Hydrobiologia
DOI 10.1007/s10750-010-0477-3

PRIMARY RESEARCH PAPER

Sustainability assessment and comparison of efficacy of four P-inactivation agents for managing internal phosphorus loads in lakes: sediment incubations

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Received: 18 May 2010 / Revised: 7 September 2010 / Accepted: 13 September 2010

Abstract A novel application of a continuous flow incubation system (CFIS) was used to assess four phosphorus (P) inactivation agents—alum, Phoslock^{TM}, a new modified zeolite (Z2G1 or Aqual-P^{TM}), and allophone—when used as sediment capping agents to manage internal P loads in lakes. The CFIS technique allowed combined efficacy and sustainability assessment, including: (1) flux measurements during simulation of stratified (anoxic) and mixed (aerobic) conditions on the same sediment through multiple cycles to assess the longevity of a range of product doses; (2) simulation of a summer algal bloom collapse and subsequent burial of the products; and (3) investigation of non-target effects on nitrification and denitrification processes at the sediment–water interface. Minimum P-removal dose rates were found to differ substantially at 80 g m^{-2} for alum, 190 g m^{-2} for Z2G1, 220 g m^{-2} for allophane and 280 g m^{-2} for Phoslock^{TM}, for similar capping layer thickness of about 2 mm, and would be effective for at least 4 years. All products temporarily suppressed nitrification and denitrification under aerobic conditions, and it may be important to minimise product application to any permanently aerobic zones, such as the littoral areas of a lake. While the aluminium (Al)-based products did not enhance Al fluxes in the CFIS, lanthanum (La) was released at a near constant rate of around 2 mg La m^{-2} day^{-1} from the Phoslock^{TM} treatments over a period of at least 14 days. Spatial variability of sediment P, bioturbation, and burial are factors that will affect upscaling these results to a whole lake.

Keywords Lake restoration · Internal P load · P-inactivation agents · Alum · Phoslock^{TM} · Modified zeolite · Allophane · Sediment capping · Phosphorus · Nitrogen · Sustainability

Introduction

The use of an active capping material layer to bind and thus block the release of phosphate (PO_4-P), measured as dissolved reactive phosphorus (DRP), from lake sediments can be thought of as a management strategy which resets the lake internal phosphorus (P) loads to zero, with all subsequent P being supplied from the catchment. The nitrogen (N) and P nutrients that drive algal growth in lakes come directly from the catchment as external loads, or they are recycled from the lake sediments as internal loads from a pool that accumulated during periods of high external loading (Søndergaard et al., 2003). The

Handling editor: P. Nõges

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Published online: 25 September 2010

sustained control of phytoplankton biomass in lakes requires the reduction of both N and P loads (e.g. Lewis & Wurtsbaugh, 2008); however, the reduction of P loading often can be the most effective approach in eutrophic lakes (e.g. Schindler et al., 2008; Welch, 2009).

External loads can be managed through catchment remediation work including restricting stock access to the lake and river inflows, enhancing riparian buffer zones, restoring marginal wetlands around the lake shores, and managing point discharges. However, while internal loads of N can be permanently removed from the lake by the microbial processes of coupled nitrification and denitrification (e.g. McCarthy et al., 2007), there is no comparable removal process for P.

Internal P loads are mainly derived from the release of PO_4-P mostly sequestered by oxidised iron species and the decomposition of organic matter in the lake sediments releasing biologically available (bioavailable) P as DRP into the water column during periods of anoxia, usually in summer (Smolders et al., 2006). Not all of the P in the lake sediments is bioavailable (Spears et al., 2007). A further complicating factor in the lakes of the Taupo volcanic zone (TVZ) of the North Island of New Zealand is that the pumice soils have naturally high P content and produce elevated DRP concentrations in the springs and stream inflows to the TVZ lakes (Timperley, 1983), exacerbating the effects of the internal P load. Consequently, many of these lakes show a tendency for nitrogen limitation (White et al., 1985) and the excess P concentrations favour cyanobacteria dominance in summer (e.g. Havens et al., 2003).

Internal P load management strategies in Northern Hemisphere countries, to reduce algal biomass and the incidence of cyanobacteria blooms, have included binding the P in the lake with a P-inactivation agent applied either as a flocculation agent to strip P from the water column or as a capping agent to coat the sediments and block the release of P during periods of bottom water anoxia (Cooke et al., 2005). The P-inactivation agent of choice is typically alum (aluminium sulphate) which, in neutral to alkaline water (pH 6.0 to 8.0), produces a flocculent gelatinous precipitate of aluminium hydroxide, $Al(OH)_3$, which is chemically relatively stable, even under the low redox states commonly encountered under anoxic conditions during summer stratification. Alum treatment effectiveness can be variable and Welch & Cooke (1999) report that "an expectation of 15 years longevity seems reasonable". Notwithstanding this, alum may be completely ineffective, or effectiveness may be short-lived, if much of the lake is covered with macrophytes that senesce during summer and contribute P to the water (Welch & Schrieve, 1994). Furthermore, the use of alum to manage internal P loads may not be appropriate for all lakes (Hickey & Gibbs, 2009). This is especially important in the low alkalinity soft waters of many of the lakes in the TVZ, and where low pH (<6.0) may produce more soluble and potentially toxic Al^{3+} ions and associated poor floc formation. Also, the alum floc is up to 5× more easily resuspended than the natural sediment (Egemose et al., 2010), potentially reducing its efficacy as a capping agent in large wind exposed lakes.

Internationally, alternative strategies to reduce internal P loadings in eutrophic lakes include sediment capping using calcite (Berg et al., 2004), modified clay minerals (Robb et al., 2003) and iron slag (Yamada et al., 1987). Other natural products that have been tested for their P-binding capability include allophane (Yuan & Wu, 2007) and a modified zeolite product, Z2G1 (recently named Aqual-P™), specifically designed as a sediment capping agent to manage internal P loads (Gibbs & Özkundakci, 2010).

With a long term commitment to the restoration of water quality in the Te Arawa/Rotorua lakes in the TVZ, the regional managers, Environment Bay of Plenty, are working towards the restoration of Lake Rotorua, a large (area 81 km^2), relatively shallow (mean depth ~ 10 m) polymictic lake which is eutrophic and experiences episodic cyanobacteria blooms following P release from the sediment during periods of thermal stratification in summer (Burger et al., 2007). Sediment capping to manage the internal loading of P is being considered as a feasible management option. However, not all P-inactivation agents have comparable binding efficacy in these low alkalinity (<30 g m^{-3} as $CaCO_3$) soft waters. In order to provide a robust comparative basis for decision-making on which P-inactivation agent might be most appropriate for use on Lake Rotorua, this study compares four P-inactivation agents (products) for their efficacy of blocking P release from Lake Rotorua sediments, their potential longevity and for any potential non-target side effects on the lake ecosystem

and the microbial communities at the sediment–water interface. The laboratory-based technique used offers a 'novel' integrated assessment approach when combined with the dose–response design.

Methods

Experimental design

The dose–response incubations were run using the continuous flow incubation system (CFIS) described in Gibbs & Özkundakci (2010) with product treatments in triplicate and four controls. As sediment release of P is largely regulated by oxygen concentrations at the sediment–water interface (Gächter & Müller, 2003; Hupfer & Lewandowski, 2008), the incubations were first run with natural lake water under aerobic conditions to simulate mixed or littoral zone conditions, and then under anoxic conditions to simulate hypolimnetic conditions after thermal stratification.

The incubations were run in the dark in a temperature controlled water bath at the summer lake water temperature of 21°C for a period of 90 days and were cycled from aerobic to anoxic on four occasions during that period to simulate annual stratification events and test longevity. Each aerobic and anoxic period was treated as a separate phase of the study representing a 'year'. On two occasions a slurry of algae was added to each incubation chamber, including controls, to simulate the collapse of a summer algal bloom based on field studies (Burger et al., 2007) and provide additional carbon and nutrients over the capping layer to simulate partial burial.

The incubations were run concurrently with the same source water from a single supply flowing through all incubation chambers. Because long-term incubations of Lake Rotorua sediment have previously been found to produce gas ebullition which could physically disturb the sediment in the incubation chambers, a cup-shaped 1-cm mesh plastic screen was fitted inside the chamber between the sediment surface and the incubation chamber cap, flat bottom of the mesh cup in contact with the sediment surface (Fig. 1), to prevent significant internal sediment disturbance.

Fig. 1 Assembled incubation chamber showing the position of the cup-shaped 1-cm mesh plastic screen which was fitted between the sediment and the cap on the incubation chamber. The flat bottom of the mesh cup was in contact with the sediment surface

P-inactivation agents

The four P-inactivation agents tested in this study were: (i) alum (aluminium sulphate solution) buffered with sodium bicarbonate to allow it to form a floc; and three granular products, (ii) Phoslock^{TM} (Robb et al., 2003) which is a bentonite clay modified with the rare earth element Lanthanum (La); (iii) Z2G1 (Gibbs & Özkundakci, 2010) which is a proprietary zeolite-based product from Scion, Rotorua, modified with an aluminium salt and (iv) allophane, which is a natural volcanic mineral rich in alumino-silicates and iron (Yuan & Wu, 2007). All granular products were sieved to remove particles >1 mm. Because the nominal P-binding capacity (g P kg^{-1}) of each product was different (Table 1), the dose rate of each product (g m^{-2}) was normalised so that there was sufficient product to nominally block the release of all bioavailable P from the top 4 cm of sediment, i.e. around 3 g P m^{-2}. This was defined as the 100% treatment. Two additional treatments, with half and double the 100% treatment dose rate (i.e. 50% treatment and 200% treatment, Table 1), provided a range of dose rates aimed at identifying treatment rates that would achieve a complete block of all phosphate

Table 1 Experimental dose rates, in g product per chamber, of the four P-inactivation agents as applied to the individual incubation chambers and the equivalent dose rate (g m^{-2}) as would be applied to a lake

Product (g m^{-2})	NPBC (g P kg^{-1})	Treatment		
		50%	100%	200%
Allophane	5	1.155 (300)	2.31 (600)	4.62 (1200)
Phoslock™	20	0.289 (75)	0.578 (150)	1.155 (300)
Z2G1	50	0.116 (30)	0.231 (60)	0.462 (120)
Alum	100	0.058 (15)	0.116 (30)	0.231 (60)

Calculations used a bioavailable *P* value of 3 g P m^{-2}

NPBC nominal P-binding capacity

released from the sediment and the dose rate required for longer-term sustained treatment. The dose–response design would allow the minimum dose rate to be calculated relative to a range of efficacy, sustainability and other management criteria. Control incubation chambers contained un-dosed sediment.

