Lake Okaro re-treatment with Z2G1 in August 2009

NIWA Client Report: HAM2009-177
February 2010

NIWA Project: BOP10223 / Okaro

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Prepared for

Environment Bay of Plenty

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Executive Summary

As part of the on-going remediation of water quality in the Te Arawa/Rotorua lakes, Environment Bay of Plenty has been testing the use of sediment capping agents to inhibit the release of phosphorus (P) from the sediment as an internal load that can drive cyanobacteria blooms. NIWA was commissioned to assess the efficacy of remediation work on Lake Okaro. In September 2007, Lake Okaro was treated with about 100 tonnes of a modified zeolite product, Z2G1, developed by Scion as a P-binding agent for sediment capping. This product had a nominal grain size of 1-3 mm. Although application using a fertilizer spreader was relatively easy, the sediment coverage was uneven and the coarse granules sank into the sediment, substantially reducing the efficacy of the treatment. Measurements of P content in the granular Z2G1 recovered from the top 4-cm sediment layer indicated that only about 10% of the potential P-binding capacity of the Z2G1 applied in 2007 had been used. Notwithstanding this, the total bioavailable P in the surficial sediment (0-4 cm depth) following that treatment was reduced by around 50%.

In August 2009, while the lake was well oxygenated throughout its depth (>7 g DO m^{-3}), the lake was treated with a further 44 tonnes of Z2G1 but in a finer grain size mostly in the range 0.1-0.4 mm, applied as a slurry 2-3m below the lake surface. The evenness of sediment coverage was assessed using sediment traps at 17 locations across the lake bed. While the mean measured areal load was 178 g m^{-2}, which was comparable with the expected areal load of 166 g m^{-2}, the coverage was, again, highly variable ranging from around 100 g m^{-2} up to 250 g m^{-2} of Z2G1. The minimum areal loading of 100 g m^{-2} was theoretically sufficient to bind all P in the surficial sediments.

Apart from the uneven lake bed coverage, the results of the trapping exercise also showed that there was substantial drift of the Z2G1 into the non-target edge waters <5 m deep. These observations indicate that further work is required on the settling and dispersal properties of the Z2G1 product and the flow-on effects to the application technique.

Additional information obtained from the August 2009 treatment included:

- The fine grain size Z2G1 was able to absorb P from the upper water column, possibly as a function of longer contact time due to the slower settling rate. There was a 50% reduction in dissolved reactive P and ammoniacal nitrogen in the upper water column following the Z2G1 application.
- The mean flux of organic matter for the deep (>5 m) traps was 1.57 g m^{-2} d^{-1}, with a large range of 0.73 to 2.31 g m^{-2} d^{-1}.
- There was a statistically significant relationship ($P << 0.001$, $r^2 = 0.77$, $n = 13$) between the amount of organic matter and the Z2G1 in each of the deep (>5 m) traps. This indicates that the fine grain Z2G1 formulation behaved like a flocculent, co-precipitating organic matter, including algae, from the water column.

- Large numbers of bullies used the sediment traps as habitats. The numbers of bullies observed in the sediment traps on retrieval correlated with the amount of organic matter in the traps. There appeared to be two distinct groupings of bullies with 4-fold higher numbers in the eastern traps. This may indicate a natural sediment focusing area in the lake attracting higher populations of bullies to the resultant food source.
- Chlorophyll fluorescence profiles as an indicator of algal biomass showed that there was a layer of algae about 1-m thick moving around the lake at about the depth of the euphotic zone (~5 m), independent of the thermal structure in the lake at that time. This layer consisted mostly of the dinoflagellate, *Peridinium sp*., in a patch with an estimated area of about one third of the lake. While the patchiness of the dinoflagellate bloom may be natural, it is possible that part of that bloom was co-precipitated with the Z2G1.
- Excluding dinoflagellate peaks, mean chlorophyll *a* concentrations at 5 m increased from 20.9 mg m^{-3} on 24th August, at the beginning of the dosing, to 30.1 mg m^{-3} on 3rd September 6 days after dosing had finished. This is consistent with natural growth rates rather than stimulated growth in response to the Z2G1 dosing.

Conclusions:

The finer grain formulation of Z2G1, applied as a slurry, gave a more consistent cover of the lake bed than the previous application of courser grain size material, but there were still substantial variations in the areal loading across the lake. This indicates that there is still work to be done to produce a product formulation and application system that will reliably and consistently deliver an even coverage of the product to the targeted zone on the lake bed.

When first applied the fine grain formulation of Z2G1 formed a cloud which was slow to settle giving a high contact time during which it adsorbed both DRP and ammoniacal nitrogen from the upper water column. The cloud coalesced into larger particles as it formed a floc which sank rapidly taking some of the algal biomass out of the water column. These changes in the properties of Z2G1 may have direct bearing on how the product is developed.

1. Introduction

As part of the on-going Environment Bay of Plenty (EBoP) programme for the water quality restoration of Lake Okaro, the lake has been treated twice (September 2007 and August 2009) with a new phosphorus (P) inactivation agent (Z2G1) applied as a thin layer to the sediment. This thin sediment capping layer was intended to block the release of P from the sediments under the anoxic conditions that develop in the bottom waters (hypolimnion) of the lake during summer stratification.

