
P-inactivation efficacy of Z2G1 as a capping agent on Lake Okaro sediment



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Executive Summary

Environment Bay of Plenty is committed to the long-term management of the water quality of the major recreational lakes in the Bay of Plenty region and the restoration of those lakes that have become degraded through excessive inputs of nitrogen (N) and phosphorus (P) from catchment development. As part of the restoration process for Lake Okaro, a whole-lake treatment is planned using the P-inactivation agent Z2G1, a modified zeolite with aluminium developed by Scion and made by Blue Pacific Minerals, to reduce the dissolved reactive phosphorus concentrations in the lake's water column in summer and thus the development of summer algal blooms of blue-green algae.

Environment Bay of Plenty contracted NIWA to independently evaluate the efficacy of the Z2G1 as a P-inactivation agent, and to identify any adverse effects. This report presents the findings of a laboratory study using lake sediment in flow through incubation tubes to test the efficacy of two application rates of Z2G1 under aerobic and anoxic conditions. The experimental design included nutrient additions of dissolved reactive phosphorus and nitrate nitrogen in the flow through water to determine the rate of P removal from the overlying water and whether the microbial functions of nitrification and denitrification were adversely affected by the presence of a thin layer of the Z2G1 on the sediment surface.

It was found that the thin layer of Z2G1 on the sediment surface altered the biogeochemistry of the sediment-water interface, as would be expected from any capping agent. The study results and effect of the changes are summarised as follows:

- Z2G1 was designed to take up P and thus represented a zone of “zero” P concentration on the sediment surface. As the efflux of DRP out of the sediment is driven by concentration gradients, the Z2G1 layer acted as a sink adsorbing P from the sediment. Similarly, P was removed from bottom water in contact with the Z2G1 layer.
- The rate of P uptake by the Z2G1 layer appeared to be limited by the availability of DRP in the pore water and thus the measured uptake rate of $30 \text{ mg P m}^{-2} \text{ d}^{-1}$ may be the mineralization rate of organic P in the Lake Okaro sediments used in this study.
- The estimated P load in the top 20 mm of Lake Okaro sediments was 1.56 g m^{-2} . At the suggested application rate of 350 g m^{-2} the P uptake would need to be 0.45 g per 100 g Z2G1 or 4.5 g P kg^{-1} which is substantially less than the theoretic adsorption capacity of 50 g P kg^{-1} .
- The diffusion of oxygen into the sediment was reduced through the Z2G1 layer to less than sediment oxygen demand allowing the sediment to become anoxic immediately below the Z2G1 layer.

- Surface deposits of Z2G1 increase the concentrations of hydrogen sulphide in the pore water of the uppermost sediment. Deposits of 700 g m^{-2} of the 1-3 mm grain size Z2G1 particles cause a diffusive flux of hydrogen sulphide from the uppermost sediment pore water into the overlying bottom water. At the suggested application rate of 350 g m^{-2} , efflux of hydrogen sulphide is unlikely to occur.
- There appeared to be no hidden problems with Z2G1 interfering with the nitrification-denitrification cycle. The strong oxygen gradients across the sediment-water interface appeared to be beneficial to the removal of $\text{NO}_3\text{-N}$ and may be responsible for the major reduction in the $\text{NH}_4\text{-N}$ concentrations observed.
- It is likely that ebullition of methane gas from within the sediments will cause local areas of disruption of the thin deposit of Z2G1 on the sediment surface and may reduce its efficiency as a P-inactivation agent.

From the results of this study it is reasonable to conclude that the application of Z2G1 will reduce the P load regenerated from the sediment. Extrapolation from the sediment cores collected from this study suggests that the reduction in DRP concentrations in the lake water column is likely to be large.

The results of this study also indicate that there is scope for a reduction in the application rate of Z2G1 by at least 50%.

1. Introduction

Environment Bay of Plenty is committed to the long-term management of the water quality of the major recreational lakes in the Bay of Plenty region and the restoration of those lakes that have become degraded through excessive inputs of nitrogen (N) and phosphorus (P) from catchment development. Although many of the degraded lakes are sensitive to N, both N and P loads need to be reduced in order to restore the lake water quality. Furthermore, because N can be permanently removed from the lake by the microbial processes of coupled nitrification and denitrification, there is often a disproportionately high internal load of P released from the sediments of the Rotorua lakes which negates the benefits of controlling the external loads.

Management strategies overseas 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 bottom water anoxia. The P-inactivation agent of choice is Alum (aluminium sulphate) which is easy to apply but has the potential to raise aluminium (Al) concentrations to toxic levels in the water column at low pH. An initial low-dose alum addition to Lake Okaro in December 2003 had limited success (Quinn et al. 2004). A new product developed by Scion and manufacture by Blue Pacific Minerals is a modified zeolite, Z2G1, which carries the P-binding agent, Al, and is thus less likely to raise the Al concentrations in the water column. Environment Bay of Plenty has decided to use this product on Lake Okaro as a “whole lake” trial to assess whether Z2G1 could be used in the restoration of other Rotorua lakes, including Lake Rotorua.

In late August or September 2007, Lake Okaro is to be treated with 100 t of Z2G1, which equates to a nominal application rate of 350 g m⁻² across the whole lake bed. While Scion have produced results which indicate that this rate will be effective, as part of the trial monitoring programme, Environment Bay of Plenty has contracted NIWA to independently evaluate the efficacy of the Z2G1 as a P-inactivation agent, and to identify any adverse effects.

1.1 Background

In 2006, a study by visiting scientist to University of Waikato, Mark McCarthy, measured differential effluxes of dissolved reactive phosphorus (DRP) from the sediments of Lake Rotorua as a function of depth and oxygen concentration. Effluxes ranged from <10 µmol P m⁻² h⁻¹ in the inshore waters up to 60 µmol P m⁻² h⁻¹ below 20m water depth under conditions of anaerobic bottom water. Using additions of

nitrate-nitrogen ($\text{NO}_3\text{-N}$), he also determined that there was a similar spatial difference in denitrification rates with N losses ranging from $100 \mu\text{mol N m}^{-2} \text{h}^{-1}$ in the inshore waters to around $250 \mu\text{mol N m}^{-2} \text{h}^{-1}$ below 20 m under anaerobic conditions. These experiments were conducted on un-modified sediment cores incubated in the laboratory under a continuous flow regime.

These findings demonstrated that lake-bed processes are important in controlling lake N removal as well as P release.

Observations from Lake Taupo after the 1995-6 Mount Ruapehu eruptions indicated that, while the fine ash (allophane) stripped all P from the water column and temporarily stopped P-release from the sediments. The ash was also thought to have eliminated the microbial community associated with nitrification of ammoniacal-nitrogen ($\text{NH}_4\text{-N}$) released from the sediments, as $\text{NO}_3\text{-N}$ disappeared from the lake water column. This effect lasted for about 12 months before $\text{NO}_3\text{-N}$ was detected in the lake again and it took about 8 years for the lake chemistry to return to the pre-eruption levels (Gibbs 2006), and for the microbial community to recover sufficiently to nitrify all of the $\text{NH}_4\text{-N}$ released from the sediments in Lake Taupo.

These observations suggest that applications of flocculation agents, designed to remove DRP from the water column and block DRP release from the sediments, may also adversely affect microbial communities within the lake.

The 2003 Alum trial in Lake Okaro showed a similar response with a sudden increase in $\text{NH}_4\text{-N}$ immediately following the dosing and a subsequent algal bloom. Without the experience from Lake Taupo, the occurrence of this bloom may have been passed off as unfortunate timing for a bloom that was already developing. While this may still be a valid explanation, the correspondence between the addition of a flocculation agent in these lakes and the appearance of $\text{NH}_4\text{-N}$ under conditions that should have converted it to $\text{NO}_3\text{-N}$ indicates that the flocculation agent may have adversely affected the microbial community, and most probably the nitrifying bacteria.

The loss of the nitrifying microbial community or reduction in nitrification efficiency would be critical to the natural removal of N from the lake through denitrification. This process may account for >50% of the N removal from the lake on an annual basis. If the addition of any P-inactivation agent has a similar effect on the microbial communities in the Rotorua lakes, this nitrogen would remain in the lake and the additional N in the readily available form of $\text{NH}_4\text{-N}$ would be likely to stimulate and sustain increased algal biomass unless all the P was removed by the flocculation agent.

The mechanism apparently affecting the nitrifying bacteria is not understood. It may be simply a toxicity issue confined to just that microbial assemblage or it may extend to sediment-water boundary diffusion or REDOX issues which also affects the mobilisation of sediment bound trace minerals such as Fe, Mn, Al, As, and Zn etc.

1.2 P-inactivation agent

At a meeting of the Sediment Processes Committee at University of Waikato (19 February 2007), two formulations, based on grain size, of the new P-inactivation agent, Z2G1, were presented by Scion, a 1-3 mm granule and a mixed <1.0 mm granule/powder. As both formulations would settle rapidly, it was decided that these products were better suited to a sediment capping application rather than a flocculation application. The difference between these two uses is the timing of application. Flocculation agents need to be applied when the lake is stratified and P levels are high in the water column so that they can be bound by the P-inactivation agent as it flocculates and sediments. Sediment capping agents need to be applied when the lake is mixed and the P is mostly confined to the sediments so that it can bind the P being released from the sediment and prevent it from diffusing up into the lake. Consequently, the application of Z2G1 to Lake Okaro would be at the end of August or beginning of September, just before thermal stratification began.

This study was designed to evaluate the efficacy and stability of the two formulations of Z2G1 applied as a sediment capping material at the proposed rate plus double that rate and to assess the effect on the microbial community in terms of nitrification, denitrification, as well as mineral mobilisation. The different treatment rate assessments were considered especially important given the lack of knowledge of the efficacy of the Z2G1 P-inactivation agent in a non iron-based geological system.

1.2.1 Objectives

Objective 1: Determine the efficacy of the Z2G1 as a P-inactivation agent on Lake Okaro sediments by (i); evaluating the efficacy of phosphate removal by Z2G1 from the sediment-overlying lake water under aerobic conditions and (ii); by evaluating the efficacy of Z2G1 at blocking phosphate release from the sediments under anaerobic/anoxic conditions

Objective 2: Identify potentially "toxic" side effects of a Z2G1 application to the lake sediments including the release of toxic metals (e.g., arsenic); trace metals that could stimulate cyanophyte growth (e.g., zinc); and any substantial modification of the microbial nitrification denitrification process. Note that toxicity testing to sediment

and water column biota is a separate issue and excluded from this study (see Martin & Hickey 2007).

2. Methods

Lake Okaro (Fig.1) was sampled on 6 June 2007 under relatively calm conditions with a 5-10 knot S-W breeze ahead of a forecast storm. The lake was in the process of mixing and a dissolved oxygen (DO) and temperature profile (Fig. 2) showed that the water column was essentially isothermal with DO saturation levels of around 60% down to 10 m, declining to around 18% at 13 m, the sediment sampling depth. Although there was no smell of hydrogen sulphide in the lake water, there was a hydrogen sulphide smell from the sediment. There was also a strong musty smell of cyanophytes in the air above the lake (See section 6, Health & Safety).