Notably, the 50 and 100% treatments of Z2G1 did not give complete surficial coverage of the sediment in the incubation chambers, although the 200% treatment (120 g m^{-2}) did. Earlier studies of Z2G1 used higher dose rates (135, 200, 270, 405, 540, 600 and 674 g m^{-2}, Vopel et al., 2008; 350 and 700 g m^{-2}, Gibbs & Özkundakci, 2010) which all provided complete coverage of the sediment.

Sampling

Sediment

Cooke et al. (2005) recommend that estimates of the total bioavailable P in lake sediments should be made on the top 4 cm because sediment P content typically decreases rapidly below that depth. In this study, we required a consistent sediment composition for the incubations. Consequently, a bulk surface sediment sample was collected in mid-summer from a depth of ~17 m in an area of Lake Rotorua where the total P content was known to be >3 g P m^{-2} in the top 10 cm (Pearson, 2007). Multiple (40) sediment cores were collected using a Jenkins corer (Mortimer, 1971) and the upper 10 cm of each core was extruded into a sediment incubation tube for transport to the laboratory, as described in Gibbs & Özkundakci (2010). The sediment cores were subsequently combined in a large plastic bucket and stirred to produce a homogenous mixture before being loaded into the incubation tubes in equal amounts and left to reconstitute under aerated lake water in a controlled temperature water bath at 21°C for 5 days. This procedure ensured that the sediment was consistent in each incubation tube and that sediment differences would not be a factor in the comparison of the four products.

During sediment collection, one sediment core was sectioned on site into 2 cm fractions down to 10 cm and the fractions stored in pre-weighed 100-ml wide-mouth polyethylene screw-cap jars for determination of bulk density, pore-water and sediment chemistry. A sample of the near-sediment overlying water in the core tube was also collected using a syringe before extruding the sediment for sectioning.

Algal slurry

About 2 kg of wet green *Enteromorpha* sp. from Lake Rotorua was washed in lake water to remove sand, then homogenised in a food blender to produce a fine slurry. A 10-ml aliquot of the slurry was added over the sediment in each incubation chamber during that phase of the experiment. The slurry was stored in sealed plastic buckets at 4°C pending use.

Incubation water

Large volumes of unfiltered surface Lake Rotorua water were collected at weekly intervals in six 100-l sealable wide-mouth black alkathene barrels lined with clean heavy-walled plastic bags (bin liners) to prevent cross contamination and to allow the water to be deoxygenated for the anoxic tests (Gibbs & Özkundakci, 2010). For the aeration phases, filtered compressed air was bubbled through an aquarium

aerator stone at the bottom of the barrel. For the anoxic phase, oxygen free dry nitrogen (N_2) was bubbled through the aerator stone in the barrel to sparge the dissolved oxygen (DO) from the system. To control pH, a short burst (30 s) of CO_2 was periodically bubbled through a second aerator stone in the bottom of the barrel. To prevent reoxygenation of the water from air in contact with the surface of the water in the barrel, the plastic bin liners were drawn tightly around the N_2, CO_2 and water draw-off tubes to produce an oxygen-free head-space above the water (Gibbs & Özkundakci, 2010). Dissolved oxygen and pH of the anoxic water were measured twice daily and adjusted as required to maintain a DO of <0.2 g m^{-3} and a pH of around 7.0 (range 6.8–7.2).

Non-target effects were assessed on nitrification and denitrification processes using lake water amended with potassium nitrate to raise the natural nitrate (NO_3-N) concentration from 390 mg N m^{-3} to around 2,070 mg N m^{-3} for the aerobic phases and from 235 mg N m^{-3} to around 1170 mg N m^{-3} for the anoxic phases.

Incubation chambers

The CFIS run was initiated after 5 days with the incubation chambers open and exposed to aerated lake water to allow reconstitution of the microbial communities in the sediment. Previous experiments with the CFIS (Gibbs & Özkundakci, 2010) showed that, with a chamber volume of 100 ml and a flow rate of 1.5 ml min^{-1}, the water in each chamber was exchanged about 24 times per day, and that it took about 24 h for the CFIS to reach a steady state after the initial disturbance of closing the chambers. Consequently, although each phase of the experiment was run for a minimum of 5 days, sampling of the inflow water from the bulk barrel and the outflow water from each incubation chamber for dissolved nutrients began at the end of the second day. In all cases, a duplicate set of water samples was collected on the last day of each phase of the experiment 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 (nominal pore size 1.2 μm) in a Swinnex® filter holder directly into the sample bottles at the time of sampling.

Analytical

The wet sediment fractions were weighed for bulk density before the pore water was extracted. After weighing, the sediment sections were shaken for 1 min with 20 ml of deionised water to partition pore-water nutrients and trace metals into the aqueous phase. This mixture was chilled to 4°C in a refrigerator and allowed to settle for 1 h. The supernatant liquid was transferred to a 50-ml plastic centrifuge tube and centrifuged at 3,000 rpm for 10 min before syringe filtering into a sample bottle containing nitric acid preservative. The residual sediment in the centrifuge tube was recombined with the original sample and dried in an air fan oven at 60°C for 24 h. The sediment from each fraction was analysed for total P (TP), total N (TN), total iron (TFe), total manganese (TMn), total arsenic (TAs), total aluminium (TAl), total zinc (TZn) and total lanthanum (TLa) following acid digestion for 2 h in aqua rega.

The decision to measure TP rather than 'bioavailable' P (dithionate extracted P) was a rationalization that, in eutrophic lake sediments, most of the particulate P would be organic and thus labile with very little refractive P. Consequently, the TP analysis would provide a reasonable estimate of the bioavailable P with an upper limit.

The acid-preserved pore water and water samples from the continuous flow incubation tubes were analysed for the total dissolved metals—Fe, Mn, As, Al, Zn and La using an ICP mass spectrometer. Non-acidified water samples were analysed for the dissolved nutrients DRP, ammoniacal-N (NH_4-N) and NO_3-N using a Lachat flow injection analyser (FIA) and standard Lachat FIA methods.

The algal slurry was analysed for dry weight after drying at 105°C and organic content was determined as the loss of weight after combustion at 550°C. 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. The 10 ml of algal slurry applied to each incubation chamber at the end of the third and fourth aerobic phases was estimated to contain 106 mg C, 15 mg N and 2.6 mg P giving an equivalent areal loading of 27.5, 3.9 and 0.68 g m^{-2} of C, N and P, respectively.

Calculation of fluxes across the sediment–water interface

Nutrient flux rates were estimated from the difference between inflow and outflow concentrations at steady state, the volume of the flow-through chamber and the flow rate through the system. Phosphorus processes and non-target effects were inferred from the changes in these fluxes:

- Phosphorus release from the sediment occurred if the flux of DRP was greater than zero; and
- phosphorus uptake occurred if the flux of DRP was less than zero.
- Nitrification suppression occurred if the flux of NH_4-N was greater than the control; and
- denitrification suppression occurred if the removal of NO_3-N from the flow-through water was less than the control under aerobic conditions.
- Under anoxic conditions, nitrification and denitrification was not expected and fluxes of NH_4-N and NO_3-N should be similar to the controls.

Longevity was estimated based on the point when P break-through occurred for each product and for each treatment. Break-through is operationally defined as an increase in the outflow water DRP concentrations above the inflow water concentration under anoxic conditions. This would indicate that the P-binding capacity of the product at that treatment dose rate has been exceeded, or the product had been buried and no longer blocked DRP release.

P-saturation measurements

The P-binding capacities of the three granular products were also measured. This was required because results from the CFIS incubations were substantially different from 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), P-saturation curves were determined at three different pH levels (6.1, 7.0 and 8.9) which encompass the normal range of pH in a lake and covered the range (pH 6.8–7.2) used in the incubations. Sampling was more frequent for the first few hours to capture the initial rapid P uptake, but was continued for about 50 h to characterise the adsorption characteristics.

The P-binding tests used 5 g of granular material in 1 l 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 3,000 rpm for 10 min. 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 and other elements by ICP-mass spectrometry.

Statistical analysis

Linear regressions were used to assess trends. A t test was used to test for significant differences between treatments of an individual product. A significance was assumed when $P < 0.05$. Statistical differences between treatments of different products were not tested because the dose rates were different for each product.

Results

Sediment chemistry

The metal content of the sediment depth fractions were generally uniform down through the core (Table 2). In contrast, TP and TN content was highest at the surface and decreased with depth. The pore water metal concentrations were highest near the surface for Al, As and Fe but increased with depth for Mn and Zn. Bulk density in the top 10 cm averaged 1.066 g cm^{-3} giving a TP content of 3.17 g P m^{-2} in the top 4 cm. This value is consistent with the estimate of 3.0 g P m^{-2} used to calculate the dose rates for the sediment incubations. Pore water DRP concentrations were not measured but literature values from a sediment core from an adjacent core site (Ru141; Motion, 2007) have been included to indicate the likely shape of the profile (Table 2).

P saturation

Time-series analysis of the uptake of PO_4-P by the granular products at three different pH levels

Table 2 Metal concentrations in the sediment, pore water and bottom water taken from the Jenkins corer tube <5cm above sediments from Lake Rotorua on 14 February, 2008

Core depth (cm)	Al	Fe	Mn	Zn	As	La	TP	TN
Sediment								
0–2	7,500	7,900	490	45	53	3.9	1,300	1.10
2–4	7,800	6,600	410	46	63	3.7	1,100	0.91
4–6	8,100	7,200	340	46	61	3.9	950	0.95
6–8	8,700	10,000	330	50	75	4.0	870	0.78
8–10	8,400	7,400	360	49	49	4.2	760	0.83
Pore water							DRP	
0–2	370	1,200	1,900	160	32.0	0.37	970	
2–4	540	620	1,000	150	51.0	0.50	1570	
4–6	160	87	4,100	390	5.3	0.33	660	
6–8	180	370	4,600	380	7.4	0.39	860	
8–10	240	390	5,900	400	11.0	0.57	660	
Bottom water	3	38	46	2.1	3.5	<0.1		
Detection limit	3	20	0.5	1	1	0.1		

Total phosphorus (TP) 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 100 g^{-1} dry weight. Pore water and bottom water concentrations are as mg m^{-3}. Pore water DRP are from core Ru141 (Motion, 2007). The analytical detection levels for metals are also reported in mg m^{-3}

demonstrated that the actual P-binding capacities were substantially different from the nominal P-binding capacities (NPBC) given by the suppliers and used to calculate the dose rates for each treatment in the sediment incubation experiment (Table 3). These results also demonstrated that the actual P-binding capacities were affected by the pH of the system (Table 3) consistent with the observations of Peterson et al. (1976).

