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LAKE RESTORATION

Effects of a modified zeolite on P and N processes and fluxes across the lake sediment–water interface using core incubations

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Abstract A new locally produced P-inactivation agent, Z2G1, was tested on sediment cores from Lake Okaro, New Zealand, for phosphorus (P) removal efficacy and any non-target side effects prior to a whole lake trial to manage internal P loading. Z2G1 is a granular product which settles rapidly, and was designed as a sediment capping material. It is a modified zeolite which acts as a carrier for the aluminium (Al)-based P-binding agent. It was found to have a high affinity for P and did not release Al into the water column. Continuous-flow incubation study results showed that a thin layer of Z2G1 ($\sim$2 mm) could completely block the release of P from the sediment under aerobic and anoxic conditions, and remove P from the overlying water in contact with the capping layer. The Z2G1 capping layer neither released metals itself nor did it induce the release of metals from the sediments, and the zeolite substrate absorbed arsenic and mercury from the geothermally influenced Lake Okaro sediments. In general, zeolites are strong cation absorbers and the zeolite substrate of Z2G1 absorbed ammoniacal nitrogen, making it the only sediment capping material to actively remove both P and N. There were, however, indications of a suppression effect on microbial denitrification by the Z2G1 capping layer under aerobic conditions. Overall, the Z2G1 sediment capping material is a highly effective P-inactivation agent which might be a useful material for managing internal P loads in eutrophic lakes.

Keywords Internal load · P-inactivation agent · Sediment capping · Lake restoration · Modified zeolite · Phosphorus · Nitrogen · Lake Okaro

Introduction

The problem of excess internal phosphorus (P) loads in lakes occurs world wide. For example, a recent study of over 14,000 lakes >1 ha in size in Great Britain found that 51% are likely to require P-reduction measures to meet the Water Framework Directive to achieve 'good status' by the year 2015 (Carvalho, 2005). Results from that study also showed strong regional patterns with Scotland having the least, and England having the highest number of lakes at risk at 18 and 88%, respectively. New Zealand has many lakes adversely affected by

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internal P loads. However, due to the high P content of their catchment soils and thus their inflow streams (Timperley, 1983), lakes in the Taupo volcanic zone (TVZ) of the North Island are more likely to require internal P load management than elsewhere in New Zealand (Parliamentary Commissioner for the Environment, 2006; Edgar, 2009).

Internal P loads are derived from the release of phosphate sequestered by oxidised iron species and the decomposition of organic matter in the lake sediments releasing biologically available (bioavailable) P as soluble phosphate 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).

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 an inactivation agent applied either as a flocculation agent to strip P from the water column or as a capping agent to seal the sediments against the release of P during periods of anoxia (Cooke et al., 2005). The P-inactivation agent of choice is typically Alum (aluminium sulphate) which, in neutral to alkaline water, produces a flocculent gelatinous precipitate of aluminium hydroxide, $Al(OH)_3$, which is chemically relatively stable, even under low redox states commonly encountered under anoxic conditions.

The effectiveness of the alum treatment usually lasts for more than just the year of treatment. In an evaluation of the effectiveness of reducing total P (TP) and longevity of alum treatments in 21 lakes across USA, Welch & Cooke (1999) found that the internal loading rate was reduced by around two-thirds and TP was reduced by around one-half for a period of 5–11 years. In some dimictic lakes, the internal loading may be controlled for at least 13 and up to 18–20 years, with a reasonable expectation of 15 years longevity (Welch & Cooke, 1999). A decline in treatment effectiveness over time was thought to be due to bioturbation and burial of the alum floc. It is likely that the continued input of P from the catchment was also a contributing factor.

While 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. In general, denitrification can remove up to 36% of the TN input to lakes (Molot & Dillon, 1993), with denitrification rates of up to 229 mg N m^{-2} day^{-1} in some hyper-eutrophic lakes (Jensen et al., 1992). Lake Rotorua, located near Lake Okaro, has highly organically enriched sediments, and mean annual denitrification rates are estimated to be around 30 mg N m^{-2} day^{-1} (White et al., 1978), and mean P release rates were found to be 44 mg P m^{-2} day^{-1} (White et al., 1978; Burger et al., 2007). Given the similarity in soil type, geothermal influence, catchment land-use and trophic condition (Hickey & Gibbs, 2009), comparable N- and P-fluxes might be expected in Lake Okaro, the focus of this study, with the high internal P load negating the benefits of controlling the external P loads from the catchments.

Internationally, attempts to reduce internal P loadings in eutrophic lakes also include sediment capping using calcite (Berg et al., 2004), modified clay minerals (Robb et al., 2003) and iron slag (Yamada et al., 1987). P-inactivation agents considered for the reduction of internal P loads in Lake Okaro were Alum and a new proprietary granular P-inactivation agent, Z2G1, that has been developed as a capping agent by Scion, Rotorua, and manufactured by Blue Pacific Minerals Ltd., Matamata, New Zealand.

Z2G1 is also an Al-based P-inactivation agent that uses zeolite clay as a carrier for the Al and does not require buffering to avoid lake water acidification as can occur using Alum in poorly buffered lakes (Cooke et al., 2005). Zeolites are good cation absorbers that can remove ammonium ions (NH_4^+; Wen et al., 2006), and the modified zeolite retains the NH_4^+ absorption properties of the base material. Z2G1 has been designed to be applied as a sediment capping material with a granular formulation that improves the settling rate and thus accuracy of treating specific areas of lake bed. This is necessary to avoid lateral drift of the capping material into the littoral zone.

Environment Bay of Plenty, the regional environmental manager, used Z2G1 on Lake Okaro (surface area 0.33 km^2) in September 2007 as a 'whole lake' trial to test its effectiveness in reducing the internal P load by blocking the release of P from the sediments, and to assess whether Z2G1 could be used in the restoration of other Rotorua lakes, including Lake Rotorua (surface area 81 km^2). The main objective of this study was to assess if Z2G1 could block the

release of P from lake sediments before undertaking the whole lake trial. We examined the P-removal efficacy of Z2G1 on Lake Okaro sediment by treating cores with two different grain sizes and dose rates of Z2G1 under aerobic and anoxic conditions. We also used the different layer thicknesses to examine the effect of the Z2G1 capping layer on the microbial processes of nitrification and denitrification and the potential release of metals such as arsenic (As) and mercury (Hg) from Lake Okaro's geothermally influenced sediments under aerobic and anoxic conditions.