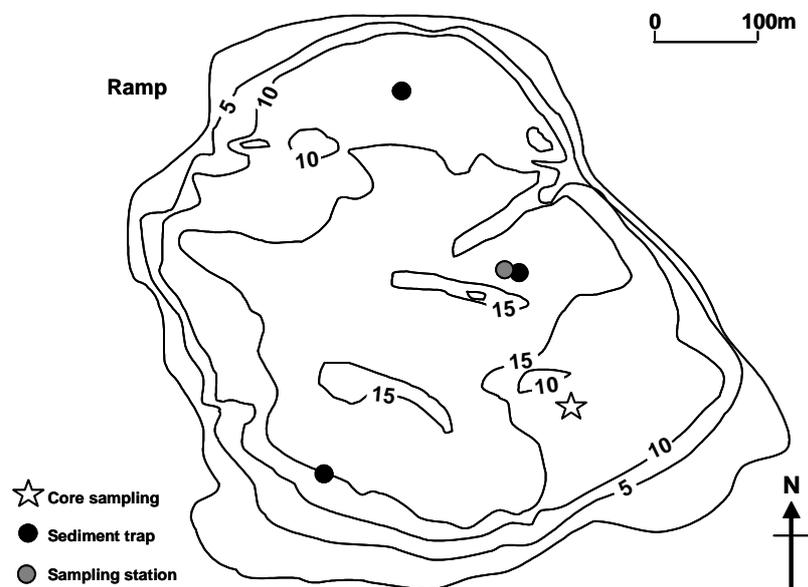


Figure 1: Lake Okaro site map showing the position from which the cores were collected (Star) relative to other lake monitoring positions used by the University of Waikato. This position was thought to be sufficiently distant from the sediment trap sites that it would not interfere with the traps.

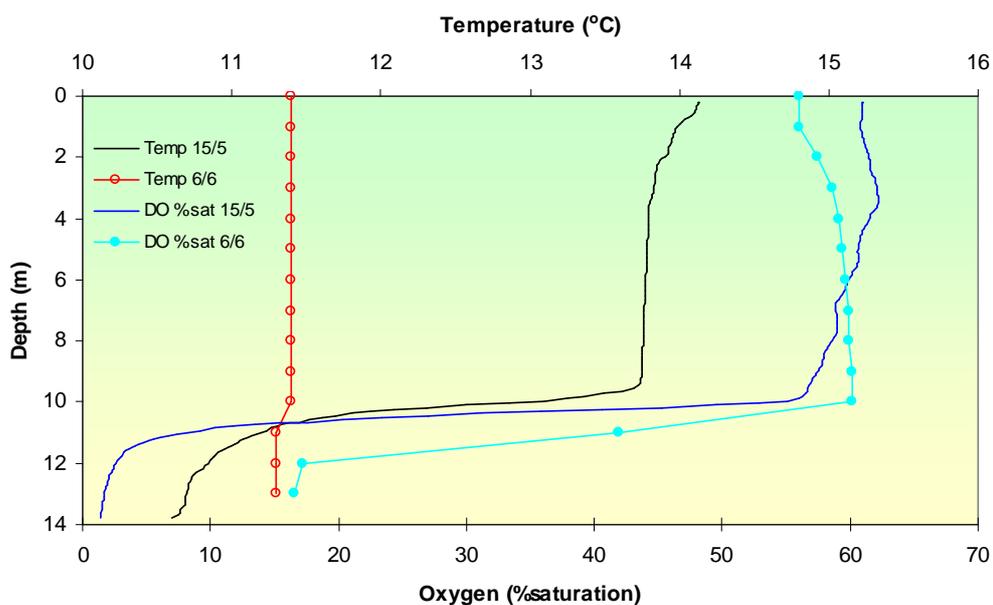


Figure 2: Temperature and oxygen (%saturation) profiles in Lake Okaro on the sampling date compared with profiles collected 3 weeks earlier. Upper water column oxygen saturation was comparable but the bottom water had oxygenated by about 18% by 6 June 2007.

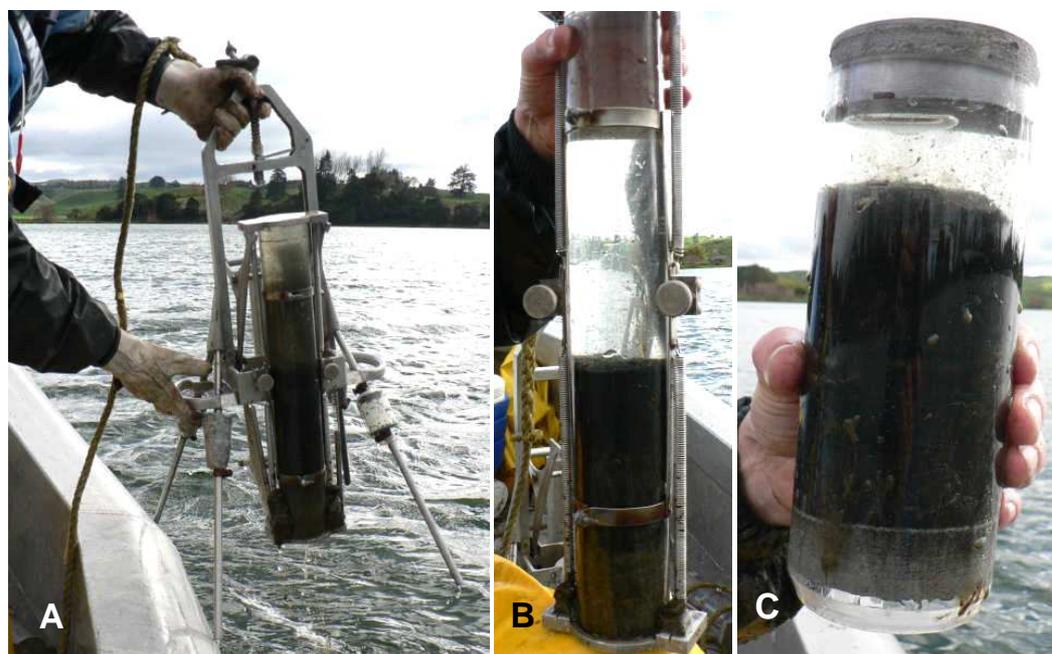


Figure 3: Photographs showing (A) a Jenkins corer being retrieved from Lake Okaro, and (B) a sediment core. Note the clear bottom water and the undisturbed sediment-water interface. (C) The sediment-water interface, after transferring from the corer tube to the incubation tube, was still essentially undisturbed.

2.1 Sediment and lake water collection

Surficial sediment samples (70 mm ID) were taken across the sediment-water interface with a Jenkins Corer (Fig. 3A) which is designed to take an undisturbed core (Fig. 3B). The sediment core was transferred to an incubation tube (Fig. 3C) by using a piston rod to push the core up and out of the corer sampling tube and into the incubation tube via a sectioning device attached to the top of the corer tube. Before transfer, the overlying water in the corer tube was sampled for nutrient analysis. Thereafter, a high-density plastic foam plug with a vent hole was inserted into the top of the incubation tube. The excess overlying water was displaced through the vent hole until the surficial 10 cm of undisturbed sediment was in the incubation tube. The sectioning device slide was closed and the corer tube removed, emptied, and rinsed. A non-vented high-density plastic foam plug was fitted into the top of the corer tube and the sectioning device, with the incubation tube still in place, was re-attached to the top of the corer tube. The foam plug was pushed into the bottom of the incubation tube using the piston rod after the sectioning device slide was opened. The loaded incubation tube was then removed from the sectioning device and stored vertical in a plastic milk crate inside a large chilli-bin filled with lake water, for transport to the laboratory.

About 400 litres of surface lake water was collected in four 100-litre plastic drums lined with large plastic bags (“Wheely-bin” liners) and sealed with water-tight lids.

2.2 Experimental design

Unfortunately, due to a combination of vibration during transport, warming, and reduced pressure causing degassing, several cores were highly mixed by the time they reached the laboratory. Consequently, it was decided to completely mix all the cores and allow them to stand for several days under aerobic lake water in the dark to equilibrate and oxidise before starting the experiment (Fig. 4A). The decision was also made to run the experiment at early summer temperatures to accelerate sediment processes and thus enhance the nutrient efflux.

2.2.1 Flow through system

Two batches of 13 incubation tubes (with top plugs removed) were set up in milk crates submerged in lake water in a controlled temperature room at 16 °C in the dark. One further incubation tube without sediment was included with one batch of tubes to act as a “material only” control. The incubation tubes were allowed to equilibrate with oxygenated water for 5 days before being treated with Z2G1 (Fig. 4B), recapped with the vented high-density foam plugs, and connected to a “flow-through” incubation system (e.g., Miller-Way & Twilley 1996; McCarthy & Gardner 2003).

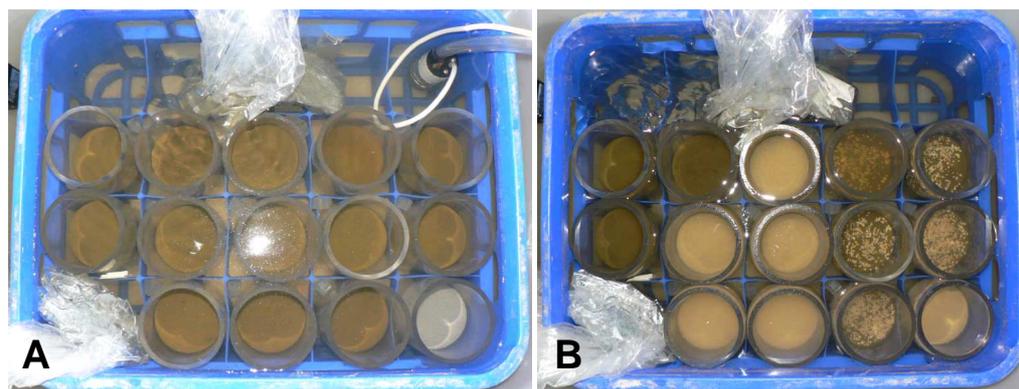


Figure 4: Incubation cores showing (A) brown sediment surface after 5 days of oxidation, and (B) the spatial distribution of the Z2G1 after application. The incubation tube order is apparent in Figure 6A. Note the bottom right hand incubation tube has no sediment and was used as the material control (blank). Plastic bags contain lead weights to hold the crates down against the buoyancy of the foam plugs in the bottom of each tube.

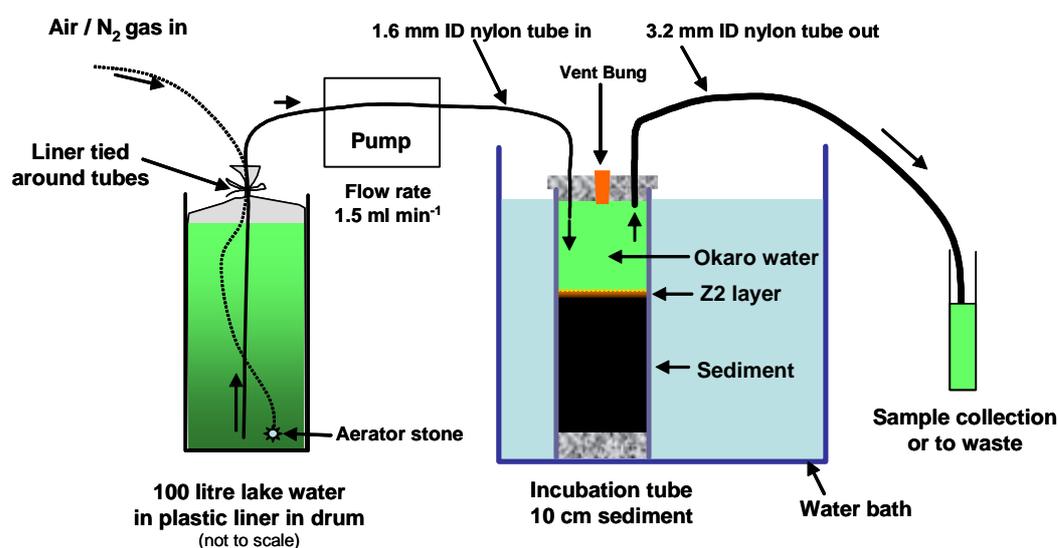


Figure 5: Schematic of flow through system (not to scale and only one tube shown). Each incubation tube had 100 mm sediment and 70 mm overlying water. Water volume = 270 mL and, at a flow rate of 1.5 mL min^{-1} , it was exchanged every 3 hours.