In September 2007, the Z2G1 product was applied at a nominal dose rate of 500 g m^{-2}, in the form of coarse granules (nominal grain size 1-3 mm) using a fertilizer spreader from a barge. The granules settled rapidly to the lake bed within the targeted zone below the 5-m depth contour, but the sediment coverage was highly variable with patches of both high and low sediment loading (mean 928 g m^{-2}; range 450-1520 g m^{-2}). This amount of variability indicated difficulties with this application method. Subsequent examination of the lake sediments for Z2G1 coverage indicated that the larger granules had also sunk into the sediment by several cm in some places, further reducing the efficacy of the sediment capping layer at blocking the release of P from the sediment.

An additional complication in assessing the efficacy of the Z2G1 as a sediment capping agent was the timing of the application relative to the oxygen concentrations in the hypolimnion. By the time of application in September 2007, the hypolimnion was anoxic and P was already being released from the sediment. Although the Z2G1 application reduced subsequent P release, there was a substantial amount of P already in the lake water column from that source. Observations of water column P concentrations through the stratified period indicated that the Z2G1 P-binding capacity may have been overwhelmed or that the capping layer had been buried by newly sedimented material from in-lake production and external inputs.

The main lessons learned from the September 2007 treatment of Lake Okaro were:

- the timing of the application is critical and must be completed while the hypolimnion is well oxygenated;
- the grain size of the Z2G1 needs to be small enough so that the granules do not sink into the nepheloid layer on the sediment surface; and
- the application technique needs to be more precise to provide an even coverage of the sediment, thus forming a coherent layer across the lake bed.

These lessons were addressed for the repeat treatment of Lake Okaro in August 2009. The application was made while the hypolimnion of the lake was well oxygenated and

a finer grain formulation of Z2G1 was used, applied as a slurry injected about 2 m below the lake surface. NIWA was asked to determine the dose rate required for the repeat treatment of the lake and to measure the evenness of the sediment coverage by the application using the slurry injection technique. This report presents sediment loading calculations and the field data associated with the re-treatment of Lake Okaro using the finer grain size Z2G1 formulation in August 2009.

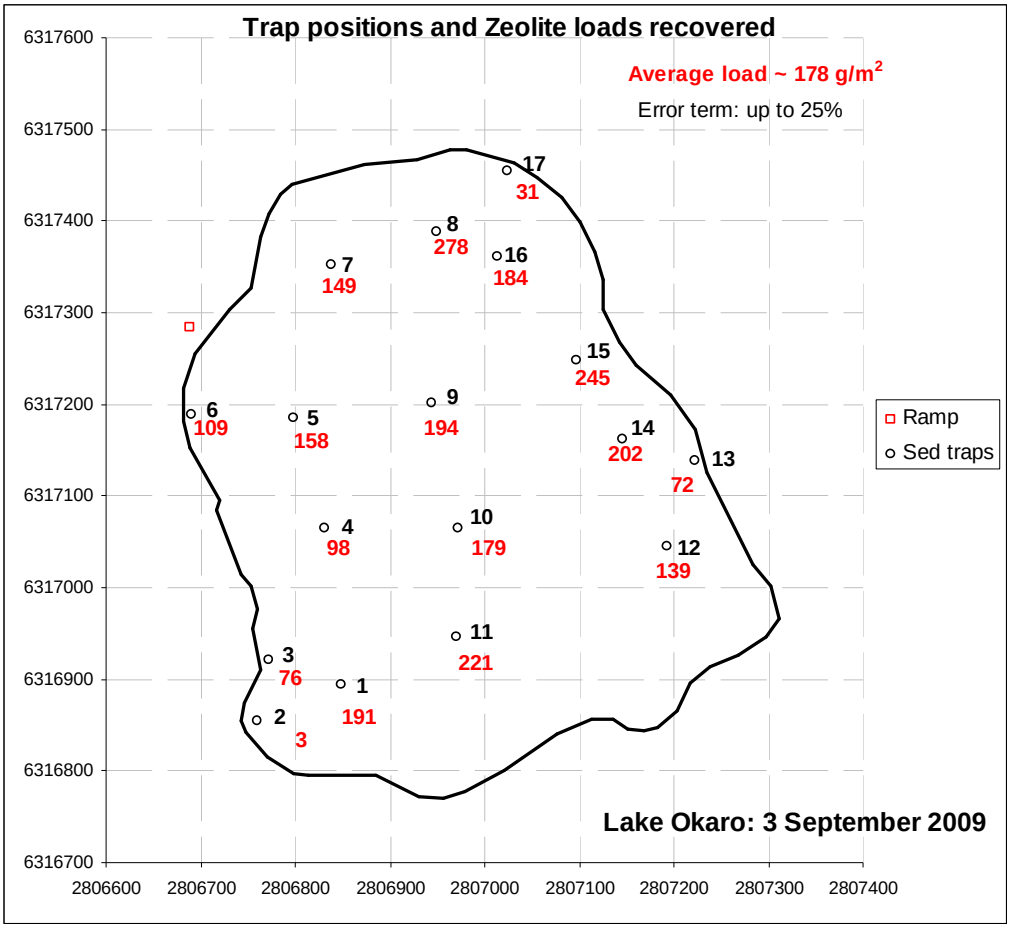

Figure 1: Schematic map of Lake Okaro showing the location of the sediment trap sampling points. Black numbers are site numbers, red numbers are the measured areal loading of Z2G1 (g m^{-2}) recovered after the August 2009 dosing (See text for error term explanation). Site 11 is the deepest site. Site 2 is the water supply intake. Sites 3, 6, 13, and 17 are littoral sites in less than 5 m water depth.