Methods

Study site

Lake Okaro, a relatively small (33 ha) low-alkalinity (HCO_3 36.8 g m^{-3}), hyper-eutrophic crater lake in the TVZ that lies in a mostly agricultural (>95% pasture) catchment. It has a mean depth 12.1 m (max. depth 18.0 m) and thermally stratifies annually between 4 and 8 m. Summer surface temperatures reach up to 23°C with hypolimnetic temperatures of around 18°C. Water clarity is variable (Secchi depth 0.6–3.6 m) associated with chlorophyll *a* concentrations ranging from 1.4 to 200 mg m^{-3} (mean 28 mg m^{-3}). Total phosphorus concentrations ranging from 18 to 573 mg m^{-3} (mean 103 mg m^{-3}) and total nitrogen concentrations range from 430 to 4,690 mg m^{-3} (mean 1,161 mg m^{-3}; Timperley & Vigor-Brown, 1986; Environment Bay of Plenty, 2006; Hickey & Gibbs, 2009). Lake Okaro has highly organically enriched sediments from agricultural catchment runoff (Forsyth et al., 1988), with high nitrogen (N) inputs from the catchment and a high internal P load (Burns, 2001) from the sediments during summer stratification. These are the main nutrient drivers of nuisance cyanobacteria blooms (Dryden & Vincent, 1986) which occur through summer and autumn. Because Lake Okaro is an important recreational lake in the Bay of Plenty region, Environment Bay of Plenty, have made a commitment to improve its water quality through the use of catchment and in-lake remediation techniques, to reduce both N and P. The sustained control of phytoplankton biomass 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). Catchment remediation work including restricting stock access to the lake, enhancing riparian buffer zones, and installing a large constructed wetland on the main inflow have been completed (Tanner, 2007) and the present focus is on managing the internal P load.

Core collection

In this study, it was assumed that releases of P from lake sediments were mainly by diffusion mostly from the top 4 cm (Cooke et al., 2005). Sediment P release rates, and the efficacy of Z2G1 as a capping agent to block that release, were measured on composite degassed sediment using a continuous-flow incubation system (e.g., Miller-Way & Twilley, 1996). Multiple sediment cores were collected from a depth of 12 m in Lake Okaro in winter (June 2006) when the lake was fully mixed, using a Jenkins Corer (Mortimer, 1971). Sampling at this time of year ensures the maximum sequestration of P into the sediments and simulates the expected time of application of the Z2G1 as a capping layer for the whole lake treatment. The top 10 cm of sediment in each core was extruded upwards into a 25-cm long incubation tube the same diameter as the corer tube (7.0 cm ID), using a manual push piston. The bottom of the incubation tube was sealed with plug of 3 cm thick high density foam (cut from a sheet with a 7.5 cm hole saw without the drill bit). This process spilled most of the overlying water. The top of each incubation tube was closed with another plug of high density foam, but with a vent hole to relieve any pressure. The vent hole was subsequently closed with a rubber bung and the incubation tube placed vertically in a rack in container of lake water for transport to the laboratory.

A sample of the near-sediment overlying water was collected for nutrient and dissolved metal analyses from one corer tube using a syringe fitted with a length of narrow-bore hard nylon tube. Four 100 l barrels of unfiltered surface lake water were also collected as the source water for the incubations. The barrels were sealable wide-mouth black alkathene barrels lined with clean heavy-walled plastic bags (bin liners) to prevent cross contamination.

Set up procedure

While the intention was to use the undisturbed sediment in the incubation tubes, sediment disturbance by degassing of methane and CO_2 during transport to the laboratory made this impossible. Consequently, the sediment in each incubation tube was stirred gently to remove remaining gas bubbles and then allowed to reconstitute under aerobic lake water for 5 days before starting the experiment.

After treatment (see below), the incubation tubes were converted to incubation chambers by closing the top with a high density foam plug with a vent port, a 2-mm ID nylon inlet tube, and a 3.5 mm ID nylon outlet tube; both tubes were inserted through the plug (Fig. 1A). With the top closed, the water space above the sediment was reduced to 2.5 cm (volume $\sim$ 100 ml) by pushing the bottom plug further up inside the incubation tube. The vent port spilled the excess water and air bubbles, and was then sealed with a rubber bung. The incubation chambers were placed vertically in a rack in a temperature-controlled water bath at 18°C (i.e., summer hypolimnion temperature), with the incubation chamber tops just under water. The experiments were run in a controlled temperature room at 18°C.

Continuous-flow incubation system

The continuous-flow incubation system (CFIS; Fig. 1B) comprised a multi-channel peristaltic pump (ex-Auto-Analyzer®) drawing water from the source-water drum and pushing it into each incubation chamber at a flow rate of 1.5 ml min^{-1}, i.e. each incubation chamber received identical water. The inflow water mixed with water in contact with the sediment in each incubation chamber and an equal volume of the mixed water was displaced via the outflow tube into individual sample collectors. The larger diameter of the outlet tube was to prevent pressure build up in the sediment under test. Apart from the Tygon® pump tube, all tubing was hard nylon (automotive brake fluid transmission tubing) which had low internal friction, and was impermeable to oxygen.

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 day^{-1}. It took about 24 h for the CFIS to reach a steady state after the initial

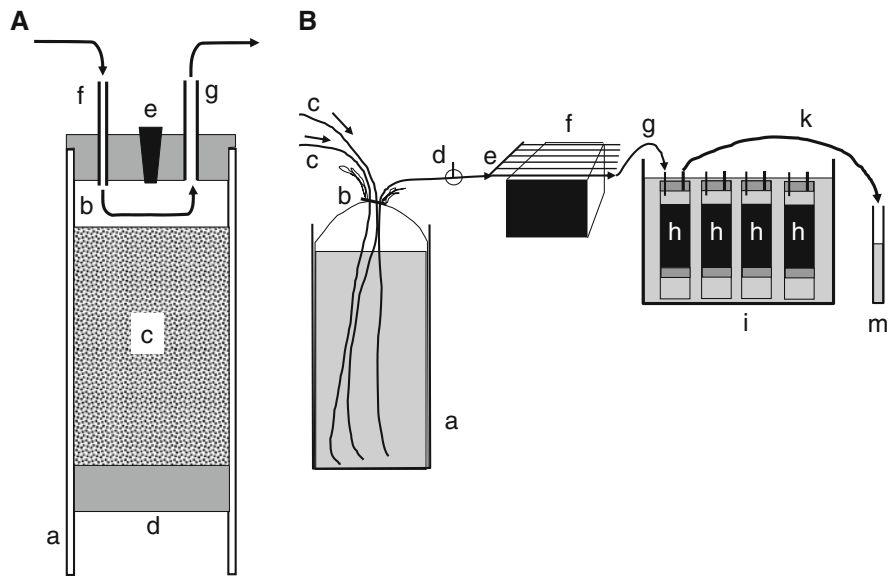

Fig. 1 **A** Schematic of the incubation chamber (*a*) with flow-through cavity (*b*) above the sediment (*c*) showing the movable bottom plug (*d*), vent hole and bung in the chamber cap (*e*), the 2-mm ID inlet tube (*f*), and the 3.5-mm ID outlet tube (*g*). **B** Schematic of the continuous-flow incubation system showing the bulk water drum (*a*) with the plastic liner (*b*) bound around the gas lines (*c*), the 3-way tap for inflow water sampling (*d*), the distribution manifold to the individual pump tubes (*e*), the multi-channel peristaltic pump (*f*), the inflow transmission tubes to each incubation chamber (*g*), the incubation chamber (*h*) submerged in a controlled temperature water bath (*i*), the outflow transmission tubes (*k*) to the sample collection tube (*m*). *Arrows* indicate flow direction

disturbance of closing the chambers. Nutrient fluxes from the sediments were estimated from the difference between inflow and outflow concentrations at steady state.

