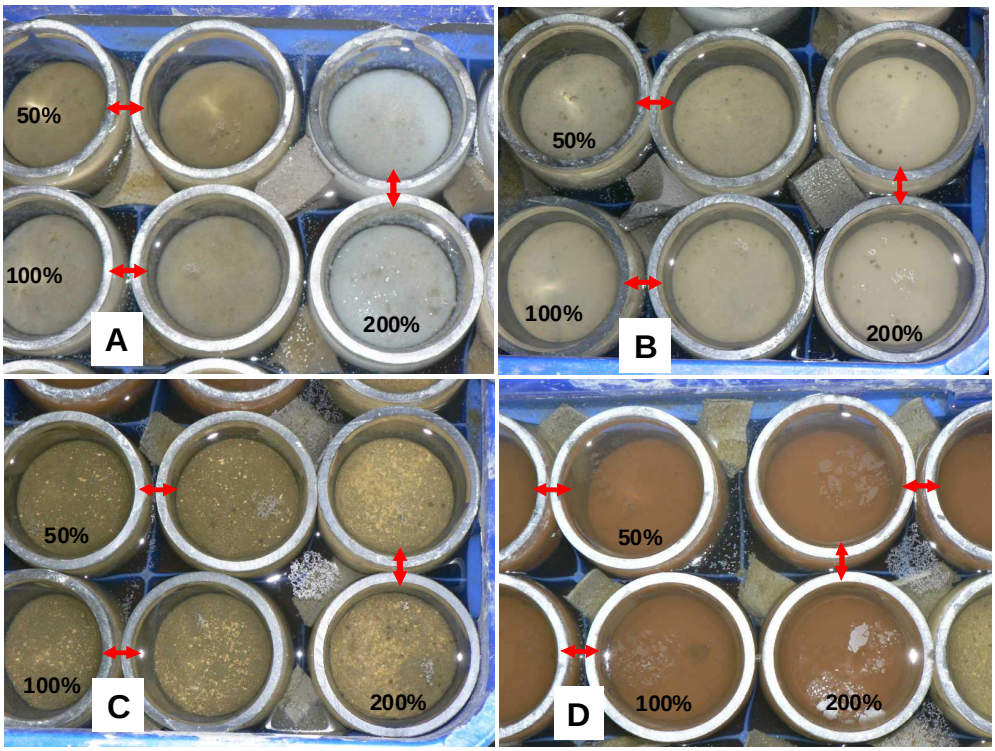

Figure 4. **A**) Alum; **B**) Phoslock™; **C**) Modified Zeolite; **D**) Allophane. Treatments are indicated by % (see text) and replicate tubes are linked by red arrows. Not all tubes shown.

After treatment it was observed that the granular (0-to-1 mm) formulation of the modified Zeolite did not evenly cover the sediment surface (Fig. 4C) compared with complete coverage by the floc formed by Alum (Fig. 4A), the fine grain sized Allophane (Fig. 4D), and the almost colloidal layer of Phoslock™ (Fig. 4B).

Because the previous study (Gibbs et al. 2007) had found gas ebullition disrupted the sediment and caused the surface layer to turn over in the incubation tube, plastic mesh screens (1-cm mesh size) were fitted in the overlying water space (Fig. 5A) to overcome this problem. The top plugs were then fitted and the continuous flow incubation process started.

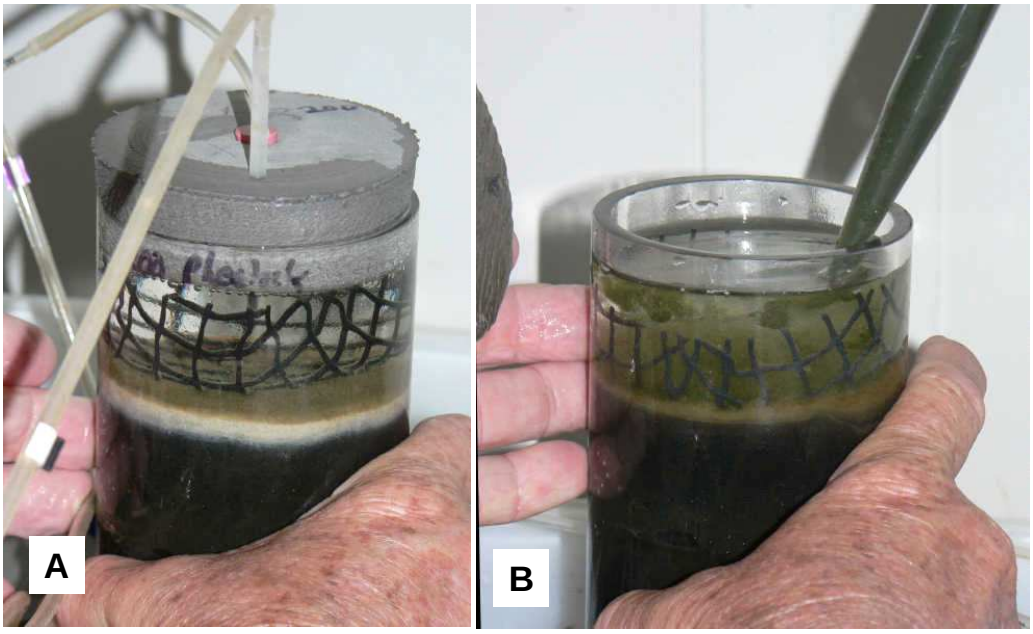

Figure 5. **A)** Incubation tube showing the positioning of the mesh screen designed to prevent sediment turn-over during ebullition; **B**) Application of the algal slurry to the core for objective 3 (see text).

The continuous flow incubation system (Fig. 6) was essentially the same as that used for the previous study of Lake Okaro (Gibbs et al. 2007). For the aerobic incubation runs, natural lake water in a drum was aerated via aeration stones using a clean air supply from outside the building, before being distributed to all incubation tubes; i.e., all incubation tubes received the same water. A new drum of lake water was used each day. Similarly, for anoxic incubation runs, the water in a drum was bubbled with oxygen-free nitrogen gas to remove the dissolved oxygen. The pH of the de-oxygenated water was adjusted to around 7 by bubbling with carbon dioxide gas (CO_2). To achieve anoxic conditions the inner liner bag was sealed around the tubes into the water and the outer liner bag was sealed around the tubes independent of the

inner bag. Because the nitrogen gas escaping from the inner liner held the outer liner under positive pressure, the resultant gas space between the bags acted as an "air-lock" to prevent oxygen from the atmosphere diffusing into the water through the plastic or via any defects in the inner plastic liner. Anoxia was achieved within 2 hours of beginning the N_2 gas bubbling and a short burst (30 seconds) of CO_2 gas was sufficient to adjust the pH down from 8.5 to around 6.8.

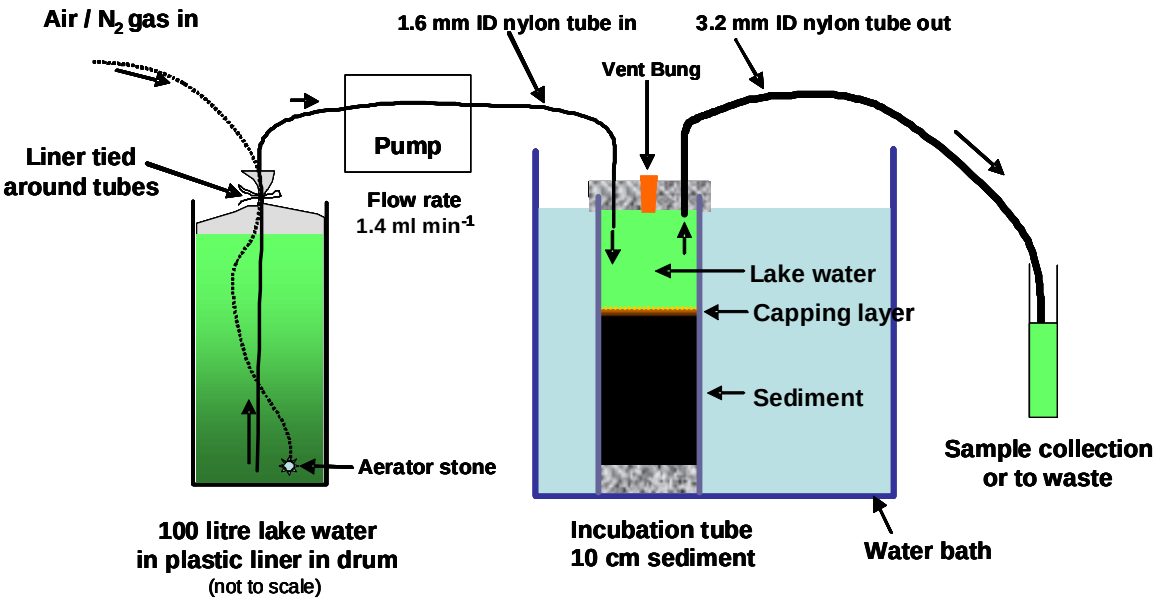

Figure 6. The continuous flow incubation system. Two liners were used in the source water drum to ensure anoxia was maintained when purging oxygen with nitrogen gas. Run temperature was 21ºC to simulate summer lake temperatures.

2.3 Treatments

The treatments used a range of dose rates applied to the sediment in the incubation tubes were based on the total available[3] P (TAP) in the top 4 cm of sediment and the nominal P-binding capacity of each capping material. The nominal P-binding capacity value (Table 1) was given by the manufacturers as the nominal maximum amount of P that can be bound by each capping material expressed as g P / kg capping material. The value for Alum is a literature estimate (Cooke et al. 2005). The choice of the top 4 cm was to conform to the standard procedure used for estimating the total available P in lake sediment (Cooke et al. 2005).

[3] Available P is that P which can be mineralised from the organic matter or unbound from metal oxides as DRP.

2.3.1 Treatment concept

Testing the four P-inactivation agents at the suppliers recommended dosing rate would demonstrate that these products worked but would provide no scientific basis for determining there efficacies i.e., is the recommended dose correct for this lake or is it more or less than is actually required. The focus of the testing in this study was not on whether these products remove P but on the dose rate where they stopped removing P i.e., the lowest dose rate that removes 100% of the TAP from the top 4 cm of Lake Rotorua sediment is the P-removal efficacy expressed as g product m^{-2}. The point where they stopped removing P is where the P-binding capacity becomes exhausted and there is P break-through i.e., free DRP appears in the overlying water column. Note, the P already bound by the product stays bound to it and is not released.

In order to compare the four different P-inactivation agents used as sediment capping materials, there needed to be a standardised approach which could normalise these materials relative to each other. Each capping agent has three different characteristics that must be considered: P-binding capacity, product formulation, and an application factor which may be derived from how the product behaves in a field-dosing situation. With each product the nominal P-binding capacity is known (Table 1), and the mass of TAP in the top 4 cm of Lake Rotorua sediment can be measured. Estimated TAP was 3 g P m^{-2}. These two values provide the basis for calculating the dose rates to compare their P-removal efficacies. Assuming the data from the suppliers is correct, dose rates calculated in this way will be less than the recommended dosing rates.

While it would seem possible to estimate the P-removal efficacies from sequential additions of DRP to these products shaken in a flask of water, those values would not include the product formulation effects (e.g., flocculation, grain size, formation of gelatinous layers) and application factors (e.g., interaction with natural sediments, consequences of the pH and REDOX environment of the sediment beneath the capping layer). Also, flask evaluations would not show any hidden “non-target” side effects such as effects on the microbial nitrification and denitrification community on the sediment-water interface, or the mobilization of toxic metals from the sediments if the REDOX conditions change across the sediment-water boundary (e.g., Gibbs et al. 2007; Vopel et al. 2008).

In this study, the dosing rates were calculated to provide sufficient capping material to bind all of the TAP in the top 4 cm of Lake Rotorua sediment. This was called the “100%” treatment. Treatments were also made at half this dosing rate, i.e., “50%”, and at twice this dosing rate i.e., “200%” (Table 1). This spread of treatments was to ensure that at least one dosing rate from each product would remain active throughout

the time-series sampling. Having found the point where there was break-through, reasons could be assessed as to why this did or did not match expectations.

Each treatment used three replicate sediment incubation tubes and there were four control (untreated) sediment incubation tubes. Because the peristaltic pump used for the continuous flow system could not handle 40 tubes simultaneously, the incubation tubes were divided into two groups with two sets of capping material treatments in each, plus two controls.

2.3.2 Sampling protocols

The experimental schedule for objectives 1 and 2 was designed to evaluate the sediments under aerobic versus anoxic conditions using both natural lake water and lake water amended with high concentrations of DRP and nitrate-nitrogen (NO_3-N). Each phase of the experiment was run for a minimum of 5 days with sampling of the inflow and outflow water for dissolved nutrients at the end of each day. In all cases the first day of each run was not sampled as previous experience demonstrated that the day-1 data was most likely to show the effects of the setting up disturbances. Also, in all cases an additional water sample was collected on the last day and preserved with nitric acid for determination of total dissolved metals. All water samples were syringe filtered through a 2.5 cm Whatman GF/C glass fibre filter in a Swinnex filter holder, directly into the sample bottles, at the time of sampling.

Table 1. Experimental dose rates (g material / core) of the four capping materials as applied to the individual incubation cores and the equivalent dose rate as would be applied to a lake. Calculations used a TAP value of 3 g P m^{-2}. (N PBC = nominal P-binding capacity). Controls had no capping material added.

N PBC (g P / kg)	Treatment	50%	100%	200%
5	**Allophane**			
	g material / core	1.155	2.31	4.62
	= g/m^2	300	600	1200
20	**Phoslock**			
	g / core	0.289	0.578	1.155
	= g/m^2	75	150	300
50	**Mod Zeolite**			
	g / core	0.116	0.231	0.462
	= g/m^2	30	60	120
100	**Alum**			
	g / core	0.058	0.116	0.231
	= g/m^2	15	30	60

To conserve lake water, the continuous flow system was turned off and the incubation tubes were left open over the weekends between aerobic runs. Before and between anoxic runs, the incubation tubes were left closed with the continuous flow system turned off and the N_2 bubbling gas at reduced flow. This was sufficient to maintain anoxic conditions in the source water drums.

The experimental schedule for objective 3 was designed to test the effect of repeated shifts from aerobic to anoxic conditions and back. This was run on the same sediment with all incubation treatments being taken through a total of four aerobic-anoxic cycles. Protocols for conserving lake water under aerobic and anoxic conditions were as above with the continuous flow regime running for at least 48 hours before sampling for dissolved nutrients. Total dissolved metals were not measured. The schedule also included a simulation of burial by detritus following an algal bloom during the aerobic phase. This was achieved by applying a slurry of enteromorpha from Lake Rotorua to the sediment surface after sampling for the aerobic phase (Fig. 5B). The slurry was made by putting fresh enteromorpha through a food blender and decanting the organic mixture from any sand. The organic mixture was divided into equal portions and stored in sealable 5-litre plastic buckets at 4ºC. Before use, the overlying water was removed leaving a thick slurry which was applied to the surface of each incubation tube, except controls, using a 10-ml pipetter. A 10-ml aliquot of the slurry, as applied to the sediment in the incubation tubes, was taken for analyses.

2.4 Analytical measurements

The wet sediment slices were analysed for bulk density before the pore water was extracted. The sediment from each slice was analysed for TAP, total nitrogen (TN), total iron (TFe), total manganese (TMn), total arsenic (TAs), total aluminium (TAl), total zinc (TZn), and total lanthanum (TLa). The filtered pore water and acid preserved water samples from the continuous flow incubation tubes were analysed for the total dissolved metals – Fe, Mn, As, Al, Zn, and La. All of these metal analyses were measured by RJ Hill Laboratories, Hamilton using an ICP mass spectrometer.

Water samples were analysed for the dissolved nutrients DRP, NH_4-N, and NO_3-N using a Lachat flow injection analyser (FIA) and standard Lachat FIA methods at NIWA.

The algal slurry was analysed for dry weight after drying at 105ºC and organic content was determined as the loss of weight after combustion at 550 ºC. The approximate C, N, and P content of the slurry was estimated from Redfield (1958) mass ratios

assuming that for algal/plant material the carbon content was 47% of the total organic content.

2.5 P-saturation measurements

Subsequent to the main study, the P-binding capacities of the three granular products were measured. This was required because results from the main study were substantially different from theoretical expectations based on the nominal P-binding capacities given by the suppliers. As the P-binding capacity of a sediment capping material is sensitive to pH (Peterson et al. 1976), they were estimated at three different pH levels (6.1, 7.0, and 8.9) which encompass the normal range of pH in a lake – pH 6.1 in an anoxic hypolimnion, pH 8.9 during an algal bloom – and at pH 7.0 which is the middle of the range (pH 6.8-7.2) used in the main study. From previous experiments it is known that P uptake by P-inactivation agents is rapid, with more than 90% occurring in the first few hours, the P-saturation experiments were run for about 50 hours to ensure complete saturation had been achieved.

The P-saturation tests used 5 g of granular material in 1 litre of distilled water containing 1 g of buffered P made by combining sodium di-hydrogen phosphate and di-sodium hydrogen phosphate in the appropriate proportions to obtain the required pH. The mixtures were shaken periodically then allowed to settle before sampling. At timed intervals, approximately 0.5 g aliquots of the settled product were removed by pipette and separated from the aqueous phase by centrifuging at 3000 rpm for 10 minutes. The liquid was discarded and the solids were washed with distilled water before analysis. The solid material was dissolved in aqua regia before analysis of bound P by ICP-Mass Spec. The ICP-MS analysis also gave a complete spectrum of the mineral content of the sample, those data were used to answer specific questions about product behaviour.

3. Results

3.1 Sediment chemistry

Analytical results for metals from the sediment slices are presented in Table 2 as mg kg^{-1} dry weight, and the pore water concentrations as mg m^{-3}. The analytical detection limits are also given. The total available phosphorus and total nitrogen content of the sediment are also given as mg kg^{-1} dry weight.