The flow through system (Fig. 5) used a separate multi-channel peristaltic pump for each batch. Each pump channel drew water from a single bulk supply (100-litre drum) and delivered it at 1.5 mL min^{-1} , via a narrow bore hard nylon tube through the foam plug, into the cavity above the sediment. Another larger-bore hard nylon tube through the foam plug provided the exit for this water after the vent hole was sealed with a rubber bung (Fig. 6A). The exit water from each incubation tube was either sampled for analysis of nutrients and trace metals (Fig. 6B) or allowed to run to waste.

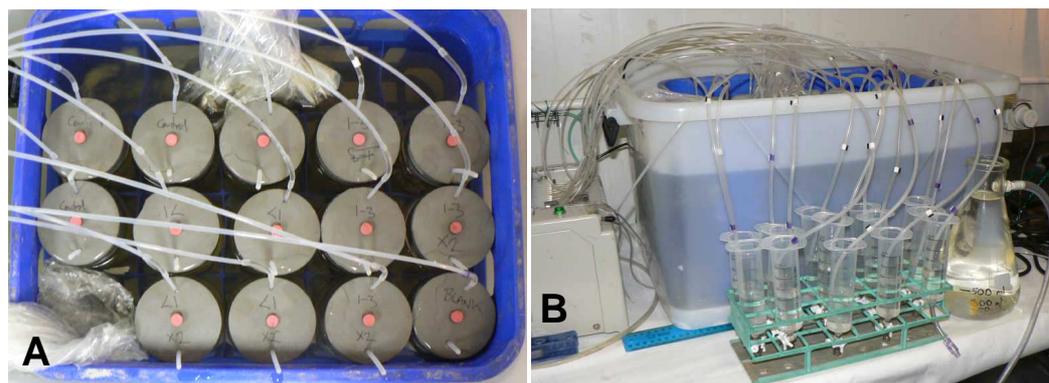


Figure 6: (A) Capped incubation tubes with inflow and out flow tubes fitted and the vent holes sealed with a rubber bung. Note the labelling is for the treatment and corresponds to Figure 4B. (B) The flow through system during a collection. All incubation cores were sampled simultaneously. After sample collection, the outlet extension tubes were fed into a flask which had an overflow outlet to waste.

2.2.2 Treatments

The Z2G1 was sieved to provide a <1 mm fraction and a 1-3 mm fraction. At 100 t for the whole lake, the estimated Z2G1 loading was about 350 g m⁻² which translated to 1.35 g per incubation tube. The two batches of sediment incubation tubes were treated in the same way: 3 tubes as controls, 3 tubes with 1.35 g of <1 mm Z2G1, 2 tubes with 2.7 g of <1 mm Z2G1, 3 tubes with 1.35 g of 1-3 mm Z2G1, and 2 tubes with 2.7 g of 1-3 mm Z2G1. The material-only tube was treated with 2.7 g of <1 mm Z2G1. (See Fig. 4B for the spatial distribution of the Z2G1 after application).

The experiments were run in paired batches with natural lake water (Table 1) and spiked lake water being run under aerobic conditions first, then being rerun under anoxic conditions, giving a total of 4 experimental runs. The spike solution was made by dissolving 0.1 g of NaH₂PO₄·2H₂O and 1.44 g of KNO₃ in a small volume of deionised water (DIW) which was added to a bulk 100-litre drum of lake water to give a nominal concentration of 200 mg m⁻³ of DRP and 2000 mg m⁻³ of NO₃-N.

Aerobic conditions were maintained by bubbling outside air through the bulk water in two of the drums, one of which was spiked. Anoxic conditions were achieved by bubbling oxygen-free nitrogen gas through the water in the other two drums, one of which was spiked. The top of the plastic bags lining the drums of anoxic water were tied around the nitrogen gas line in and the water outlet line to the peristaltic pump to exclude air contact with the surface of the water in the drum and thus maintain a hypoxic atmosphere over the water.

Note that deoxygenating natural water with just nitrogen gas also removes the dissolved carbon dioxide (CO₂) and, in hindsight, CO₂ should have been bubbled through the water to compensate for this. Consequently, the pH of the anoxic water was around 8.6 compared with the aerated natural water at around pH 7.6.

Table 1: Nutrient concentration (mg m⁻³) in surface and bottom waters of Lake Okaro at the time of sediment collection, 6 June 2007.

	Nutrient concentrations (mg m ⁻³)		
	DRP	NH ₄ -N	NO ₃ -N
Surface	31	409	69
Bottom	185	2967	0

2.3 Sampling

The inflow and outflow water from each incubation tube was sampled daily including just before analysis of all samples on the final day of the aerobic and anoxic runs. Water samples for nutrient analyses were filtered immediately and stored frozen except for the final samples which were analysed immediately after filtration. Water samples for trace metals were filtered and preserved with distilled nitric acid and sent to RJ Hill Laboratories for analysis of total dissolved metals.

At the end of the flow-through experiments, microprofiles of oxygen and H₂S were measured normal to the sediment surface from a position above the sediment surface to a maximum depth of 20 mm. Profiles were measured in one incubation tube from each treatment. From other replicate incubation tubes, the Z2G1 layer was removed from the sediment surface by suction (Fig. 7) for analysis separate from the upper 20 mm of sediment. The Z2G1 was washed with DIW using two cycles of constant shaking for 10 minutes then centrifugation at 4000 rpm for 10 minutes. The supernatant water was discarded between cycles and replaced with fresh DIW.

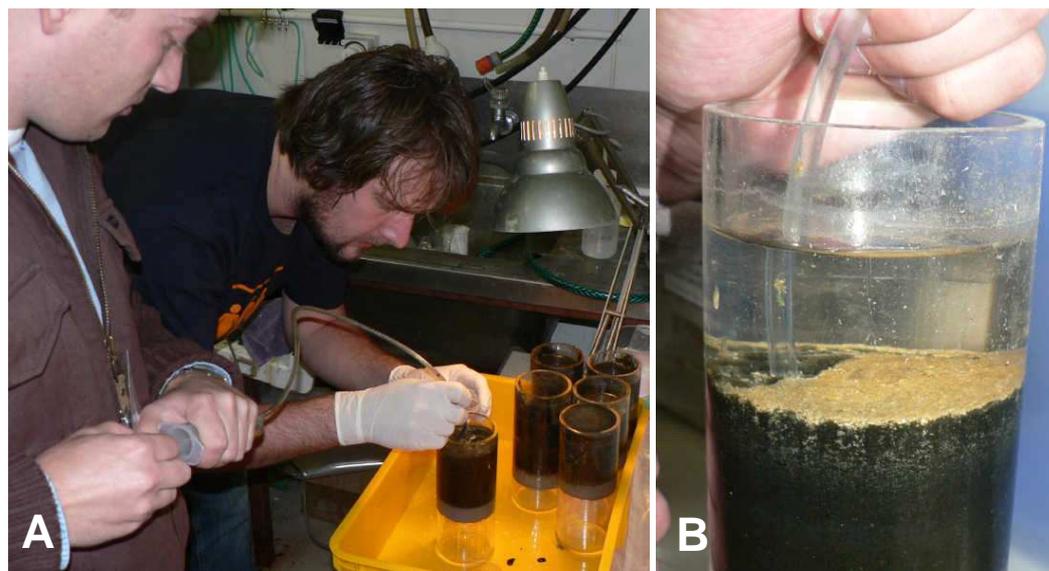


Figure 7: (A) Removing the layer of Z2G1 from the sediment surface in the incubation tube; (B) A close-up of the suction process at the sediment surface.

All samples were dried at 105 °C for 24 h, and homogenised by grinding with a mortar and pestle. Samples were then digested in aqua regia at 90 °C for two hours before analysis for metals and trace elements by ICP-MS.

2.4 Analyses

Time series water samples were analysed for DRP, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ on a Lachat flow injection analyser using standard methods. Time series water samples for total dissolved metals were analysed for iron (Fe), manganese (Mn), aluminium (Al), zinc (Zn), and arsenic (As) by ICP-MS. The extracted sediment and Z2G1 samples were analysed for 32 major and trace elements by ICP-MS but only the P data will be reported.

3. Results

With continuous flow incubations, the expectation is for an equilibrium to become established such that the differences in analyte concentrations between inflow and outflow in each incubation tube does not change over time. Consequently, the experiments were run for about 100 hours to allow the incubations to reach a steady state. The results were evaluated to confirm that a steady state had been reached and, in the aerobic experiments the data from the first two days were discarded as being an artefact of incubation tube disturbance before equilibrium was established. In the anoxic experiments, only the data from the first day was discarded as the incubation tubes appeared to have stabilised by day 2.

3.1 Water column

3.1.1 Nutrients

Data for DRP, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ in the flow through water from the 4 experiments, aerated natural lake water, aerated spiked lake water, anoxic natural lake water, and anoxic spiked lake water, are presented in a series of graphs of mean data from the 3 replicates (Figs. 8 and 9). These graphs show the outflow relative to inflow concentrations for each of the treatments from day 3 to day 5 of the aerobic experiments, and day 2 to day 5 of the anoxic experiments.

Equilibrium is indicated where the time-series line is horizontal. A sloping line indicates a change was occurring for some reason. The steeper the slope the greater the change. For example, the $\text{NO}_3\text{-N}$ data from the anoxic spike experiment (Fig. 9) shows a rapid increase which is due to an oxygen leak into the bulk water after day 2. This was most likely caused by a tear in the plastic liner letting air into the headspace above the water in the drum, despite vigorous bubbling with oxygen-free nitrogen.

3.1.2 Metals

Total dissolved metal data are presented in Table 1 and show little difference between treatments. Note that the anoxic spike treatments were not completely anoxic after the first 2 days and the oxygen concentration had risen to around 20% saturation by day 5. We believe that this was caused by a tear in the plastic liner allowing air into the headspace above the bulk water.

3.1.3 Sediments and Z2G1

The concentrations of P in the Z2G1 removed from the treated incubation tubes relative to the original product in the two size fractions tested are presented in Figure 10. Concentrations of P in the upper 20 mm of sediment from the same incubation tubes relative to untreated sediments are also presented in Figure 10.