Experimental design

In order to achieve rapid settling of Z2G1 as a capping layer in Lake Okaro, a 1–3 mm grain size was used at a dose rate of 350 g m^{-2}. Experimental treatments used this dose rate and 700 g Z2G1 m^{-2} in the CFIS in one set (three replicates of each treatment) of incubation chambers. The 1–3 mm grain size material was sieved from a bulk <3 mm grain size Z2G1 sample. Because fine-grained materials have a greater surface area per unit mass and thus potentially could absorb more P, this was tested by treating a second set of incubation chambers with the same dose rates of the residual <1 mm grain size. Control treatments where chambers containing bare sediment, and a single blank treatment consisted of a chamber dosed with 700 g m^{-2} of <1 mm grain size Z2G1 without sediment, to distinguish between trace metals released from the Z2G1 and releases from the sediment because of the Z2G1 capping layer. The 1–3 mm grain size treatments and controls were run in triplicate, and the <1 mm grain size treatments were run in duplicate.

Two identical experiments were set up and run concurrently, one with natural lake water and the other with natural lake water amended with nutrients to evaluate natural and potential fluxes of N and P. The nutrient amendments increased the DRP concentration to about 200 mg DRP m^{-3} (sodium dihydrogen phosphate) and the nitrate (NO_3-N) concentration to about 1,500 mg NO_3-N m^{-3} (potassium nitrate). The NO_3-N amendment was also used to check the effect of Z2G1 capping layer on denitrification. No ammoniacal-N (NH_4-N) was added.

Aerobic versus anoxic treatments

As sediment release of P can be predominantly regulated by oxygen concentrations at the sediment–water interface (Gächter & Müller, 2003), each experiment was first run with natural lake water under aerobic conditions, to simulate mixed or littoral zone effects, and then under anoxic conditions to simulate hypolimnetic conditions after thermal stratification.

The bulk lake water for aerobic tests was aerated using an aquarium air stone and filtered air from outside the laboratory. Lake water was made anoxic using the plastic liner as an air barrier bound tightly around two gas lines and the pump line to the CFIS installed in the bulk water drum. One gas line was used to continuously bubble oxygen-free dry nitrogen gas through the bulk water to remove all dissolved oxygen. Anoxia was achieved in about 1 h. The other gas line was used to bubble CO_2 gas into the anoxic water as required (30-s bursts) to adjust the pH to around 7.5. A nylon Luer lock three way tap in the pump line allowed the bulk water to be sampled for measuring pH and DO. The plastic bag trapped the excess N_2 gas under positive pressure in the headspace, preventing any significant diffusion of oxygen into the water from the atmosphere.

Sampling

Each experimental condition was run for 5 days. Sample collection was daily after the first day. For nutrient analyses, 50 ml water was collected from each chamber in an open 50 ml plastic syringe (plunger removed) with a tap in place of the needle. Refitting the plunger enabled the sample to be syringe-filtered into a sample bottle without an intermediate transfer step. Inflow water samples were drawn by syringe from the three way tap in the pump line. Filtration was through a 2.5 cm Whatman® GF/C glass fibre filter in a 2.5 cm Swinnex® filter holder. A 10 ml aliquot of each filtered sample was transferred to a specially prepared sample bottle containing nitric acid preservative for trace metal analysis.

At the completion of the experiment, the incubation chambers were opened and samples of the Z2G1 capping layer material were recovered from each chamber under low vacuum and placed in plastic centrifuge tubes. The sediment adhering to the Z2G1 capping material was removed by sequential washing with deionised water, which was discarded. The recovered Z2G1 and a similar amount of fresh Z2G1 as a reference material were dried at 105°C for 24 h before being ground to a fine powder with a mortar and pestle. The Z2G1 samples and a dried ground sample of untreated sediment were digested using aqua regia solution at 90°C for 2 h before analysis for metals and trace elements.

P-saturation

In order to determine the maximum P-binding capacity of Z2G1 and its P-uptake rate, 5 g of the <3 mm grain size product were placed in 1 l of water containing 200 mg P (2 g $NaH_2PO_4{\cdot}2H_2O$). The mixture was shaken vigorously for 1 min then allowed to settle for 10 min before removing about 0.5 g of granules by suction tube. The mixture was shaken and sampled at timed intervals over a period of 200 h to provide a time-series uptake curve. The samples were centrifuged immediately on collection (3,000 rpm for 10 min) and the aqueous phase was discarded. The samples were rinsed twice with deionised water before drying, grinding and digestion as above.

Analytical

The nutrient bottles were frozen at −20°C pending batch analysis for DRP, NO_3-N and ammoniacal-N (NH_4-N) on a Lachat flow injection analyser (FIA) using standard Lachat methods for freshwaters. The acidified water samples were analysed for the metals iron (Fe), manganese (Mn), aluminium (Al), zinc (Zn) and As, using an ICP-mass spectrometer (ICP-MS) and the Z2G1, and sediment sample digests were analysed for metals and trace elements using an ICP-MS.

Sediment bulk density was determined on an aliquot of wet sediment, and was calculated from the water loss from a measured volume of sediment after drying at 105°C for 24 h.

Statistical analysis

A T-test was carried out to test for significant differences between dose rates and grain size with natural and nutrient enriched lake water. Due to the limited sample size (3), significance was assumed when $P < 0.05$.

Results

P-binding capacity

The P-uptake results (Fig. 2) showed a rapid uptake of DRP over the first few hours with uptake reaching a plateau of around 20,000 mg P kg^{-1} Z2G1 dry weight over the 200 h experiment. As the fitted curve

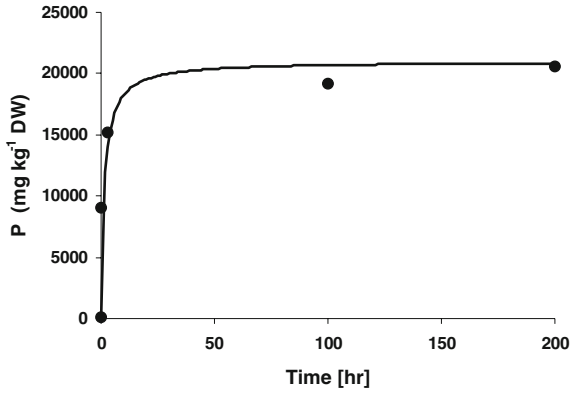

Fig. 2 Time-series total P concentration changes in Z2G1 over the 200 h P-saturation experiment. Curve modelled to account for the measured (*dots*) rapid initial uptake and final concentration, gives an indication of maximum P-binding capacity of Z2G1

indicates little increase after 24 h, this is a best estimate of the P-binding capacity of Z2G1. The use of sodium di-hydrogen phosphate as the source of the DRP gave the solution a pH of around 6.