Bulk density in the top 10 cm averaged 1.066 g cm^{-3}. This means there are 66 kg of dry sediment in each m^3. Assuming that the diffusion of biologically available P comes from the top 4 cm, then it comes from 2.64 kg dry weight sediment m^{-2}. Using the average concentration of available P in the top 4 cm i.e., 1.2 g kg^{-1} dry weight, this gives a total available P content of 3.17 g P m^{-2}. This is consistent with the estimate of 3.0 g P m^{-2} used to calculate the dose rates for the sediment incubations.

Table 2. Metal concentrations in the sediment, pore water, and bottom water taken from the Jenkins corer tube <5 cm above sediments from Lake Rotorua on 14 February 2008. Total available phosphorus (TAP) and total nitrogen (TN) in the sediments are included. Sediment concentrations are as mg kg^{-1} dry weight except for TN which is given as g $100g^{-1}$ dry weight. Pore water and bottom water concentrations are as mg m^{-3}. The analytical detection level for metals are as reported by R.J. Hill Laboratories Ltd.

Slice depth (cm)	**Al**	**Fe**	**Mn**	**Zn**	**As**	**La**	**TAP**	**TN**
Sediment (mg kg^{-1} dw)								(g $100g^{-1}$ dw)
0 - 2	7500	7900	490	45	53	3.9	1300	1.10
2 - 4	7800	6600	410	46	63	3.7	1100	0.91
4 - 6	8100	7200	340	46	61	3.9	950	0.85
6 - 8	8700	10000	330	50	75	4.0	870	0.78
8 - 10	8400	7400	360	49	49	4.2	760	0.83
Pore water (mg m^{-3})								
0 - 2	370	1200	1900	160	32.0	0.37		
2 - 4	540	620	1000	150	51.0	0.50		
4 - 6	160	87	4100	390	5.3	0.33		
6 - 8	180	370	4600	380	7.4	0.39		
8 - 10	240	390	5900	400	11.0	0.57		
Bottom water (mg m^{-3})	3	38	46	2.1	3.5	<0.1		
Detection limit (mg m^{-3})	3	20	0.5	1	1	0.1		

3.2 Objective 1

"Determine the efficacy of the four P-inactivation agents as sediment capping materials on Lake Rotorua sediments".

The P results from the continuous flow incubations using natural lake waters in aerobic and anoxic conditions are given as mean effluxes relative to the inflow water DRP concentration for each capping material (Fig. 7). Effluxes have units of mg m^{-2} d^{-1} with negative values indicating a loss of DRP from the overlying water and positive values indicating an increase of DRP in the overlying water. An increase in DRP is interpreted as DRP released from the sediment.

Under aerobic conditions, all capping materials caused a reduction in DRP concentration greater than in the control. This indicates that the four capping materials were removing DRP from the overlying water. The loss of DRP in the controls under aerobic conditions was most likely due to uptake by Fe and Mn oxides in the sediments. There was a difference in the DRP removal between capping materials and between treatments for Allophane and the modified Zeolite. Alum and Phoslock™ removed the most DRP from the water column, followed by Allophane then the modified Zeolite. Both Allophane and the modified Zeolite showed a small trend of increasing DRP removal with increasing dose rate (Fig. 7).

Under anoxic conditions DRP was released from the control sediments at a rate of around 27 mg m^{-2} d^{-1} (Fig. 7). Lower effluxes from the capping material treatments indicated that the release of DRP from the sediments was being blocked. At all levels of treatment the capping materials Alum, Phoslock™, and Allophane completely blocked the release of DRP from the sediments and had the capacity to remove additional DRP from the overlying water column. Except for Allophane, which had an apparently constant DRP removal rate, there was an increase in the removal of DRP from the overlying water column with increasing treatment.

The modified Zeolite at the 50% and 100% treatments was not able to block the release of DRP from the sediment (Fig. 7) despite having a theoretically higher P-binding capacity than Phoslock™ and Allophane. At the 200% treatment, the modified Zeolite did completely block the DRP release and had the capacity to remove additional DRP from the overlying water column, comparable with the other capping materials. Because the increase in blocking efficiency was not a gradient, with the 50% and 100% treatments blocking similar amounts of DRP release, it is likely that the partial blocking was a result of the observed incomplete coverage of the sediment surface by the granular (0-to-1 mm) formation of this product, compared with the much finer grain size and complete sediment coverage by the other products (Fig. 4).

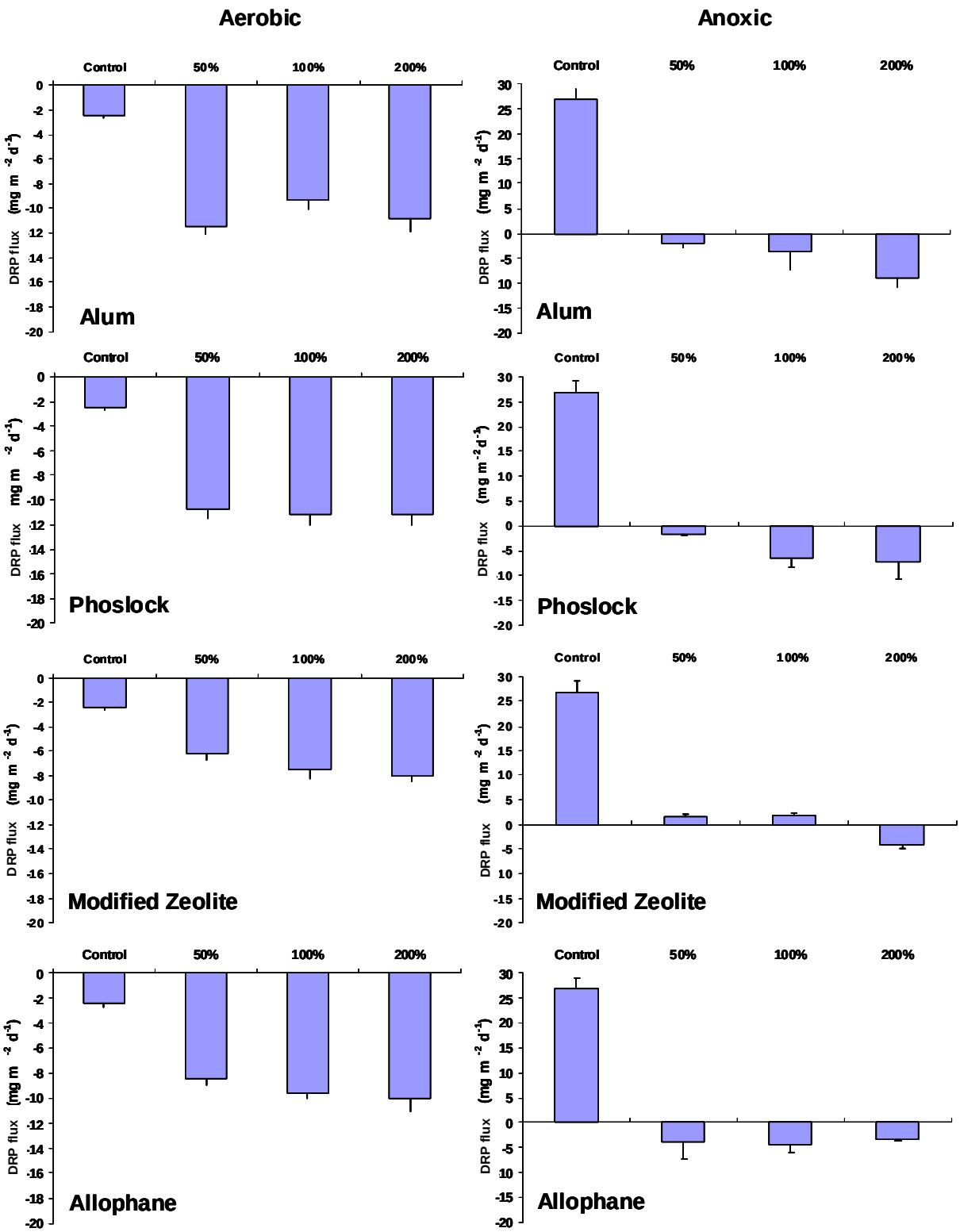

Figure 7. Phosphorus: Mean DRP effluxes for each capping material treatment under aerobic and anoxic conditions in natural lake water. Negative values indicate DRP uptake; positive values indicate DRP release from the sediment. (Error bars = 1SD).

3.3 Objective 2

"Identify any potentially adverse side effects of these P-inactivation agents on key microbial processes at the sediment-water interface".

The microbial processes of concern are those that regulate the removal of nitrogen through mineralisation, nitrification and denitrification. As these processes affect the efflux and thus concentration of DIN species in the lake water column, the changes in NH_4-N and NO_3-N concentrations were also examined in detail. Compared with the control concentrations, an **increase** in NH_4-N concentrations would indicate a net suppression of nitrification processes. A **reduction** in the relative loss of NO_3-N in the water compared with the control would imply a net suppression of denitrification processes. Microbial nitrification-denitrification processes occur at the aerobic-anoxic interface in the sediment and stop when the overlying lake water becomes anoxic. Both effects occur together, although there may not be a stoichiometric relationship.

The NH_4-N and NO_3-N results from the continuous flow incubations using natural lake waters in aerobic and anoxic conditions are given as mean effluxes relative to their inflow water concentrations for each capping material (Figs. 8, 9).

3.3.1 NH_4-N

These results show that each capping material had a different and apparently dose-related effect on the efflux of NH_4-N from the sediment (Table 3). Under aerobic conditions the lowest Alum treatment (50%) results showed no difference between inflow and outflow NH_4-N concentrations, which was a suppression of the efflux seen in the control (Fig. 8). As the dose rate increased, the efflux of NH_4-N became measurable. This efflux was suppressed at the 100% treatment dose rate, but was enhanced to almost double the control in the 200% treatment. Under anoxic conditions this pattern was reversed with the 50% and 100% Alum treatment dose rates enhancing the NH_4-N efflux while the 200% treatment suppressed it relative to the control.

Under aerobic conditions the lowest Phoslock™ treatment (50%) results were similar to the control suggesting no effect. However, the NH_4-N efflux increased significantly with increasing dose rate and was 5-fold greater than the control at the 200% treatment with a mean increase of 287% relative to the control (Table 3). This represents a significant suppression of microbial nitrification processes. Under anoxic conditions the pattern of NH_4-N efflux increase with increasing dose rate was still observed but the magnitude of the increase was minimal (Table 3).

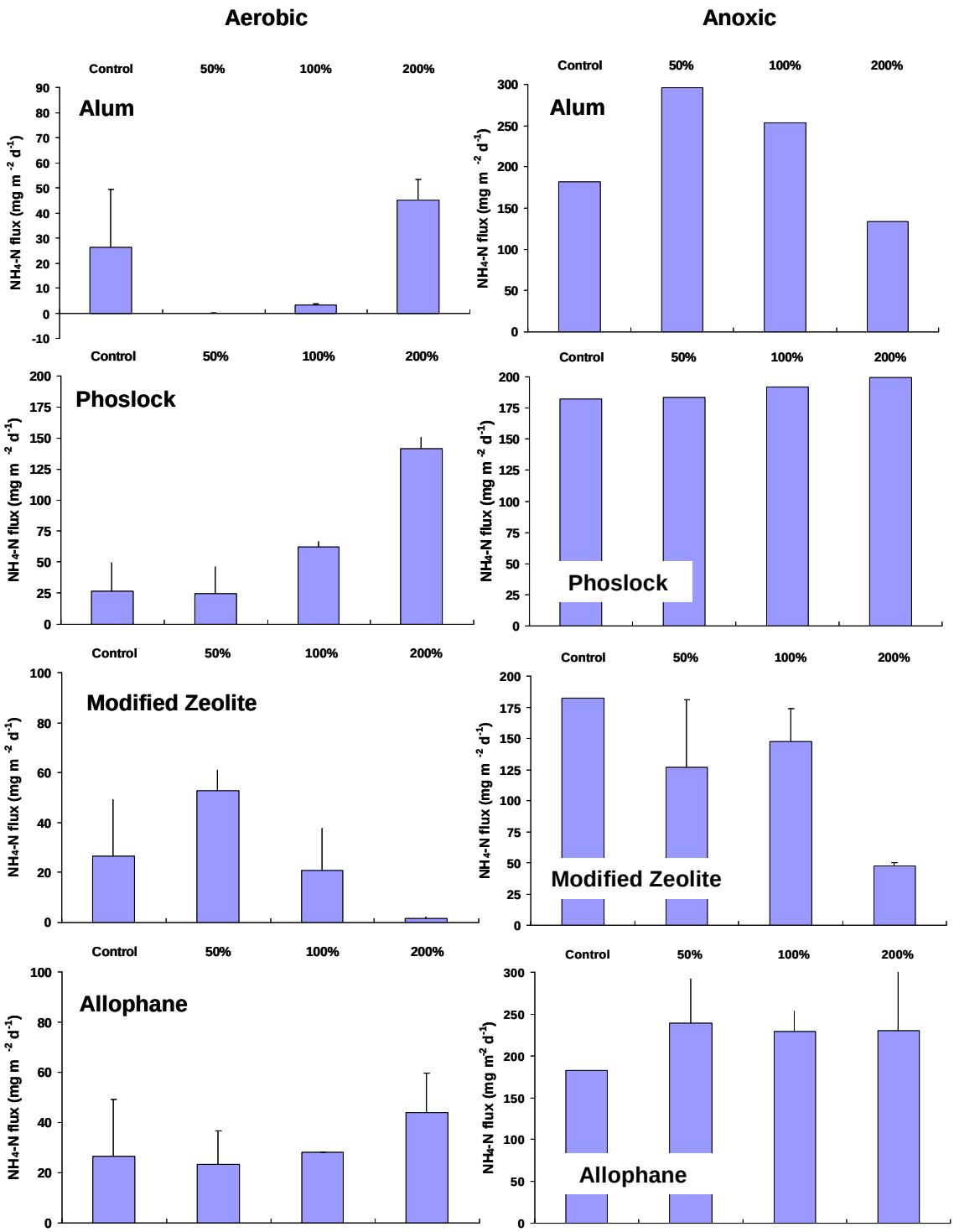

Figure 8. Ammonium: Mean effluxes for each capping material treatment under aerobic and anoxic conditions in natural lake water. An increase over the control is an indication of suppression of the nitrification process. (Error bars = 1SD).

The modified Zeolite was expected to remove NH_4-N from the water column (Besser et al. 1998) but, under aerobic conditions, the lowest (50%) treatment showed an enhancement of the NH_4-N efflux relative to the control. At higher dose rates the NH_4-N efflux was suppressed and the suppression increased with increasing dose rate. The 200% treatment dose rate suppressed the NH_4-N efflux to near zero (Table 3). This is consistent with NH_4-N adsorption onto the Zeolite mineral substrate of this product (Besser et al. 1998). The pattern of increasing NH_4-N efflux suppression with increasing dose rate was present under anoxic conditions and there was no apparent enhancement of the efflux rate at the lowest treatment (Fig. 8). Note that the NH_4-N adsorption estimates (Table 3) are based on the 200% treatment only as that was the only treatment that gave complete sediment coverage for this product.

The Allophane treatments under aerobic conditions had minimal effect on NH_4-N with only a small increase in efflux for the 200% treatment (Fig. 8). Under anoxic conditions there was an increase of about 30% in the NH_4-N efflux for all treatments.

3.3.2 NO_3-N

All capping materials caused some reduction (suppression) of denitrification in the sediments (Fig. 9). The mean reduction was variable and different between aerobic and anoxic conditions for each capping material (Table 3).

Table 3. Non-target effects of the capping materials on nitrification, expressed as % NH_4-N in the control (values below 100 indicate adsorption by the product while values above 100 indicate enhanced release), and denitrification expressed as % suppression relative to the control. These values are means for the three treatments. (* 200% treatment data used only, as other treatment dose rates did not give complete sediment coverage).

	Alum	Mod Zeolite*	Phoslock™	Allophane
Nitrification				
Aerobic conditions	170	4	287	120
Anoxic conditions	125	26	105	131
Denitrification				
Aerobic conditions	43	37	48	17
Anoxic conditions	6	13	14	5

The least suppression was by Allophane and greatest was by Phoslock™ under aerobic conditions. Under anoxic conditions Allophane and Alum had the least effect on denitrification while the modified Zeolite and Phoslock™ had the greatest effect, although this was substantially less than their aerobic effects. Because both the reduction in NO_3-N removal and the enhancement of NH_4-N release occurred

simultaneously, these results indicate that denitrification in natural lake was suppressed significantly under aerobic but only slightly under anoxic conditions.