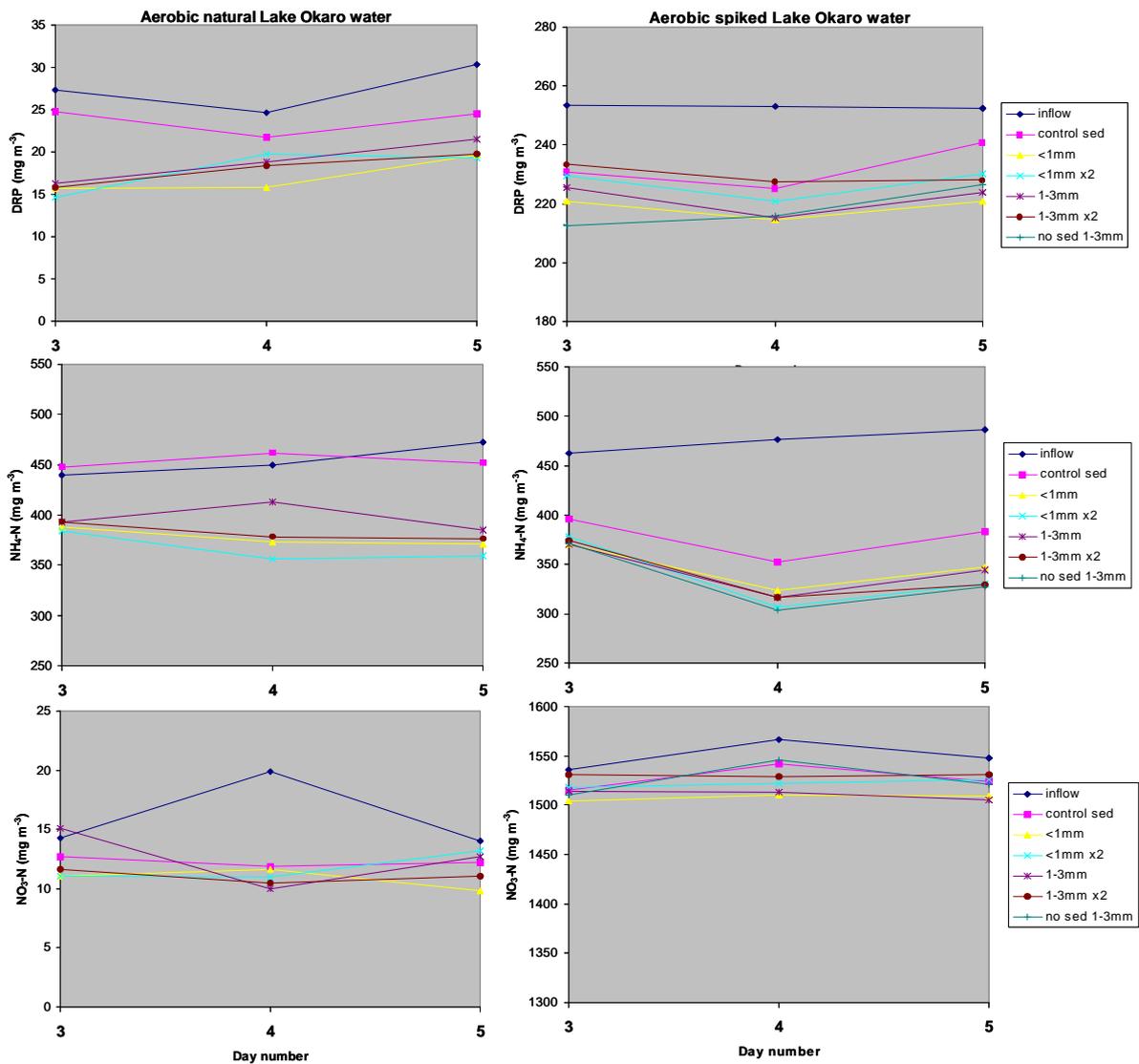


Figure 8: Graphs showing the nutrients results from the aerobic incubations in natural lake water and spiked lake water. The “no sediment” tube was in the spiked experiment. Values are the means of 3 replicate measurements, error bars are omitted for clarity.

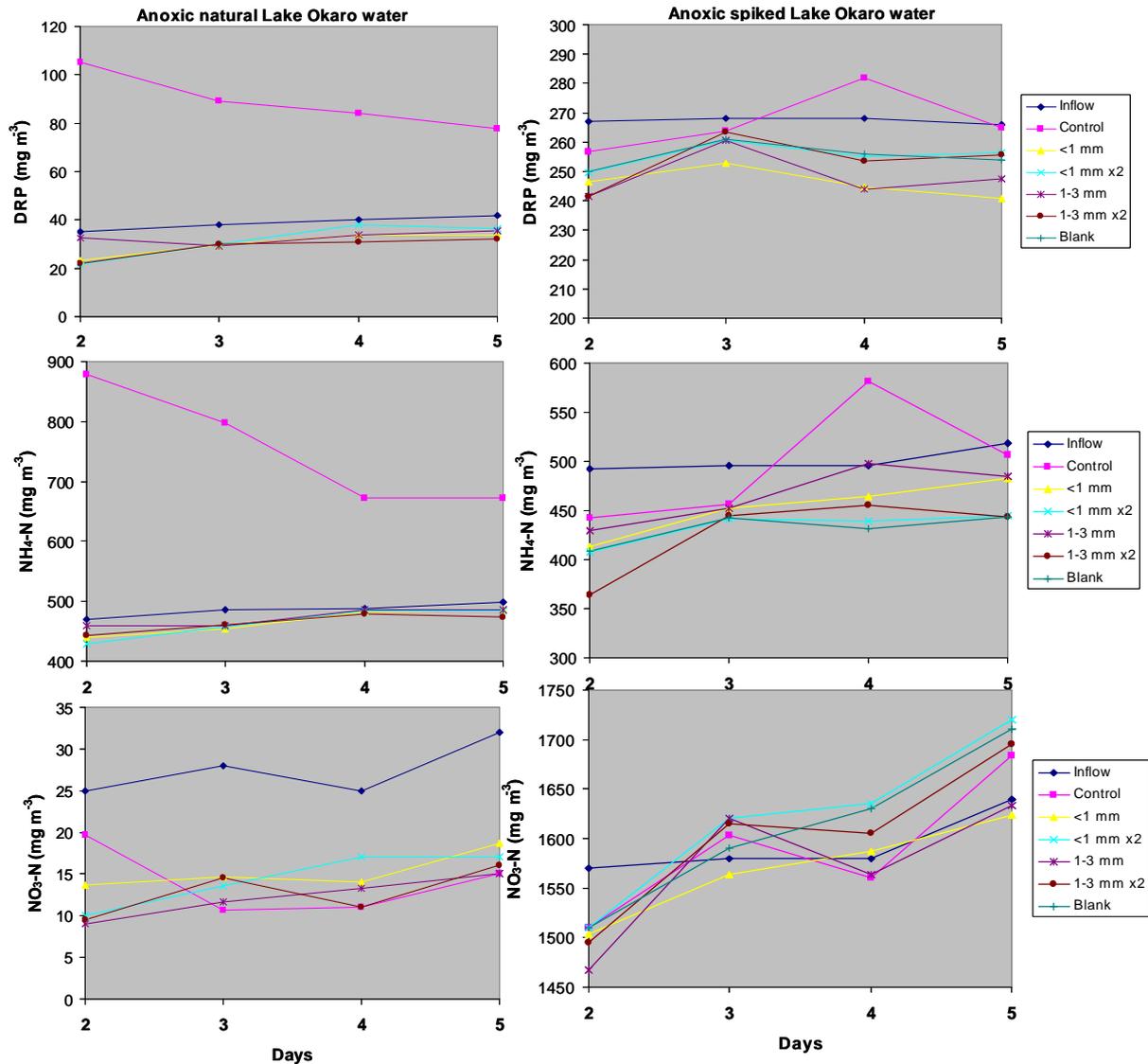


Figure 9: Graphs showing the nutrients results from the anoxic incubations in natural lake water and spiked lake water. The “no sediment” tube was in the spiked experiment. Values are the means of 3 replicate measurements, error bars are omitted for clarity. The spike experiment become hypoxic after day 2 –see text.

Table 2: Total dissolved metals concentrations in the outflow water relative to the concentrations in the inflow (lake surface) and lake bottom waters.

	Fe (g.m ⁻³)	Mn (g.m ⁻³)	Al (g.m ⁻³)	Zn (g.m ⁻³)	As (g.m ⁻³)	DO (% sat)	pH
Lake Okaro							
Surface water	0.027	0.002	0.013	0.127	0.003	56.50	
Bottom water	0.510	0.197	0.009	0.029	0.004	16.50	
Aerobic							
Control	0.027	0.002	0.013	0.127	0.003	92.10	7.70
<1 mm	0.027	0.003	0.018	0.088	0.003	87.40	7.69
<1 mm (x2)	0.030	0.005	0.014	0.070	0.003	89.00	7.65
1-3 mm	0.030	0.007	0.007	0.115	0.003	89.40	7.69
1-3 mm (x2)	0.033	0.004	0.011	0.068	0.003	90.20	7.63
Materials blank	0.037	0.003	0.022	0.095	0.003	89.10	7.62
Anoxic (natural)							
Control	0.068	0.018	0.023	0.061	0.004	<0.5*	8.10
<1 mm	0.025	0.010	0.036	0.055	0.003	<0.5*	8.30
<1 mm (x2)	0.020	0.006	0.009	0.025	0.003	<0.5*	8.20
1-3 mm	0.030	0.011	0.009	0.045	0.003	<0.5*	8.00
1-3 mm (x2)	0.027	0.009	0.008	0.030	0.003	<0.5*	8.00
Anoxic (Spiked)							
Control	0.025	0.005	0.006	0.036	0.003	22.00	8.50
<1 mm	0.030	0.018	0.010	0.036	0.003	22.10	8.52
<1 mm (x2)	0.023	0.006	0.010	0.012	0.003	22.80	8.63
1-3 mm	0.038	0.012	0.007	0.042	0.003	24.00	8.44
1-3 mm (x2)	0.025	0.006	0.006	0.012	0.003	25.00	8.59
Materials blank	0.020	0.002	0.011	0.018	0.003	24.00	8.73

* measured in bulk supply

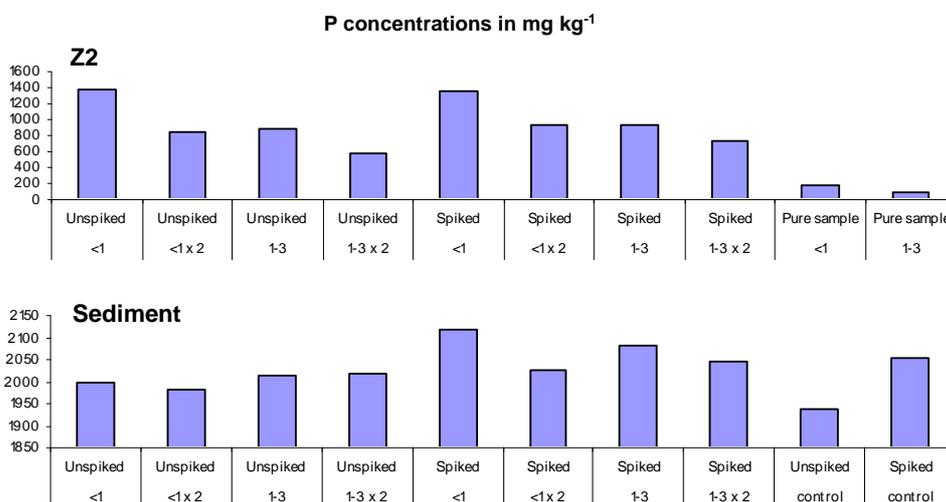


Figure 10: Phosphorus concentrations measured in the Z2G1 removed from the sediment in the incubation tubes relative to the original product, and in the upper 20 mm of sediment from the same tubes relative to the untreated controls.

3.1.4 Vertical microprofiles of dissolved oxygen and hydrogen sulphide

No oxygen and hydrogen sulphide microprofiles were measured in the sediment cores containing oxygenated bottom water and being treated with 350 g m^{-2} of Z2G1 particles $<1 \text{ mm}$ (Figs. 11A and 12A) due to disturbance by gas bubbles (ebullition).

Addition of only 350 g m^{-2} of 1-3 mm Z2G1 particles to the sediment cores resulted in a patchy surface deposit instead of a homogenous surface layer. The microprofiles in this treatment were measured between patches of Z2G1 surface deposit.