Sediment coverage

Sediment coverage was judged visually. The sediment coverage by the 1–3 mm grain size 350 g m^{-2} layer was incomplete with large gaps between the Z2G1 granules (Fig. 3B), while the <1 mm grain size 350 g m^{-2} layer gave almost complete coverage (Fig. 3A). At the 700 g m^{-2} dose rates, the 1–3 mm grain size still did not achieve complete coverage of the sediment.

P-fluxes

Sequential analyses of the inflow and outflow DRP concentrations from the incubation chambers showed that the system was at equilibrium from the beginning of the sampling at the end of day 2 and through to the final sampling on day 5 (Fig. 4). Concentrations higher than those of the inflow (Fig. 4, control) indicate that DRP was released from the sediment. Concentrations lower than the inflow (Fig. 4, all treatments) indicate that the Z2G1 blocked the release of DRP from the sediment as well as absorbing DRP from the lake water above the sediment.

Under aerobic conditions, DRP was removed from the overlying water column in all incubation

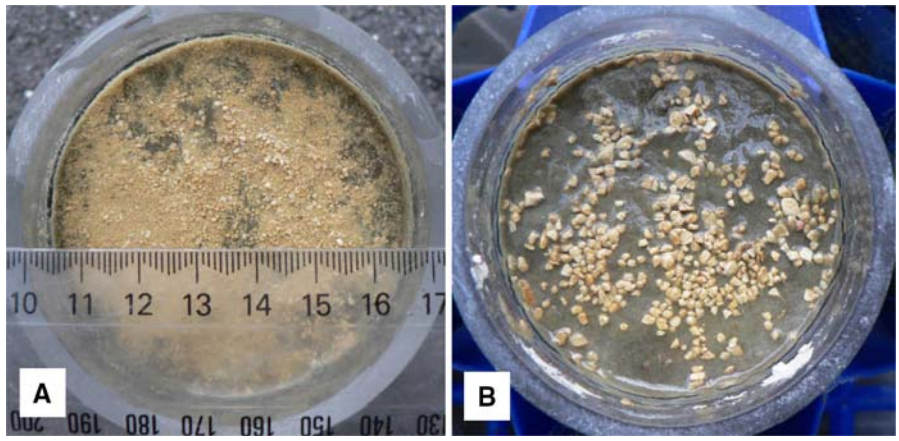

Fig. 3 Comparison of sediment coverage by Z2G1 at a dose rate of 350 g m^{-2} for (**A**) < 1 mm grain size, and (**B**) 1–3 mm grain size. Ruler shows scale in cm

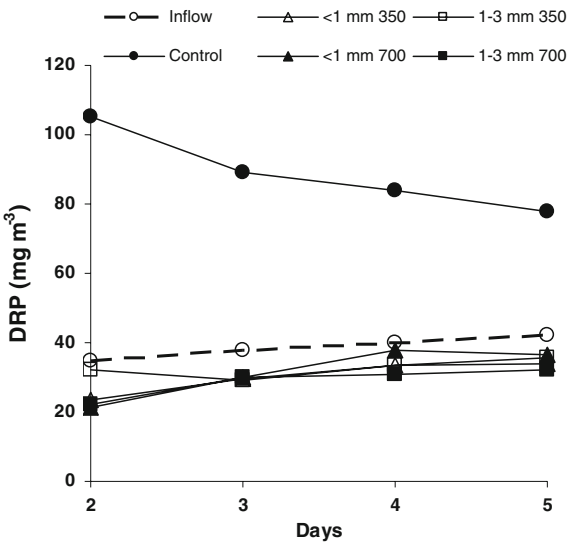

Fig. 4 Sequential analyses of DRP concentrations (mean of 3) in the inflow and outflow water from the anoxic natural lake water chambers over days 2–5. Graph key values 350 and 700 are dose rates of Z2G1 in g m^{-2}

chambers including the control (Fig. 5A). The results showed that all of the Z2G1 treatments sequestered a similar amount of P which was about double the amount sequestered by the natural sediment from the natural lake water. There was no statistically significant (T-test; $P < 0.05$) difference between dose rates ($P > 0.05$). Adding DRP to the lake water enhanced the amount of DRP sequestered, but while the lower dose rate of each grain size appeared to sequester more than the higher dose rate, the difference was not statistically significant ($P > 0.05$).

Under anoxic conditions, DRP was released into the overlying water column in the control with natural lake water, but not with DRP-amended lake water (Fig. 5B). In the incubation chambers dosed with Z2G1, the release of DRP from the sediments was blocked and some of the DRP in the overlying water column was sequestered. While there was no statistically significant (T-test; $P < 0.05$) difference between dose rates ($P > 0.05$) for the <1 mm grain size, there was a significant difference ($P < 0.02$) between dose rates for the 1–3 mm grain size, with higher sequestration of P at the higher dose rate. In the chambers exposed to DRP-amended lake water, the amount of P sequestered by the Z2G1 treatments was higher than in the control, but not as high as in the aerobic incubations. The lower dose rate of each grain size sequestered significantly ($P < 0.02$) more *P* than the higher dose rate, but overall there was no statistically significant ($P > 0.05$) difference with grain size (Fig. 5B).

N-fluxes

The NH_4-N-fluxes under aerobic and anoxic conditions (Fig. 6) showed that Z2G1 absorbed NH_4-N released from the sediment and from the overlying water. Under aerobic conditions and natural lake water (mean NH_4-N concentration 450 mg m^{-3}), there was little or no change in the NH_4-N concentrations from the control chambers, while the incubation chambers treated with Z2G1 had significantly reduced NH_4-N concentrations (Fig. 6A). The addition of NO_3-N to the natural lake water (NO_3-N 1,540 mg m^{-3}; no change to the NH_4-N concentration) produced a greater loss of NH_4-N from all chambers (Fig. 6A). There was no statistically significant