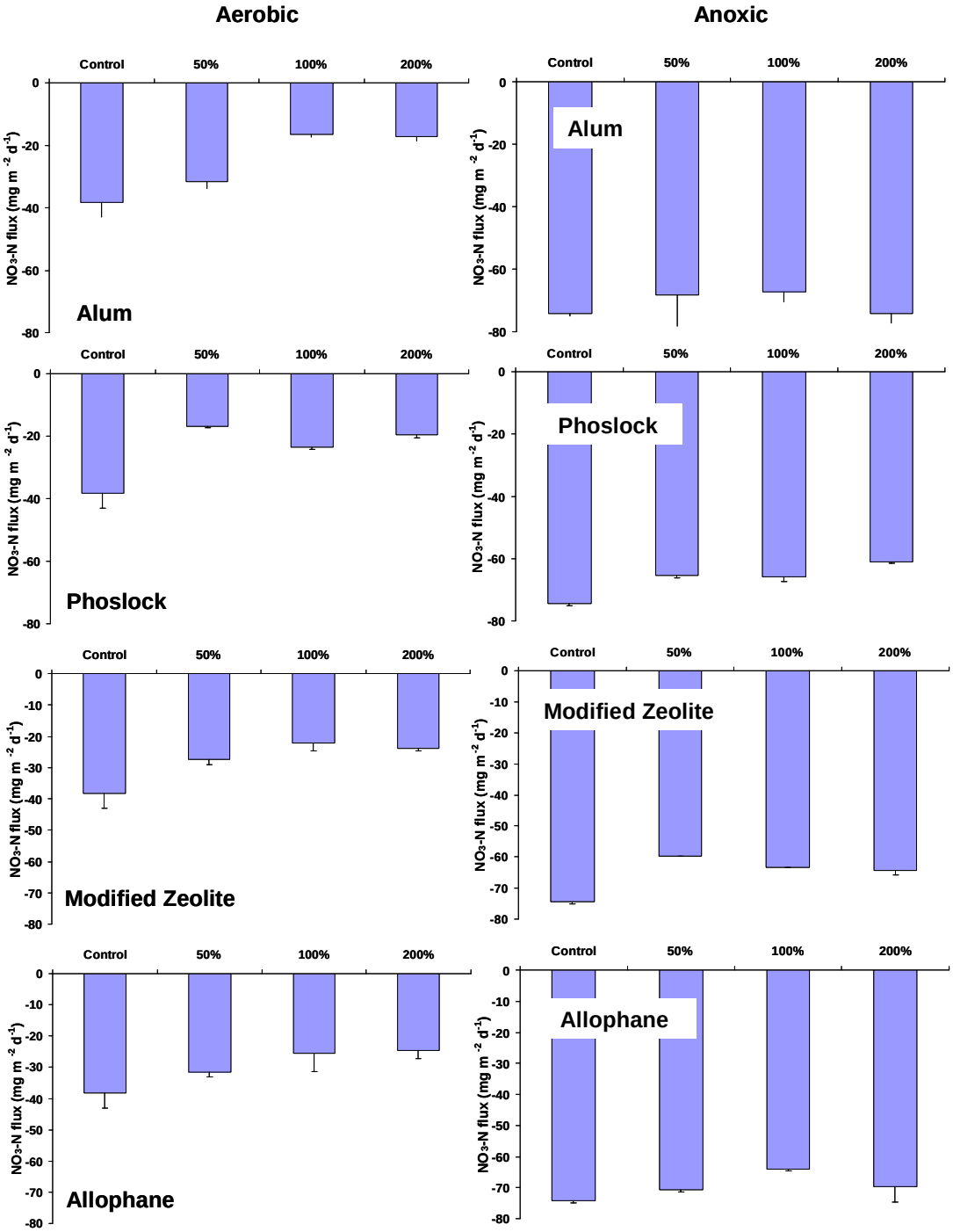

Figure 9. Nitrate: Mean effluxes for each capping material treatment under aerobic and anoxic conditions in natural lake water. A reduction in the loss of nitrate relative to the control is an indication of a reduction in denitrification. (Error bars = 1SD).

3.3.3 Metals

A possible consequence of applying a capping material to the sediments of a geothermally-influenced lake is the release of toxic metals such as arsenic from the sediments as the capping material alters the boundary conditions across the sediment-water interface (Gibbs et al. 2007). Another possibility is that sediment contact may allow the P-binding elements in the capping material to leak into the water column e.g., Al or La. Comparative plots of the metal concentrations for Fe, Mn, and Zn under aerobic and anoxic conditions are presented in Appendix A. Comparative plots of total dissolved Al, As, and La are presented in Figures 10, 11, and 12, respectively. Variability in the inflow water metal concentrations were due to different drums of source water being used for each daily run between the aerobic and anoxic experiments. The same lake water source was used for each incubation tube.

Iron (Fe), Manganese (Mn), and Zinc (Zn)

Although general patterns were apparent, the high variability in the results suggest that most were not statistically different from the controls. Under aerobic conditions, Fe concentrations were low except in the modified Zeolite highest treatment (Fig. A1). Under anoxic conditions, Fe was released from the sediment and the data suggest that Allophane had the highest release rate.

Manganese data showed higher than expected concentrations in the water column under aerobic conditions (Fig. A2), which indicated that the oxygen levels in the incubation tubes were below 5 g m^{-3}. Under anoxic conditions, both Allophane and the modified Zeolite appeared to produce more Mn that the Alum or Phoslock™.

There was high variability in the Zn data (Fig. A3) with some individual incubation tubes producing elevated Zn concentrations while the remainder showed a decrease in Zn relative to the inflow water.

Aluminium (Al)

A small increase in the amount of total dissolved Al was observed in all treatments under aerobic and anoxic conditions (Fig. 10). Although Alum and the modified Zeolite were both Al based materials, there appeared to be more Al associated with the Phoslock™ and Allophane treatments. Not withstanding this, the amounts measured were minor, and there was not obvious leaching of Al from the Al-based capping materials.

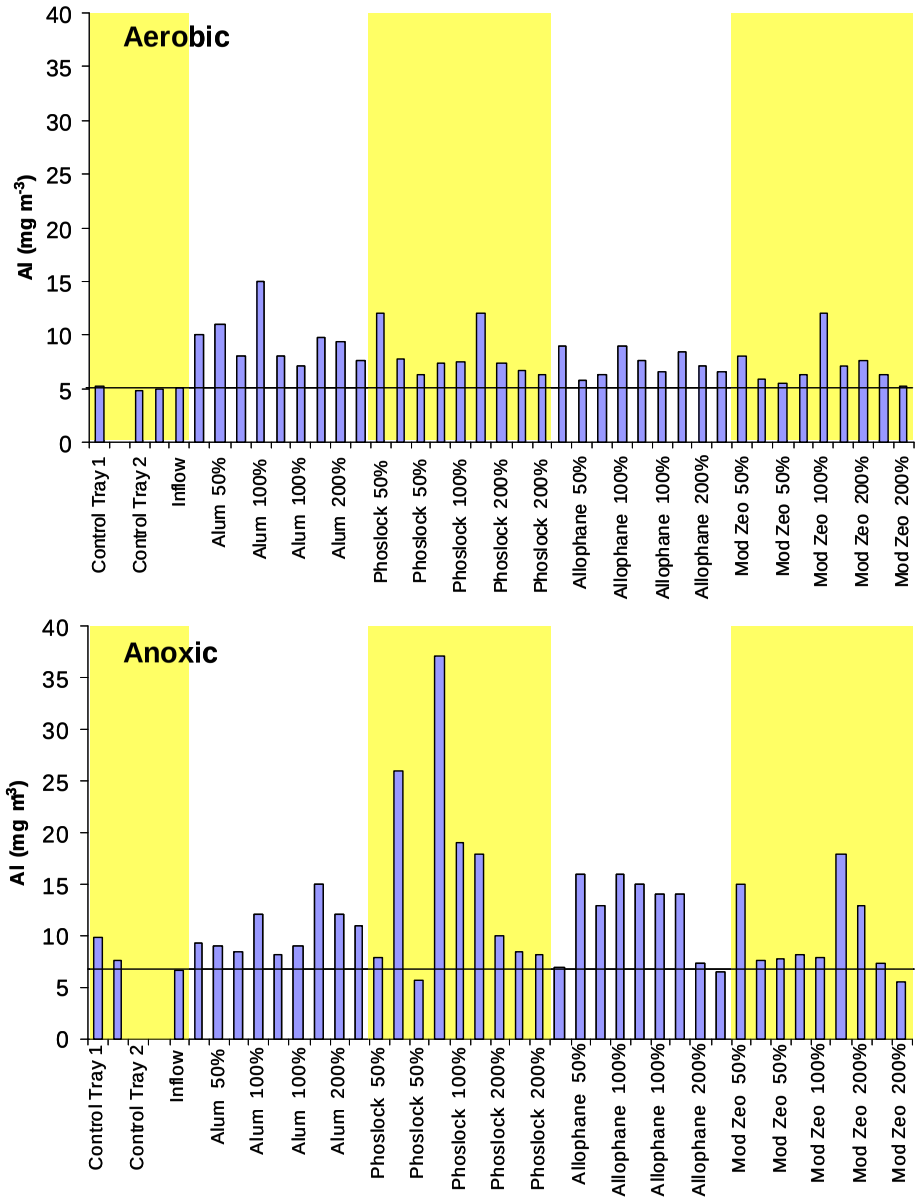

Figure 10. Comparative plots of the total dissolved Aluminium (Al) concentrations from the incubation tubes under aerobic and anoxic conditions. The horizontal line is the measured concentration in the inflow water. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals an efflux of about 0.5 mg m^{-2} d^{-1})

Arsenic (As)

The As data (Fig. 11) showed a pattern of slightly higher concentrations from the Phoslock™ and the modified Zeolite treatments under both aerobic and anoxic

conditions. The greatest increase relative to inflow was for the aerobic modified Zeolite.

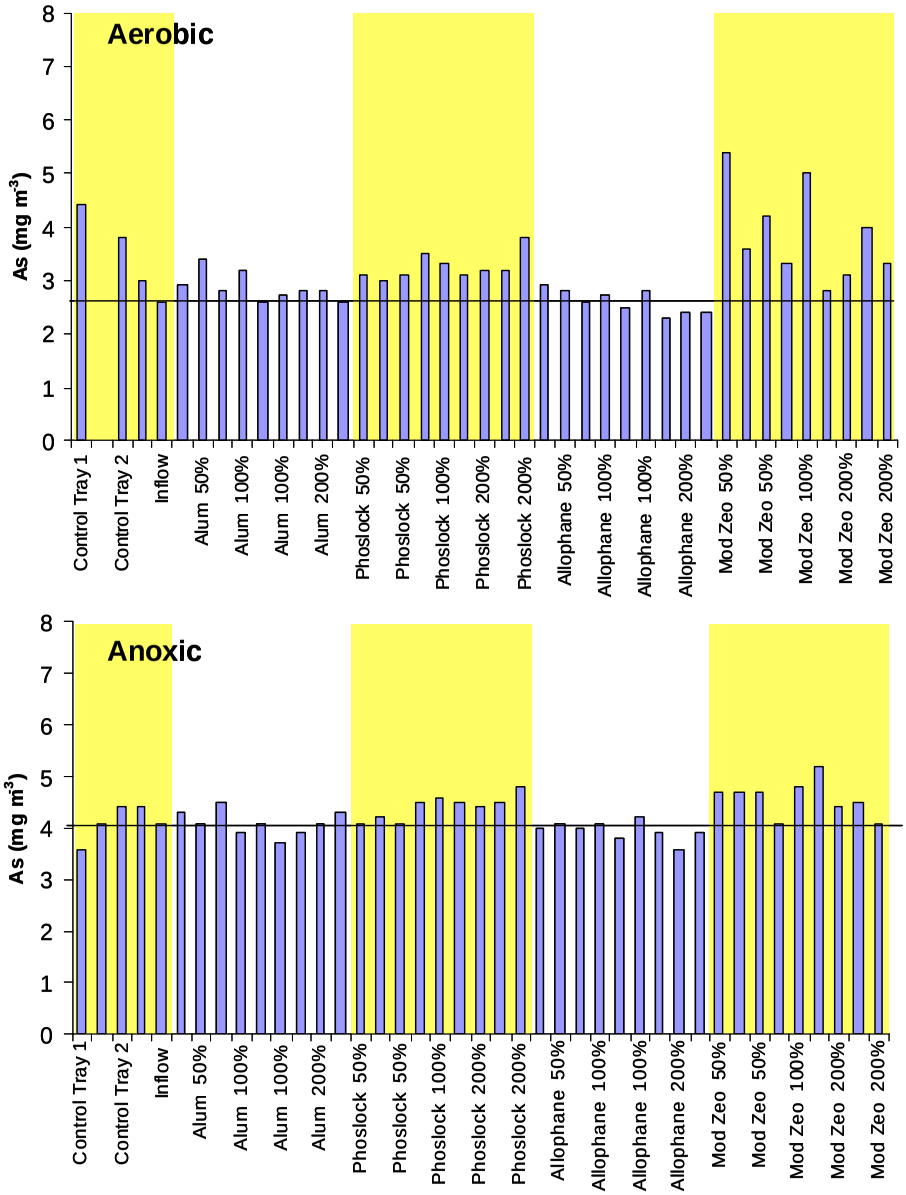

Figure 11. Comparative plots of the total dissolved Arsenic (As) concentrations from the incubation tubes under aerobic and anoxic conditions. The horizontal line is the measured concentration in the inflow water. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals an efflux of about 0.5 mg m^{-2} d^{-1}).

Lanthanum (La)

These data (Fig. 12) showed that Phoslock™ was leaking La into the water column under both aerobic and anoxic conditions in similar proportions.

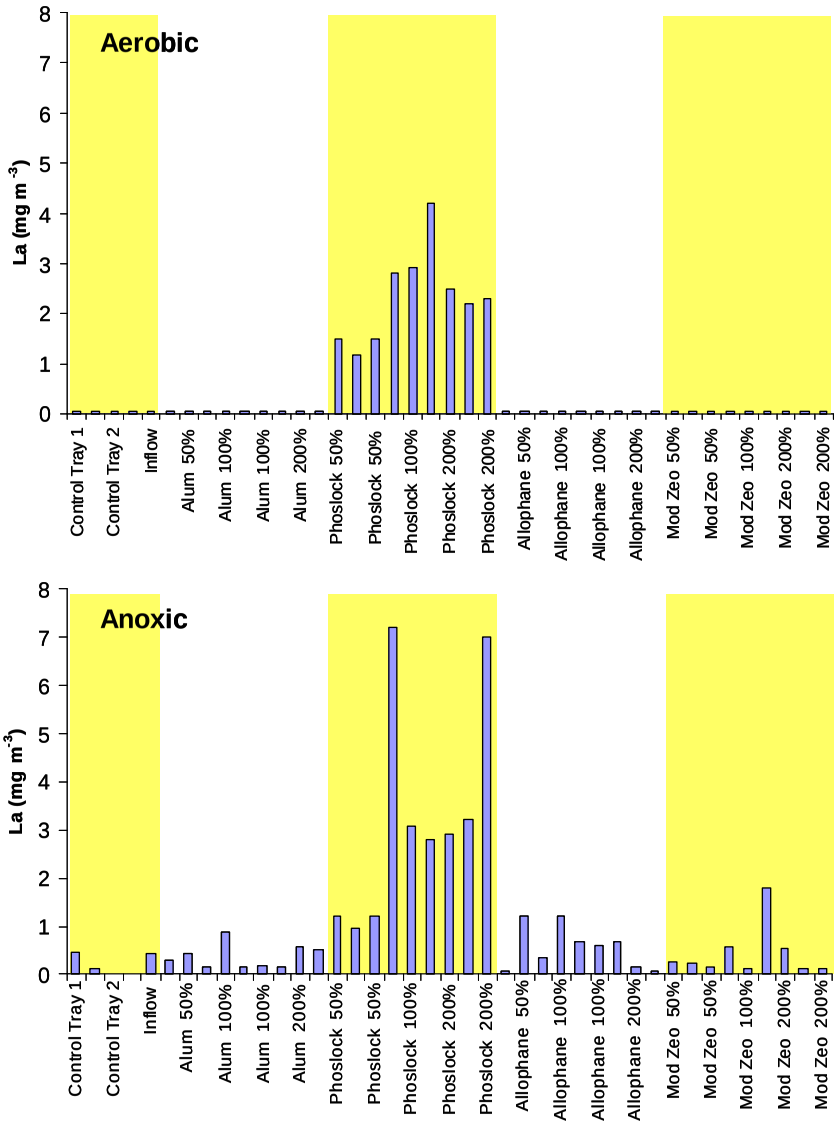

Figure 12. Comparative plots of the total dissolved Lanthanum (La) concentrations from the incubation tubes under aerobic and anoxic conditions. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals an efflux of about 0.5 mg m^{-2} d^{-1}).

These concentrations (4-7 mg m^{-3}) are comparable with La concentrations measured during toxicity testing (Clearwater 2004; Clearwater & Hickey 2004; Martin &

Hickey 2004). They are lower than the 45 mg La m^{-3} derived from the regulatory chronic ecotoxic threshold concentration of 1 g Phoslock™ m^{-3} (ERMA 2001) (See Glossary). They represent an efflux of about 2 mg m^{-2} d^{-1}, which would be diluted substantially if mixed into the whole volume of a lake.

3.3.4 DRP and NO_3-N additions

To further explore the effects of the capping materials on microbial nitrification and denitrification, the inflow water was amended with phosphate and nitrate solutions to raise the DRP and NO_3-N concentrations to around 200 mg m^{-3} and 2000 mg m^{-3}, respectively. These are levels that might be expected in hypolimnetic waters at different phases of stratification. Full results are presented in Appendix B.

In general, the DRP removal by most capping material treatments from the inflow water amended with DRP under aerobic conditions was greater than for the natural water concentrations. The greater DRP removal was therefore most likely a function of the higher diffusion rate into the sediment due to the high DRP concentrations in the overlying water column. The exceptions were the lowest Alum treatment (50%) which had less than half the natural water DRP removal (Fig. B1) and the modified Zeolite (Fig. 13, aerobic) which had consistently lower DRP removal, although the pattern of increasing DRP removal with increasing dose rate was still present.

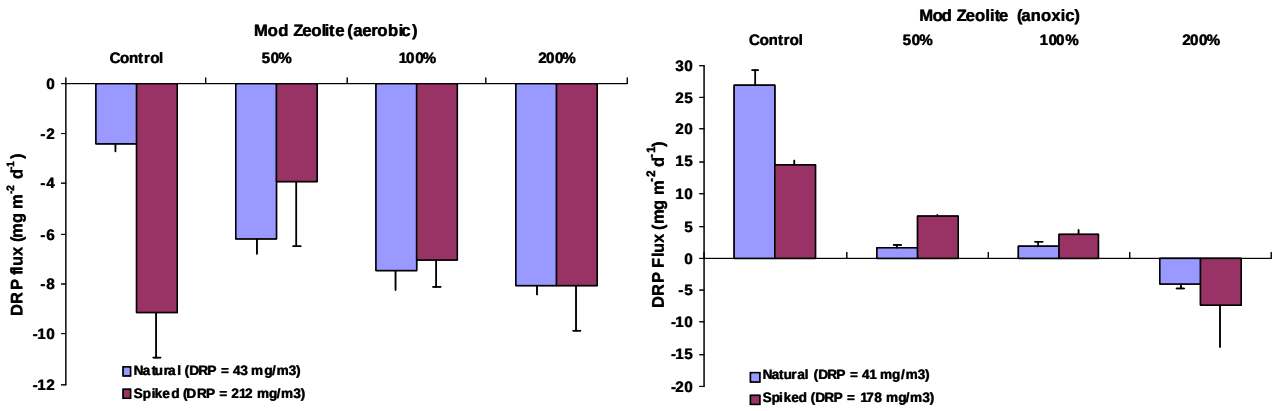

Figure 13. **Modified Zeolite:** comparison of dissolved reactive phosphorus (DRP) effluxes in natural water (blue) and natural water amended with high DRP and NO_3-N concentrations (red) under aerobic and anoxic conditions.