The surface of the sediment core-overlying water was in contact with the atmosphere during all microprofiling measurements. Consequently, diffusion of oxygen from the atmosphere resulted in a gradual oxygenation of those treatments that were previously deoxygenated.

Oxygen penetration depth and diffusive oxygen uptake

Our measurements in cores treated with Z2G1 at a rate of 700 g m^{-2} revealed that surface deposits of $<1 \text{ mm}$ Z2G1 particles had a larger effect on oxygen penetration depth (OPD) and diffusive sediment oxygen uptake (DOU) than the deposits of 1–3 mm Z2G1 particles (compare Figures 11B and D). Oxygen penetrated bare sediment $\sim 2.6 \text{ mm}$. Addition of a surface deposit of Z2G1 particles $<1 \text{ mm}$ (700 g m^{-2}) decreased the oxygen penetration by $\sim 0.5 \text{ mm}$ (19%). This lower penetration corresponds with a higher DOU indicated by a steeper oxygen concentration gradient in the $\sim 0.8 \text{ mm}$ -thick diffusive boundary layer (DBL) above the Z2G1 deposit (Fig. 11B).

Surface deposits of Z2G1 impede the diffusion of dissolved gases to a different degree than the underlying sediment does (K. Vopel, unpublished data). Such difference should cause a discontinuity in the slope of vertical concentration profiles of solutes that diffuse across the interface between the two substrates. Inspection of the oxygen concentration profiles in Figure 11 (black symbols), however, did not reveal such discontinuity indicating that oxygen did not diffuse to the depths of the lower boundaries of the Z2G1 surface deposits. The surface deposits of Z2G1 were apparently 2–3 mm thick so that diffusion of oxygen from the bottom water towards the underlying sediment oxygenated the pore water of the surface Z2G1 deposit but not necessarily the pore water of the underlying sediment. Consequently, the vertical position of the chemocline (interface between oxygenated and hydrogen sulphide containing sediment pore water) shifted upwards from a position at some depth in the sediment into the surface layer of Z2G1.

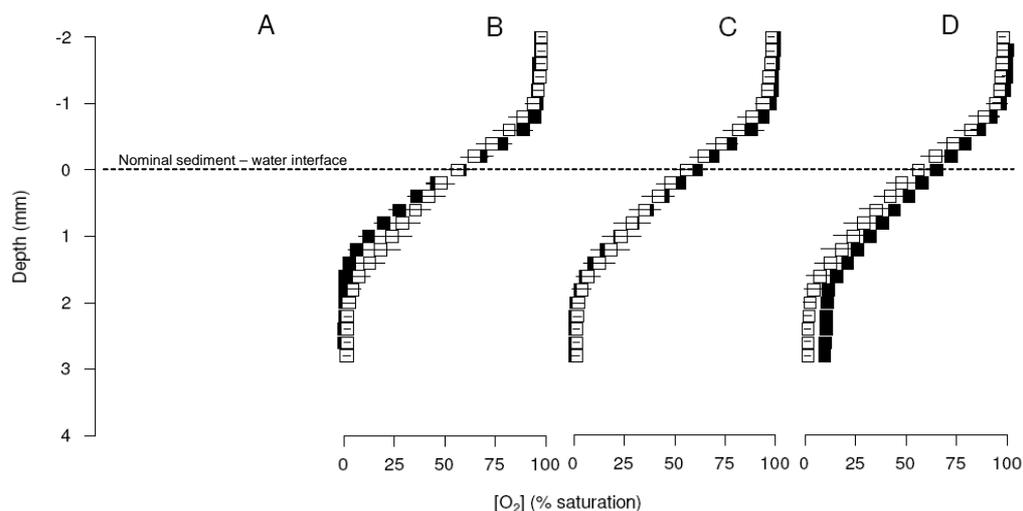


Figure 11: Graph showing vertical microprofiles of dissolved oxygen measured from a position 2 mm above bare sediment (white symbols, control) or sediment surface deposits of Z2G1 (black symbols) to the depth of anoxic sediment or surface deposit. The Z2G1 deposits resulted from addition of (A, B) <1 mm Z2G1 particles and (C, D) 1–3 mm Z2G1 particles at a rate of (A, C) 350 g m⁻² and (B, D) 700 g m⁻². The dashed line indicates the surface of the bare sediment or the Z2G1 deposit. Horizontal error bars represent ± 1 SD (n = 3). Note that the vertical axis is in mm.

Pore water concentrations of hydrogen sulphide, oxygenated bottom water

Hydrogen sulphide was detected in the pore water of the untreated sediment cores below a depth of 2 mm (Fig. 12). Note that we measured concentrations of the dissolved hydrogen sulphide gas but not the concentration of the total dissolved reduced sulphur. The pore water concentration of hydrogen sulphide is a function of the pore water pH. Consequently, changes in the concentration of hydrogen sulphide along the vertical profile do not necessarily indicate a change in the concentration of the total dissolved reduced sulphur but may also result from change in the pore water pH.

Our measurements revealed that surface deposits of Z2G1 increase the pore water concentration of hydrogen sulphide in the uppermost 20 mm of the sediment (Fig. 12). Thick surface deposits of larger particles (700 g m⁻², 1–3 mm particle size) caused the largest increase. The pore water of sediment cores treated with Z2G1 at a rate of 700 g m⁻² contained hydrogen sulphide starting at 1 mm depth (Fig. 12D).

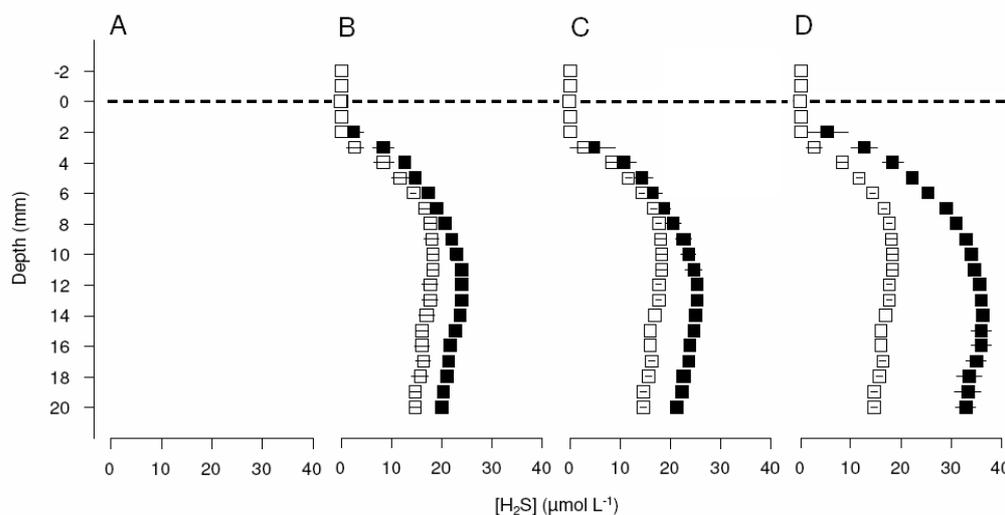


Figure 12: Graph showing vertical microprofiles of hydrogen sulphide measured from a position 2 mm above bare sediment (white symbols, control) or sediment surface deposits of Z2G1 (black symbols) to 20 mm depth. The bottom water was oxygenated. The Z2G1 deposits resulted from addition of (A, B) $< 1\text{ mm}$ Z2G1 particles and (C, D) $1\text{--}3\text{ mm}$ Z2G1 particles at a rate of (A, C) 350 g m^{-2} and (B, D) 700 g m^{-2} . The dashed line indicates the surface of the bare sediment or the Z2G1 deposit. Horizontal error bars represent $\pm 1\text{ SD}$ ($n = 3$). Note that the vertical axis is in mm.

Pore water concentrations of hydrogen sulphide, hypoxic bottom water

Our measurements in the hypoxic sediment cores (Fig. 13) confirmed the finding from measurements in cores that contained oxygenated bottom water: surface deposits of Z2G1

- 1) increased the sediment pore water concentrations of hydrogen sulphide; and
- 2) shifted the position of the chemocline upwards from the underlying sediment into the surface deposit.

The vertical displacement of the chemocline was more pronounced under conditions of hypoxic bottom water compared to that under conditions of oxygenated bottom water. Sediment cores treated with $1\text{--}3\text{ mm}$ Z2G1 particles at a rate of 700 g m^{-2} leaked hydrogen sulphide into the bottom water (Fig. 13 D).

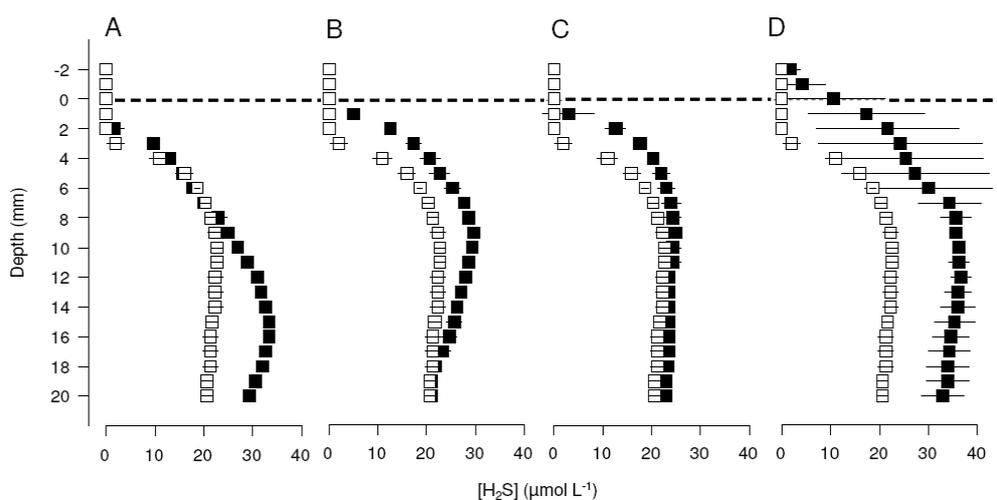


Figure 13: Graph showing vertical microprofiles of hydrogen sulphide measured from a position 2 mm above bare sediment (white symbols, control) or sediment surface deposits of Z2G1 (black symbols) to 20 mm depth. The bottom water was hypoxic. The Z2G1 deposits resulted from addition of (A, B) <1 mm Z2G1 particles and (C, D) 1–3 mm Z2G1 particles at a rate of (A, C) 350 g m^{-2} and (B, D) 700 g m^{-2} . The dashed line indicates the surface of the bare sediment or the Z2G1 deposit. Horizontal error bars represent ± 1 SD (n = 3). Note that the vertical axis is in mm.

4. Discussion

4.1 Phosphorus

4.1.1 Incubations

The results from the aerobic experiment (Fig. 14) using non-spiked natural lake water showed that DRP was removed from the overlying water column by the natural sediments, presumably by the oxidised iron in the sediment. However, there was a larger reduction in DRP concentration in the outflow water from the sediments capped with the Z2G1 treatments than the control indicating that Z2G1 was also adsorbing P from the water column. Similar results were obtained from the spiked lake water (Fig. 14). Although the difference between the control and treated incubations were proportionally not as great, both control and treated incubations removed a larger mass of P from the overlying water indicating that P-removal was affected by concentration and thus was a function of the diffusion gradient across the sediment-water interface.