Time-series results from the P-saturation tests showed that while there was an initial rapid uptake of P by all three products and a continued increase in P uptake in the allophane and Z2G1 tests, there was a statistically significant reduction in the amount of P bound by the Phoslock™ at pH 6.1 ($P < 0.002$, $r^2 = 0.977$, $n = 4$) over the 50 h period of the test. This reduction was positively correlated (Fig. 2) with a statistically significant reduction in the La content of the Phoslock™ ($P < 0.05$, $r^2 = 0.850$, $n = 4$) at a similar rate. Decreases in the P and La content of Phoslock™ over time at similar rates also occurred at pH 7.0 but not at pH 8.9 (Fig. 2).

Table 3 Comparison of the measured P-binding capacities (g P/kg) of each P-inactivation agent (product), at the specified pH after 50 h, with the nominal P-binding capacities given by the suppliers

Product	P-binding capacity			
	Nominal	Measured		
		pH 6.1	pH 7.0	pH 8.9
Z2G1	50	21.5[a]	21.5[a]	11.6[a]
Phoslock™	20	11.6[b]	11.3[b]	15.1
Allophane	5	16.3	16.0	9.5

[a] P-binding capacity still increasing

[b] P-binding capacity decreasing after an initial high

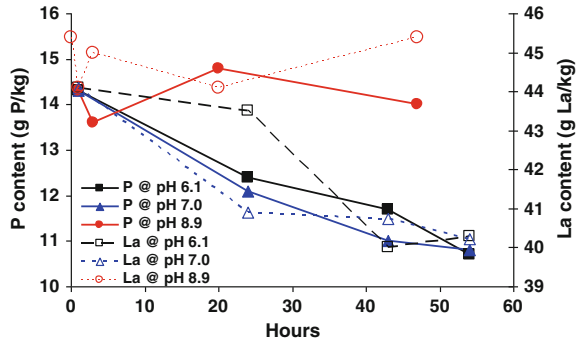

Fig. 2 Time series changes in the P (*solid symbols*) and La (*open symbols*) content of Phoslock™ at pH 6.1, 7.0 and 8.9 during the P-saturation experiment

Analyses of the elemental content of the three raw granular products (Table 4) showed that allophane had the highest content of Al, Fe, Mn and P while Phoslock™ had the lowest content of most elements except Mg and La.

Phosphorus incubations

During the first aerobic phase, all treatments caused a reduction in DRP concentration in the flow-through water greater than in the controls (Fig. 3; aerobic). There were small non-significant ($P > 0.05$) differences in the amount of DRP removal between treatments for allophane and Z2G1. Alum and Phoslock™ removed the most DRP from the water, followed by allophane then Z2G1. Both allophane and Z2G1 showed a small trend of increasing DRP removal with increasing dose rate. None of these differences were statistically significantly different ($P > 0.05$).

During the first anoxic phase DRP was released from the control sediments at a rate of 26.9 ± 2.2 mg m^{-2} day^{-1} (Fig. 3; anoxic). At all levels of treatment the products 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. The Z2G1 at the 50 and 100% treatments was not able to block the release of DRP from the sediment (Fig. 3; anoxic). At the 200% treatment, which had complete sediment coverage, Z2G1 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. 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 P results from the extended incubation study, with three further anoxic phases plus two algal inoculations, showed substantial increases in DRP concentrations associated with sediment release during each anoxic phase and reductions during each aerobic phase (Fig. 4). The DRP concentrations in the outflow water from the control incubations were lower than those in the inflow water due to sequestration by iron and manganese in the bare sediment. However, after the addition of the algal slurry, DRP concentrations in the outflow water during the aerobic phase were higher than those in the inflow water.

Results from the treatments with the four products showed similar patterns except that DRP concentrations during the anoxic phases were lower than those in the controls (Fig. 4). In all treatments, the Z2G1 blocked the least P released from the sediment. Even at the highest treatment (200%; Fig. 4), P break-through occurred during the second anoxic phase. In contrast, allophane blocked the most P released from the sediment with P break-through apparently occurring during the fourth anoxic phase in all treatments. For alum, P break-through occurred in the 200% treatment during the third anoxic phase and in the 50% treatment during the third anoxic phase for Phoslock™ (Fig. 4).

Nitrogen incubations

The NH_4-N results show that each product had a different and apparently dose–rate related effect on the flux of NH_4-N from the sediment (Fig. 5). 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 NH_4-N flux seen in the control (Fig. 5; alum, aerobic). As the dose rate increased, the flux of NH_4-N became measurable with suppression in the 100% treatment, but enhancement to almost double the control in the 200% treatment. Under anoxic conditions this pattern was reversed with the 50 and

Table 4 Selected mineral content (mg/kg dry weight) of the three granular P-inactivation agents (products) determined by ICP-mass spectrometry for each product as supplied and used in this study

Product	Elemental composition								
	Na	K	Mg	Ca	Al	Fe	Mn	La	P
Allophane	280	170	1,008	972	68,075	30,610	675	28	1,321
Phoslock™	2,278	161	7,505	1,233	11,701	4,498	29	45,380	130
Z2G1	11,213	7,080	1,877	9,761	21,752	4,457	278	20	118

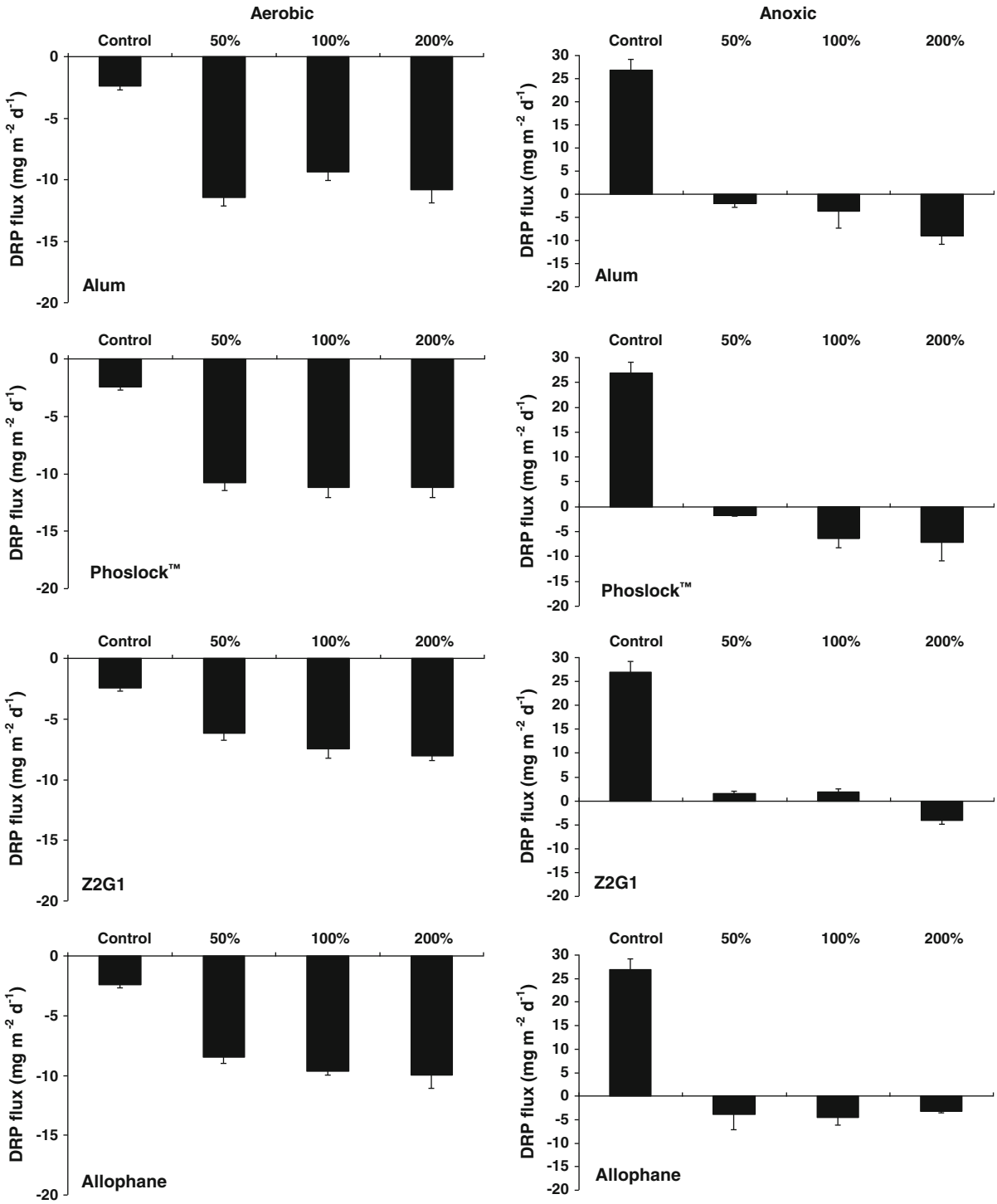

Fig. 3 Mean dissolved reactive phosphorus (DRP) fluxes for each of the product treatments and controls under aerobic and anoxic conditions in natural lake water. The 100% treatment dose rates were normalised by nominal P-binding capacity to block the release of the estimated 3 g P m^{-2} in the top 4 cm of sediment. The 50 and 200% treatments were half and twice the 100% treatment dose rates, respectively. Negative values indicate DRP uptake; positive values indicate DRP release from the sediment (*Error bars* = 1 SD)

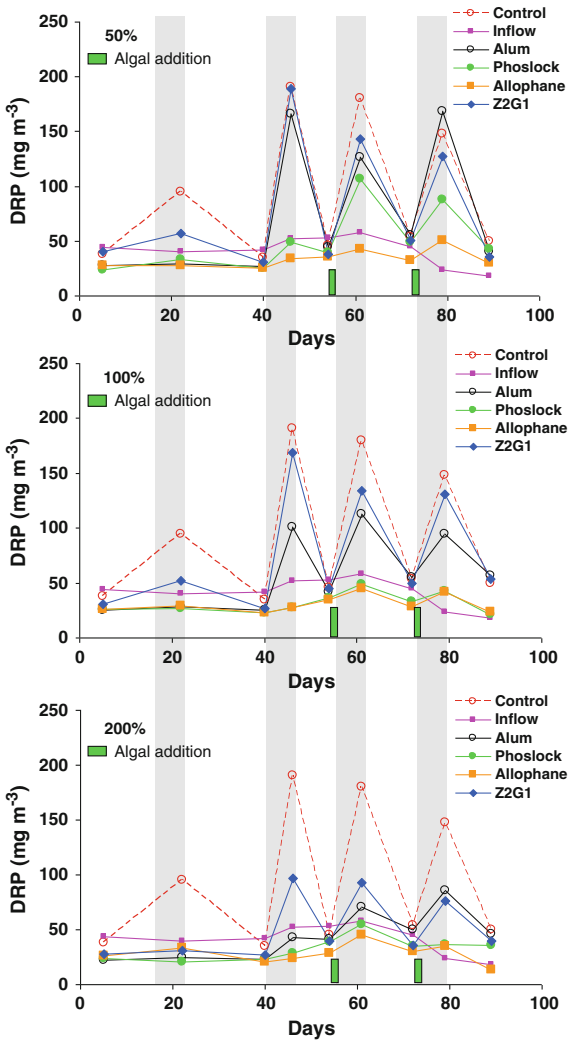

Fig. 4 Time series of mean dissolved reactive phosphorus (DRP) concentration changes in the inflow and outflow waters from the extended study relative to the four P-inactivation agents (products) for the three treatments 50, 100, and 200%. *Grey-shaded vertical bands* indicate the periods of anoxia; *blocks* indicate when the algal slurry was applied

100% alum treatments enhancing the NH_4-N flux while the 200% treatment suppressed the NH_4-N flux relative to the control (Fig. 5; alum, anoxic).