Under anoxic conditions and with DRP amended lake water, the capping materials blocked the release of DRP from the sediments to a similar degree as for the anoxic natural water and most treatments removed more DRP from the inflow water than

from the natural water. This is again consistent with a higher diffusion rate into the sediment due to the high DRP concentrations in the overlying water column. The exception was the Modified Zeolite at 50% and 100% treatment dose rates, which blocked less DRP release from the sediment than in the natural water tests (Fig. 13, anoxic).

The use of elevated NO_3-N concentrations examined the denitrification potential of the sediment and thus the effect of the capping materials on that potential. Under aerobic conditions, the results showed enhanced releases of NH_4-N from the Alum and Allophane treatments (Figs. B1, B4) but a suppression of the NH_4-N efflux relative to controls from the modified Zeolite and the higher Phoslock™ treatments (Figs. B2, B3). Under anoxic conditions, there was a reduction in the NH_4-N efflux for all treatments, including controls, relative to the natural lake water. This is consistent with the NO_3-N being an oxygen source for microbial processes of denitrification in the sediment. This effect can be seen as enhanced NO_3-N losses, relative to natural lake water incubations, from all treatments of all capping materials and the controls (Figs. B1 to B4).

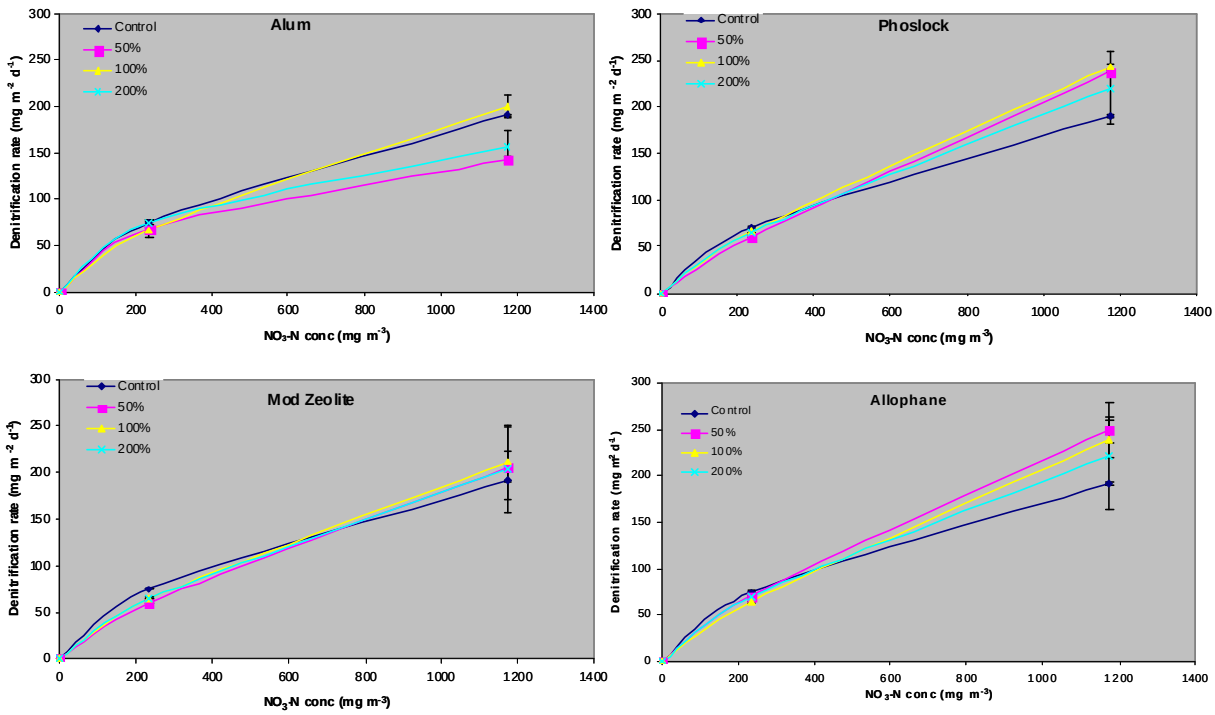

Figure 14. Denitrification potentials as estimated from the loss of nitrate (NO_3-N) at different concentrations under anoxic conditions for all capping materials at all treatments.

The estimation of denitrification potentials and thus the effect of these capping materials on those microbial processes (Fig. 14) show that, with the exception of Alum, there was a slight increase in denitrification potential associated with each capping material treatment. However, because of the variability in the results, this apparent enhancement may not be statistically significant. The reduction in denitrification rates for two of the Alum treatments does not follow a pattern associated with the level of treatment and thus may also be natural variability. These results indicate that the denitrification potential of the sediment was not adversely affected by the capping material at the dose rates used.

3.4 Objective 3

"Evaluate longevity of these P-inactivation agents through repeated cycles of aerobic / anaerobic conditions".

Longevity tests were designed to give an estimate of how long the capping layers would remain effective and thus the time between re-treatments.

3.4.1 DRP

The P results of this phase of the study are presented as time-series graphs (Fig. 15), which includes the initial aerobic and anoxic cycle, to give four complete aerobic-to-anoxic-to-aerobic cycles. The results presented are for the last day before the switch from aerobic to anoxic or from anoxic to aerobic. The "saw-tooth" pattern to the data reflects the shift from aerobic conditions (low DRP concentration) to anoxic condition (high DRP concentrations). The difference in maximum DRP concentration in each anoxic cycle for each capping material is an indication of how well that material is likely to perform in the years following the initial application. The initial performance of each capping material has been described in detail (section 3.2).

For the longevity estimates, the results of interest are when "break-through" occurs for each capping material and for each treatment. Break-through occurs when the capping material P-uptake capacity has been exceeded or the material has been buried and it no longer prevents DRP accumulation in the lake water column. This is seen as an increase in water column DRP concentrations above the inflow water concentration.

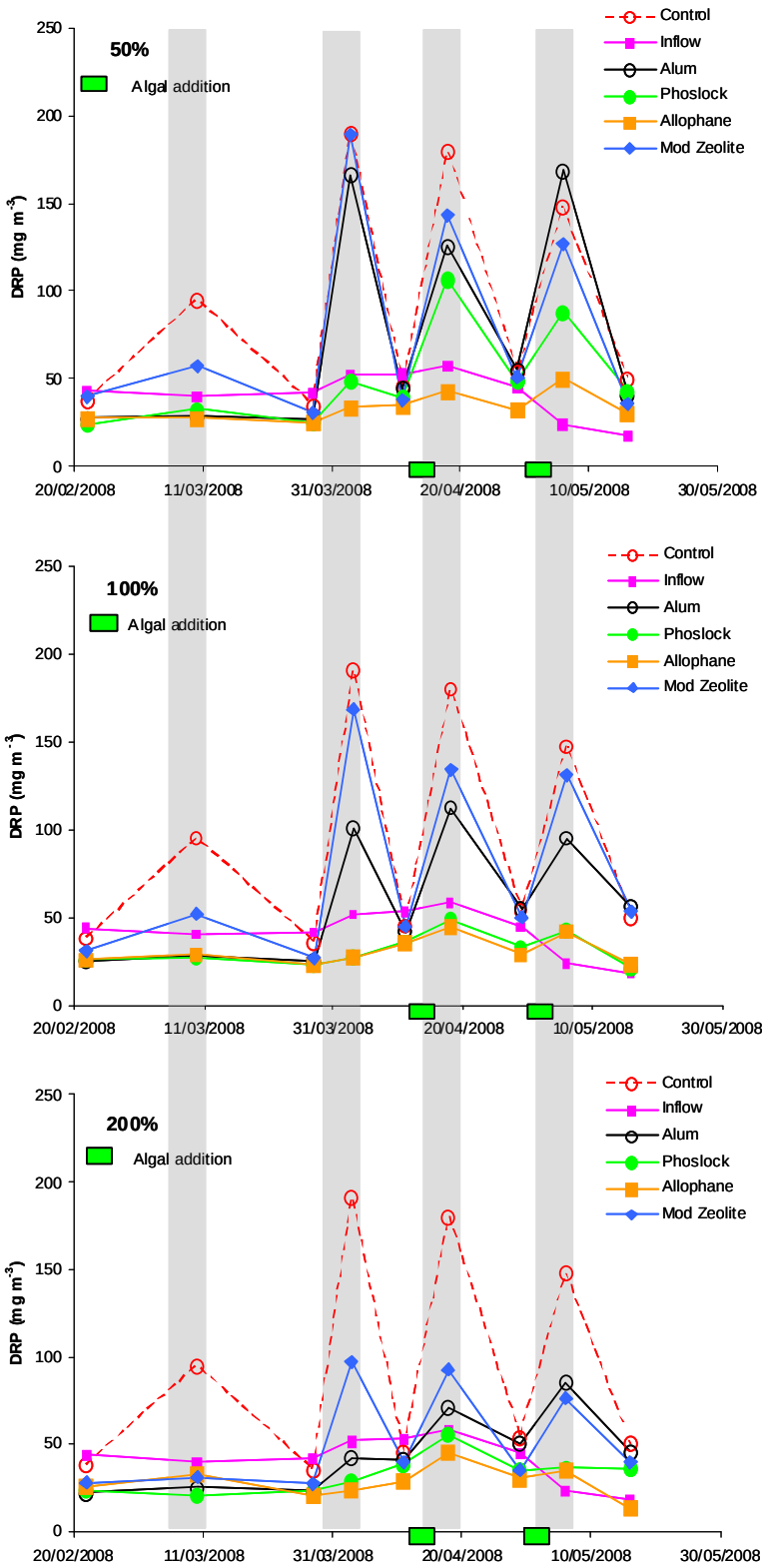

Figure 15. Time series of mean dissolved reactive phosphorus (DRP) concentration changes in the inflow and outflow waters from the longevity experiment. Grey shaded bands indicate the periods of anoxia; green blocks indicate when the algal slurry was applied.

Break-through is a function of the P-uptake capacity of the capping material, the dose rate, and the mass of DRP in contact with the capping material. In the continuous flow incubation system, there was a continuously renewed supply of DRP in the inflow water as well as the efflux of DRP from the sediment. There was also the spot inoculation with an algae slurry on two occasions to add DRP from decomposition and to test for burial effects.

The algal slurry was added to the treated incubation tubes at the end of the 3rd and 4th aerobic cycles to simulate the collapse of an algal bloom. The incubation tubes were closed and left without circulation for 2 days to allow the slurry to settle and decomposition to begin. Analyses of the algal slurry as added are given in Table 4. As annual loadings, these applications are equivalent to a sedimentation rate 156 mg m^{-2} d^{-1} organic matter (dry weight) which is comparable with the sedimentation rate of 200 mg m^{-2} d^{-1} organic matter (dry weight) measured in lake Okaro in September 2007 (Wright-Stow et al. 2008).

Table 4. Mean composition of the algal slurry added to the incubation tubes.

Algal slurry mean composition as added to each incubation tube					
Mass / tube (mg)			**Application rate** (g m^{-2})		
C	N	P	C	N	P
106	15	2.6	27.5	3.9	0.68

The measured DRP efflux in controls under anoxic conditions was 27 mg m^{-2} d^{-1}. Since the capping materials induce anoxic conditions in the sediments beneath them (Gibbs et al. 2007), there will be a continuous DRP efflux from the sediments that will take up part of the P-binding capacity of the capping material. The efflux from the Lake Rotorua sediments was estimated to be about 0.1 mg P d^{-1} per tube. As the total mass of P in the top 4 cm of the incubation tubes was estimated to be 12.2 mg P, it is expected that it would take at least 122 days to release all of the available P in the sediment. As the incubations ran for around 90 days, the experiment was unlikely to be affected by P depletion in the sediments.

The water flowing through the incubation tubes had a DRP concentration of 41-43 mg m^{-3} for the natural lake water, which was equivalent to the addition of about 0.08 mg P d^{-1}. The DRP amendment water, at 212 and 178 mg m^{-3}, would have added 0.43 and 0.36 mg P d^{-1} to the incubation tubes during that phase of the study. As these waters were in contact with the capping materials, the DRP in those waters would also take up part of the P-binding capacity of the capping material. The two spot inoculations of algae to the incubation tubes also added P to the system (Table 4). From these data,

the cumulative mass of DRP in contact with the capping material can be estimated (Fig. 16) to enable assessment of the longevity of the capping materials.

The nominal P-uptake capacities of the capping material in each incubation tube at the 50%, 100%, and 200% treatments were 5.8, 11.6 and 23.2 mg P, respectively. These levels are marked on the cumulative P supply curve with arrows (Fig. 16). As this graph is drawn with the same X-axis as the time-series data (Fig. 15), the intersection of the arrow with the cumulative DRP curve indicates the date (X-axis) when break-through might be expected. Break-through before that date was interpreted as lower than expected, and after that date was interpreted as better than expected.

At the 50% treatment dose rate, the modified Zeolite results showed break-through in the 1st anoxic cycle (before 11/03/2008) which is lower than expected (Fig. 16). Alum showed significant DRP break-through in the 2nd anoxic cycle, which is consistent with expectations. Phoslock™ showed break-through after the 2nd anoxic cycle, which is at a higher P-uptake capacity than expected (Fig. 16). However, the 50% Allophane treatment did not show break-through until the 3rd anoxic cycle, which indicates a much higher P-uptake capacity than expected or that some other factor was affecting the results.

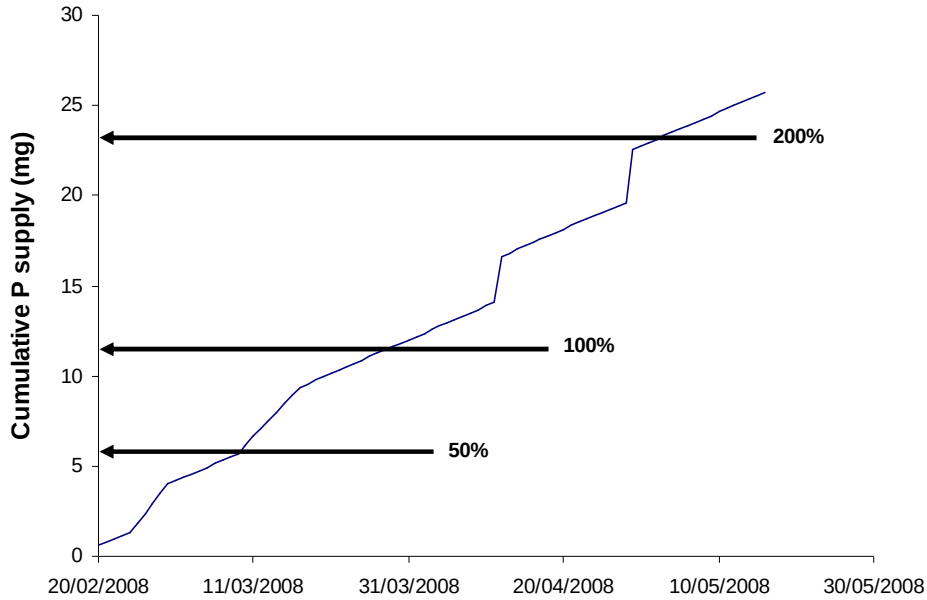

Figure 16. Cumulative phosphorus supply to the incubation tubes relative to the treatments (dose rates) of 50% (5.8 mg), 100% (11.6 mg), and 200% (23.2 mg). Burst through should have occurred for each treatment level about the date when the cumulative P curve exceeded the nominal P-binding capacity indicated for that treatment.

At the 100% treatment dose rate, a similar pattern was observed with the modified Zeolite treatment results being lower than expected. The 100% Alum treatment results were also lower than expected, although the DRP concentrations associated with the Alum break-through were much lower than at the 50% treatment dose rate (Fig. 15). Break-through for the Allophane and Phoslock™ treatments occurred after the 3rd anoxic cycle, which was much higher than expected (Fig. 16), and the increase in DRP concentration relative to the inflow water was small compared with the control (Fig. 15; 100%).

At the 200% treatment dose rate, the modified Zeolite treatment had a DRP break-through during the 2nd anoxic cycle, which was much lower than expected (Fig. 16), although the level of DRP concentration increase was less than for the 50% and 100% treatments. For Alum, the 200% treatment results indicated a break-through during the 3rd anoxic cycle, which is much lower than expected, although the increase in DRP concentration relative to the inflow water was small compared with the control (Fig. 15; 200%). Break-through for the Allophane and Phoslock™ 200% treatments occurred about the 4th anoxic cycle, which is consistent with expectations (Fig. 16).

3.4.2 NH_4-N and NO_3-N

The results for the equivalent N changes associated with these DRP results are presented separately in Appendix C.

The NH_4-N results (Fig. C1) show that after the initial anoxic period, the release of NH_4-N from the sediments was comparable for all capping materials over the 2nd and 3rd anoxic periods. However, through the 4th anoxic cycle there were marked differences in the NH_4-N effluxes between some capping materials, with significant enhancement by the 50% Alum treatment and a significantly lower efflux for the 200% modified Zeolite. There was a trend over time of increasing NH_4-N concentrations under anoxic conditions. Highest concentrations were in the 4th anoxic period which may be associated with the addition of two lots of algal slurry covering the capped sediment.

The NO_3-N results (Fig. C2) show that denitrification was not significantly affected by the capping materials. However, the complete removal of NO_3-N after the additions of algal slurry indicate that burial of the capping material removed any inhibition effects restoring the full denitrification potential of the Lake Rotorua sediments.

The significant increase in NH_4-N coinciding with the complete removal of free NO_3-N by denitrification is consistent with the uninhibited release of NH_4-N from the

sediments as microbial processes shift from anoxic to anaerobic, and sulphate (SO_4^{2+}) is used as the energy source for sediment microbial processes.

3.5 P-saturation experiment

Time-series analysis of the uptake of PO_4-P by the capping materials at three different pH levels demonstrated that the actual P-binding capacities were substantially different from the nominal P-binding capacities given by the suppliers and used to calculate the dose rates for each treatment in the sediment incubation experiment (Table 5). These results also demonstrated that the P-binding capacities were affected by the pH of the system (Table 5) consistent with the observations of Peterson et al. (1976). These pH effects were sufficient to account for the measured versus nominal P-binding capacity differences.