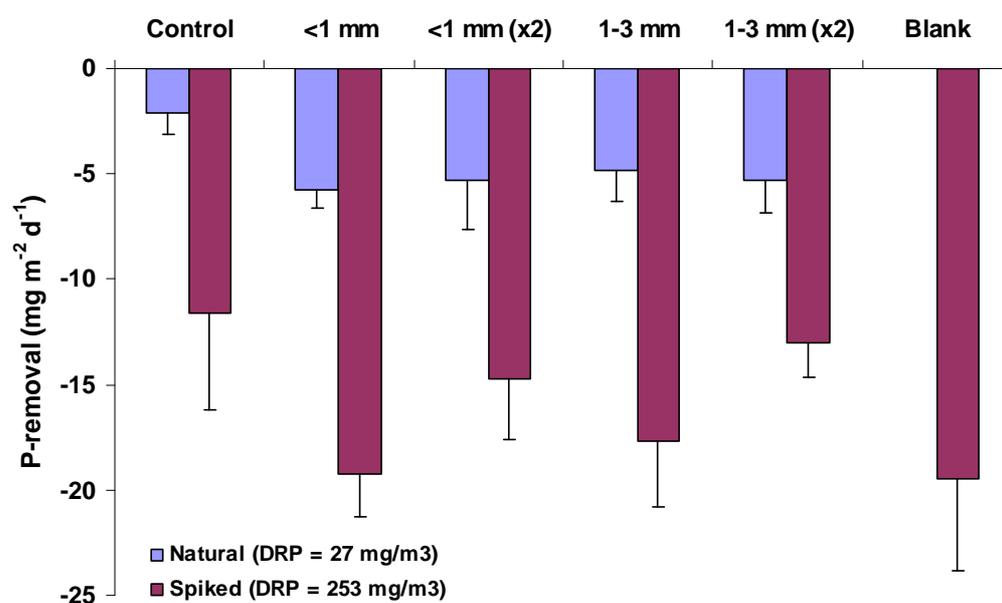


Figure 14: Mean (error bar = 1 SD) P-removal from water column over the last 3 days of incubation at different treatments in the incubation tubes under aerobic conditions. Treatments were at 350 g m⁻² or 700 g m⁻² (i.e., x2). The “blank” was a material blank with no sediment but treated with <1 mm Z2G1 at the highest rate, 700 g m⁻².

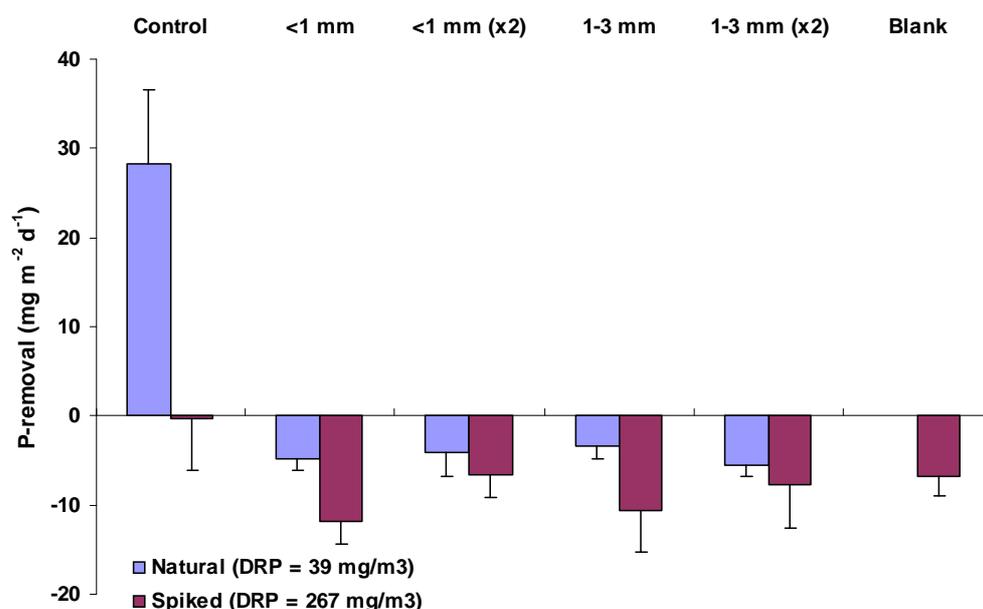


Figure 15: Mean (error bar = 1 SD) P-removal from water column over the last 4 days of incubation at the different treatments in the incubation tubes under anoxic conditions. Treatments were at 350 g m⁻² or 700 g m⁻² (i.e., x2). The “blank” was a material blank with no sediment but treated with <1 mm Z2G1 at the highest rate, 700 g m⁻².

The results from the anoxic experiment (Fig. 15) using non-spiked natural lake water showed that DRP was released into the overlying water column by the natural sediments, as expected. However, there was minimal release or removal of DRP by the control sediments using spiked lake water. This is consistent with sediment release being a diffusive process. Surface lake water had 30 mg m⁻³ DRP whereas the bottom waters had a much higher concentration of about 185 mg m⁻³ when collected (Table 1). If the DRP concentration in the bottom waters of the lake reflect concentrations close to the maximum possible by sediment release, then the spike at 267 mg m⁻³ was higher than that maximum and there was no concentration gradient to draw the DRP out of the sediment by diffusion.

In contrast to this apparent diffusive flux balance, there was a reduction in DRP from the overlying water in all incubations treated with Z2G1. As we have demonstrated that DRP was released from the control sediments in natural water, the “natural water” results for the Z2G1 treatments include the removal of the DRP released from the sediment i.e., the actual P-removal rate was about 32-34 mg m⁻² d⁻¹, most of it being from sediment release.

Using the above logic, in the spiked experiment, the efflux of DRP from the sediments would be minimal because of overlying water has a higher concentration of DRP than

would typically occur in the bottom waters of the lake. Consequently, the P-removal rate appears to be much lower at $7\text{-}12 \text{ mg m}^{-3} \text{ d}^{-1}$. However, Z2G1 is known to remove DRP and when applied to the sediment surface, it should effectively become a thin layer with no free DRP. This means that the Z2G1 drives the diffusion process into and out of the sediment, binding the DRP released from the sediment before it can reach the overlying water and removing DRP from the overlying water as that P diffuses down into the Z2G1 layer. Thus, assuming the diffusive flux of P beneath the Z2G1 is of similar magnitude as that in the non-spiked anoxic control, the actual P-removal rate by the Z2G1 capping layer is likely to be about $34\text{-}39 \text{ mg m}^{-2} \text{ d}^{-1}$. That is essentially the same as in the non-spiked anoxic experiment.

4.1.2 Z2G1 uptake

Confirmation that the Z2G1 is actually removing DRP is seen in the P content of Z2G1 before and after use (Fig. 10). The amount of P removed by each Z2G1 treatment can be calculated from those ICP-MS data by correcting for the P content of the raw Z2G1 and the actual weight of Z2G1 applied to each incubation tube treatment (Fig. 16).

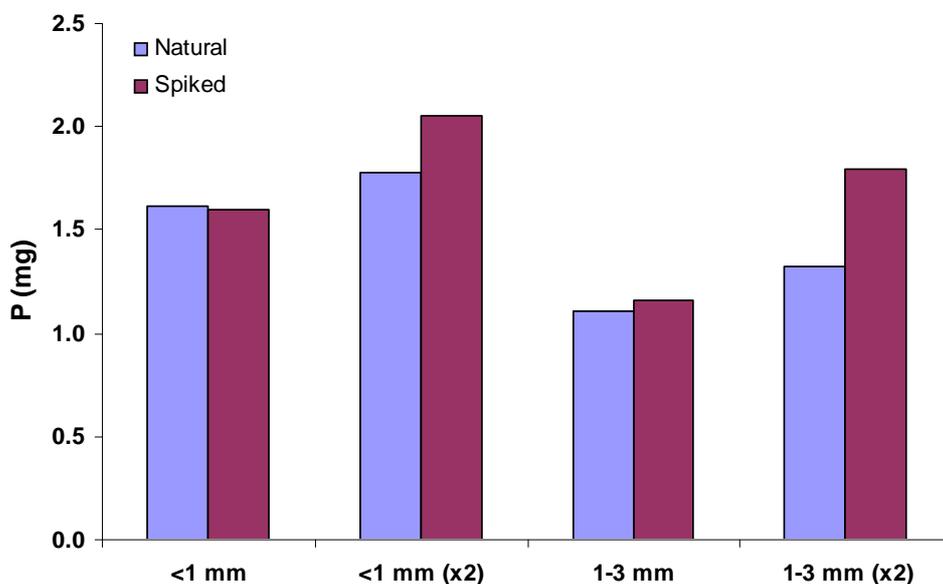


Figure 16: Net increase in the mass of P in the Z2G1 applied to the incubation tubes at the different treatments and rates.

These mass data converted to P-removal rates over the 14 days from application to extraction give an overall mean rate of $28.8 \text{ mg m}^{-2} \text{ d}^{-1}$ with a range from $21\text{-}38 \text{ mg m}^{-2} \text{ d}^{-1}$.

$\text{m}^{-2} \text{d}^{-1}$. Quantitatively, within experimental errors, these removal rates are essentially the same as those estimated from the nutrient efflux data at about $32\text{-}34 \text{ mg m}^{-2} \text{ d}^{-1}$ from natural water and about $34\text{-}39 \text{ mg m}^{-2} \text{ d}^{-1}$ from the spiked experiment.

The apparent differences in the amount of P in the Z2G1 from different treatments (Fig. 16) may be function of particle size with smaller particles having a larger active surface area. The differences may also be a function of the % coverage of sediment by the Z2G1. For example, if there was a stoichiometric uptake of P by Z2G1, the differences would have been proportional to the amount of Z2G1 applied to the sediment. Instead, P uptake by the double layer of $<1 \text{ mm}$ Z2G1 was only marginally greater than the single layer which implies the amount of P available for uptake is limited by a rate process, i.e., the rate of supply from within the sediments.

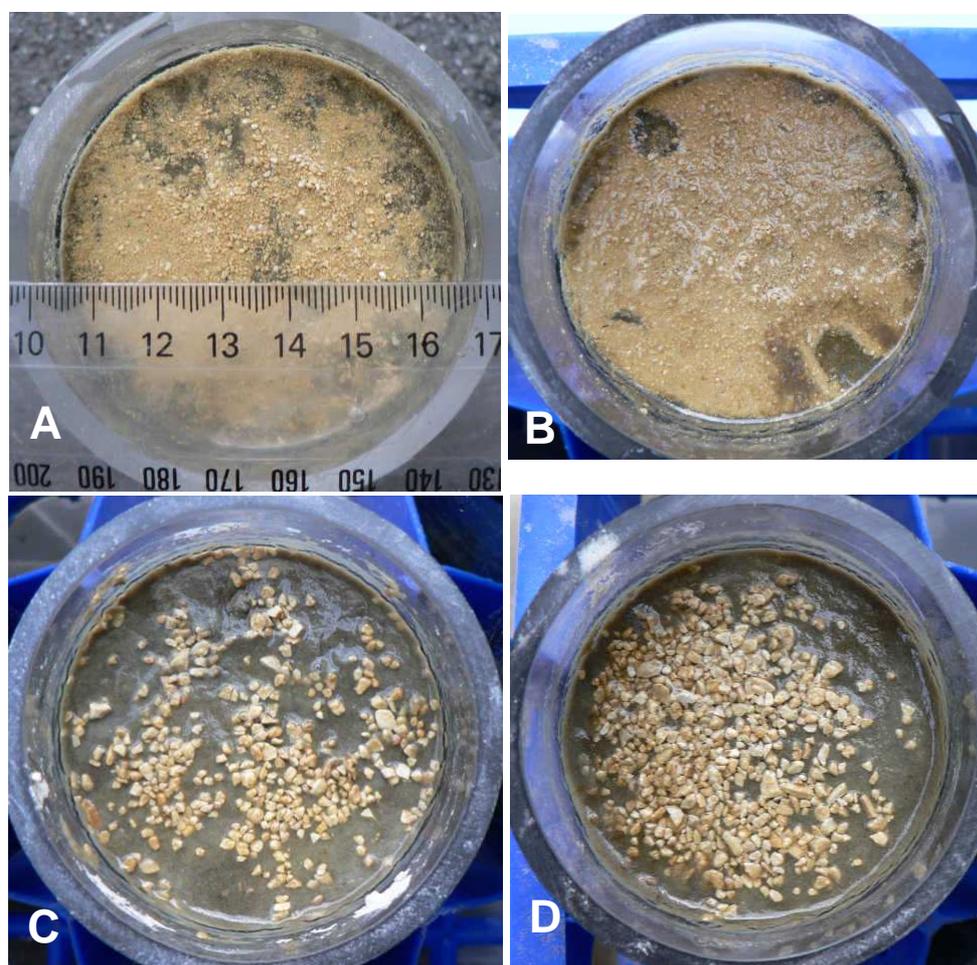


Figure 17: Sediment coverage by the application a single dose of $<1 \text{ mm}$ Z2G1 (A) or $1\text{-}3 \text{ mm}$ Z2G1 (C) compared with a double dose of $<1 \text{ mm}$ Z2G1 (B) or $1\text{-}3 \text{ mm}$ Z2G1 (D). A single dose was 1.35 g of Z2G1. Tube scale as per (A).