Under aerobic conditions the lowest Phoslock^{TM} treatment (50%) results were similar to the control suggesting no effect. However, the NH_4-N flux increased substantially with increasing dose rate and was fivefold greater than the control at the 200% treatment (Fig. 5; Phoslock^{TM}, aerobic). Under anoxic conditions the pattern of NH_4-N flux increase with increasing dose rate was still observed but the magnitude of the increase was relatively small (Fig. 5; Phoslock^{TM}, anoxic).

The Z2G1 was expected to remove NH_4-N from the water column (Besser et al., 1998; Nguyen & Tanner, 1998), but under aerobic conditions, the lowest (50%) treatment showed an enhancement of the NH_4-N flux relative to the control ($P < 0.005$). However, at higher dose rates the NH_4-N flux was suppressed and the suppression increased with increasing dose rate with almost complete suppression of the NH_4-N flux in the 200% treatment (Fig. 5; Z2G1, aerobic). This is consistent with NH_4-N adsorption onto the zeolite mineral substrate of this product compared to other New Zealand zeolites (Nguyen & Tanner, 1998). The pattern of increasing NH_4-N flux suppression with increasing dose rate was also present under anoxic conditions but there was no apparent enhancement of the flux rate at the lowest (50%) treatment (Fig. 5; Z2G1, anoxic).

In contrast to the other product treatments, allophane treatments under aerobic conditions had minimal effect on NH_4-N with only a small increase in the NH_4-N flux for the 200% treatment (Fig. 5; allophane, aerobic). Under anoxic conditions, there was an increase of about 30% in the NH_4-N flux for all allophane treatments (Fig. 5; allophane, anoxic).

The NH_4-N results from the extended incubation study for all treatments of the four products showed similar patterns to those for DRP (Fig. 4) with higher concentrations during the anoxic phases than during the aerobic phases (Fig. 6). The non-target effects noted during the initial aerobic and anoxic phases (Fig. 5) were largely gone by the end of the second aerobic phase. The exception was the enhanced release of NH_4-N from the 200% treatment of Phoslock^{TM} (Fig. 6). Addition of the algal slurry resulted in substantial increases in the NH_4-N flux from all treatments during the anoxic phases and subsequent aerobic phase (Fig. 6). The apparently higher NH_4-N fluxes for the treatments than controls in the final (fifth) aerobic phase may be an artefact due to pump tube failure.

For NO_3-N, all product treatments caused variable but statistically significant ($P < 0.05$) reductions in the amount of NO_3-N removed from the flow-through natural lake water under aerobic conditions (Fig. 7; aerobic). The greatest reduction (48%) occurred in the Phoslock^{TM} treatments although similar levels of reduction ($\sim$43%) also occurred in the 100 and 200%

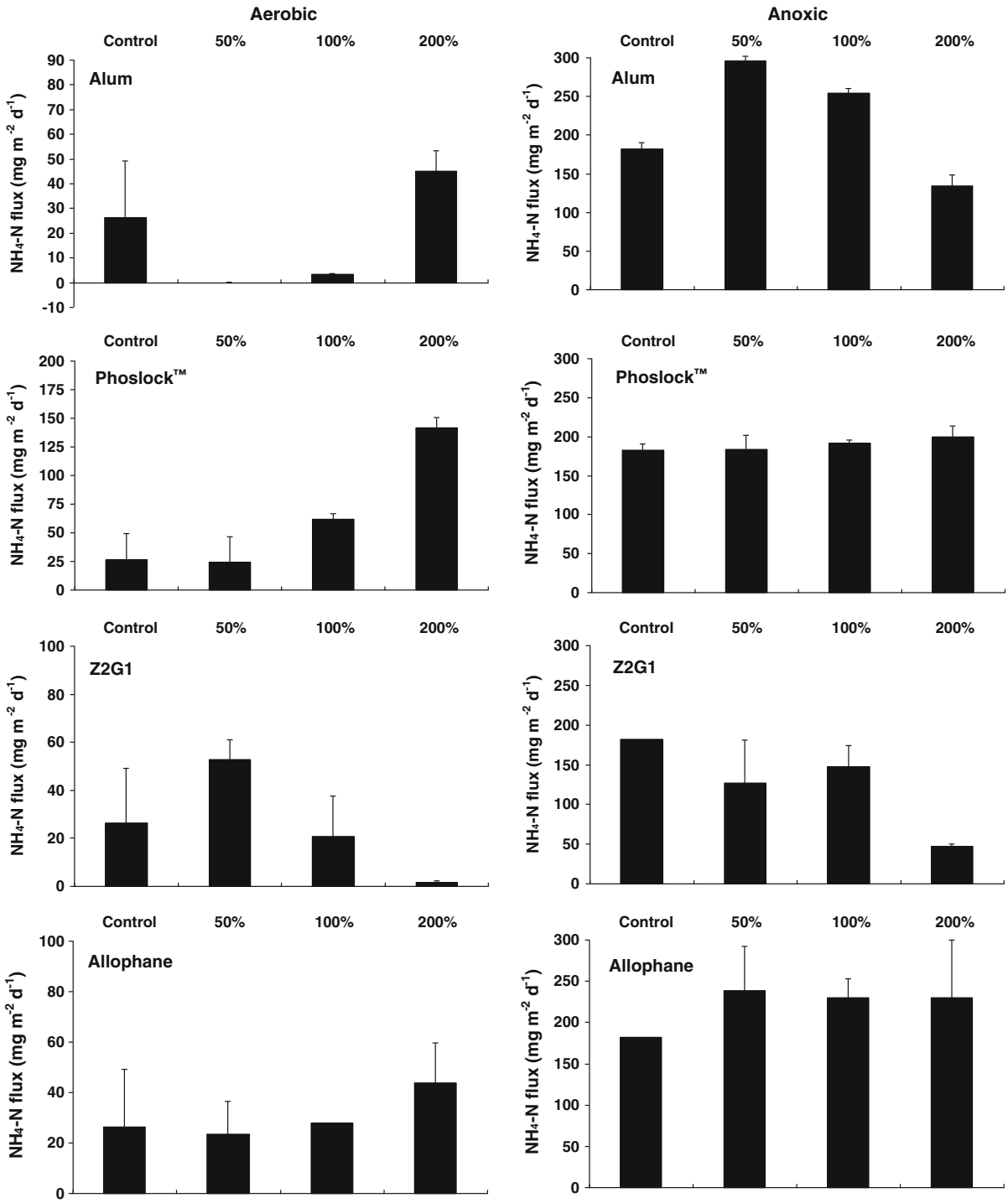

Fig. 5 Mean ammoniacal nitrogen (NH_4-N) fluxes for each of the product treatments and controls under aerobic and anoxic conditions in natural lake water. Concentrations of NH_4-N in the aerobic and anoxic lake water were 68 and 82 mg m^{-3}, respectively. An increase over the control under aerobic conditions is an indication of suppression of the nitrification process (*Error bars* = 1 SD)

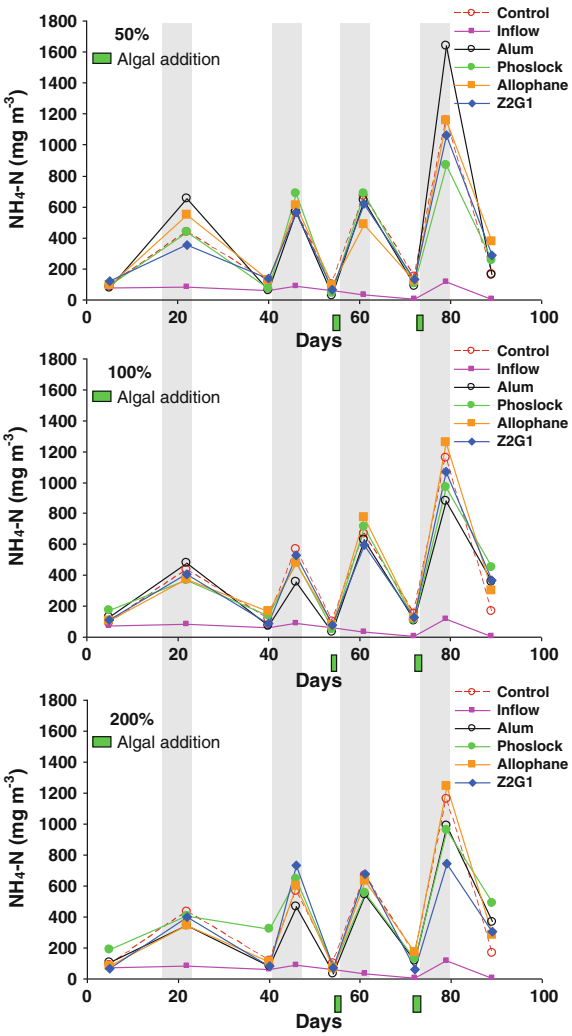

Fig. 6 Time series of mean ammoniacal nitrogen (NH_4-N) concentration changes in the inflow and outflow waters from the extended study relative to the four P-inactivation agents (products) for the three treatments 50, 100, and 200%. *Grey-shaded vertical bands* indicate the periods of anoxia; *blocks* indicate when the algal slurry was applied

alum treatments. Allophane treatments caused the least reduction (17%) of the NO_3-N removal, while Z2G1 caused a 37% reduction at the 200% treatment. With the exception of Phoslock™, the decrease in the reduction of NO_3-N under aerobic conditions appeared to be dose–rate dependent with the greatest reductions in the highest product treatments (Fig. 7; aerobic).