Table 5. Comparison of the measured P-binding capacities of each capping agent, at the specified pH after 50 hours, with the nominal P-binding capacities given by the suppliers. (* P-binding capacity still increasing; ** P-binding capacity decreasing after an initial high).

Capping Material	**P-binding capacity** (g P / kg product)			
	Nominal	**Measured**		
		pH 6.1	pH 7.0	pH 8.9
Modified Zeolite	50	21.5*	21.5*	11.6*
Phoslock™	20	11.6**	11.3*	15.1
Allophane	5	16.3	16	9.5

The measured P-binding capacity of the modified Zeolite was still increasing after 50 hours. This is consistent with a granular product having a slower uptake response as the P is initially rapidly adsorbed on the surface of the granule and then slowly diffuses deeper into the granules before it can be permanently bound. By regression modelling, the predicted maximum P-binding capacity at the test experiment pH of 7.0 would be about 23 g P / kg. This is less than half the nominal P-binding capacity given (Table 5). This value is consistent with the P-binding capacity of around 20 g P / kg estimated for this product in the previous Lake Okaro study (Gibbs et al. 2007).

In contrast, the measured P-binding capacity of Phoslock™ at pH 6.1 and 7.0 reached an initial maximum of around 14 g P / kg before decreasing again. The P-binding capacity was still decreasing after 50 hours (Fig. 17). While the initial rapid P-uptake

is consistent with the very fine, almost colloidal appearance of this material when shaken in water, it is not certain why the P-binding capacity of Phoslock™ was declining over time. A possible explanation could be the simultaneous loss of the active ingredient, La, from the product over the same period (Fig. 17) (See section 4.3.3). Regression slopes of the reduction in P and La content over time at pH 6.1 were similar at 0.0646 and 0.0843, respectively, which supports the concept of an apparent link between a decline in the P-binding capacity and the loss of La from the Phoslock™ capping material. At pH 8.9, the P-binding capacity of Phoslock™ was relatively stable at a mean of around 15 g P / kg for over 100 hours. The estimated P-binding capacity at the test experiment pH of 7.0 was about 12 g P / kg. This is just over half the nominal P-binding capacity given.

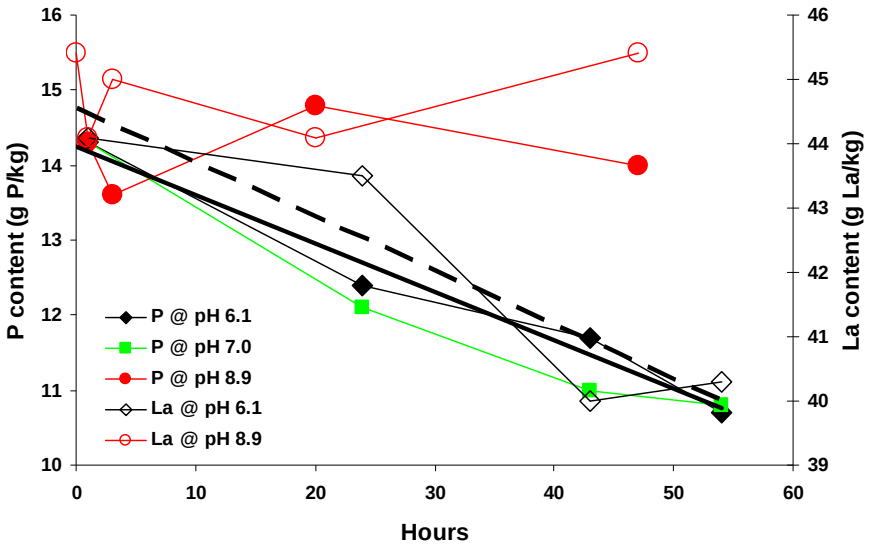

Figure 17. Time series analyses of the P (solid symbols) and La (open symbols) content of Phoslock™ at high and low pH during the P-saturation experiment. Solid regression line for P content at pH 6.1 has the equation Y = 0.0646*X + 14.25, r^2 = 0.9771; dashed regression line for the La content at pH 6.1 has equation Y = 0.843*X + 44.55, r^2 = 0.8503. The P content decrease at pH 7.0 was similar to the decrease at pH 6.1.

While the measured P-binding capacity of Phoslock™ was highest at high pH, the measured P-binding capacity of Allophane was highest at the low pH (Table 5) and, after an initial rapid uptake, was relatively stable at each pH level over 50 hours. The mean P-binding capacity at the experiment pH of 7.0 was about 16 g P / kg. This is more than 3 times greater than the nominal P-binding capacity given.

Analysis of Allophane showed that it had more than 3 times the aluminium and almost 8 times the iron content of modified Zeolite (Table 6). Both Al and Fe have a high affinity for P.

Table 6. Selected mineral content of the three granular capping materials determined by ICP-mass spec for the raw material as supplied and used in this study.

Material	Elemental composition (mg / kg dw)								
	Na	K	Mg	Ca	Al	Fe	Mn	La	P
Allophane	280	170	1008	972	68075	30610	675	28	1321
Modified Zeolite	11213	7080	1877	9761	21752	4457	278	20	118
Phoslock™	2278	161	7505	1233	11701	4498	29	45380	130

4. Discussion

4.1 Efficacy of P-removal

The use of a capping material layer to bind and thus block the release of DRP from lake sediments can be thought of as a management strategy which resets the lake to zero internal DRP loads with all DRP being supplied from the catchment. If the capping material is applied at a sufficient rate per unit area to block 100% of the available DRP in the upper sediment and is not disturbed, this should be true. The tests conducted in the course of this study have determined the relative DRP removal rates for each of the four capping materials tested. The capping materials were applied at rates calculated to give complete removal of all available DRP in the top 4 cm of Lake Rotorua sediment (i.e., 100%) as well as half and double that rate (i.e., 50% and 200%, respectively), based on the nominal P-binding capacities given by the suppliers (Table 1). The results of these tests over a 90-day period demonstrated that the actual P-binding capacities of each capping material was substantially different from the nominal P-binding capacities given. The reason for these differences may reflect sediment effects or that the nominal P-binding capacity value given was incorrect. For Alum, modified Zeolite, and Phoslock™ the actual P-binding capacities were lower than expected while the actual P-binding capacity of Allophane was much higher than expected.

The inconsistency between the experimentally derived P-removal efficacy values and those calculated using the nominal P-binding capacity values was most obvious in the longevity experiment. There, only the 200% treatments for Alum, modified Zeolite, and Phoslock™ produced results that approached expectations while even the 50% treatment of Allophane exceeded expectations.

Expectations were that the actual P-binding capacity of each capping material would be exceeded at their nominal P-binding capacity, as indicated by P break-through.

The longevity results considered all DRP inputs to the incubation tubes including the P released from the sediment beneath the capping layer, the continuous supply of new DRP in the lake water pumped through the incubation tubes, and the decomposition of simulated senescing algal blooms and detritus falling to the sediment. In the continuous flow incubation system, the daily mass of P supplied in the lake water (0.08 mg d^{-1}) was similar in magnitude to the efflux of DRP from the sediment (0.10 mg d^{-1}). Based on the cumulative DRP curve (Fig. 16), the break-through times for all of the capping materials were different from the theoretical times indicated for each treatment and dose rate.

The longevity results showed that Alum and the modified Zeolite capping materials applied at the 100% dose rate did not control DRP concentrations during the second anoxic cycle. In the 200% treatment, Alum controlled DRP concentrations during the second anoxic cycle but the modified Zeolite did not. The cause of the lower than expected performance for Alum appeared to be related to the disturbance of the light Alum floc by the inflow water currents. This disturbance effect makes Alum unsuitable for use on Lake Rotorua where large wind fetch and deep mixing would destroy the capping layer. Conversely, the lower than expected performance for modified Zeolite appeared to be a function of the range of grain sizes of the formulation not giving a complete coverage of the sediment, especially at the 50% and 100% treatments. It is possible that a finer grain size would be more effective. However, as this was the same formulation successfully used on the Lake Okaro sediments at higher dose rates, these results also suggested that the P-binding capacity of modified Zeolite was lower than the nominal value given.

The 50% Phoslock™ treatment controlled DRP concentrations through to the second anoxic cycle and the 100% treatment controlled DRP concentrations through the third anoxic cycle, which appeared to match theoretical expectations. However, increasing the dose further to the 200% treatment did not increase the DRP control beyond the third anoxic cycle, suggesting that its P-binding capacity had been exhausted before the fourth anoxic cycle sampling. This suggested that the P-binding capacity of Phoslock was lower than the nominal value given.

In contrast to Phoslock™, the 50% Allophane treatment controlled DRP concentrations through to the fourth anoxic cycle, which was about 2-4 times more effective than theoretical expectations. This suggested that the P-binding capacity of Allophane was much higher than the value given. However, the same level of DRP control was also achieved at the 100% and 200% treatment, which indicates that there may be a layer thickness effect as well as the P-binding capacity of the Allophane. Because there was no break-through even at the 50% treatment, it is likely that the actual P-removal efficacy dose rate will be less than the dose rate used in the 50% treatment. Further work should be undertaken to determine the lowest dose rate required to achieve effective control of DRP over an extended period.

The supplementary assessment of Phoslock™, modified Zeolite, and Allophane after the main study was completed, showed that the P-binding capacity of these materials was strongly influenced by pH, consistent with the findings of Peterson et al. (1976). The measured P-binding capacities at the experimental pH of around 7 where much lower than expected for Phoslock™ (12 g P/kg measured compared with 20 g P/kg given) and modified Zeolite (23 g P/kg measured compared with 50 g P/kg given).

Conversely, Allophane had a much higher than expected P-binding capacity (16 g P/kg measured compared with 5 g P/kg given) which is consistent with the estimate of 2-4 times more effective obtained from the longevity experiment. Of interest, the mineral analysis of Allophane (Table 6) indicates that the P-binding sites were likely to be associated with Al and Fe. Because the active ingredient in the modified Zeolite was Al, which is also the active ingredient in Alum, it is reasonable to assume that the pH effect on Alum would be comparable with that of modified Zeolite. Thus the estimated P-binding capacity of Alum would be around 45 g P/kg compared with 100 g P/kg given.

These values were used, together with the analytical results from objective 1 and the sediment P, content to calculate the P-removal efficacy of each capping material i.e., the amount of each capping material required to block 100% of the TAP that could be released from the top 4 cm of Lake Rotorua sediments (Fig.18). These dose rates give a direct comparison the P-removal efficacy of the four P-inactivation agents if these were applied to Lake Rotorua in the formulations as supplied for the tests in this study.

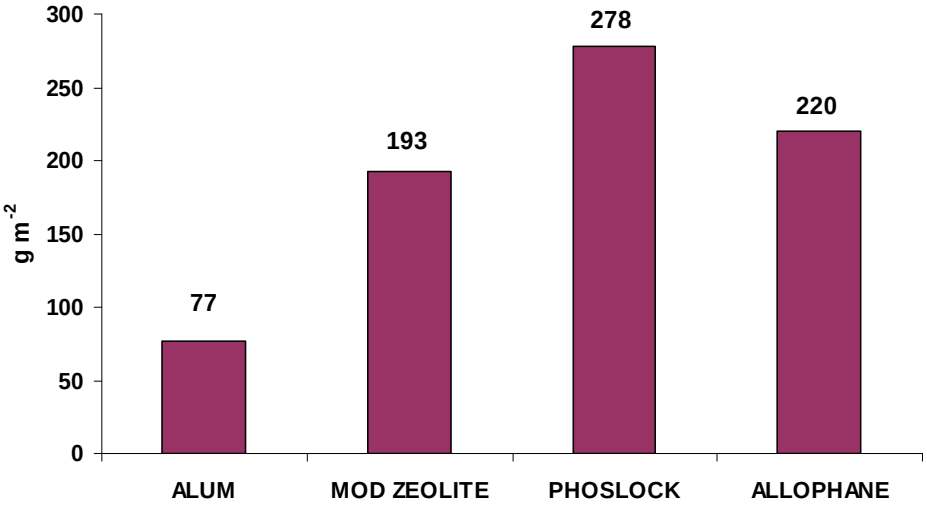

Figure 18. **P-removal efficacy comparisons:** Estimated required dose rate (g m^{-2}), based on the measured P-binding capacity of each capping material, to completely block the release of DRP from the top 4 cm of Lake Rotorua sediments (TAP content = 3.168 g m^{-2}). This assumes the capping materials have the same formulation as the products supplied for testing.

4.2 Longevity of P-removal

While these capping materials may be highly effective in blocking DRP release from the sediment when first applied, the continued input of DRP from the catchment (inflow water) will gradually take up part of the P-binding capacity of the capping material so that the material eventually becomes "saturated", i.e., the P-binding capacity is exhausted and the capping material stops adsorbing new DRP inputs. Also, subsequent deposition of detritus from the inflows and senescing algae will eventually bury the capping material and provide a new source of DRP above the capping layer. These factors affect the longevity of the capping material application and, thus, how often the lake must be treated to control the DRP concentrations in the water column.

A key factor in determining how long a sediment capping treatment will remain effective in a lake is the mineralisation rate of the sediment organic matter into DRP and its subsequent diffusion out of the sediments. Because the P-saturation experiment demonstrated that these capping materials rapidly adsorb PO_4-P and can become saturated within a few hours of exposure, the P-removal is limited by the mineralization rate in the sediment. This rate was estimated to be around 27 mg m^{-2} d^{-1} for Lake Rotorua sediments. Assuming that the measured TAP in the top 4 cm of sediment, at 3.168 g m^{-2}, is an average for the lake, it would take 117 days for the TAP to be released and adsorbed. During that 117 day period, external DRP sources from the stream inflows and sedimenting detritus will compete for the available binding capacity of the capping agent from above. Also any disruption of the capping material layer will reduce its ability to adsorb the mineralised P from the sediments.

Another important consideration is whether the bound P is released again under anoxic conditions. The longevity experiment was taken through four cycles of anoxic-to-aerobic conditions to simulate seasonal changes over a period of "four years". The results of the 50% Allophane and 200% Phoslock™ treatments, which were closest to their respective P-removal efficacy values, showed that the P bound on these products was not released during the anoxic phase (Fig. 15) and the capping materials continued to remove P released from the sediment and from the overlying water column and detritus through at least "3-years".

This means that if the sediments were treated with any of the capping materials at application rates based on their respective P-removal efficacy values (Fig. 18), the undisturbed capping layer should remain effective for at least four years. Given that the P is permanently bound to the capping layer and not released under anoxic conditions, the lake would effectively be "reset" and subsequent re-treatments would only be needed to control P released from sediments that subsequently bury the capping layer. In this study and the previous study, using Lake Okaro sediments

(Gibbs et al. 2007), the capped sediments produced methane gas bubbles which had the potential to disrupt the sediments. The effects of gas ebullition on the integrity of the capping layer would require testing in the lake where the amount of disturbance could be measured. Observations from the Alum treatments showed that the Alum floc was very easily disturbed. Disturbance of the capping layer during the initial four months following treatment could reduce both the effectiveness of the P removal and thus the longevity of the treatment.

4.3 Non-target effects

All capping materials had non-target effects which impacted on the microbial processes of nitrification and denitrification. These two processes are linked but are considered separately here. These results are **net effects** of one or more processes.

4.3.1 Nitrification effects

Under aerobic conditions, microbial nitrification oxidises NH_4-N released from the sediment into NO_3-N at the sediment-water interface. The action of the capping material layer was to reduce nitrification, which was seen as an increase in the amount of NH_4-N in the water column. This non-target effect appeared to be dose-rate dependent and, while mean nitrification effect results are given in Table 3, the effects of capping material application rates at the P-removal efficacy rates can be estimated from the NH_4-N efflux rates (Fig. 8) and the experimental dose rates (Table 1).

Phoslock™ at the 200% treatment dose rate of 300 g m^{-2} was close to its P-removal efficacy dose rate of 280 g m^{-2} (Fig. 18) and thus the expected non-target effect would be NH_4-N at around 5 times the control. Alum at the 200 % treatment dose rate of 60 g m^{-2} was only 75% of its P-removal efficacy dose rate of 80 g m^{-2}. As the effect was dose-rate dependent and was increasing non-linearly with increasing dose rate (Fig. 8), it is likely that the Alum non-target effect would also release NH_4-N at around 5 times the control. In contrast, Allophane at the 50% treatment dose rate of 300 g m^{-2} was around 36% higher than its P-removal efficacy dose rate of 220 g m^{-2}. As there was minimal effect by Allophane on nitrification at the 50% treatment dose rate (Fig. 8), this is unlikely to change.

Modified Zeolite at the 200% treatment dose rate of 120 g m^{-2} was only around 60% of its P-removal efficacy dose rate of 220 g m^{-2}. At the 200% treatment dose rate, modified Zeolite blocked the release of almost all the potential NH_4-N release from the sediments due to the adsorption of NH_4-N onto the Zeolite base material. At almost double that treatment dose rate the expectation would be for a complete

blockage of NH_4-N release from the sediments, consistent with the higher dose rates used in the earlier Lake Okaro study (Gibbs et al. 2007). However, while these results appear to be in contrast with the likely non-target effects on nitrification by Phoslock™ and Alum, the adsorption of the NH_4-N by the modified Zeolite is a net effect that may be masking the impact on nitrification.

Under anoxic conditions, nitrification (and denitrification) does not occur at the sediment surface. However, there were some changes in NH_4-N effluxes attributable to these capping agents (Fig. 8). The adsorption of NH_4-N by the modified Zeolite still occurred and is likely to be more effective at the higher dose rate if applied at its P-removal efficacy dose rate.

4.3.2 Denitrification effects

Under aerobic conditions, microbial denitrification reduces the NO_3-N produced by the nitrifiers at the sediment-water interface. The special conditions for this reaction are that 1) anoxic sediments are close the surface allowing nitrification to occur within the surfacial sediments and 2) the NO_3-N produced can diffuse down into the anoxic zone where the NO_3-N occurs and nitrogen is released as N_2 gas. A non-target effect suppressing denitrification was seen as higher NO_3-N concentrations than in the controls (Fig. 9, Aerobic), and P-removal efficacy dose-rate-adjusted suppression results are similar to those given in Table. 3, i.e., Phoslock™ 49%, Alum 58%, Allophane 13%, and modified Zeolite 42%.