In terms of aerial coverage of the sediments by the Z2G1, the small differences in P mass between the single dose and the double dose of <1 mm Z2G1 (Fig. 16) are associated with the small increase in the % sediment coverage by these 2 treatments (Fig. 17A and B). Conversely, the larger differences in P mass between the single and double layers of 1-3 mm Z2G1 (Fig. 16) are consistent with the much larger increase in the % sediment coverage by these 2 treatments (Fig. 17C and D).

From the above, it is clear that the product Z2G1 applied as a capping agent is efficient at stopping the release of P from the sediment into the overlying water and has the ability to remove P from the overlying water coming in contact with it as a layer on the sediment surface. From the incubation experiments, the data shows that the removal process was continuous and essentially constant over the incubation period. The agreement between the amount of P lost from the water in the continuous flow incubations and the net increase in the amount of P in the Z2G1 on the sediment in the incubation tubes over the 14-day period of the experiment, implies that the P-removal rate is largely a function of diffusion processes which can limit the availability of free DRP in contact with the Z2G1 where it can be removed. These data also indicate that the capacity of the Z2G1 to take up P was not reached during the 14-day period of the incubation experiment.

4.1.3 Rough calculations and reality check

From the ICP-MS data (Fig.10), the mean total P content of the sediment was about 2000 mg P kg⁻¹ dry weight. The wet sediment had a bulk density of 1039 kg m⁻³, therefore 1 m³ of wet sediment will have 39 kg dry weight of sediment. If the top 20 mm of sediment is the source of most of the diffusive flux of DRP then that flux is coming from 0.78 kg of sediment. Thus, on an aerial basis, the total amount of P stored in that 20 mm layer (including refractory and non-refractory P) is about 1.56 g m⁻².

Consequently, the proposed Z2G1 application rate of 350 g m⁻² is required to block the release of up to 1.56 g P m⁻². This is a P uptake of 0.45 g P per 100 g Z2G1, which is less than the P uptake capacity of Z2G1 (50 mg P g⁻¹) and may explain why the P uptake capacity of the Z2G1 was not exceeded during the incubation experiment.

As a reality check, the theoretical bottom water concentrations of DRP can be calculated without the Z2G1 application. Assuming that the diffusive flux implied from the incubation tube experiments at around 30 mg m⁻² d⁻¹ is the release rate from the sediments and all the P stored in the top 20 mm is eventually released, it would take about 50 days for the DRP concentrations to reach maximum concentrations.

With a hypolimnetic depth of 10 m, the expected concentration would be in the order of 160 mg m^{-3} . This is less than but comparable with the concentration measured in the bottom waters at the time of sampling (Table 1), indicating that the sediment efflux estimate for Lake Okaro is in the correct order of magnitude.

4.2 Other factors

Other data collected during this experiment included the changes across the sediment-water interface with the different treatments of Z2G1, indicating that the layer of Z2G1 is affecting the sediment biogeochemistry. As the Z2G1 was designed as a sediment capping agent, this was expected and these data give an indication of the likely effects and their relative importance to the ecology of the lake.

4.2.1 Pore water oxygen and hydrogen sulphide

Data from this study indicate that the Z2G1 layer reduces the rate of diffusion of oxygen into the sediments and allows the sediments immediately below the Z2G1 layer to become anaerobic. Our data do not indicate a complete blockage of oxygen, rather that the rate of diffusion of oxygen through the Z2G1 layer was less than the sediment oxygen demand immediately below that layer. Consequently, the surface deposits of Z2G1 increase the concentrations of hydrogen sulphide in the pore water of the uppermost sediment. Deposits of 700 g m^{-2} 1–3 mm Z2G1 particles caused a diffusive flux of hydrogen sulphide from the uppermost sediment pore water into the bottom water that could adversely affect benthic fauna in the sediment and on the sediment surface (e.g., Koura). However, at the nominated application rate of 350 g m^{-2} an efflux of hydrogen sulphide is unlikely to occur, unless the Z2G1 layer on the sediment is disturbed.

4.2.2 Ebullition

Ebullition of gas from the sediments of Lake Okaro is a feature of that lake and is likely to vary seasonally due to changes in the bottom water temperature (Liikanen et al. 2002). Raising the temperature of the incubation tubes from 11°C to around 16°C increased gas production in the incubation tubes and consequently, ebullition. Although gas bubbles that developed deep in the sediments were not analysed, they were probably mostly methane, from anaerobic fermentation of organic matter (acetate) in the sediments, as most of the CO_2 produced would dissolve in the pore water. The rate of gas bubble production appeared to be less in the incubation tubes with high $\text{NO}_3\text{-N}$ concentrations in the overlying water.

We observed that the Z2G1 layer had developed a physically cohesive structure after 14 days. This layer was strong enough to bind the sediment surface in a jelly-like sheet. The cohesive nature of the layer was sufficient to prevent the upwards passage of small gas bubbles. Consequently, the sediment in several of the incubation tubes became positively buoyant with the upper 5-cm thick portion separating from the rest of the sediment and rising to the top of the incubation tube after the 5-day hypoxic incubations. In several incubation tubes the gas bubbles coalesced into bubbles which were large enough to disrupt the Z2G1 layer as they burst out of the sediments. The result of this vigorous ebullition or “burping” was either an opening torn in the Z2G1 layer or a flap of sediment folded over, burying part of the Z2G1 layer (Fig. 18).

While the overturn of sediments may be an artefact of the sediment in the tubes, it is clear that once the Z2G1 layer is established and the diffusion of oxygen into the sediments is reduced, anaerobic processes will rapidly develop and the production of gas bubbles may reduce the efficiency of the capping layer. Liikanen et al. (2003) observed that the ebullition of methane was closely related to the efflux of DRP and $\text{NH}_4\text{-N}$ from the sediment with significant increases in these effluxes as ebullition increased. It is unknown whether the expected ruptures through the cohesive surface layer will enhance or suppress the efflux of nutrients from the sediment by entrainment of sediment pore water into the overlying water column.



Figure 18: After a gas bubble has “burped”, the Z2G1 layer was buried beneath 4 cm of sediment. P in the newly exposed sediment would not experience the P-removal effects of the Z2G1 treatment.

4.2.3 Nitrogen dynamics

The results of the nitrogen tests (Figs. 8 and 9) indicate that the basic processes of nitrification and denitrification were not disrupted by the Z2G1 application although there were some interesting effects.

Ammoniacal-nitrogen concentrations were high in the lake water and thus not added to the nutrient spike. Under aerobic conditions with non-spiked lake water, the $\text{NH}_4\text{-N}$ concentrations were unchanged in the controls but reduced rapidly in all of the Z2G1 treatments (Fig. 19). With spiked lake water, there was a loss of $\text{NH}_4\text{-N}$ from all incubation tubes including the controls and the material blank.

Under anoxic conditions, the non-spiked controls released a large amount of $\text{NH}_4\text{-N}$ into the overlying water while the Z2G1 treated sediments showed a net loss of $\text{NH}_4\text{-N}$ comparable with losses from the Z2G1 treatments under aerobic conditions (Fig. 20). With spike lake water, there was less release of $\text{NH}_4\text{-N}$ from the controls but greater loss of the $\text{NH}_4\text{-N}$ from the Z2G1 treated sediments (Fig. 20).

These results indicate that Z2G1 has the ability to remove $\text{NH}_4\text{-N}$ from the overlying water column and to block the release of $\text{NH}_4\text{-N}$ from the sediments. An alternative explanation is that the Z2G1 somehow facilitates denitrification.

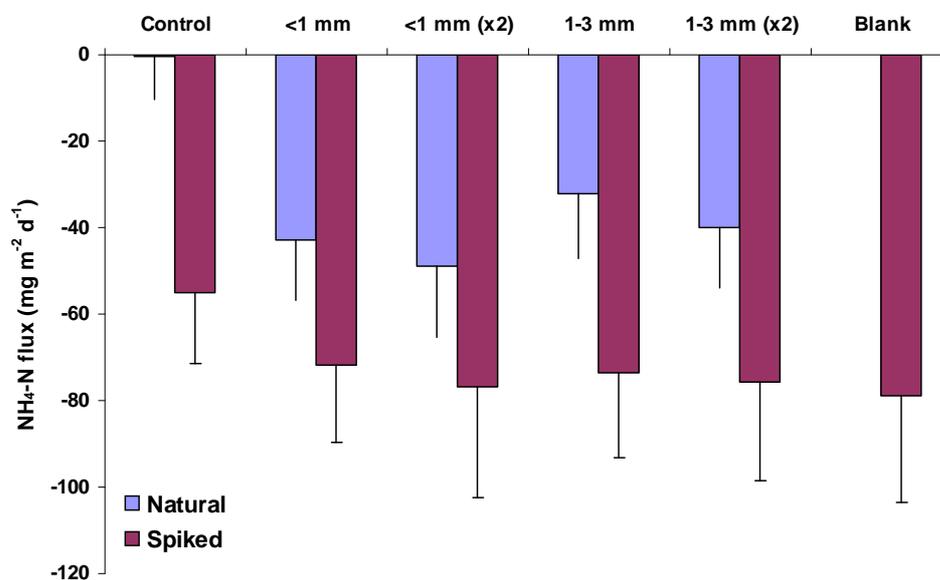


Figure 19: Aerobic incubation results (means, error bar = 1 SD) showing the effect of Z2G1 on the $\text{NH}_4\text{-N}$ in the overlying water under natural (blue) and spiked (red) conditions. The spike contained 1500 mg m^{-3} of $\text{NO}_3\text{-N}$ and 200 mg m^{-3} of DRP.