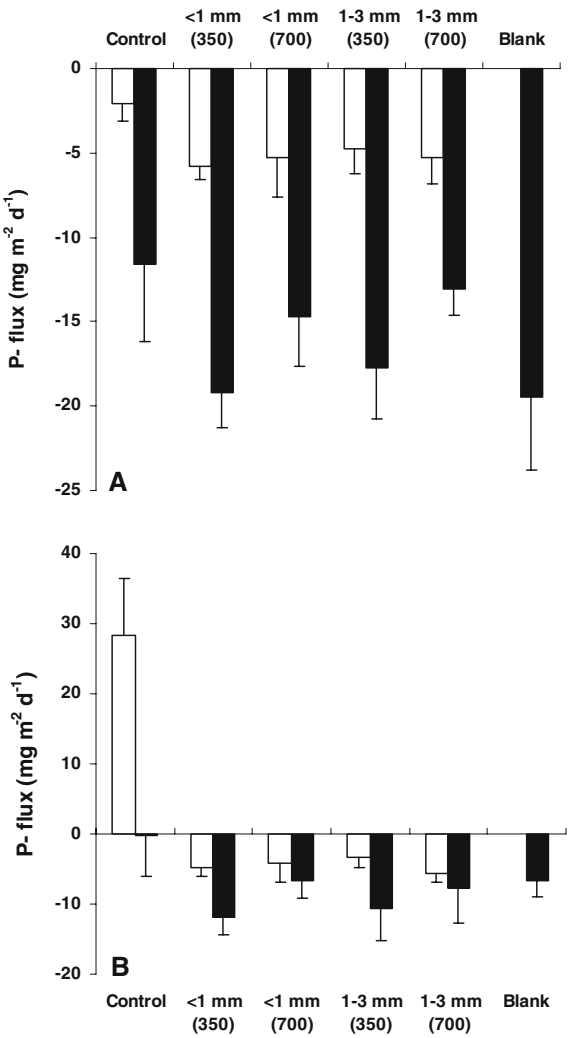

Fig. 5 **A** P-fluxes (mg m^{-2} day^{-1} ± 1 SD) in the sediment incubation chambers under aerobic conditions using natural lake water (*open bar*, DRP concentration 27 mg m^{-3}) and amended lake water (*solid bar*, DRP concentration 253 mg m^{-3}); **B** P-fluxes (mg m^{-2} day^{-1} ± 1 SD) in the sediment incubation chambers under anoxic conditions using natural lake water (*open bar*, DRP concentration 39 mg m^{-3}) and amended lake water (*solid bar*, DRP concentration 267 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of <1 mm grain size Z2G1 applied to an incubation tube without any sediment using amended lake water only

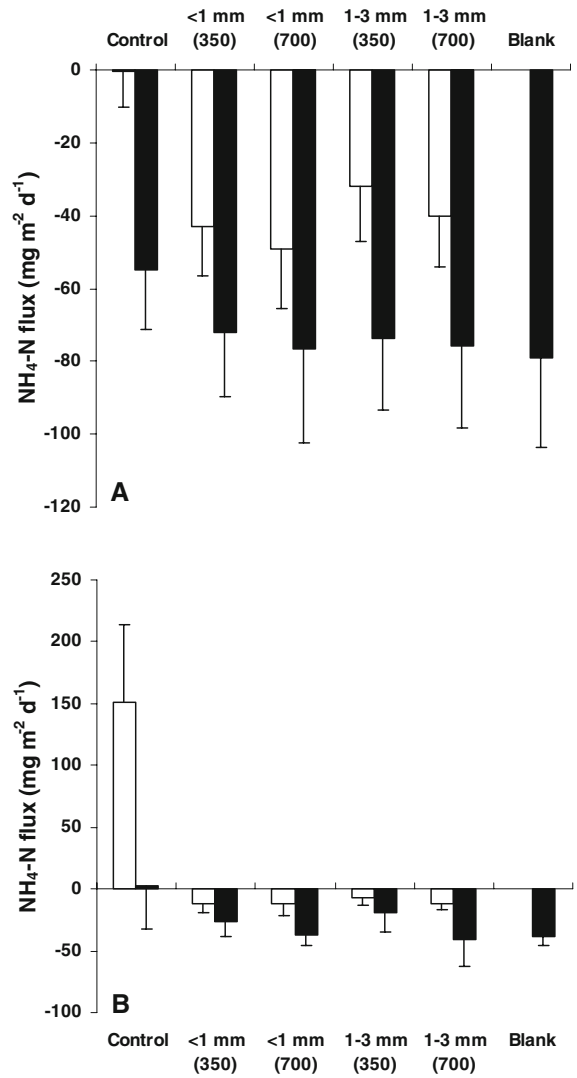

Fig. 6 **A** NH_4-N-fluxes (mg m^{-2} day^{-1} ± 1 SD) in the sediment incubation chambers under aerobic conditions using natural lake water (*open bar*, NH_4-N concentration 450 mg m^{-3}) and lake water amended with NO_3-N (*solid bar*, NO_3-N concentration 1,540 mg m^{-3}); **B** NH_4-N-fluxes (mg m^{-2} day^{-1} ± 1 SD) in the sediment incubation chambers under anoxic conditions using natural lake water (*open bar*, NH_4-N concentration 480 mg m^{-3}) and lake water amended with NO_3-N (*solid bar*, NO_3-N concentration 1,590 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of <1 mm grain size Z2G1 applied to an incubation tube without any sediment using amended lake water only

(T-test; $P < 0.05$) difference between dose rates ($P > 0.05$).

Under anoxic conditions, there was a significant release of NH_4-N from the control sediments with natural lake water (mean NH_4-N concentration 480 mg m^{-3}), but not with the lake water amended with NO_3-N (1,590 mg m^{-3}) (Fig. 6B). In contrast, the incubation chambers treated with Z2G1 had significantly reduced NH_4-N concentrations (Fig. 6B). The addition of NO_3-N to the natural lake water (no

change to the NH_4-N concentration) produced a greater loss of NH_4-N from all chambers (Fig. 6B). There was no statistically significant (T-test; $P < 0.05$) difference between dose rates with natural lake water ($P > 0.05$). With the addition of NO_3-N, the higher dose rates appeared to have a greater loss of NH_4-N, although this difference was not statistically significant ($P > 0.05$).

The NO_3-N-fluxes under aerobic conditions (Fig. 7) showed N reductions in all treatments. With natural lake water (NO_3-N concentration 17 mg m^{-3}), the loss of NO_3-N from the Z2G1-treated chambers was similar to the loss from the control, and there was no statistically significant (T-test; $P < 0.05$) difference between dose rates ($P > 0.05$). With the lake water amended with NO_3-N (NO_3-N concentration 1,540 mg m^{-3}), there was a significant increase in the loss of NO_3-N from all chambers. The loss of NO_3-N from the chambers treated with Z2G1 was equal to or greater than the loss from the control chambers. The apparent difference between dose rates, with the lower dose rate producing a greater NO_3-N loss than the higher dose rate, was highly significant ($P \ll 0.001$).