2. Methods

2.1 Sediment P

In order to determine the minimum dose rate for the Z2G1 re-treatment of Lake Okaro, sediment cores were taken from Lake Okaro at 4 locations equivalent to sediment trap site numbers 1, 7, 12, and 16 (Fig. 1) in May 2009. The cores were collected with a Jenkins Corer to ensure an undisturbed sediment-water interface. Examination of the cores showed apparent layers of sediment on top of the Z2G1 granular material applied in September 2007 (Fig. 2). The Z2G1 granules were mostly at a depth of around 4 cm but they were also visible at depths down to at least 6 cm. The top 4 cm of each core was sectioned off and passed through a 0.5 mm sieve to remove the Z2G1 granules which were retained for analysis by ICP-mass spectrometer to determine their total P absorption. The sediment sections were dried at 105ºC and analysed for total recoverable P by R.J. Hill Laboratories Ltd. Note that "total recoverable P" will be greater than "total biologically available P", giving a maximum P concentration in the sediment. Results of these analyses are presented in Table 1.

Table 1: **Total recoverable P** is the amount of bioavailable phosphorus that could potentially be released from the top 4 cm of sediment at 4 locations, sites 1, 7, 12, and 16 (Fig. 1), measured in May 2009; **Z2G1 applied in 2007** is the estimated amount applied at each location in 2007 from 2007 trap data; **Recovered Z2G1** is the amount of the 2007 Z2G1 granules recovered from the top 4 cm of a 70 mm diameter sediment core at each location in May 2009; **Total P in recovered Z2G1** is the amount of P in the 2007 Z2G1 recovered from those sediment cores. (* = best estimate).

Core site	**1**	**7**	**12**	**16**
Total recoverable P (mg/kg -dry weight)	870	980	990	930
Z2G1 applied in 2007 (g/m^2)	930*	1110	1335	1230
Recovered Z2G1 (g/m^2)	120	228	150	285
Total P in recovered Z2G1 (mg/kg)	2083	1690	1643	2010

2.2 Dosing

The mean residual total recoverable P content in the top 4 cm of lake sediment was used to determine the minimum amount of Z2G1 required to treat the lake below the 5-m depth contour. The top 4 cm of sediment is recommended for assessing bioavailable P content when calculating minimum dose rates (Cooke et al. 2005). Assuming that the surface sediment bulk density (1.037 g/cm^3) was unchanged from

that previously measured (Gibbs et al. 2007), the mean TAP content of around 950 mg/kg (Table 1) converts to an areal load of around 1.5 g m^{-2}. Based on a maximum P-binding capacity for Z2G1 of around 20 g P /kg (Gibbs et al. 2007), the theoretical dose rate required to block the release of the estimated 1.5 g P m^{-2} from the sediments of Lake Okaro was 75 g m^{-2} Z2G1. This equates to a minimum total Z2G1 application of 20 tonnes (Table 2).

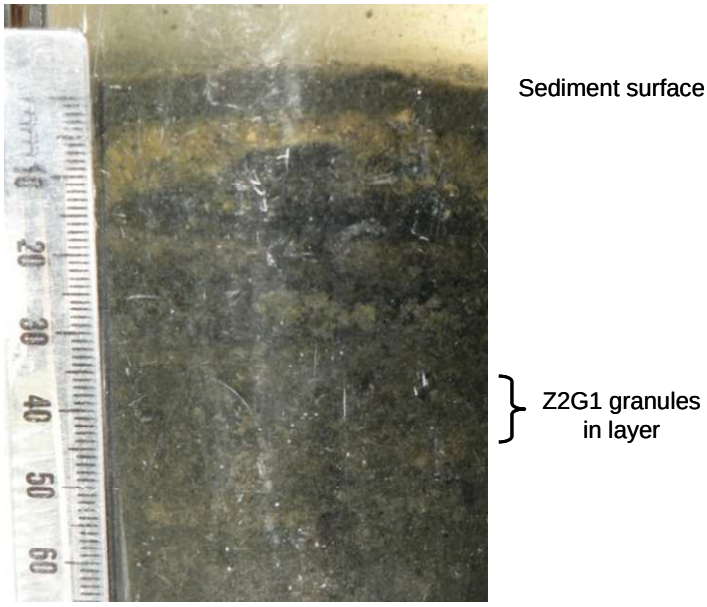

Figure 2: Lake Okaro sediment core taken 31 July 2009 showing several different coloured layers of recently sedimented material on top of the layer of Z2G1 (glossy black) at a depth of around 4 cm below the sediment surface.

Table 2: Z2G1 application (tonnes) table to achieve different sediment coverage loadings (g m^{-2}) and the maximum theoretical P absorption capacity (uptake) from the sediment. The surface area of Lake Okaro is 0.33 km^2, the lake bed area below 5 m depth is estimated to be 20% smaller at 0.26 km^2.