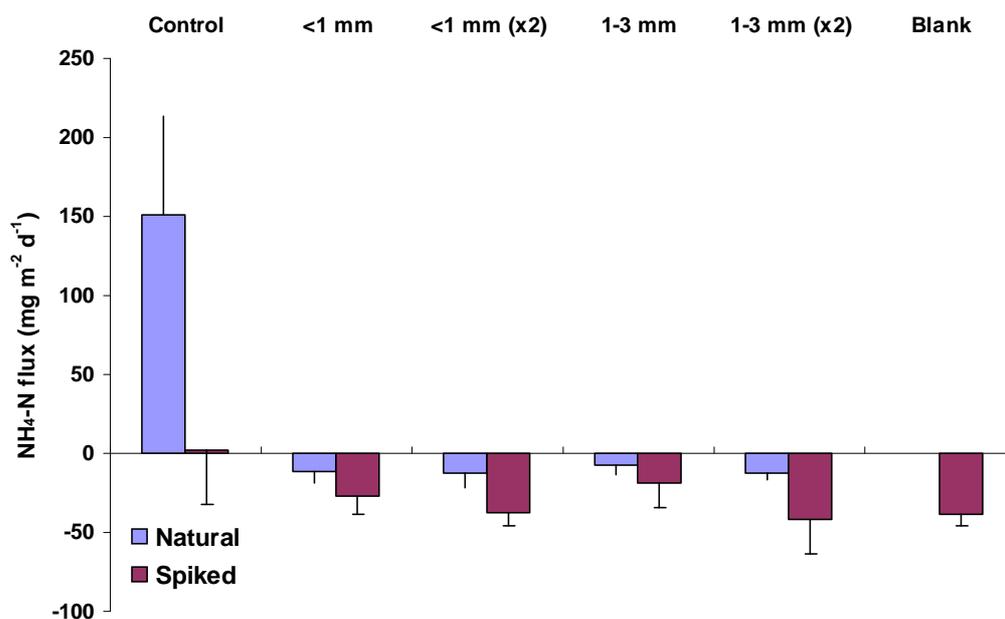


Figure 20: Anoxic incubation results (means, error bar = 1 SD) showing the effect of Z2G1 on the NH₄-N in the overlying water under natural (blue) and spiked (red) conditions. The spike contained 1500 mg m⁻³ of NO₃-N and 200 mg m⁻³ of DRP.

Under aerobic conditions with non-spiked lake water, the NO₃-N concentrations were reduced by a similar but small amount in the controls and in all of the Z2G1 treatments (Fig. 21). With spiked lake water, there was a much larger loss of NO₃-N from all incubation tubes including the controls and the material blank. A possible explanation for these losses is that the sediments were anoxic very close to the surface, as indicated by the H₂S profiles (Fig. 12 and 13), and that denitrification was occurring. The reason for the greater loss of NO₃-N from the spiked than non-spiked incubations would be a function of diffusion – the higher concentration of NO₃-N in the overlying water would enhance the diffusion of the NO₃-N across the sediment-water boundary into the anoxic sediment.

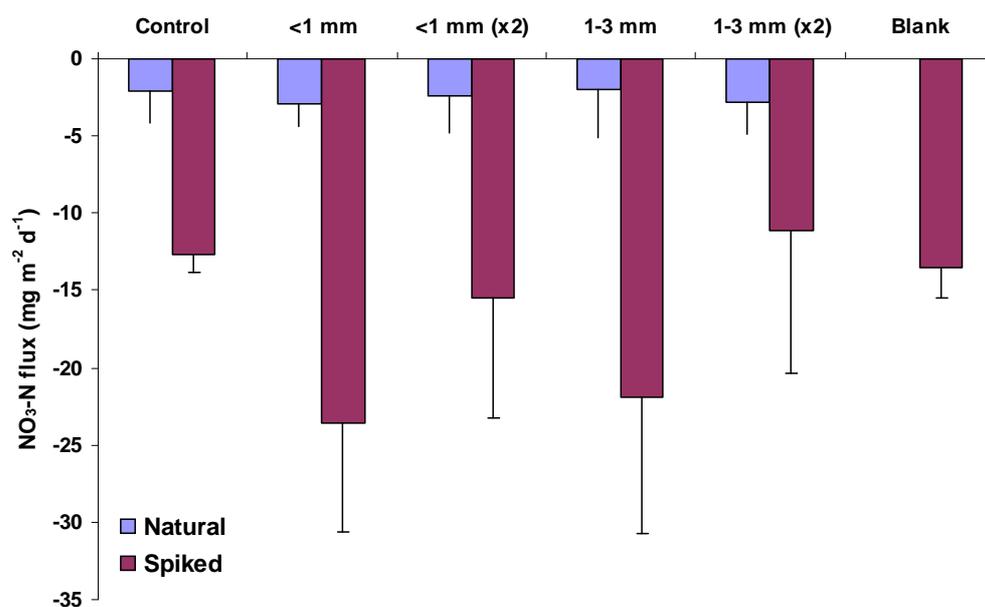


Figure 21: Aerobic incubation results (means, error bar = 1 SD) showing the effect of Z2G1 on the NO₃-N in the overlying water under natural (blue) and spiked (red) conditions. The spike contained 1500 mg m⁻³ of NO₃-N and 200 mg m⁻³ of DRP.

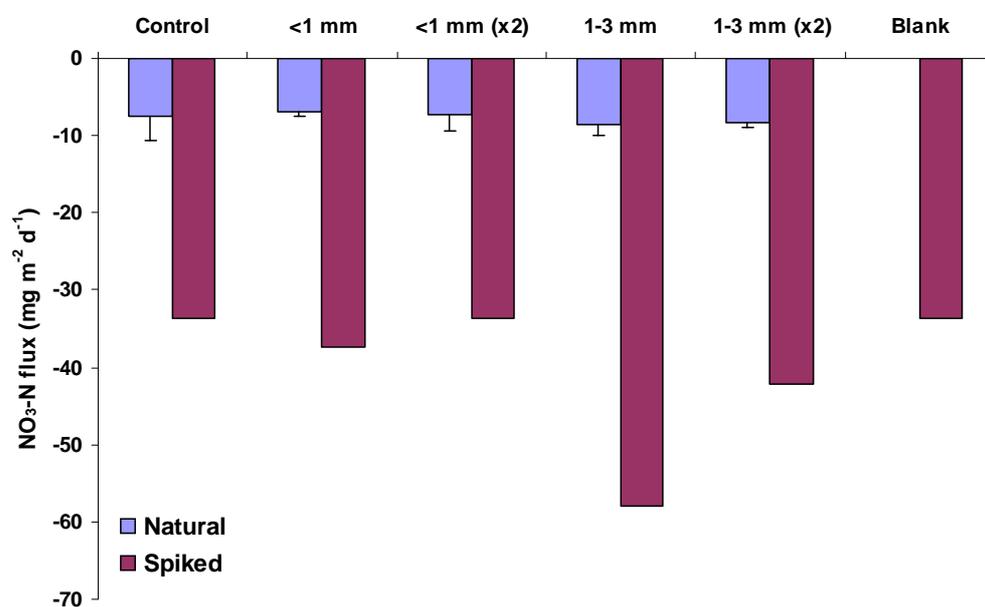


Figure 22: Anoxic incubation results (means, error bar = 1 SD) showing the effect of Z2G1 on the NO₃-N in the overlying water under natural (blue) and spiked (red) conditions. The spiked results are from the day 2 sampling while the incubations were still anoxic, and consequently there are no error bars. The spike contained 1500 mg m⁻³ of NO₃-N and 200 mg m⁻³ of DRP.

Similar results were obtained under anoxic conditions with a greater reduction in $\text{NO}_3\text{-N}$ concentrations than under aerobic conditions (Fig. 22). The same explanation of denitrification also applies for these losses.

Unfortunately, the spiked anoxic experiment became partially oxygenated over the duration of the incubation and this can be seen as an overall increase in the $\text{NO}_3\text{-N}$ concentrations in the incubation results (Fig. 9). However, as the $\text{NO}_3\text{-N}$ concentrations increased substantially over the spike concentration this indicates that there was some level of nitrification occurring.

5. Summary

- The data presented in this report demonstrate that the P-inactivation Z2G1 applied as a capping agent is capable of blocking P released from the sediment under anoxic conditions.
- The data also demonstrate that Z2G1 can remove DRP from the overlying water column under aerobic and anoxic conditions.
- The mean P-removal rate measured was around $30 \text{ mg m}^{-2} \text{ d}^{-1}$. This removal rate appears to be limited by diffusive processes and may reflect the mineralisation rate of P in the sediments of Lake Okaro.
- The estimated amount of total P stored in the upper 20 mm of sediment was up to 1.56 g P m^{-2} . At 350 g m^{-2} , this is an uptake of 0.45 g P per 100 g of Z2G1 or 4.5 g P kg^{-1} . This is substantially less than the theoretical P adsorption capacity of Z2G1 at 50 g P kg^{-1} .
- Surface deposits of Z2G1 increase the concentrations of hydrogen sulphide in the pore water of the uppermost sediment. Deposits of 700 g m^{-2} of the 1-3 mm grain size Z2G1 particles cause diffusive flux of hydrogen sulphide from the uppermost sediment pore water into the overlying bottom water. At the suggested application rate of 350 g m^{-2} , efflux of hydrogen sulphide is unlikely to occur.
- While modification of the biogeochemistry across the sediment-water interface by the surface deposit of Z2G1 was expected, there appear to be no hidden problems with Z2G1 interfering with the nitrification-denitrification cycle. The strong oxygen gradients across the sediment-water interface appear to be beneficial to the removal of $\text{NO}_3\text{-N}$ and may be responsible for the major reduction in the $\text{NH}_4\text{-N}$ concentrations observed.
- Ebullition of methane gas from within the sediments will cause disruption of the thin deposit of Z2G1 on the sediment surface and may reduce its efficiency as a P-inactivation agent.

These results indicate that there is scope for a reduction in the application rate of Z2G1 by at least 50% from the proposed rate of 350 g m^{-2} . This conclusion is based on the apparent 10-fold excess P-removal capacity of the Z2G1. The benefit of a lower

application rate would be to give a greater buffer against the possibility of the diffusive flux of hydrogen sulphide into the overlying bottom water observed with the higher application rate of 700 g m^{-2} .

6. Health and safety

Not all hazards are immediately apparent when planning field work. Although all the required physical precautions were taken for operating a research boat on a small inland water and life jackets were worn through the whole period on the lake, there was a hidden hazard associated with the lake itself and the critical state of over-turn (winter mixing) combined with the presence of a cyanophyte bloom.

At turnover, anaerobic bottom water enriched with dissolved gases (hydrogen sulphide (H_2S), carbon dioxide (CO_2) and methane (CH_4)) is brought to the surface. Normally the toxic H_2S would be rapidly oxidised to harmless sulphate in the water column. If turnover is vigorous, there is insufficient time for that oxidation and free H_2S can be released into the air. This process can be exacerbated by degassing i.e., dissolved gases form bubbles as the pressure is reduced. In extreme conditions where dissolved gases were at saturation levels, degassing can be very rapid causing columns of bottom water to rise to the surface in “limnetic eruptions”

Although there was no smell of sulphide in the lake water at the time of sampling, there was a strong musty smell of cyanophytes in the air above the lake.

The cyanophyte smell permeated my clothing and skin and was subsequently difficult to wash off (I could still smell it on my hands 3-days later). An effect of this “aerosol” of cyanophyte vapour was to produce feelings of discomfort and nausea as well as a headache. The onset of these symptoms was insidious over the 3-hour sampling period and are possible symptoms of cyanophyte poisoning. Retrospectively, this was a hazardous situation that was only mitigated by the breeze on the day. Based on these observations, caution should be exercised when working for extended periods on this lake during a cyanophyte bloom. Breathing apparatus and water-proof clothing may be necessary under certain conditions.

7. Acknowledgements

We thank the laboratory staff, especially Margaret McMonagle and Graham Bryers for their co-operation in getting a rapid turn-around of the large number of sample analyses between the first and second experiments and immediately afterwards. Their efforts were greatly appreciated.

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