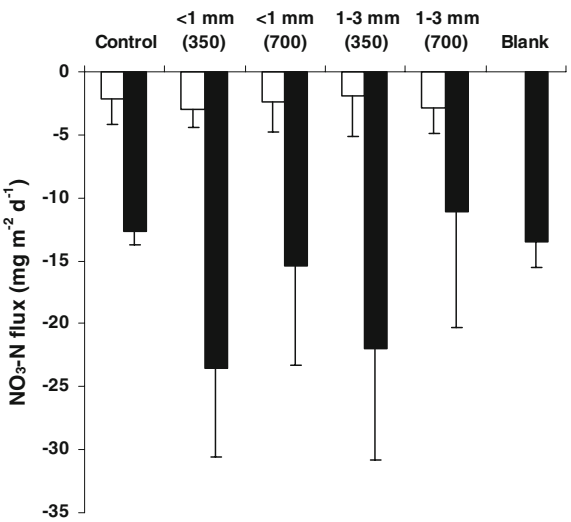

Fig. 7 NO_3-N-fluxes (mg m^{-2} day^{-1} ± 1 SD) in the sediment incubation chambers under aerobic conditions using natural lake water (*open bar*, NO_3-N concentration 17 mg m^{-3}) and lake water amended with NO_3-N (*solid bar*, NO_3-N concentration 1,540 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of <1 mm grain size Z2G1 applied to an incubation tube without any sediment using amended lake water only

Metal fluxes

The fluxes of metals between the sediment and water column in the incubation chambers were generally small (Table 1). Even when the incubation chambers were taken to anoxia, the concentrations of metals in the water from the chambers were generally much lower than in the water sample collected from just above the sediment in the corer tube at the time of sampling (Table 1). This may indicate that the bottom water metal concentrations were augmented by disturbance of the pore waters during coring.

Sediment and Z2G1

The wet sediment had a bulk density of 1,039 kg m^{-3}, therefore 1 m^3 of wet sediment will have 39 kg dry weight of sediment. The TP content of the sediments was 2,000 mg kg^{-1} dry weight (Table 2), and therefore each 1 cm thick slice of wet sediment had an areal TP content of 780 mg P m^{-2}. This indicates a potential internal P load of up to 3.12 g P m^{-2} from the top 4 cm of sediment. Note that TP is a maximum which will be greater than the total bioavailable P.

Metal and trace element analyses of different fractions of Z2G1 (Table 2) showed considerable variability in composition between different size fractions, which may be a function of the grain size or the analytical procedure. Analyses of the recovered Z2G1 (Table 2, used) showed that the finer material had statistically significant (T-test; $P < 0.05$) higher P concentrations ($P < 0.001$) than the coarser material, and that the <1 mm grain size had adsorbed about 45% more P than the 1–3 mm grain size. This was consistent with the significantly ($P < 0.001$) higher (~60%) aluminium content of the <1 mm than the 1–3 mm grain size Z2G1. There were no statistically significant differences in P absorption by Z2G1 of either grain size from the incubation chambers exposed to natural lake water or P-amended lake water (Table 2, +P) (<1 mm: $P = 0.22$; 1–3 mm: $P > 0.05$), indicating that the majority of the P absorbed was from the sediment.

Comparison of the other elemental composition of the new and recovered Z2G1 with that of the sediment shows that there were elemental changes occurring in the Z2G1 in contact with the sediments. For example, the sediment had a higher Fe content than the Z2G1 applied. The Fe content in the recovered Z2G1 was

Table 1 Total dissolved metal concentrations (g m^{-3}) and dissolved oxygen (% saturation) in the outflow water relative to the inflow water (lake surface) and lake bottom water from just above the sediments in the corer tube

Sample	Fe (g m^{-3})	Mn (g m^{-3})	Al (g m^{-3})	Zn (g m^{-3})	As (g m^{-3})	DO (% sat)
Lake Okaro						
Surface water	0.027	0.002	0.013	0.127	0.003	56.5
Bottom water	0.510	0.197	0.009	0.029	0.004	16.5
Aerobic chambers						
Control	0.027	0.002	0.013	0.127	0.003	92.1
<1 mm (350)	0.027	0.003	0.018	0.088	0.003	87.4
<1 mm (700)	0.030	0.005	0.014	0.070	0.003	89.0
1–3 mm (350)	0.030	0.007	0.007	0.115	0.003	89.4
1–3 mm (700)	0.033	0.004	0.011	0.068	0.003	90.2
Blank (< 1 mm 700)	0.037	0.003	0.022	0.095	0.003	89.1
Anoxic chambers						
Control	0.068	0.018	0.023	0.061	0.004	<0.5
<1 mm (350)	0.025	0.010	0.036	0.055	0.003	<0.5
<1 mm (700)	0.020	0.010	0.036	0.055	0.003	<0.5
1–3 mm (350)	0.030	0.011	0.009	0.045	0.003	<0.5
1–3 mm (700)	0.027	0.009	0.008	0.030	0.003	<0.5

Table 2 Concentrations (mg kg^{-1} dry weight) of metals and trace elements in Lake Okaro sediment and different fractions of Z2G1, measured by ICP-MS

Sample	Grain size (mm)	P	Al	Fe	Mn	Zn	As	Hg	Na	K	Ca	Mg
Sediment		2,000	10,700	17,800	315	78	38	13.1	565	1,980	2,430	1,500
Z2G1 new	<3	110	18,100	3,200	200	57	8	0.6	10,200	6,560	8,410	1,570
Z2G1 new	<1	180	24,800	5,700	275	60	9	0.7	12,200	8,220	5,260	1,810
Z2G1 new	1–3	80	14,900	5,100	170	37	9	0.5	12,800	8,220	5,260	1,430
Z2G1 used	<1	1,380	29,700	9,100	250	96	17	9.9	2,760	8,910	3,000	735
Z2G1 used	1–3	900	19,000	6,400	150	43	11	8.3	4,360	9,200	2,860	520
Z2G1 used + P	<1	1,360	28,800	8,300	295	90	19	9.3	2,420	12,600	2,820	665
Z2G1 used + P	1–3	940	18,400	8,300	310	48	14	7.0	3,910	11,500	2,880	590

Results are means of three analyses of each digest. Used Z2G1 is material recovered from the sediment surface at the end of the incubation experiment; +P indicates those samples were exposed to the P-amended lake water

about double after the 14-day incubation period. While this change may have been due to precipitation of Fe onto the zeolite matrix during the Z2G1 recovery under aerobic conditions, other changes occurred which would require a different mechanism. Arsenic and mercury increased in the Z2G1 indicating absorption of these elements from the geothermally influenced sediment. Sodium, calcium and magnesium decreased and potassium increased, especially in the Z2G1 recovered from the chambers exposed to P and NO_3-N-amended lake water (Table 2, +P), indicating ionic exchange processes.

Discussion

Comparisons between control and treatment fluxes under aerobic and anoxic conditions show that, at the dose rates used in this study, the thin layer of Z2G1 was capable to completely block the release of P from the sediments of Lake Okaro. Under natural lake water and anoxic conditions, the higher dose rate of the 1–3 mm Z2G1 removed significantly more P than the lower dose rate, consistent with a better coverage of the sediment surface. Of interest, however, the lower dose rate of Z2G1 at both grain sizes removed

significantly more P from the water column than the higher dose rate when the phosphate concentration was increased under anoxic conditions. The increase in P content of the Z2G1 recovered from the treated sediment cores relative to the unused Z2G1 confirmed that the Z2G1 was removing the P, and that it was not only the passive action of the granular material on the sediment surface. These results also show that the <1 mm grain size absorbed around 45% more P than the 1–3 mm grain size in both the natural and phosphate-enriched incubations for the same period of sediment exposure. This is consistent with the finer material having a greater active surface area than the coarser material (e.g. Wen et al., 2006).