Under anoxic conditions, denitrification would only occur if NO_3-N from an external source was injected into the hypolimnion. The anoxic phase of this study showed essentially total denitrification of the NO_3-N in the lake water flowing through the incubation tubes although there was an apparent small effect on denitrification in the presence Phoslock™ and modified Zeolite.

4.3.3 Other non-target effects

The testing for trace metal release from the sediments showed that there were no apparent adverse effects from the use of these sediment capping agents. Arsenic release was not statistically different between treated and controls and Al release from Alum and modified Zeolite were also similar to the other treatments and the control. These results (Fig. 15) did, however, show that the active ingredient of Phoslock™, Lanthanum, was being released from that capping material in contact with the Lake Rotorua sediment.

La was present at similar concentrations (3-4 mg La m^{-3}) in the water from the treatments using Phoslock™, measured after 7 and 21 days. These concentrations are comparable with those measured during toxicity testing (Clearwater 2004; Clearwater & Hickey 2004; Martin & Hickey 2004). They are 10 times lower than the 45 mg La m^{-3} derived from the regulatory chronic ecotoxic threshold concentration of 1 g Phoslock™ m^{-3} (ERMA 2001) (See Glossary), leading to the conclusion that this level of La is unlikely to have any toxic effect on the environment. Supporting this conclusion is the clinical use of La as a "safe" phosphate binder during renal dialysis (Persy et al. 2006), treatment level 1 g La per day.

The persistent release of La from Phoslock™ in the incubation tubes was consistent with advice from the supplier, Phoslock Water Solutions Ltd., that La leaching occurs in soft waters with low DRP, but the free La will bind with DRP and alkalinity in the water column (Sarah Groves, Phoslock Water Solutions Ltd., pers. comm.). Clearly complete DRP binding was not happening as the free La was measured in the filtered water. This implies that there was insufficient DRP in the water to be sequestered by the La released. During the toxicity testing, addition of DRP caused trout toxicity to decline (Hickey, pers. comm.) supporting this hypothesis. This raises a concern that, if the sediments are treated at the P-removal efficacy dose rate but the mineralisation process at around 27 mg P m^{-2} d^{-1} takes 117 days to release all of the TAP from the sediment, then there will always be a lack of DRP for the La release to sequester until the P-binding capacity is exhausted. That would imply that there would most likely be a persistent leaching of free La from the Phoslock™ capping material for up to 117 days after the application. Note that the observed La concentrations from the sediment incubation tubes were net values after P sequestration was complete.

Compared with Al, little is known about the environmental impact and toxicity of La on aquatic biota. It is stated that La, is "extremely toxic to salmonid fishes and water fleas" at concentrations around 1000 mg La m^{-3} (Peterson et al. 1976) based on toxicity tests undertaken in that study. Unfortunately, their tests failed to identify an LD_{50} for trout or Daphnia as all fingerlings died within 24 hours at 1000 mg La m^{-3} and Daphnia mortality exceeded 50% at a concentration of 600 mg La m^{-3}. A study by Barry & Meehan (2000) determined the acute and chronic toxicity (48-h EC_{50}) of La to water fleas (*Daphnia carinata*) to be 43 mg m^{-3} in soft water (i.e., equivalent to Lake Rotorua water) and 1180 mg m^{-3} in hard waters. That information was included in Borgmann (2005).

An estimated chronic no observed effect concentration (NOEC) value of 4.3 mg m^{-3} may be obtained by dividing the soft water acute value by 10 (ANZECC 2000). The water concentrations in this study approached or exceeded this threshold (Fig. 12),

although the importance for whole lake applications is not known. However, there were "inconclusive" indications of elevated La concentrations found in some trout and Koura tissues (livers) after the Phoslock™ treatment of Lake Okareka (Landman et al. 2007; McIntosh 2007). Therefore, the significance of La release was require further investigation.

The toxicity tests by Barry & Meehan (2000) were conducted at pH 7.5-7.8 which is higher than the natural pH of Lake Rotorua water at the sediment at pH 6.8. While pH is known to be an important factor in the solubility and toxicity of Al in aquatic environments, e.g., chronic 21-42 d LC_{50} of Al at pH <6.5 (all between pH 4.5 and 6.0) for trout is 15-106 mg m^{-3} compared with 34-7100 mg m^{-3} at pH >6.5 (ANZECC 2000), there have been no studies of the effect of pH on La solubility or toxicity in aquatic ecosystems.

The study by Peterson et al. (1976) tested the P uptake of La and Al at a range of pH values from 2 to 11 and demonstrated large differences in a soft pond water (Fig. 19). Of significance, the P-uptake was strongly affected below pH 6 compared with pH 4 for Al. In this study we estimated the P-binding capacities of La and Al at three pH values (Table 5) and observed an apparent loss of La from Phoslock™ over 50 hours at pH values of 7.0 and 6.1 (Fig. 17). These data suggest that, as with Al, there may also be a pH effect on La toxicity in the aquatic ecosystem.

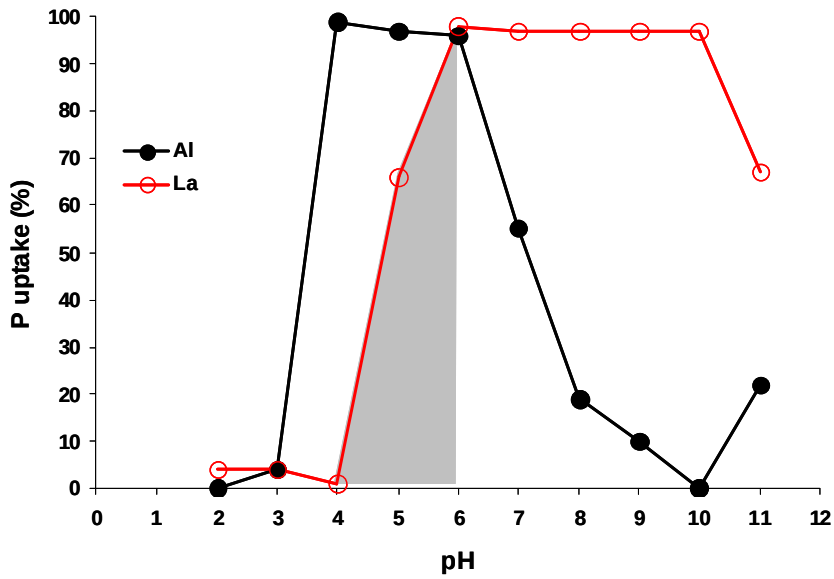

Figure 19. P-uptake changes for Al and La at a range of pH in pond water. Redrawn from Peterson et al. (1976). Shaded area indicates the pH zone where La may become soluble.

This could be an important factor when considering the use of Phoslock™ on Lake Rotorua, which is a geothermally-influenced lake. It was demonstrated in the earlier study on Lake Okaro (Gibbs et al. 2007) and Lake Rotorua sediment (Vopel et al. 2008) that capping the sediments changes the REDOX conditions across the sediment surface. Apart from respiration and CO_2 production, this allows H_2S production to move into the capping layer. As the dissociation of H_2S releases S^{2-} and H^+ ions, the pH in that zone would fall. Literature values suggest the pH could go as low as pH 4 in geothermally influenced sediments (e.g., Rusch et al. 2005). Vopel et al. (2008) did not measure such low pH with Phoslock™ (ΔpH ~0.5-0.8) in the cores tested. However, if the pH falls below 6, the P-uptake by La would decrease and the La could potentially become mobile (Fig. 19).

Apart from pH effects, the report on Phoslock™ from the National Industrial Chemicals Notification and Assessment Scheme, Australia, (NICNAS 2001) noted that "there is a possibility that under saline conditions the lanthanum may be exchanged for ions such as sodium which could lead to elevated lanthanum levels in the water". Geothermal fluid in the Rotorua lakes region has high sodium levels which, in combination with the low sediment pH effect, could favour mobilization of La from the Phoslock™ in contact with Lake Rotorua sediments.

With the NICNAS (2001) comments about potential sodium effects in mind, the buffered phosphate solutions used in the P-saturation tests were made up using sodium phosphate salts. Consequently, it is possible that the apparent loss of La in those tests was a combination of both low pH and high sodium (~10% of seawater). If this hypothesis is correct, then low pH and potentially high sodium in the sediment beneath the Phoslock™ capping layer on Lake Rotorua sediment may be the cause of the persistent leaching of La observed.

While original toxicity testing may have seen the initial release of La from Phoslock™, as acknowledged by the suppliers, the persistent release of La when Phoslock™ is in contact with Lake Rotorua sediments may be a site specific effect.

There is little information on the effects on benthic organisms living in or on lake sediments of chronic exposure to La. Our data show that there was no indication that the release rate (~2 mg m^{-2} d^{-1}) was slowing over a period of 21 days. Consequently, there was no indication of how long the release would continue, or where that La ends up in the ecosystem and to what effect. Further investigation is needed to resolve these issues.

5. Summary

5.1.1 Alum (Al based)

Alum had the highest P-removal efficacy of the capping materials tested (Fig. 18) but one of the poorest longevity results. This failure to perform as expected is related to pH effects and the ease of disturbance of the Alum floc on the sediment surface. There are four issues that need to be considered when using Alum in a lake.

1. Although Alum appears to be easy to apply being a liquid, the P-removal action only occurs when it forms a floc. Consequently, in lakes such as Lake Rotorua with low natural buffering capacity, the Alum solution must be buffered when applied to initiate the flocking action and thus sedimentation to form the cap. The buffer must also control the pH during floc formation.

2. The P-binding capacity of Alum is pH sensitive with maximum (95%) efficiency over the pH range of 4 to 6 (Fig. 19). At the lower pH there is a significant risk of toxic Al^{3+} ions being released into the water column. At pH levels around 7, the P-binding efficiency is reduced by 55% and at pH 8-9 (equivalent to a moderate algal bloom) the P-binding efficiency is around 10-20%. Lake Rotorua sediment in the incubation system had a pH of 6.8, which would account for the lower than expected results seen in the longevity experiment.

3. Alum treatment at its P-removal efficacy rate under aerobic conditions could enhance the release of NH_4-N from the sediment by up to a factor of 5 and would suppress denitrification by almost 60%, greatly increasing the retention of N in the lake. The enhanced release of NH_4-N is consistent with field observations on Lake Okaro (Paul et al. 2008).

4. As the Alum cap is a floc, it is easily disturbed by water currents, consequently there is a high probability of wind-induced mixing disturbing the Alum floc, on the sediment.

Recommendation: Alum should not be used as a capping material on Lake Rotorua.

5.1.2 Modified Zeolite (Al based)

While the modified Zeolite had the next highest P-removal efficacy, the 0-to-1 mm grain size product used in this study had the lowest longevity rating of all capping

materials tested. This failure to perform as expected is related to pH effects and grain size. There are several things to consider when using modified Zeolite.

1. This product had a high performance rating in the earlier Lake Okaro sediment tests (Gibbs et al. 2007) using 350 and 700 g m^{-2} dose rates, which gave a near complete coverage of the sediment surface. The same formulation used in this study at lower dose rates only approached complete sediment coverage at the 200% treatment dose rate of 120 g m^{-2}. However, as that dose rate was lower than the estimated P-removal efficacy dose rate on Lake Rotorua sediments, an increase to the P-removal efficacy dose rate is likely to improve the sediment coverage and longevity rating of this product.

2. As a granular product, modified Zeolite is easy to apply and, at dose rates comparable with the P-removal efficacy, it would settle rapidly to form a stable layer on the sediment. A finer grain size may improve the sediment coverage and thus make better use of the high P-binding capacity of this product.

3. Timing of application is an important issue with modified Zeolite. Because this product settles rapidly, it does not have the contact time to strip DRP from the lake water column. Consequently, this product should be applied when the lake is mixed and the DRP in the water column has been sequestered by the Fe and Mn in the sediments. The optimal timing would be just as thermal stratification begins in spring and the oxygen concentrations in the hypolimnion are still higher than 6 g m^{-3}, which is the upper threshold for mobilising Mn and thus the P bound to that metal.

4. The modified Zeolite was the only capping material tested that was capable of binding NH_4-N released from the sediment. Coupled with its P-binding capacity, ease of application, and rapid settling, the added capability of controlling NH_4-N release from the sediment makes this an attractive product for managing internal nutrient loads in lakes. However, as with Alum and Phoslock™, modified Zeolite suppressed denitrification by around 40% under aerobic conditions, a factor which would increase N retention in the lake.

Recommendation: Finer grain sizes should be tested for improved sediment coverage.

5.1.3 Phoslock™ (La based)

Phoslock™ is a field tested commercial product that effectively blocked the release of DRP from the sediments. However, as with the two Al based products, the P-binding capacity of Phoslock™ was sensitive to pH. There are several issues that need consideration when using Phoslock™.

1. In contrast to the Al based capping materials, the highest P-binding capacity for Phoslock™ was at high pH and there was a marked reduction in P-binding capacity at the pH of natural Lake Rotorua sediments and lake water.

2. Application can be either as a granule/powder or as a slurry. Applied as a granule, the product settles rapidly to form the sediment cap. Rapid settling has the same seasonal timing considerations as for the modified Zeolite. In contrast, the slurry application method allows the product to rapidly disperse in the water column where the slow settling rate gives sufficient contact time to strip DRP from the water column before it forms a sediment cap. While this is a disadvantage for a capping material where the product could drift beyond the targeted treatment area, it is an advantage when applied to a lake where the hypolimnion has elevated levels of DRP; i.e., the time of application of Phoslock™ is not critical.

3. Phoslock™ applied at its measured P-removal efficacy dose rate, greatly enhanced (5-fold) the release of NH_4-N from the sediment in the incubation tubes under aerobic conditions. This was much greater than expected from the ~50% suppression of denitrification. These two net effects could lead to an increase in dissolved inorganic nitrogen concentrations in the water column and greater retention of N in the lake.

4. There was a small, persistent release of La from the Phoslock™ capping layer at around 2 mg La m^{-2} d^{-1}, and La concentrations in the water column were around the NOEC of 4.3 mg m^{-3} derived from the acute and chronic EC_{50} of 43 mg m^{-3} for *Daphnia carinata* in soft water (Barry & Meehan 2000). The persistent release of La appears to be related to low pH and high sodium concentrations, both of which are more likely in the geothermally influenced sediments of Lake Rotorua. i.e., this may be a site specific effect. The La release may also be a feature of this product, as indicated by the supplier, which becomes apparent when there is insufficient DRP to bind with that La. From the study data, there was no indication of how long the La release would continue or the fate of the La or its chronic effects.

Recommendation: The longevity of the La release from Phoslock™ should be investigated, along with the fate of that La in the aquatic ecosystem of a lake.

5.1.4 Allophane (natural clay)

Allophane has a P-removal efficacy rate between those of Phoslock™ and modified Zeolite. Applied at this rate Allophane is likely to have few major non-target effects although it was sensitive to pH. There are several issues that need consideration when using Allophane:

1. As with Alum and modified Zeolite, the highest P-binding capacity of Allophane was at the natural sediment and lake water pH of around 7. This is consistent with the extremely high Al mineral content (3 times higher than modified Zeolite). However, unlike modified Zeolite where the Al has been added, the Al in Allophane is part of the natural crystal structure of this clay.

2. Allophane as supplied, consisted of a mixture of grain sizes with the very fine particles remaining in the water column for a considerable time – similar to the dispersed Phoslock™. When it did eventually settle it formed a cohesive layer completely covering the sediment.

3. Applied at its P-removal efficacy rate, Allophane is unlikely to substantially enhance the release of NH_4-N under aerobic conditions as was found with Phoslock™ and Alum treatments. However, Allophane did cause suppression of denitrification under aerobic conditions but the predicted effect, at around 13%, would be much lower than was caused by the other three capping materials.

4. Because the break-through point for the Allophane was not achieved within the experimental treatment range, the minimum dose rate required for Lake Rotorua sediments is uncertain. Consequently, the P-removal efficacy value provided for Allophane (Fig. 18) is a “best estimate”. Of significance is that this estimate is less than the lowest (50%) treatment dose rate used in this study.

Recommendations: Further tests should be conducted to determine the minimum dose rate of Allophane required to achieve 100% P-removal from the top 4-cm of Lake Rotorua sediment.

6. Conclusions

The four capping materials tested on Lake Rotorua sediments each have the capability of blocking all of the DRP released from the sediment during periods of anoxia, when applied at their P-removal efficacy rates. Those rates are a function of the total available P in the upper sediment (top 4 cm), the measured P-binding capacity of the capping materials, and the interactions between the capping material and the sediment. The estimated P-removal efficacies of the four P-inactivation agents as supplied for testing on Lake Rotorua sediments are:- Alum 80 g m^{-2}, modified Zeolite 190 g m^{-2}, Phoslock™ 280 g m^{-2}, and Allophane 220 g m^{-2}.

Adverse or non-target side effects suppressed nitrification under aerobic conditions resulting in substantially enhanced releases of NH_4-N (~5 fold increases) from the sediments by Alum, and Phoslock™. Allophane did not appear to affect nitrification and modified Zeolite reduced the release of NH_4-N from the sediments by adsorption onto the Zeolite base material. Also under aerobic conditions, all of the capping materials suppressed denitrification by 13% to 58% - Alum had the greatest effect while Allophane had the least.

From the longevity experiments, if these capping materials were applied to Lake Rotorua sediments at their respective P-removal efficacy rates and left undisturbed, they should remain effective for at least four years. Burial due to sedimentation and disruption by gas ebullition from the sediments could reduce that expectation.

Based on the instability of the Alum floc as a capping material, we recommend that Alum is not used on Lake Rotorua.

Based on the enhanced release of N from the sediments, all products caused suppression of denitrification under aerobic conditions, although Allophane had the least effect. We recommend that none of these capping materials be used in the permanently aerobic zones of a lake.

We recommend specific further investigations of Allophane (determining the minimum dose rate), modified Zeolite (effects of reducing the grain size), and Phoslock™ (determining the longevity and fate of low levels of La leaching into the aquatic environment).