Assume 80% of lake area in hypolimnion (0.26 km^2)		
Application (tonnes)	**Loading (g/m^2)**	**P uptake (g/m^2)**
55	**208**	**4.16**
50	**189**	**3.78**
45	**170**	**3.40**
40	**151**	**3.02**
35	**132**	**2.64**
30	**113**	**2.26**
25	**95**	**1.90**
20	**76**	**1.52**

Dosing was achieved by mixing the Z2G1 (grain size range from 0.1–0.4 mm) with lake water (1:1 weight:volume) and injecting the resultant slurry through spreader nozzles about 2-3 m below the lake surface from a barge (Fig. 3). The application was made over a short period (3-4 days) with the barge using a GPS-based positioning system to follow a path of decreasing circuits around the lake. The total amount of Z2G1 applied was 44 tonnes which equates to an areal loading of 166 g m^{-2}, assuming an even coverage.

Figure 3: Application of the Z2G1 as a slurry, via spreader nozzles on the hoses from the boom across the back of the barge. The Z2G1 was mixed with lake water in the stainless steel mixing bowl at the back of the barge. The plumes of slurry can be seen deep in the water behind the barge. Photo by M. Gibbs. (See also cover photo).

2.3 Sediment traps

Sediment traps were used to assess the evenness of the sediment coverage with Z2G1. A total of 17 sediment "mat" traps were deployed across the bed of Lake Okaro on 31 July 2009 (Fig. 1). The mat traps (Fig. 4) consisted of a weighted plastic frame holding a flat sheet (0.1 m^2) of artificial grass (Astroturf™) placed on the sediment surface using a light rope bridle. The mat traps were retrieved on 3rd September, after the re-treatment of the lake with Z2G1 was complete. It was apparent that the mat

traps had been used by bullies as a resting place and, as each trap was raised to the surface, the numbers of bullies present were counted, before they swam out of the trap.

Figure 4: Sediment "Mat" trap uses 0.1 m^2 of artificial grass in a weighted flat tray placed on the lake bed to assess the evenness of the sediment coverage by the Z2G1 application. Trap from site 1 – the Z2G1 has settled between the artificial grass fibres but local variability in coverage also shows Z2G1 on top of the fibres. Three bully wallows can be seen on the left-hand edge of the mat (red arrows).

During the lifting of the mat traps, some fine material was lost from around the edge of the trap due to sloughing. In most traps the zone of sloughing represented around 5% of the surface area of the trap. However, in some traps the loss may have been larger but would not have exceeded 25% of the trap surface area. A 25% loss represents a band 2 cm wide around all sides of the trap from which all sediment was lost – this degree of sloughing was not observed.

The sediment flux in each trap was determined by washing the Astroturf™ mat into a bucket to recover the Z2G1 and organic sediment. Large detritus (e.g., aquatic weed drift fragments) and snails were removed by hand picking and discarded. The sediment was dried in aluminium oven trays at 105°C and weighed. The trays were then heated to 450°C for 3 hours to remove organic carbon. The loss of weight from the dry weight was calculated as the organic component of the sedimenting material while the weight of ash left on the tray was calculated as the Z2G1. Note that the non-

Z2G1 inorganic matter in each trap was likely to be about the same as or slightly more than the organic content at ~2.5 g m^{-2}, and the resultant error, at around 1-2% of the total inorganic matter caught in the trap, was considered to be trivial and thus ignored.

2.4 Water column effects

Water samples were collected at the surface and just above the lake bed at the deepest site (site 11, Fig. 1; Table 3) at the time of deploying the sediment traps, 31 July 2009, and at intervals through the dosing of the lake with Z2G1, 20-28 August, and when the sediment traps were removed, 3 September 2009. During the dosing of the lake, additional water samples were taken from a depth of 5 m and from three additional sites along the north-south axis of the lake (sites 8, 9, and 10; Fig. 1). These samples were analysed for dissolved reactive phosphorus (DRP), ammoniacal nitrogen (NH_4-N), and nitrate+nitrite nitrogen (NO_3-N). Samples taken during the dosing were also analysed for chlorophyll *a* as an estimate of algal biomass. All analyses used NIWA analytical facilities and the routine analytical methods used in the NIWA laboratory.

At the time of each sampling, an in-situ recording sonde (RBR XR420f CTD + Chl) was used to record the temperature and dissolved oxygen concentrations, and chlorophyll fluorescence, as an indicator of algal biomass, through the depth of the water column at the deepest site, site 11, at depth intervals of less than 1 m. These profiles were also measured at the three additional sites along the north-south axis.

3. Results and Discussion

3.1 Sediment P and P adsorbed into Z2G1

The analysis of the sediment cores (Table 1) showed that the mean total recoverable P content of 950 mg/kg (dry weight) was about 50% of the P content (2000 mg/kg dry weight) measured prior to the September 2007 Z2G1 application. Assuming the same surface sediment bulk density (1.037 g/cm^3) this indicates that the P content in the sediment had declined from 3.15 g m^{-2} to around 1.5 g m^{-2}, a reduction of around 50%. Measurement of the total P content in the recovered Z2G1 granules (Table 1) showed that the mean P content of the Z2G1 was 1856 mg/kg (dry weight) indicating that most of that P reduction could be attributed to P-uptake by the Z2G1.