Under aerobic conditions and natural lake water concentrations, the natural sediment in the control also removed P from the overlying water column. This is consistent with iron oxides and oxyhydroxides in the natural sediment sequestering phosphate from the water in contact with the sediment (Søndergaard et al., 2003). Adding more phosphate to the overlying aerobic water increased the concentration gradient between the water column and the sediment, inducing a greater uptake flux. These results indicate that under aerobic conditions, internal P loads in Lake Okaro are unlikely to occur.

Under anoxic conditions and natural lake water concentrations, P was released from the sediment in the control cores, but there was still a reduction of P in the Z2G1-treated sediment cores. This indicates that we had achieved anoxic conditions and that in the anoxic control cores, phosphate sequestered by iron under aerobic conditions had been released under the resultant reducing conditions (Perkins & Underwood, 2001). It also indicated that Z2G1 was sequestering the phosphate released from the iron and had sufficient P-binding capacity to also remove some of the P from the overlying water column. Adding more phosphate to the overlying water increased the amount of P removed by the Z2G1, but caused the P release flux from the control sediments to reduce to near zero. This apparent anomaly can be explained if the mechanism for release of P from the sediments is considered, namely chemical or molecular diffusion as a function of concentration gradient with movement of a compound towards the low concentration. Under natural lake water, the P concentrations in the sediment pore water can be expected to be very much higher than in the lake water (Enell & Löfgren, 1988), causing the observed efflux of P. Increasing the overlying water P concentrations reduced the concentration gradient to near zero causing the efflux also to be reduced to near zero. This indicates that the pore water P concentrations were likely to be in the order of 200 mg m^{-3}.

Efficiency of Z2G1 uptake of ions

From the analysis of the Z2G1 granules recovered from the incubation cores, it is clear that particle size of the granular material has a strong influence on the efficiency of Z2G1 to bind P, with the finer material being around 50% more efficient than the coarser material. Based on the efflux of P from the anoxic untreated sediments of up to 38 mg m^{-2} day^{-1}, and the additional reduction in P from the water column of up to 15 mg m^{-2} day^{-1}, Z2G1 has a P-uptake rate of at least 53 mg m^{-2} day^{-1}.

This P-uptake rate would be effective on lakes in New Zealand and around the world with similar sediment P release rates. For example, Burger et al. (2007) measured P release rates of 2.1–85.6 mg P m^{-2} day^{-1} in nearby Lake Rotorua (mean rate 44 mg P m^{-2} day^{-1}), values which included both seasonal changes and differences between sites at different depths. White et al. (1978) also estimated a mean sediment P release of $\sim$44 mg m^{-2} day^{-1} in Lake Rotorua. Penn et al. (2000) measured seasonal variations in P release rates of 3–38 mg P m^{-2} day^{-1} in hyper-eutrophic Onondaga Lake, USA. The similarity in P release rates from these three lakes is consistent with P release being limited by the rate of diffusion across the sediment–water interface (Perkins & Underwood, 2001).

The zeolite substrate in Z2G1 also absorbed NH_4^+ from water and this was seen in the NH_4-N flux data. The aerobic results showed that Z2G1 absorbed a mean of 40 mg NH_4-N m^{-2} day^{-1} from the overlying water across all treatments, but with apparently higher absorption rates by the <1 mm than the 1–3 mm grain size material, however, not statistically significant. Addition of NO_3-N to the incubation water almost doubled the NH_4-N absorption rates to around 75 mg m^{-2} day^{-1} with maximum values of >100 mg m^{-2} day^{-1}, and induced a comparable reduction of NH_4-N in the controls. The extra NH_4-N reduction in the presence of high NO_3-N concentrations is consistent with coupled nitrification–denitrification.

However, while these results show that nitrification is occurring, they do not show whether there has been suppression of the nitrification by the Z2G1. As nitrification biochemically oxidises NH_4-N to NO_3-N, an adverse effect on nitrification would result in an increase in NH_4-N in the water column. Any increase in NH_4-N in these experiments was masked by the uptake of NH_4-N by the zeolite substrate.

Under anoxic bottom water conditions, nitrification and thus denitrification would not be expected at the sediment–water interface (Downes, 1988), and the DIN released from the sediments would all appear as NH_4-N, as seen in the controls where the NH_4-N efflux was up to 212 mg m^{-2} day^{-1}. Notwithstanding this, the Z2G1 capping layers absorbed all of the NH_4-N released from the sediments as well as additional NH_4-N from the water column. These results indicate that Z2G1 could absorb NH_4-N at up to almost 300 mg m^{-2} day^{-1} under anoxic conditions. As the NH_4-N absorption capacity of the Z2G1 was not tested, it is uncertain how long this uptake would continue. A best estimate from this study would indicate an NH_4-N absorption capacity of around 4.5 mg NH_4-N g^{-1} Z2G1, which is comparable with other New Zealand zeolites (e.g. Nguyen & Tanner, 1998).

Potential effects of sediment capping on benthic fauna

While not specifically part of this study, it is important to recognise that excessive applications of capping materials are undesirable as they may cause unexpected effects such as Fe release from the sediments (Douglas et al., 2008). Low dose rates based on laboratory estimates of the internal P load were preferred because these are sufficient to bind the P release without smothering sensitive benthic biota, an unacceptable ecological outcome. These comments are supported by a study by Vopel et al. (2008), who showed that excessively thick capping layers (>2-mm), caused the reduction–oxidation (redox) boundary to move out of the sediment into the capping layer thus completely blocking oxygen diffusion into the sediment. The sediment immediately below the capping layer became anaerobic, which would smother infauna, and had the potential to release metals and sulphides which could diffuse out of the capping layer. Vopel et al. (2008) also tested Z2G1 at a range of dose rates with a dose rate of 400 g m^{-2} of <125 μm sieved Z2G1 producing a layer about 2 mm thick. This suggests that the <1 mm grain size, 350 g Z2G1 m^{-2} treatments in this study probably had a thickness of around 2 mm, and thus were at the top end of an acceptable dose rate range without causing adverse effects on benthic fauna. However, in other studies, it was found that macrozoobenthic organisms were not affected by layer thickness of calcite and applications achieving up to 5 mm were taken into consideration to compensate for possible mechanical instability of the capping agent (Berg et al., 2003).

The implications from the different grain size results are that the larger granules did not completely block oxygen diffusion into the sediment and thus would be less likely to smother benthic biota. They would also settle faster and make application of the capping layer to selected areas of lake bed more precise. Low residence time of the material in the water column could also be beneficial in reducing the impact on zooplankton. Kirk & Gilbert (1990) for example showed that population growth rate of rotifers was reduced by coarse clay in the water column.