7. Acknowledgements

We would like to thank Branwen Hughes and Kathryne Farnsworth for collecting lake water and assistance with daily sampling of the incubation tubes, Graham Bryers for the rapid analytical turn around of the thousand or more water samples produced during this study, and Chris Hickey and Kit Rutherford for valuable discussion during the preparation of this report.

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9. Appendix A

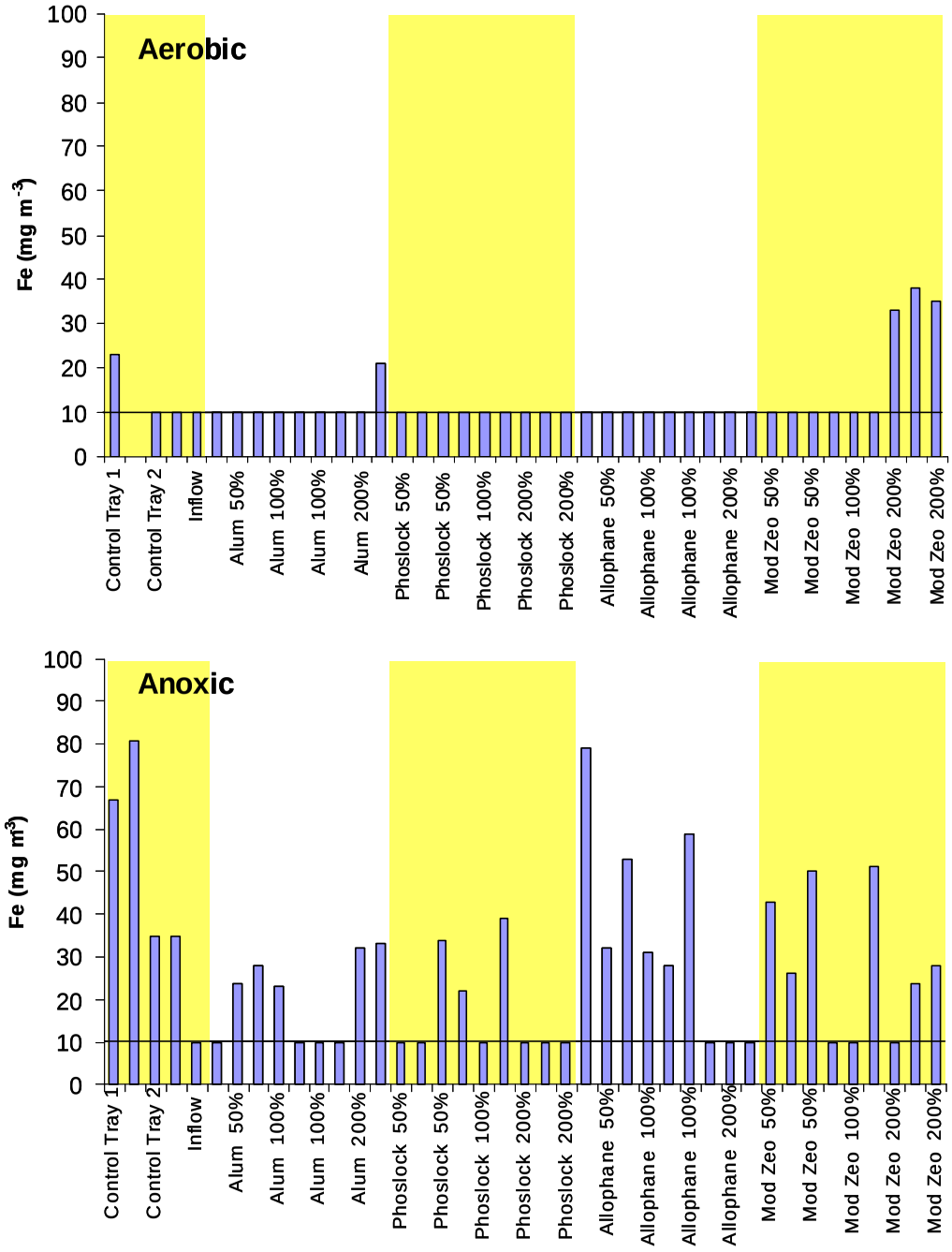

Figure A1. Comparative plots of the total dissolved Fe concentrations from the incubation tubes under aerobic and anoxic conditions. The horizontal line is the measured concentration in the inflow water. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals an efflux of about 0.5 mg m^{-2} d^{-1}).

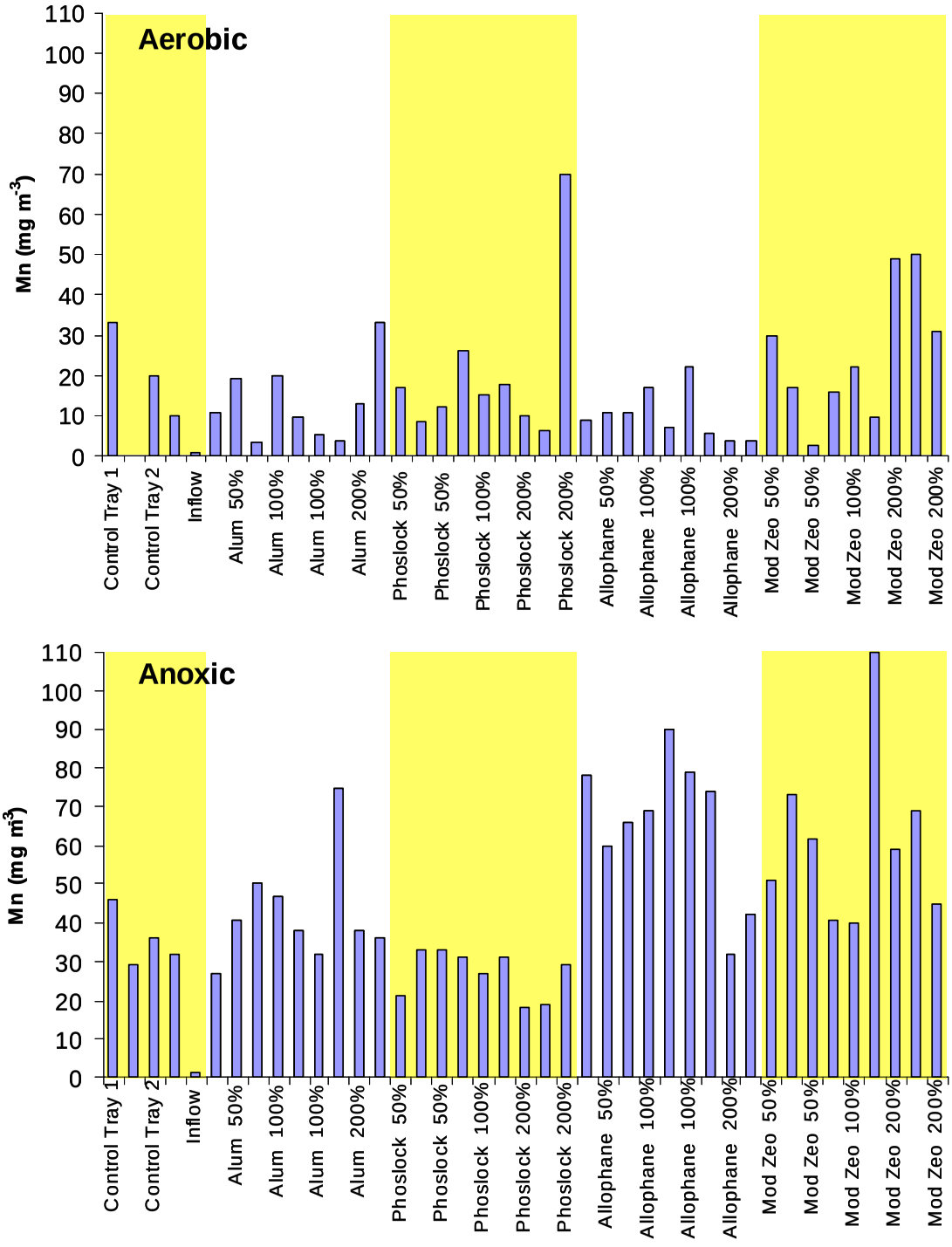

Figure A2. Comparative plots of the total dissolved Mn concentrations from the incubation tubes under aerobic and anoxic conditions. Mn concentrations were essentially zero in the inflow water. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals an efflux of about 0.5 mg m^{-2} d^{-1}).

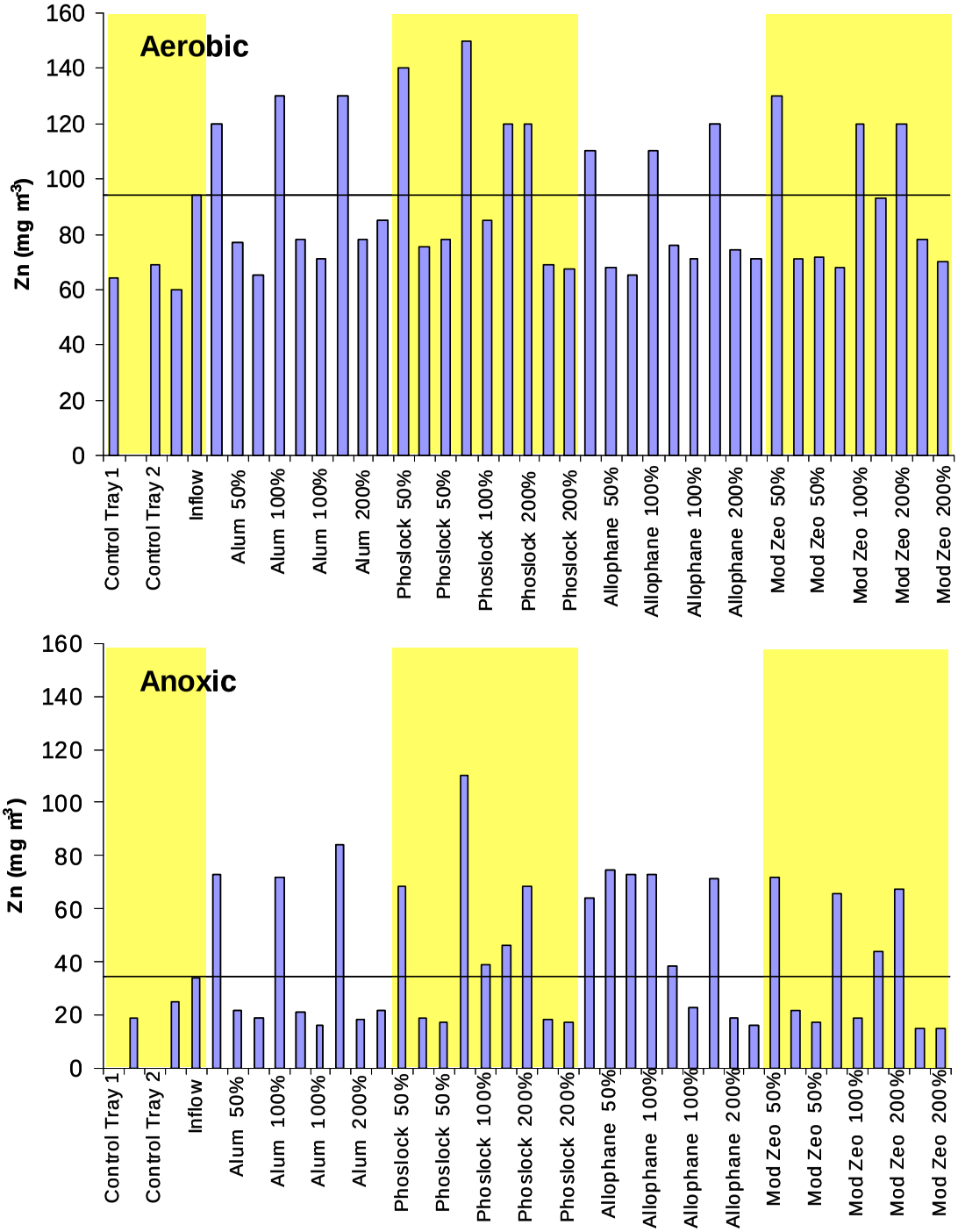

Figure A3. Comparative plots of the total dissolved Zn concentrations from the incubation tubes under aerobic and anoxic conditions. The horizontal line is the measured concentration in the inflow water. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals an efflux of about 0.5 mg m^{-2} d^{-1}).

10. Appendix B

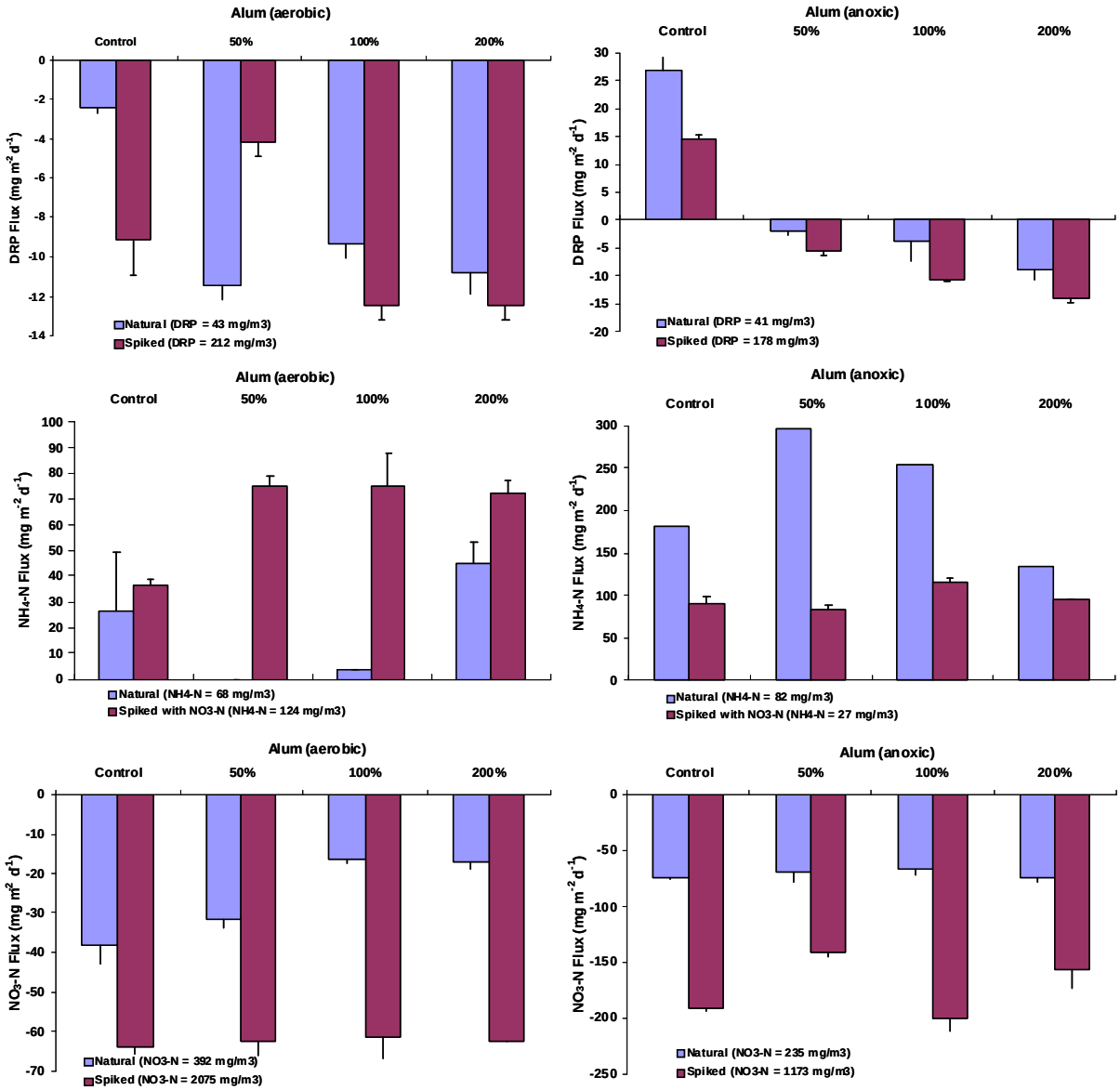

Figure B1. **Alum**: comparison of dissolved reactive phosphorus (DRP), ammonium (NH_4-N), and nitrate (NO_3-N) effluxes in natural water (blue) and natural water amended with high DRP and NO_3-N concentrations (red) under aerobic and anoxic conditions.