The addition of NO_3-N to the lake water overwhelmed the suppression effects of the products seen at the natural lake water concentration (Fig. 7; aerobic). There was no statistically significant ($P > 0.05$) difference between controls and treatments for alum but there was a significant ($P < 0.05$) reduction in the NO_3-N removal relative to control in the 200% Phoslock™ treatment (Fig. 7; Phoslock™, aerobic). Although the results were variable, Z2G1 and allophane both appeared to enhance the removal of NO_3-N relative to the controls. These enhancements were highly significant ($P \ll 0.001$) at the 200% Z2G1 and the 50% allophane treatments (Fig. 7; aerobic).

There were small but non-significant ($P > 0.05$) differences between the controls and product treatments under anoxic conditions in natural lake water (Fig. 7; anoxic). In contrast with anoxic water amended with high NO_3-N concentrations, there were statistically significant ($P < 0.05$) increases relative to controls for the removal of NO_3-N in the Phoslock™ and allophane treatments. The differences in the Z2G1 and alum treatments were not significant ($P > 0.05$).

In the extended incubation study for all treatments of the four products, the NO_3-N patterns were the inverse of those for DRP and NH_4-N (Figs. 4, 6) with lower concentrations during the anoxic phases than during the aerobic phases (Fig. 8). The non-target effects noted during the initial aerobic and anoxic phases (Fig. 7) were present until the addition of the algal slurry. This resulted in the complete removal of NO_3-N during the final anoxic phase (Fig. 8).

Metals

The main metals of interest were aluminium (Fig. 9), Lanthanum (Fig. 10) and iron (Fig. 11). Under aerobic conditions after 7 days incubation, the concentrations of these three metals in the outflow waters were variable between treatments including controls and between products. The Al and Fe results (Figs. 9, 11; aerobic) showed variability that was probably 'noise' due to ebullition as there was no consistent pattern, except for consistently higher Fe concentrations in the 200% Z2G1 treatment (Fig. 11; aerobic). In contrast, the La results showed elevated La concentrations (1.2–4.2 mg m^{-3}) relative to controls in the outflow water from all Phoslock™ treatments but not from the other products (Fig. 10; aerobic). There was significantly ($P < 0.05$) more La in the

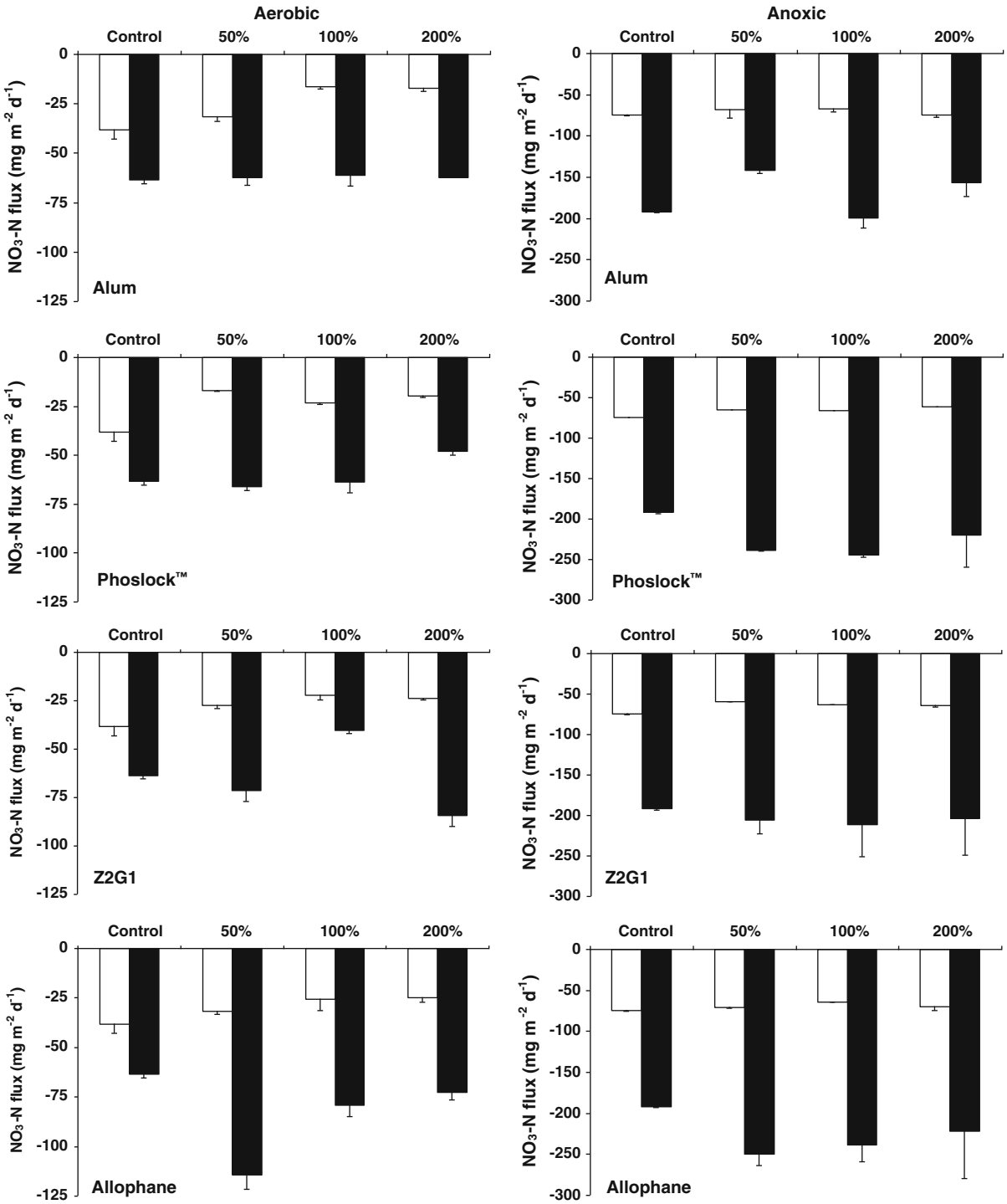

Fig. 7 Mean nitrate nitrogen (NO_3-N) fluxes for each of the four product treatments and controls under aerobic and anoxic conditions in natural lake water (*open bars*; NO_3-N concentrations: aerobic 390 mg m^{-3}, anoxic 235 mg m^{-3}) and NO_3-N amended lake water (*solid bars*; NO_3-N concentration aerobic 2,075 mg m^{-3}, anoxic 1170 mg m^{-3}). A reduction in NO_3-N removal relative to the control under aerobic conditions is an indication of suppression of the denitrification process (*Error bars* = 1SD)

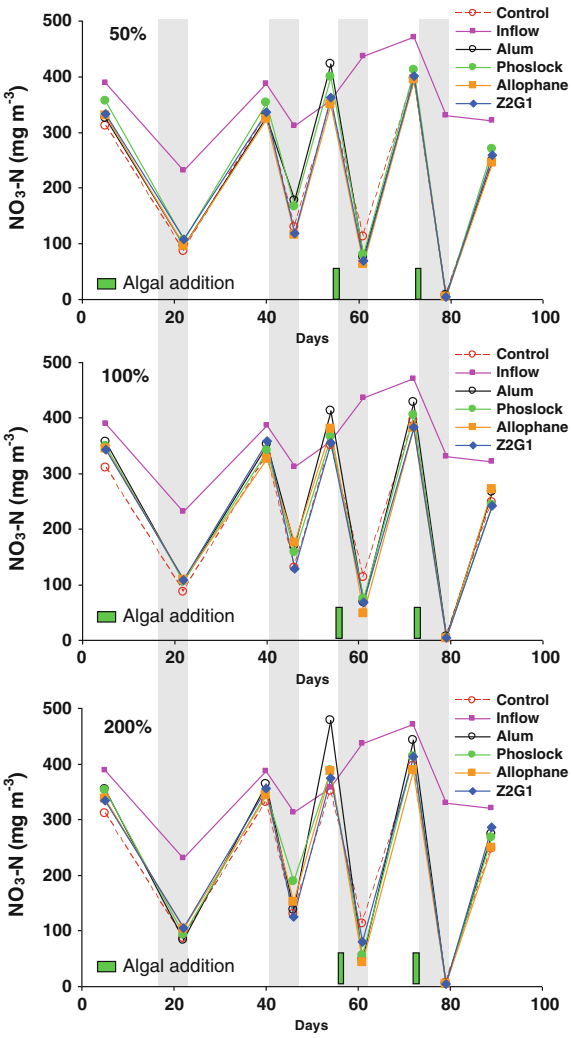

Fig. 8 Time series of mean nitrate nitrogen (NO_3-N) concentration changes in the inflow and outflow waters from the extended study relative to the four P-inactivation agents (products) for the three treatments 50, 100, and 200%. *Grey-shaded vertical bands* indicate the periods of anoxia; *blocks* indicate when the algal slurry was applied

outflow water from the 100 and 200% Phoslock^{TM} treatments than the 50% treatment.

Under anoxic conditions after 14 days incubation, there were generally higher metal concentrations and higher variability in the outflow water from most incubation chambers. The main exception was Al in the alum treatments (Fig. 9; anoxic) which were not significantly different ($P > 0.05$) from the aerobic condition results. Phoslock^{TM} produced the highest Al concentrations and allophane produced the most consistent increase. However, there was no discernable pattern to these increases.

Elevated concentrations of La (1–7.2 mg m^{-3}) were still present in outflow water from the Phoslock^{TM} treatments but at slightly higher concentrations to those measured under aerobic conditions (Fig. 10: anoxic). There was still significantly ($P < 0.05$) more La in the water from the 100 and 200% Phoslock^{TM} treatments than the 50% treatment. In contrast to the aerobic results, there were highly variable but low concentrations of La in the waters from the other products (Fig. 10; anoxic). The DRP concentrations in the outflow water from the Phoslock^{TM} incubations were >20 mg m^{-3}.

Under anoxic conditions, there were variably high concentrations of Fe in the water from the control sediments and from the 50 and 100% treatments of allophane (Fig. 11). There were also high Fe concentrations in the alum, Phoslock^{TM} and Z2G1 treatments but no discernable pattern.