However, the greater density of coarse grain size capping agents could cause them to sink into sediment where the surface has a nepheloid layer, potentially rendering them ineffective as a capping layer. Consequently, a lower dose rate of the <1 mm grain size material could be as effective as the 350 g m^{-2} dose rate used in these tests, as it would be less likely to completely block oxygen diffusion and less likely to sink into the sediments, while retaining a relatively rapid settling rate.

Potential effects of sediment capping on denitrification

Under aerobic conditions, any NO_3-N in the overlying water in contact with the anoxic sediments would most likely be removed by denitrification (e.g. Downes, 1988). Consequently, the loss of NO_3-N from all incubation chambers under aerobic conditions is consistent with denitrification. The addition of high NO_3-N concentrations produced a larger reduction in NO_3-N confirming denitrification activity and indicating that the denitrification potential of

the Lake Okaro sediments was in excess of 30 mg N m^{-2} day^{-1}.

Any adverse effect on denitrification by the Z2G1 capping layer would be expected to result in a reduction in the rate of removal of NO_3-N under aerobic conditions. Comparison of the mean denitrification potential values shows a highly significant dose-rate effect with lower potentials in the 700 g m^{-2} than in the 350 g m^{-2} treatments at around 35 and 50% for the <1 mm and 1–3 mm grain size, respectively. Although not conclusive, this dose rate and thus layer thickness-dependent reduction in denitrification indicates partial suppression of denitrification by the Z2G1-capping material. While the Z2G1 may only be affecting the denitrification microbial community, it is more likely that the nitrification microbial community was also being affected.

The implication of a 50% reduction in denitrification means that additional N would be available in the water column for algal production. This effect may have been the cause of an increase in NH_4-N concentrations for a short period after an Alum application to Lake Okaro (Paul et al., 2008). As the apparent suppression effect occurred under aerobic conditions in the laboratory, it may be very important to avoid application of this, or any other capping material, to the permanently aerobic zones of a lake, such as the littoral zone. Consequently, accurate application of the capping material on the lake bed is very important.

Effect of Z2G1 on metal fluxes

A vertical shift of the redox boundary into the sediment capping layer could potentially lead to the release of redox-sensitive metals that are mobile under anaerobic conditions (Himmelheber et al., 2008). Although the layer thickness of the Z2G1-capping material had the potential to enhance metal mobilisation from the sediments, there was little or no effect on metal fluxes from the sediments under aerobic or anoxic conditions. A small increase of 0.005 and 0.013 g m^{-3} in Al under aerobic and anoxic conditions, respectively, from the 350 g m^{-2} of the <1 mm grain size treatments was not seen in the other treatments, including the higher dose rates. The lack of significant changes in metal concentrations in the overlying water column, even under anoxic conditions, may be attributed to the zeolite substrate which is a good cation absorber. The Al content in the Z2G1 recovered from <1 mm grain size treatments was variable, but higher than in the new Z2G1, consistent with Z2G1 absorbing Al from the sediments. Apart from P, Z2G1 absorbed a range of metals from the sediment including Fe, Al, As, Hg and K. Reduction in Na, Ca and Mg content indicates an ionic exchange process may also be occurring between the zeolite substrate and the geothermally influenced sediments. These exchanges may also reflect the soft water and low alkalinity characteristics of Lake Okaro.

In this study, we found Lake Okaro sediment contains about 2 g P kg^{-1} dry weight, which is consistent with other studies (e.g. Trolle et al., 2008) and gives a potential P load of about 0.78 g P m^{-2} per cm thick layer. With a P-binding capacity of around 20 g P kg^{-1} dry weight, the Z2G1 application rate of 350 g m^{-2} is capable of absorbing about 7 g P m^{-2} of sediment, which is equivalent to all of the P in the top 8 cm of sediment, assuming a uniform P content. However, as the majority of P released for internal loads has been found to come from the top 4 cm of the sediments (e.g. Cooke et al., 2005; Heggie et al., 2008), the dose rate of 350 g Z2G1 m^{-2} may be up to twice the required treatment rate for Lake Okaro. However, P releases have also been shown from sediment depths of up to 20 cm (Søndergaard et al., 2003), but these contribute only a small part of the total P release.

The relative sediment coverage by the different grain size Z2G1 particles at the same dose rates showed that capping material particle size was important. While the larger particle size increased the settling rate and thus improved the ability to apply Z2G1 to selected areas of a lake bed, it reduced the coverage of the sediment per unit mass of material applied. The degree of sediment coverage affected the efficiency of the capping layer. Both grain size treatments completely blocked the release of P from the sediments indicating that the larger grain size granules could absorb P released from the sediments across the gaps between the granules. However, subsequent analysis of the Z2G1 granules recovered from the sediments showed that the <1 mm grain size material had absorbed around 50% more P than the 1–3 mm grain size material over the 14-day incubation period. This greater P absorption is consistent with the expected higher P-removal efficiency by finer

material. However, as no P was released from either grain size treatments, the extra P in the <1 mm grain size treatments implies a faster P release with the more complete coverage. This is also consistent with the blocking of oxygen diffusion into the sediments and the movement of the redox boundary into the <1 mm capping layer, as suggested by Vopel et al. (2008).

Conclusions

This study shows that the Z2G1 P-inactivation agent is an effective sediment capping material which completely blocked the release of P from the sediments under anoxic conditions, at the dose rates tested, on sediment cores in the laboratory. It also retained the cationic characteristics of the zeolite substrate, adsorbing some metals including As and Hg, as well as NH_4^+ from the water in contact with it and completely blocked the release of NH_4-N from the sediments at the dose rates tested. Consequently, Z2G1 is the only known sediment capping agent that inactivates both P and N.

The study results indicate a potential for Z2G1 to inhibit nitrification and denitrification under aerobic conditions. This means that Z2G1 could enhance N retention in the lake, if it was applied in the permanently aerobic zones (e.g. littoral zone) of a lake. This would be especially important in Lake Okaro where the narrow permanently aerobic littoral zone above 5 m is the only habitable area of lake bed for most of the year. In order to protect that habitat, any sediment-capping agent would need to be applied only to the lake bed below 5 m. This would require great precision in the treatment of the lake. Given that the granular nature of Z2G1 allows it to settle very quickly through the water column, Z2G1 will be more easily applied to that targeted zone than Alum or most other P-inactivation agents.

While the results from this laboratory incubation study indicate that Z2G1 has high potential for reducing the internal P and N loads from a lake when used as a sediment capping agent, it is not possible to extrapolate from these results to a whole lake situation with certainty. Consequently, Z2G1 needs to be tested in a whole lake study to give more clear conclusions about its usability as a lake restoration method, and the long term effects (several or many years) of an addition should also be investigated.

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