Regression analysis showed a statistically significant (P = 0.05, r^2 = 0.8968, n = 4) inverse relationship between the residual sediment P and the adsorbed P content in the Z2G1 recovered from that sediment (Fig. 5), which is also consistent with the P reduction being due to P-uptake by the Z2G1granules.

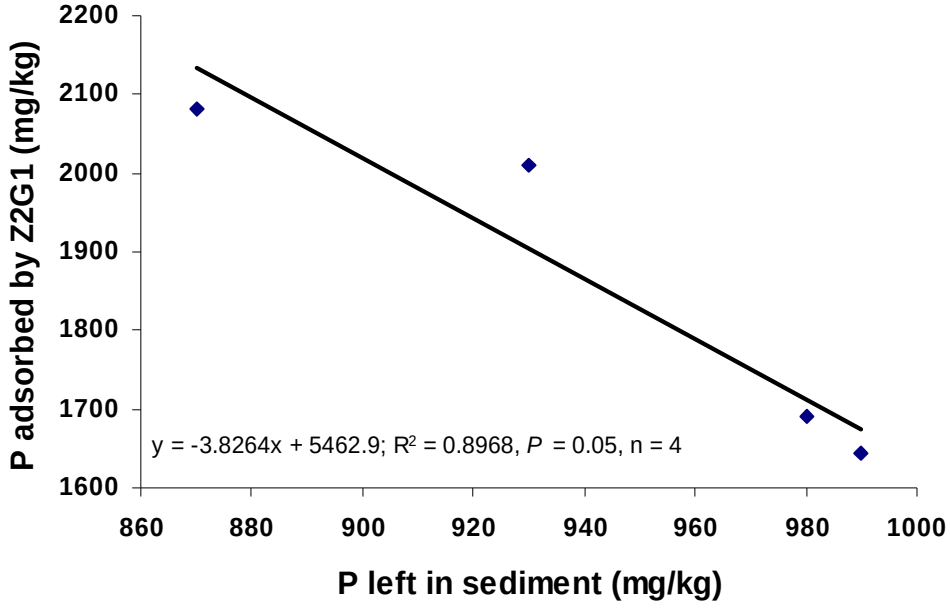

Figure 5: Regression analysis of the relationship between residual P left in the sediment and the P adsorbed by the Z2G1 sieved from that sediment.

The sediment trapping data following the 2007 Z2G1 application was limited due to loss of several key traps. Although best estimates of the amount of Z2G1 applied to the lake bed at the locations where the sediment cores were collected are given in Table 1, these are only indicative as the overall application in 2007 was spatially highly variable ranging from 400 g m^{-2} to over 1500 g m^{-2}. Within these limitations and recognising the potential for large errors, a mean estimate of the amount of Z2G1 applied would be around 930 g m^{-2}, using all the deep trap data from the 2007 application. Assuming that the mean total P content of all the Z2G1 granules was the same as the measured mean of 1.856 g P/kg, the mean P-removal would be around 1.73 g m^{-2}. As the original sediment P load was estimated to be around 3.2 g m^{-2}, this amount of P-removal would leave a residual P load of around 1.47 g m^{-2}, which is consistent with the initial estimate of around 1.5 g m^{-2} used to calculate the minimum dose rate for the 2009 application (section 2.2).

Further evaluation of the P adsorbed into the Z2G1 granules recovered from the sediment indicates that most of the P binding capacity of that application was not used. The P-saturation data (Gibbs & Özkundakci, 2010) show that Z2G1 can adsorb up to 20,000 mg P/kg and yet the recovered Z2G1 had only around 2,000 mg P/kg after being in the lake sediment for 2 years (Table 1). This suggests that when the large granules sank into the sediment, they were only able to remove P from the sediment immediately surrounding them and thus the capping layer became largely ineffective.

The finer grain-size Z2G1 applied in the 2009 application is not expected to sink into the sediment and thus should remain effective as a sediment cap.

3.2 Sediment trap data and evenness of coverage

With the total amount of Z2G1 applied at 44 tonnes, the expectation would be for an areal loading of Z2G1on the sediment of 166 g m^{-2}, assuming an even coverage. The trap data (Table 3; Fig. 1) indicate that the Z2G1 coverage was variable across the lake bed and that the mean dose rate was around 178 g m^{-2}. Correcting for under-trapping due to the potential loss of fine sediment from the trap edges during retrieval (estimated error term around 5% but possibly ranging up to 25%), the actual mean coverage was likely to be around 187, with an overall range of 100 mg m^{-2} up to 250 g m^{-2}.

Table 3: Sediment trap results showing the measured areal loading of Z2G1 (g m^{-2}) and the measured organic sedimentation flux (g m^{-2} d^{-1}) over the 35 day deployment of the mat traps in the hypolimnetic (>5 m depth) and littoral (<5 m depth) zones. The number of bullies per trap were as counted just before lifting the trap out. (+ indicates that some bullies may have left the trap before it reached the surface.)