Of the other metals measured (Mn, Zn and As), Mn concentrations were higher under the anoxic conditions in the outflow water from all product treatments than under aerobic conditions. Although there were no discernable patterns to the concentration differences between treatments, there were significant ($P < 0.05$) increases in concentration relative to the controls for alum, allophane and Z2G1. There was no significant ($P > 0.05$) difference between the Phoslock^{TM} treatments and the controls. For Zn, there was an apparent reduction in concentration in the outflow waters relative to the inflow water for all treatments and controls but no discernable pattern to the variability between treatments or products. The changes in the As concentrations did not show any discernable relationship with treatment in any product although the mean concentrations were around 0.5 mg m^{-3} higher in the water from the Phoslock^{TM} and Z2G1 treatments than in the control (4 mg As m^{-3}).

Discussion

The four products tested in this study all have the capacity to block the release of P from the sediment when applied as capping agents. The amount of each product required to achieve a complete block of all the releasable P in top 4 cm of sediment (3.17 g m^{-2})

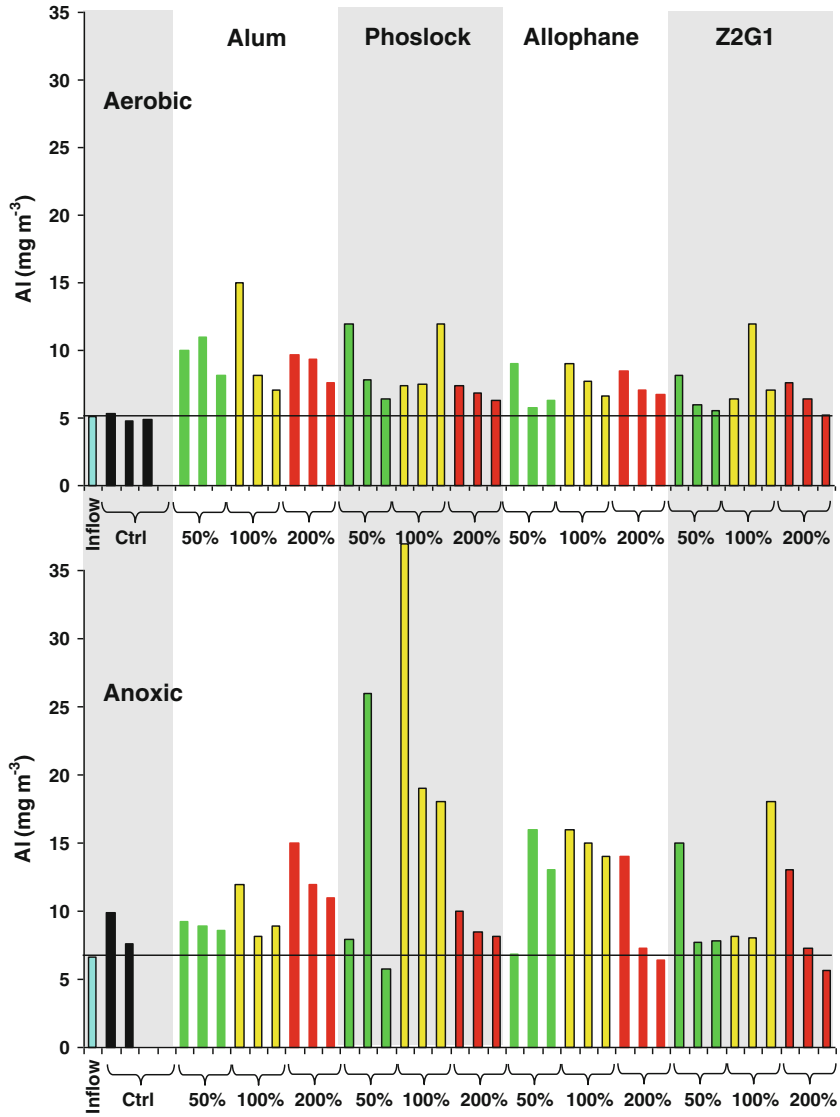

Fig. 9 Total dissolved Aluminium (Al) concentrations from the incubation chambers under aerobic and anoxic conditions. The *horizontal line* is the measured concentration in the inflow water. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals a flux of about 0.5 mg m^{-2} day^{-1})

varied as a function of the P-binding capacity of the product and the interaction between the product and the biogeochemistry of the lake water and sediments being treated. Grain size of a capping agent can change the diffusivity across the sediment–water interface (Vopel et al., 2008). However, as all granular products had a similar grain size (<1 mm), grain size should not have affected the results. We also found that all products affected the microbial processes of nitrification and denitrification at the sediment–water interface and that the extent of the effect was different for each product.

Efficacy of P-removal

We estimated the amount of each product required to block all the P in the top 4 cm based on nominal P-binding capacities (NPBC) of the products from literature data (alum) and information obtained from the suppliers i.e. the calculations an engineer managing a lake might reasonably make. Our results show that the actual P-binding capacities, at the pH of the lake water and sediment, were substantially different from the NPBCs provided for each product (Table 3). These were overestimated by about twofold

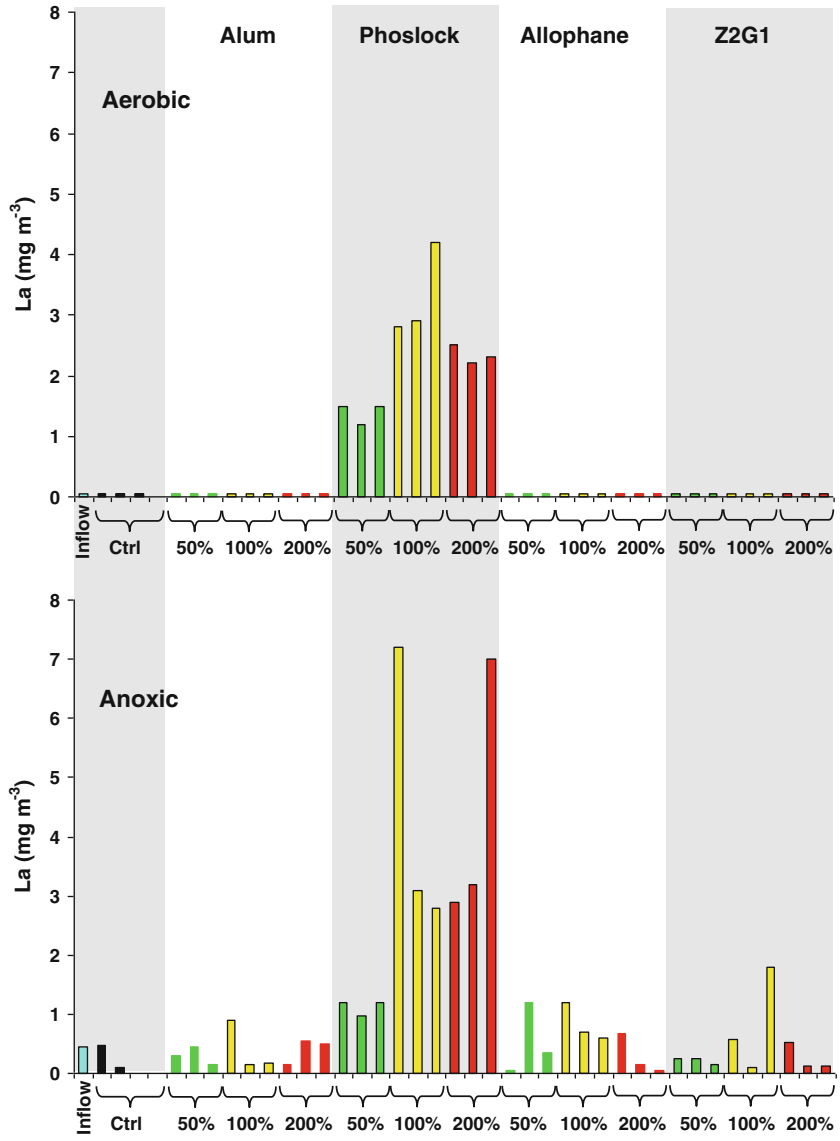

Fig. 10 Total dissolved Lanthanum (La) concentrations from the incubation chambers under aerobic and anoxic conditions. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals a flux of about 0.5 mg m^{-2} day^{-1})

for both Phoslock™ and Z2G1, and underestimated by about threefold for allophane at circum-neutral pH. It is not clear why these differences occurred but we know that P-uptake is a function of grain size (surface area) and pH. However, it emphasises the need to validate the actual P-binding capacity of the product as supplied. A P-saturation curve was not developed for alum and the best estimate for actual P-binding capacity at 45 g P kg^{-1} (cf. 49 g P kg^{-1}, Hickey & Gibbs, 2009) was obtained by regressing the P-flux data for alum with the P-flux data from the other products.

Although the incorrect NPBC values affected the calculation of the treatment dose rates for the incubations, and although the central treatment of the treatment range was not normalised to 100% removal of the potential P release, this did not negate the comparisons. The P-removal efficacies were calculated from the data obtained from the incubation chambers and are expressed as the minimum areal load of each product required to block the release of all P from Lake Rotorua sediment (Table 5). The minimum areal loads calculated from the measured P-removal efficacies, which include the effects of contact with the sediment and lake water were higher than the theoretical areal loads calculated from the measured P-binding capacities (Table 5). However, these differences were relatively small and may be