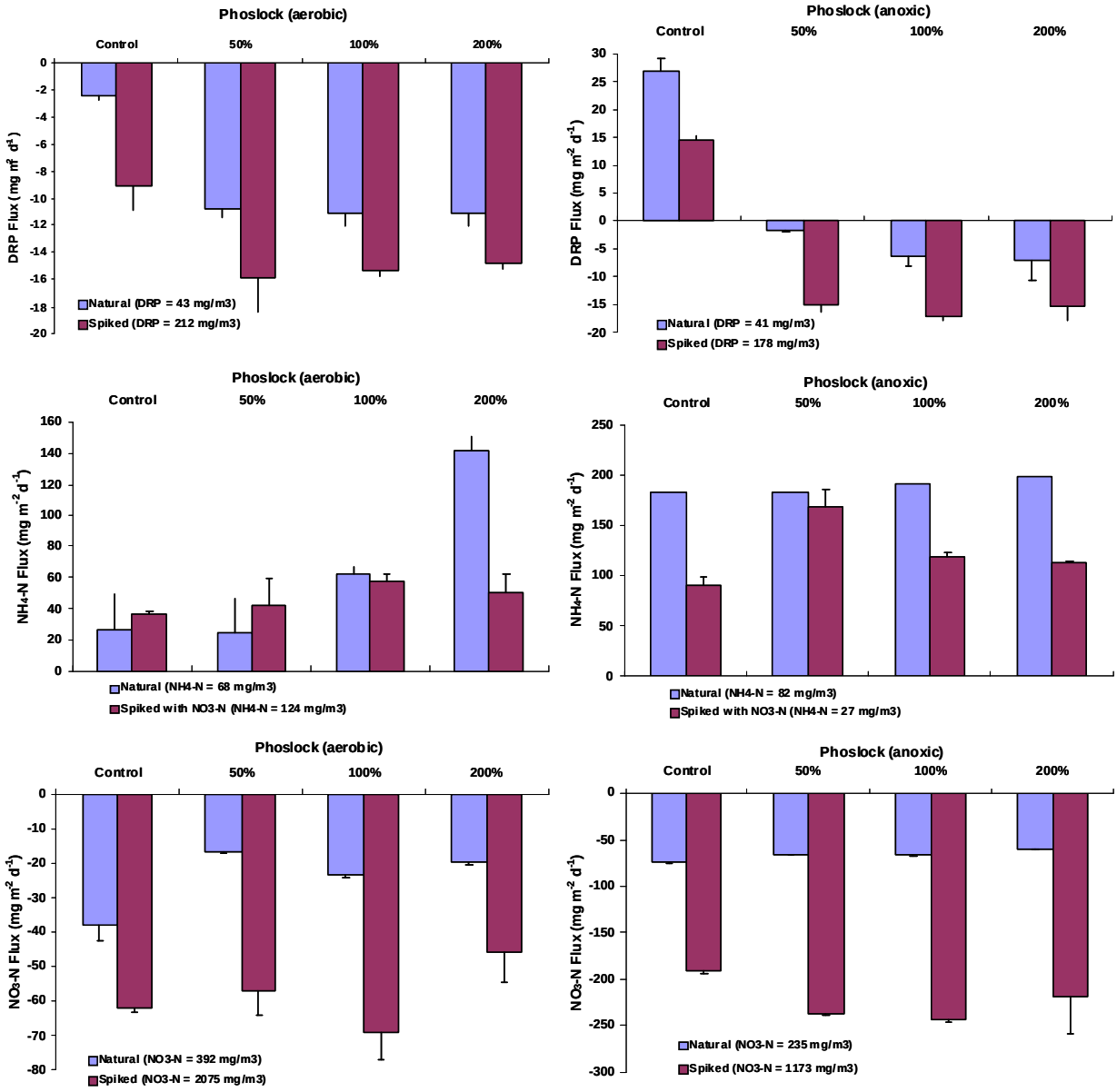

Figure B2. **Phoslock**™: comparison of dissolved reactive phosphorus (DRP), ammonium (NH_4-N), and nitrate (NO_3-N) effluxes in natural water (blue) and natural water amended with high DRP and NO_3-N concentrations (red) under aerobic and anoxic conditions.

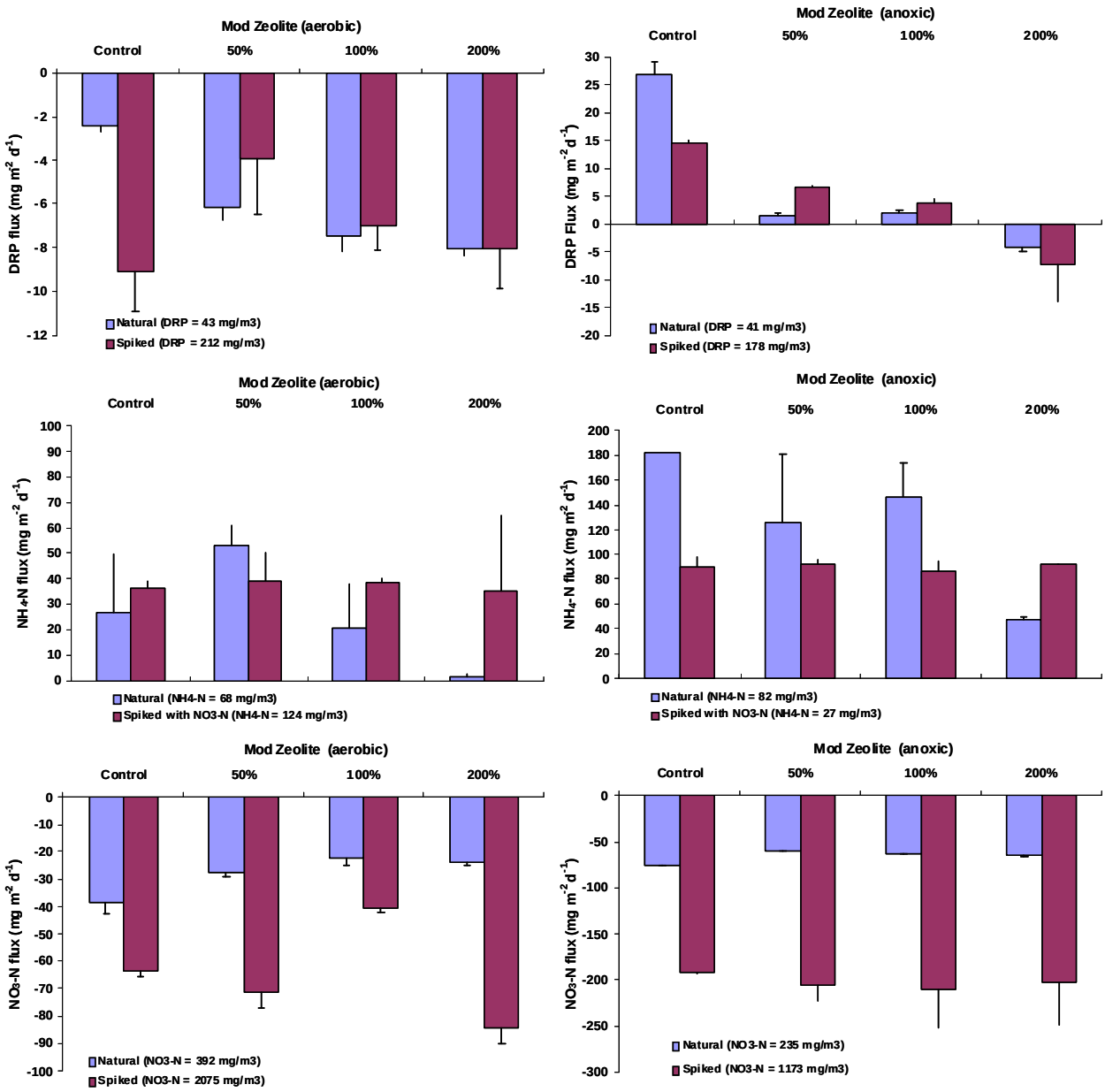

Figure B3. **Modified Zeolite**: comparison of dissolved reactive phosphorus (DRP), ammonium (NH_4-N), and nitrate (NO_3-N) effluxes in natural water (blue) and natural water amended with high DRP and NO_3-N concentrations (red) under aerobic and anoxic conditions.

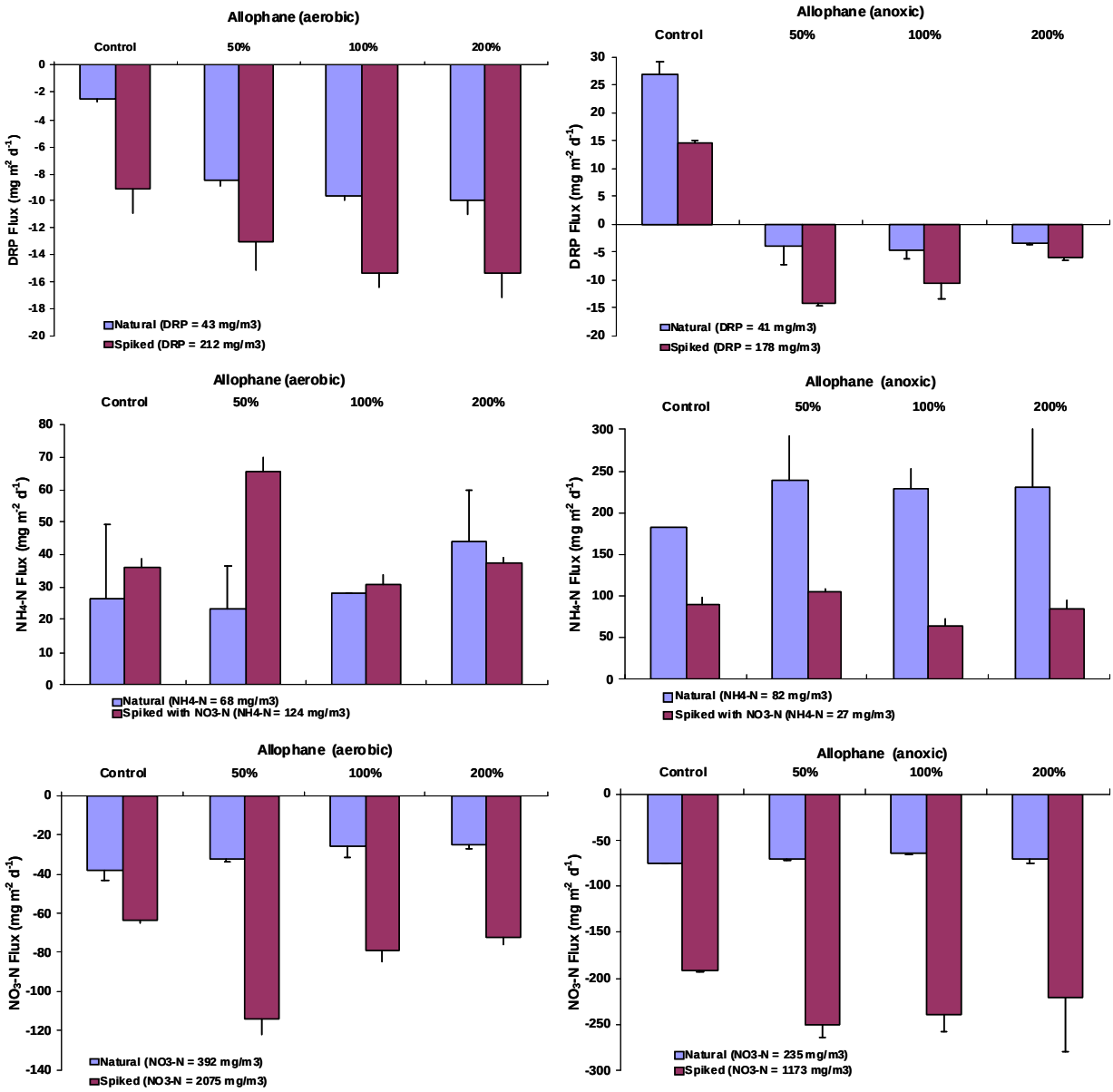

Figure B4. **Allophane**: comparison of dissolved reactive phosphorus (DRP), ammonium (NH_4-N), and nitrate (NO_3-N) effluxes in natural water (blue) and natural water amended with high DRP and NO_3-N concentrations (red) under aerobic and anoxic conditions.

11. Appendix C

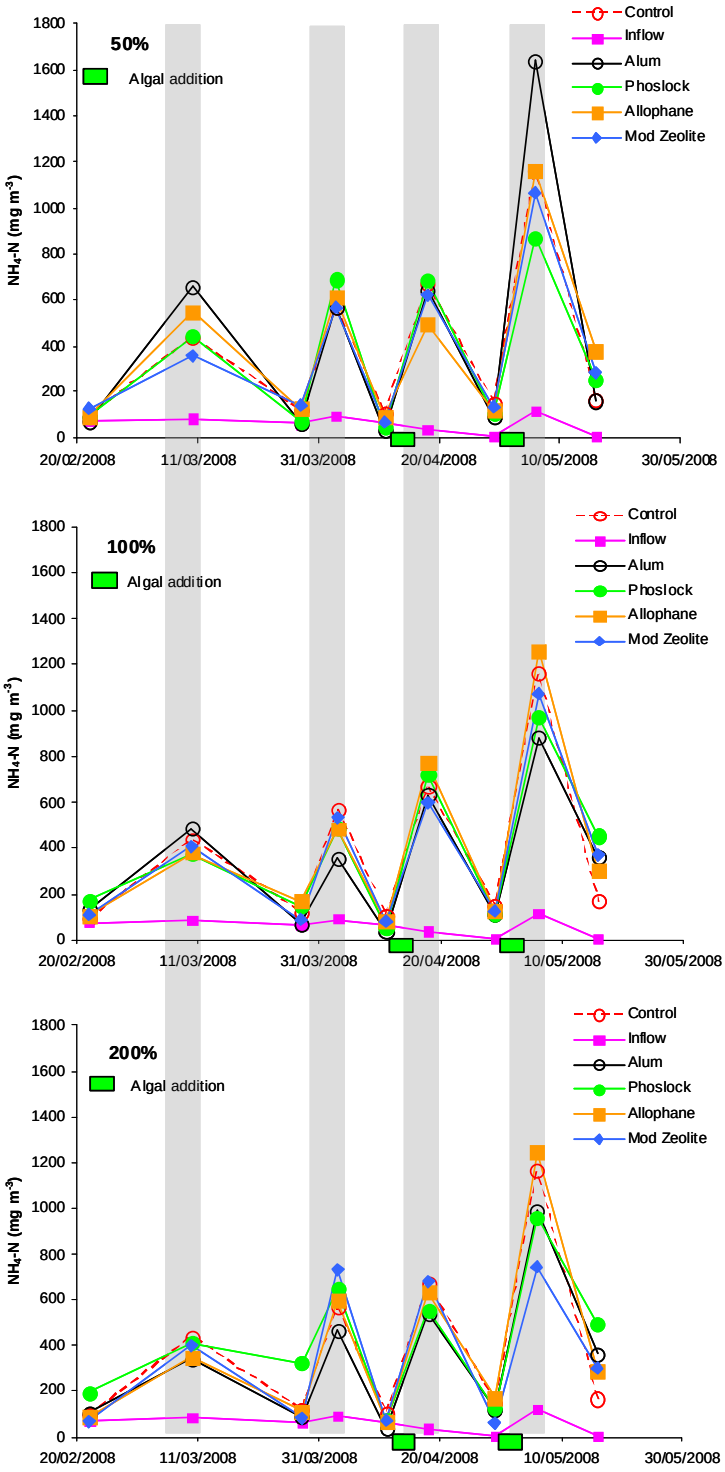

Figure C1. Time series of mean NH_4-N concentration changes in the inflow and outflow waters from the longevity experiment. Grey shaded bands indicate the periods of anoxia; green blocks indicate when the algal slurry was applied.

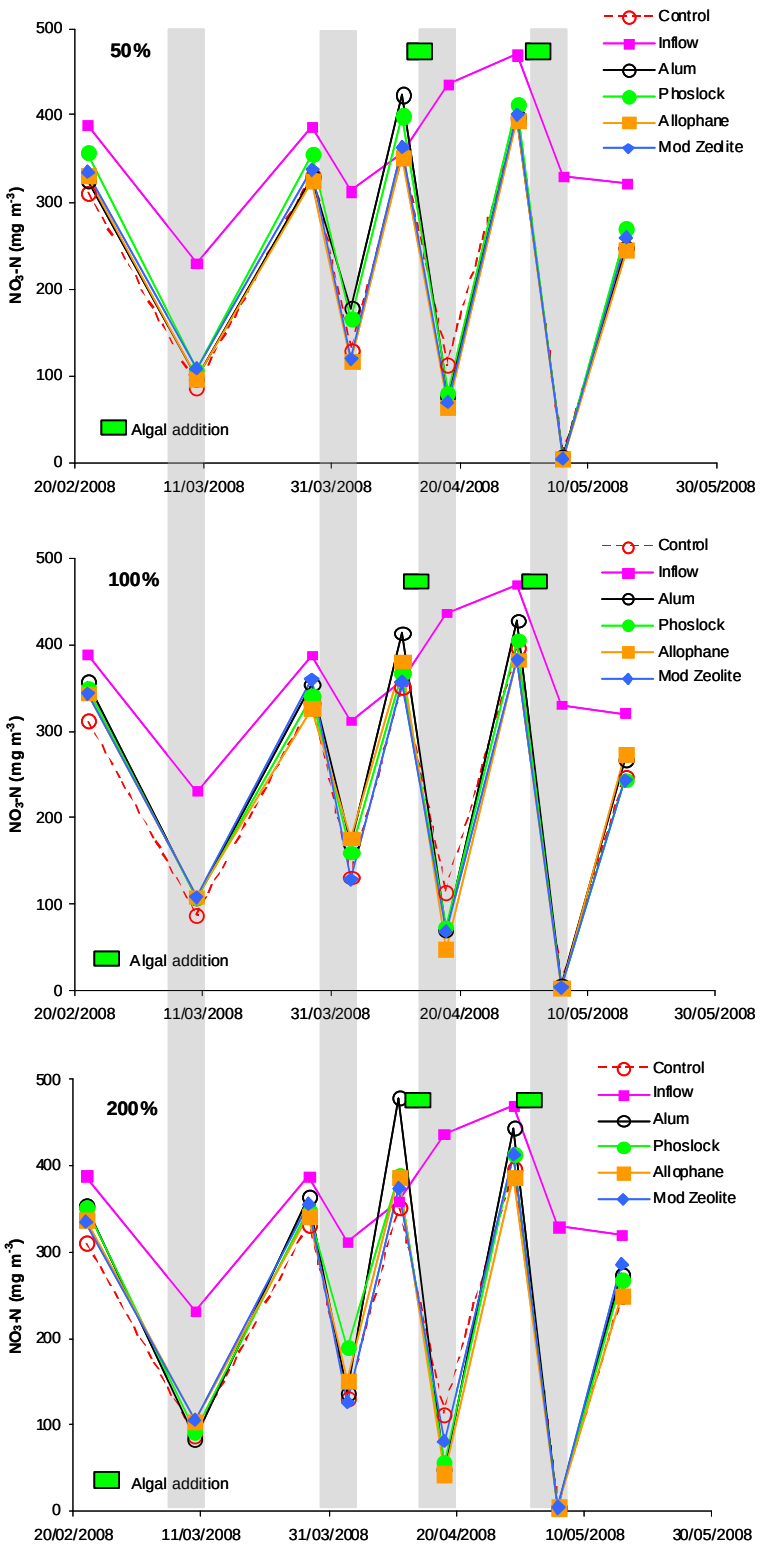

Figure C2. Time series of mean NO_3-N concentration changes in the inflow and outflow waters from the longevity experiment. Grey shaded bands indicate the periods of anoxia; green blocks indicate when the algal slurry was applied.