Lake Okaro sediment trap data - 3rd September 2009												
Hypolimnetic												
Trap site	**1**	**4**	**5**	**7**	**8**	**9**	**10**	**11**	**12**	**14**	**15**	**16**
Depth (m)	14.9	12.7	14.8	10.3	13.5	15.5	13.8	17.2	11.5	14.4	14.0	14.0
Z2G1	191.0	98.2	158.4	148.7	277.9	193.5	179.0	221.0	138.9	201.7	245.4	183.6
Sediment flux	1.83	0.75	1.30	0.73	2.24	2.25	1.36	1.94	1.04	1.67	2.31	1.39
Bullies	3+	3+	1+	2+	7+	0+	16+	5+	12+	20+	20+	0+
Littoral												
Trap site	**2**	**3**	**6**	**13**	**17**							
Depth (m)	5.3	4.2	3.1	4.3	3.6							
Z2G1	3.2	76.1	108.5	71.8	30.8							
Sediment flux	0.73	0.88	0.76	0.43	0.17							
Bullies	0	2+	0	0	0							

Figure 6: Fine Z2G1 granules form a cloud in the water column as it mixes. This cloud can drift with lake currents before it settles to the lake bed.

The spatial variability of the Z2G1 across the lake bed indicates that the hypolimnion sediment was most likely covered with at least 100 g m^{-2} with much lower coverage in the littoral zone (<5 m deep) and essentially no Z2G1 in the immediate vicinity of the water supply intake. The presence of Z2G1 in the 4 littoral sediment traps indicates that the finer particle size material has drifted from the application path. This apparent drift was observed during the application as the Z2G1 formed a slow sinking cloud in the upper water column (Fig. 6). This indicates that further work is required to produce a product formulation and application technique that will get the capping material down to the lake bed quickly.

3.3 Water column effects

3.3.1 Nutrients

The time-series of nutrient data (Fig. 7) shows that there was a step-wise reduction in the concentrations of DRP and NH_4-N in the surface water during the application of the Z2G1 slurry. This indicates that the fine material had sufficient contact time to absorb the soluble nutrients from the upper water column. This is consistent with observations of the slurry dispersion as a cloud during application (Fig. 6). The reductions in DRP and NH_4-N concentrations were around 50% of their initial concentrations when the dosing started. There was no reduction in NO_3-N in the surface waters.

In the bottom waters there was only a small decrease in DRP concentration attributable to the Z2G1 treatment but no apparent effect on NH_4-N. There was a small reduction in NO_3-N concentration, although this was a step change rather than a continuous decrease.

These results may indicate a change in the effective contact time between the Z2G1 and the nutrients in the lower water column as it settles. This could be due to a change in relative buoyancy as the fine Z2G1 particles clump together, causing them to settle faster. A comparable effect is seen in estuaries where clay particles floc together as they meet the saline water and form larger particles which are less buoyant and settle quickly. Why flocculation should happen with Z2G1 in a lake situation is uncertain, although it may be a property of finely ground zeolite substrate.