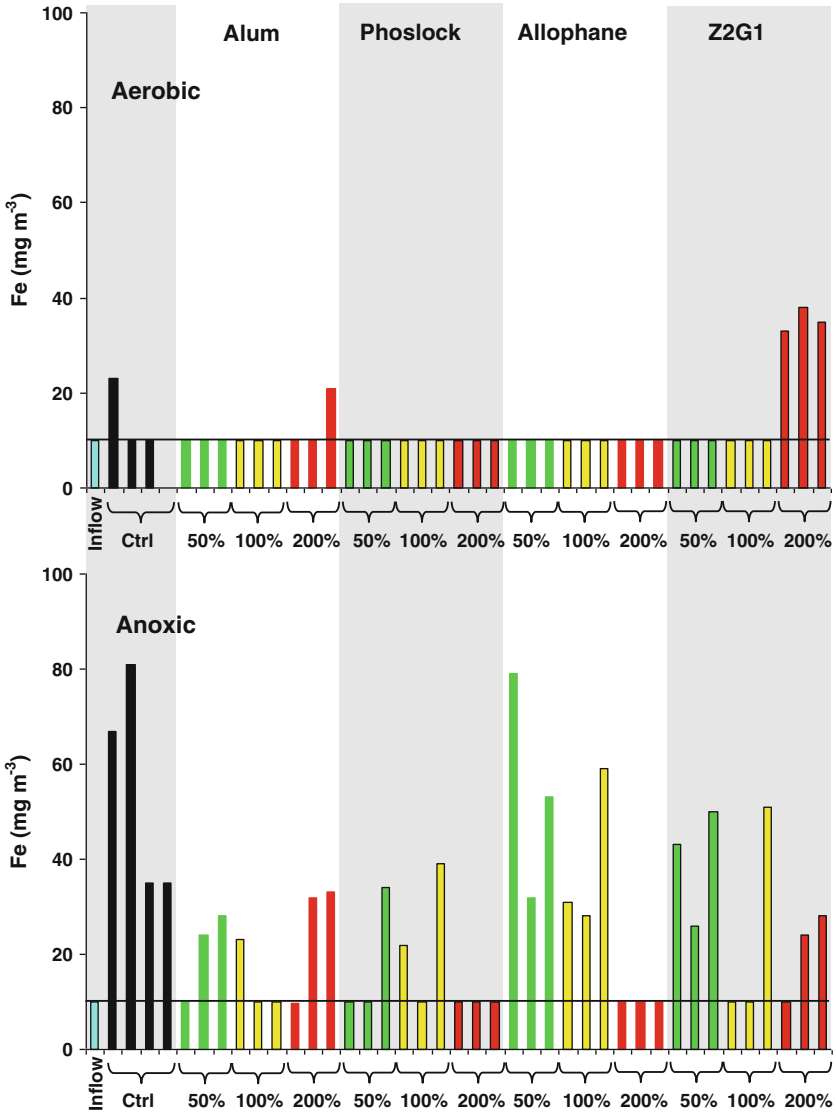

Fig. 11 Total dissolved iron (Fe) concentrations from the incubation tubes under aerobic and anoxic conditions. The *horizontal line* is the measured concentration in the inflow water. Treatments are in triplicate and highlighted bands separate the four capping materials. (1 mg m^{-3} equals a flux of about 0.5 mg m^{-2} day^{-1})

due, in part, to the low alkalinity (25 g m^{-3} as $CaCO_3$) and geothermal influence of Lake Rotorua water (Timperley & Vigor-Brown, 1986) and the additional P load from the overlying lake water.

Sustainability of P-removal

While the four products tested in this study may be highly effective in blocking P release from the sediment when first applied, the continued input of DRP from the catchment (i.e. inflow water) will eventually exhaust the residual P-binding capacity of the capping material, so that the capping layer eventually becomes "saturated" (Fig. 12). Also, subsequent deposition of detritus from the inflows and senescing algal blooms will replenish the P in the sediment and eventually bury the capping layer

Table 5 Comparison of the P-removal efficacy with the measured P-binding capacity of each product expressed as the minimum areal load (g m^{-2}) required to block the release of all P from the sediment used in the incubation chambers, i.e. 3.17 g P m^{-2}

P-inactivation agent	Alum	Z2G1	Allophane	Phoslock™
P-removal efficacy	80	190	220	280
P-binding capacity	70	150	200	260

P-removal efficacy values include the effects of contact with the lake water and sediments. Results are rounded to two significant figures and no estimates of error terms are included

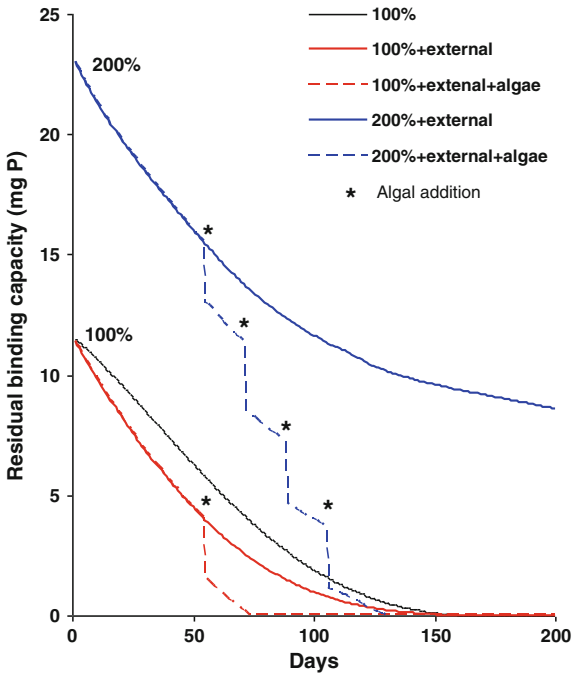

Fig. 12 Theoretical residual binding capacity curves derived using fitted polynomials for the 100 and 200% treatments based on a sediment P flux of 27 mg m^{-2} day^{-1} and the mean uptake rates of P from the flow-through water by all products over the first 60 days. The 100% curve assumes P uptake from sediment release only, while the '+ external' curves include the uptake from the overlying water, and '+ algae' curves include the effect on longevity if an additional load associated with the collapse of one or more spring–summer algal blooms. Algal P mass data were derived from the algal slurry phases of this study (*asterisk* algal addition)

providing a new source of DRP above the capping layer (e.g. Welch & Cooke, 1999). These factors affect the longevity of the product application and are major limitations to the period of effective control of the sediment-derived DRP contribution to the water column.

Another key factor in determining how long a sediment capping treatment will remain effective in a lake is the mineralisation rate of the organic P in the sediment into DRP and its subsequent diffusion out of the sediments. The P-saturation measurements demonstrated that these products rapidly adsorb PO_4-P and become saturated within a few hours of exposure at high P concentrations. Consequently, P released from the sediment will be rapidly bound by the capping layer and P-removal will be limited by the rate of mineralisation of the P in upper layers of sediment and upwards diffusion, not the mass of P in g m^{-2}. The net anaerobic mineralisation rate was estimated to be around 27 mg m^{-2} day^{-1} for the Lake Rotorua sediment used in this study.

The capping layer affects the redox potential in the sediment inducing anaerobic conditions below the layer (Vopel et al., 2008). This implies that, once the capping layer is applied, all of the P in the sediment that can be mineralised will be released and bound in the capping layer, even if the overlying lake water becomes fully aerobic again.

Assuming that the measured total available P in the top 4 cm of sediment, at 3.17 g m^{-2}, is an average for the lake, and the mineralisation rate was constant, it would take 117 days for all of that P to be released and adsorbed. In reality, the net mineralisation rate is likely to decrease as the amount of P in the sediments decreases and the diffusion gradients decrease. Interestingly, the sediment cap creates a very strong gradient by removal of that P. A simulation of this effect, calculated from the decrease in the mineralisation rate and diffusion gradient, (Fig. 12) shows that the reduction over time of the theoretical P binding capacity of a 100% treatment is not linear, and it would take longer (i.e. >117 days) for that capacity to become exhausted. The effect of the external P additions is to use the P-binding capacity faster and, following an algal bloom, that capacity might be rapidly exhausted. The step change (Fig. 12; 10% + external + algae) probably overestimates an additional P supply to the sediment, but serves to illustrate the indicative effect of uncontrolled external P sources.

In the 200% simulation (Fig. 12), the P-binding capacity of the product is not exhausted before all the sediment P is blocked. However, the P-binding capacity of the product will continue to decline due to P uptake from the external sources. In this simulation, the algal additions represent successive seasonal/annual algal blooms and show that the P-binding capacity of the product is not exhausted until after the 4th season/year. This suggests a longevity of at least 4 years. However, if the external sources of P were also managed and algae blooms did not occur, a 200% treatment should continue to remove P for many years (c.f. Welch & Cooke, 1999).

A key point to note is that if the dose rate is applied based only on the available P content in the sediment, the treatment will not block all of the P released from the sediment and a higher dose rate is needed to allow for the P-binding capacity used by

the external P load (Hickey & Gibbs, 2009). Also any disruption of the capping layer would reduce its ability to block the release of P from the sediments.

Another important consideration is whether the bound P to the product is released again under anoxic conditions. The longevity trial was taken through four cycles of anoxic-to-aerobic conditions to simulate seasonal changes over a period of '4 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. 4). This indicates that these capping materials either continued to remove any P released from the sediment or that they had already adsorbed all the bioavailable P from the sediment, and still had enough P-binding capacity to remove additional P from the overlying water column and detritus through at least '4 years'.

The Z2G1 treatments were too low, even allowing for the overestimated nominal P-binding capacity value, and demonstrate that the physical properties of the product are also important, i.e. there is a minimum quantity required to give complete coverage of the sediment. Based on the study by Vopel et al. (2008), an areal loading of the <1-mm grain size granular products at around 200 g m^{-2} would provide a complete coverage of the sediment with a capping layer thickness of 1–1.5 mm. The alum treatment should have produced a similar layer thickness but was easily disturbed by the very weak currents associated with the flow-through water in the incubation chambers, and this may have contributed to the apparent failure of some of the alum treatments. Resuspension of the fresh alum floc by lake currents can be as much as 5× easier than the natural sediment (Egemose et al., 2010).

Overall, these results suggest that all products, if applied at their P-binding efficacy value dose rates, would have a longevity of at least 4 years provided the external loads were also managed and the capping layer was not buried or disturbed by lake currents induced by wave action.

Scaling to whole lake application

The results from this study provide minimum dose and sustainability measures for the four sediment capping products. However, major scaling factors should also be considered in regard to product choice and method suitability for lake-scale application, including: sediment surface-area to lake-volume ratios (shallow lakes are susceptible to sediment resuspension and transport); depth-induced pressure effects (affecting gas ebullition and pore-water mass transfer); spatial variability in amount of bioavailable P in the natural lake sediment; and disturbance of the capping layer by benthic biota through bioturbation. Each of these scale factors may significantly affect the efficacy and selection of product for application to P management in a specific lake situation.

Non-target effects

In an earlier sediment incubation study using Z2G1 material from the same batch, there were indications of suppression of microbial processes affecting coupled nitrification and denitrification at the sediment–water interface under aerobic conditions (Gibbs & Özkundakci, 2010). These non-target effects were evaluated, and we found that all products induced apparent suppression of coupled nitrification and denitrification under aerobic conditions.

Microbial nitrification by *Nitrosomonas* sp. and *Nitrobacta* sp. cause the NH_4-N released from the sediments to be oxidised to NO_3-N under aerobic conditions. Suppression of the nitrification process results in an increase in the flux of NH_4-N from the sediment under aerobic processes. Increased net fluxes of NH_4-N occurred with all products, except Z2G1 which adsorbs NH_4-N, and were dose-dependent (Fig 5). The magnitude of the effect on nitrification, as indicated by the % change in NH_4-N flux over controls compared with treatments closest to their measured optimal P-removal dose, differed for each product (Table 6). The near complete blocking of NH_4-N release by Z2G1 was expected from the earlier study because of zeolite adsorption of NH_4-N (Gibbs & Özkundakci, 2010). The nearly fivefold enhancement of the NH_4-N release by Phoslock™ indicates a substantial effect on the nitrification process to rates comparable with anaerobic sediments (Fig. 5). This suggests that the suppression effect may relate to the capping layer thickness reducing the diffusion of oxygen to the nitrifiers as observed by Vopel et al. (2008). Alum and allophane also had enhanced NH_4-N release, but at much lower levels of

Table 6 Non-target effects of the capping materials on nitrification, expressed as % change in NH_4-N relative to the control (negative values indicate adsorption by the product while positive values indicate enhanced release), and denitrification expressed as % suppression relative to the control

Microbial process	Alum	Phoslock™	Z2G1	Allophane
Nitrification				
Aerobic	70	457	−94	−11
Anoxic	−26	9	−74	31
Denitrification				
Aerobic	55	49	37	17
Anoxic	0	18	13	−5
Denitrification potential				
	−18	15	6	30

Denitrification potentials were estimated from nitrate additions using anoxic data only. All values are for the treatments closest to P-removal efficacy dose rates, i.e. 200% treatment data for alum, Phoslock™ and Z2G1, 50% treatment data for allophane

70 and 66%, respectively, than the 457% enhancement by Phoslock™.

Under anoxic conditions nitrification would not be expected and the magnitude of the effects were reduced (Table 6). The effect by Phoslock™ was not statistically ($P > 0.05$) different to the control. However, while allophane caused a 31% increase in NH_4-N release, both alum and Z2G1 caused a reduction (Table 6).

Since the zeolite substrate in Z2G1 adsorbs NH_4-N, it was not possible to determine whether this product affected the nitrification process. However, because denitrification at the sediment–water interface relies on the diffusion of nitrate across the oxic–anoxic boundary and is, in the absence of external nitrate supply, controlled by nitrification, an effect on nitrification would produce a corresponding effect on denitrification. The NO_3-N flux data under aerobic conditions (Fig. 7) show that less NO_3-N was removed from the product treatments than from the controls indicating a net suppression of denitrification by all products. The magnitude of the suppression effect was different for each product with alum causing the greatest suppression effect at 55% reduction in NO_3-N removal and allophane the least at 17% reduction (Table 6). The 37% reduction in NO_3-N removal by Z2G1 was less than for Phoslock™ (47%) but indicates that Z2G1 probably has an effect on the nitrification process. However, that effect may in part be due to a reduction in the availability of NH_4-N to be nitrified.

Under anoxic conditions, the magnitude of the effects on denitrification were minimal although the 18 and 13% reductions in NO_3-N removal by Phoslock™ and Z2G1, respectively, relative to controls were significant ($P < 0.05$).

The addition of NO_3-N to the CFIS was to evaluate any effects of the products on denitrification potential. With the exception of alum, all products appeared to enhance the denitrification potential in the sediment (Table 6) with the 30% enhancement by allophane being significant ($P < 0.05$). These results are consistent with the NO_3-N data from the extended study (Fig. 8) which showed that denitrification increased in all treatments after the addition of the algal slurry, suggesting that any affect on denitrification by these products might be short-term. As the algal slurry was a carbon source, this response also indicates that the cause of the denitrification suppression effect may have been caused by carbon limitation associated with the capping layer thickness.

Non-target effects also include the possible release of metals from the sediments into the water column by the capping layer changing the redox potentials at the sediment–water interface (Vopel et al., 2008) or from the product used as the capping layer. All of the products caused a small increase in soluble (filterable) Al under aerobic conditions relative to the control (Fig. 9; aerobic). However, under anoxic conditions, the two Al-based products, alum and Z2G1, did not enhance the Al concentrations beyond the level of increase in the control (Fig. 9; anoxic) and there was no dose–response with any capping agent. This indicates that the variable Al concentrations may have been due to entrainment of pore water by ebullition through the capping layer.

In contrast to Al, soluble La was only found in the water from the Phoslock™ treatment under aerobic conditions (Fig. 10; aerobic). Low but variable concentrations of La were also reported from the other products and controls under anoxic conditions (Fig. 10; anoxic) but these may also be associated with entrainment of pore water by ebullition through the capping layer. The presence of soluble La in the water from the Phoslock™ treatments was unexpected as La rapidly binds with P to form insoluble LaP (e.g. Hickey & Gibbs, 2009) which would have been sedimented in the incubation chambers or

removed by the syringe filtering step during sample collection. That the La was present under both aerobic and anoxic conditions at around the same concentration suggests that it was being leached from the Phoslock™ by dissolution in the lake water rather than the release being solely a function of sediment pH or redox potential. This is consistent with the significantly ($P < 0.05$) lower release from the 50% treatments indicating a dose–rate related release process. Leaching of similar levels of La from Phoslock™ used in water treatments has been reported in other studies (e.g. Pablo et al., 2009; Lürling & Tolman, 2010).

The leaching of La from Phoslock™ is also consistent with the observations from the P-binding capacity determinations which showed an initial rapid uptake of P by the Phoslock™ then a reduction in both P and La content in the product over time at pH 6.1 and 7.0 (Fig. 2). The lake water in the incubation chambers was maintained in the pH range 6.8–7.2. The rate of leaching was low at an equivalent of 2 mg m^{-2} day^{-1} but did not change over the 14 day period of the incubation. This suggests that the leaching was rate-limited and may be associated with an ion-exchange process in the in the low alkalinity (25 g m^{-3} as $CaCO_3$), soft (hardness 13.7 g m^{-3} as $CaCO_3$) lake water.

While La salts are used as a "safe" phosphate binder in kidney dialysis (Persy et al., 2006), it is unknown whether there are ecological consequences for the benthic community in a lake from the low level leaching of La at the sediment surface. Literature studies (e.g. NICNAS, 2001; Borgmann et al., 2005) have shown low toxicity to midge larvae (Clearwater, 2004) and *Daphnia* in the water column (Barry & Meehan, 2000). In contrast, a fish kill was reported to have occurred 3 days after the treatment of Deep Creek dam, a low alkalinity (33 g m^{-3} as $CaCO_3$), and presumably low hardness, water supply reservoir in New South Wales, Australia, with 55 tonnes of Phoslock™ in April 2007 (Pablo et al., 2009); reservoir volume about 3000 megalitres. The associated investigation found that La was released from the Phoslock™ granules when diluted with water, consistent with our findings in this study. That investigation found that: (i) the reservoir water collected 3 days after the application was toxic to juvenile rainbow fish (*Melanotaenia duboulayi* Castelnau) and the cladoceran *Ceriodaphnia dubia* Richard; (ii) "Phoslock™ dispersed water was acutely toxic to *C. dubia* and *M. duboulayi* at concentrations at or approaching the licensed application rate"; and (iii) "the dam water remained toxic to *C. dubia* over the 8-week period, although toxicity decreased during this time." In contrast to these findings, Lürling & Tolman (2010), after testing Phoslock™ with *Daphnia magna*, concluded that "no major detrimental effects on *Daphnia* are to be expected from Phoslock™ or its active ingredient lanthanum when applied in eutrophication control." Their study was conducted in water with higher hardness (88 g m^{-3} as $CaCO_3$), which is an important factor in reducing metal toxicity to fish and invertebrates (Pascoe et al., 1986). For example Al is reported to be >17-fold more toxic in soft water (Borgmann et al., 2005) and the toxicity of La may be similarly enhanced.

The P-binding properties of the natural Fe component in the sediment may have been affected by the application of the four products as sediment capping layers. At the 200% treatment with Z2G1, soluble Fe was released from the sediment under aerobic conditions (Fig. 11; aerobic). This would be an indication that the sediment beneath the capping layer was anaerobic (cf. Vopel et al., 2008) with entrainment of pore water by ebullition through the capping layer. In contrast, under anoxic conditions soluble Fe was released from the sediment in the controls and all treatments except the 200% Phoslock™ and allophane treatments (Fig. 11; anoxic). However, because of the high variability in the anoxic Fe data, these differences may also be due to ebullition effects.

Conclusions

The use of the CFIS to compare four P-inactivation agents used for managing internal P loads in lakes allows steady-state chemical conditions to be established for flux measurements. While the use of a homogenous mixed sediment in the incubation chambers does not allow these results to be extrapolated to the whole lake, it does reduce the natural variability in lake sediments which could mask some of the effects observed in this study. Conditions not accounted for were depth/pressure effects and bioturbation (i.e. physical mixing) as there were very few macroinvertebrates (chironomids, oligochaetes) present in the bulk sediment mixture. This study

determined that all four products, when applied at their P-removal efficacy dose rates for a specific lake, are capable of blocking the release of P from the sediments of that lake.

However, there are physical properties that must also be considered. Primarily, the efficacy of these P-inactivation agents is a function of pH and water hardness. In particular, the formation of the alum floc is dependent on high alkalinity, either natural or supplied via a buffer added during dosing, where the water is soft. The minimum dose rate may need to be greater than the P-removal efficacy dose rate if the product does not completely cover the sediment. Although alum is widely used to manage internal P-loads in lakes in the northern hemisphere, the light fluffy nature of this product as a floc may not be a suitable product to use as a sediment capping agent in a very large shallow lake such as Lake Rotorua, where wind-induced wave action can resuspend the fine surficial sediments over large areas of the lake. In contrast, the granular products appeared to form cohesive layers across the sediment surface in the chambers, making the capping layer less susceptible to suspension by lake currents.

Applied at their P-removal efficacy dose rates, all products had an initial adverse effect on microbial nitrification and denitrification under aerobic conditions. Although this effect may only persist for a few weeks, it could adversely affect the benthic biota in the littoral zone of the lake, while the enhanced release of N into the water column could stimulate algal growth. Consequently, it would be advisable to minimise application of these products to permanently aerobic sediment zones in a lake. In this respect, the granular products have more chance of remaining within a targeted sediment zone than a floc such as alum, which may drift around the lake with the lake currents as it settles. Alkalinity and hardness of the lake water should also be considered before treating any lake with these products.

Acknowledgments We would like to thank D. Bremner, M. van Kooten, B. Hughes and K. Farnsworth for collecting the sediment and hundreds of litres of lake water, assistance with set up and daily sampling of the incubation chambers over the 90 day experiment, G. Bryers for the rapid analytical turn around of the thousand or more water samples produced during this study, and K. Rutherford for valuable discussion during the preparation of this manuscript. This study was funded by the Foundation for Research Science and Technology (FRST) contract CO1X0305, 'Restoration of aquatic ecosystems' and Environment Bay of Plenty under their programme for restoration of the Te Arawa/Rotorua Lakes.

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