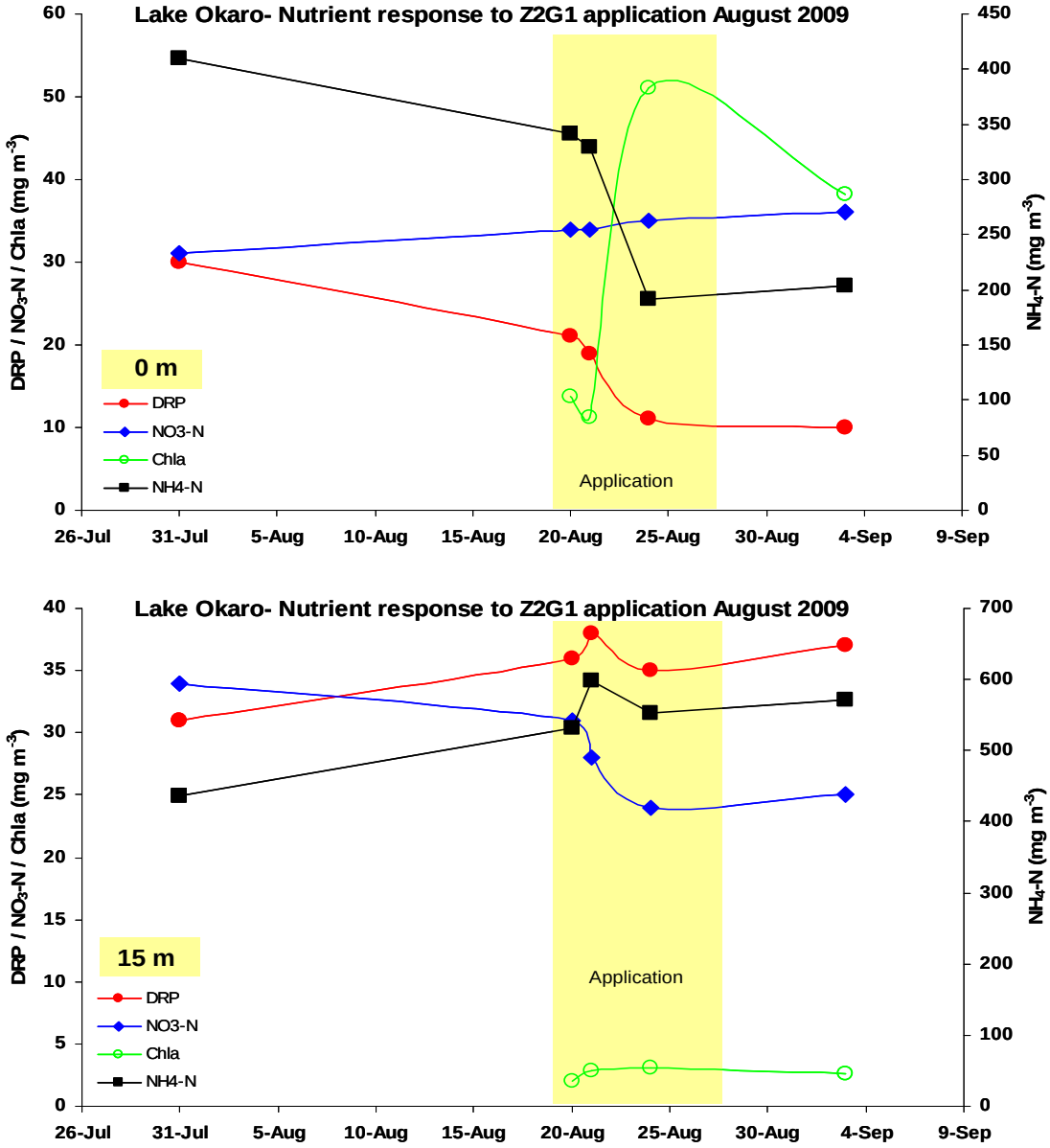

Figure 7: Surface (0 m) and bottom (15 m) water nutrient data from the deep site, trap Site 11). (Note the different right-hand axis scale for ammoniacal nitrogen (NH_4-N).

3.3.2 Sedimentation

The organic sediment flux data (Table 3) shows that the amount of organic matter caught on the traps was variable with a mean value of 1.28 g m^{-2} d^{-1} and a range from 0.17 to 2.31 g m^{-2} d^{-1}. While some variability would be expected, this range is very large but may be due to the inclusion of both shallow and deep traps in the analysis. The mean flux value for the deep (>5 m) traps was 1.57 g m^{-2} d^{-1} with a range from 0.73 to 2.31 g m^{-2} d^{-1}. Possible explanations for this high variability could include

flocculation and co-precipitation of the organic matter (including algae) from the water column with the Z2G1 material and / or natural sediment focusing with the lake circulation currents.

3.3.3 Flocculation

Evidence of flocculation was seen as a statistically significant relationship (P <<0.001, r^2 = 0.77, n = 13) between the organic sediment flux and the amount of Z2G1 in each >5 m deep trap (Fig. 8). These data suggest that the fine grain Z2G1 has the capacity to remove some organic matter from the water column as it settles.

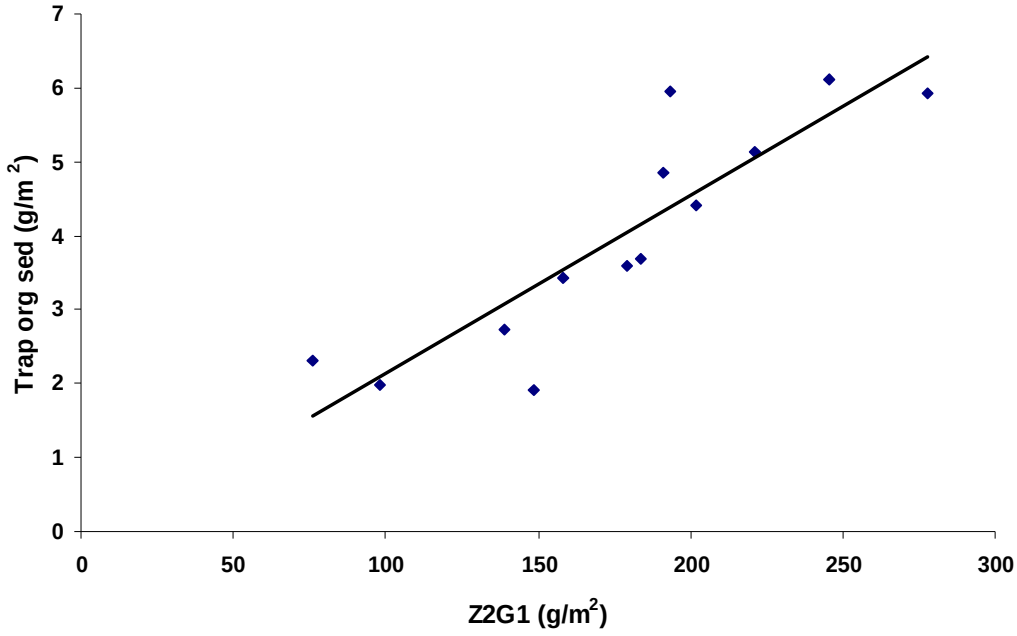

Figure 8: Statistically significant relationship between the amount of organic sediment and the Z2G1 caught in each mat trap (P <<0.001, r^2 = 0.77, n = 13). (Excludes the <5 m deep traps).

There was also an interesting pattern to the number of bullies observed in each trap, with higher numbers occurring in the eastern traps (Fig. 9) than in the traps elsewhere around the lake at depths greater than 5 m.

Further analysis of the number of bullies per trap below 5 m depth indicated two distinct populations which have been grouped as low (<10/trap; Green group, Fig. 9) and high (>10/trap; Yellow group, Fig. 9). This is an arbitrary separation but regression analysis (Fig.10) shows that there was a statistically significant relationship (P <0.05, r^2 = 0.58, n = 7) between the number of bullies and the organic sediment

content of the traps for the <10/trap group (regression excluded traps with no bullies). There was a similar relationship for the >10/trap group but this was not statistically significant ($P = 0.15$, $r^2 = 0.72$, $n = 4$) due to the small sample size.

Notwithstanding this, the slopes of the regression equations suggest that there were four times as many bullies in the yellow group traps than in the green group traps.

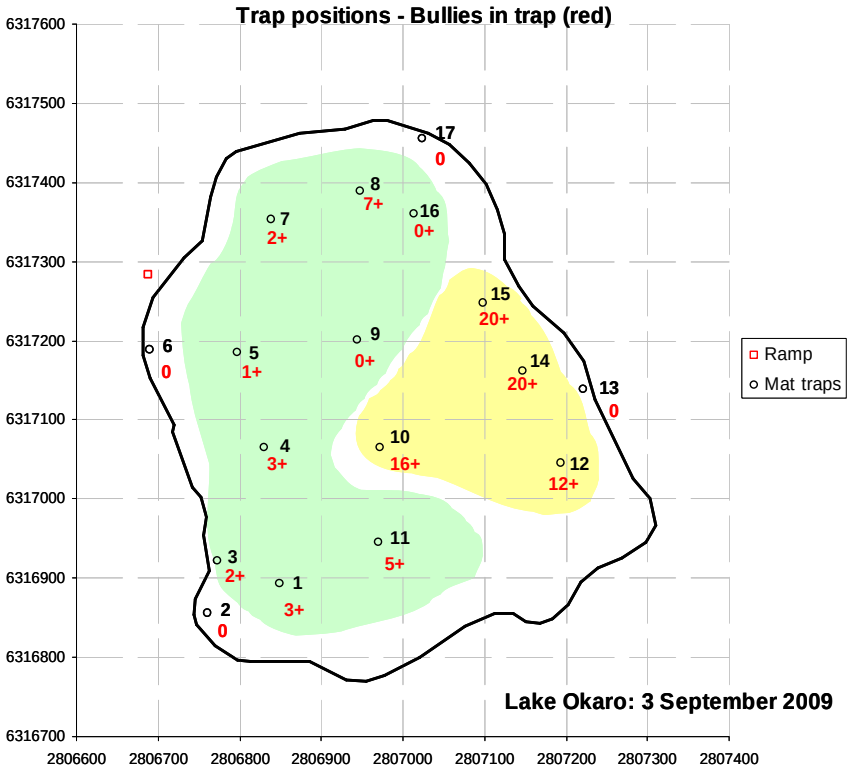

Figure 9: Distribution pattern of bullies observed in the mat traps. Red numbers are the number of bullies observed in each trap (black number; Table 3) as it was retrieved. The + indicates that some bullies may have left the trap before it reached the surface. Coloured groupings link trap sites with high (yellow) or low (green) numbers of bullies per trap.

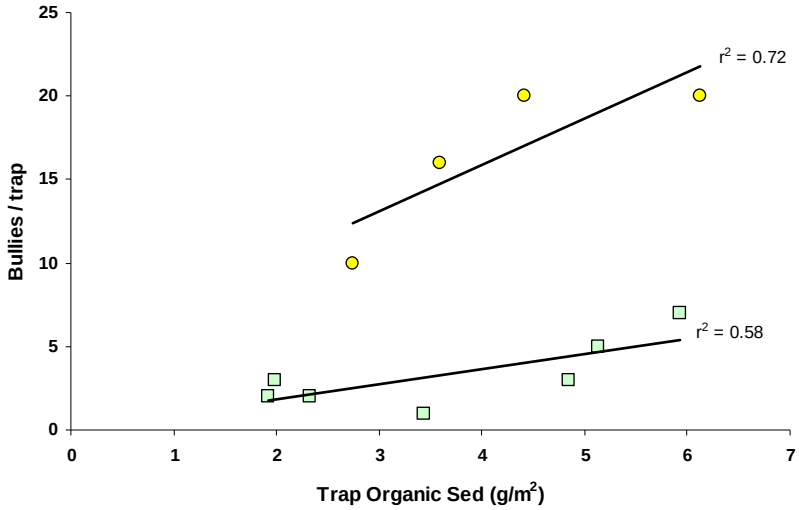

Figure 10: Relationships between the number of bullies per trap and the amount of organic sediment in each trap in the green and yellow groupings (Fig. 9; see text).

As there is only one species of bully (*Gobiomorphus cotidianus*) in Lake Okaro (Dave Rowe, NIWA, pers. comm.), the apparent separation is not a reflection of different species. There were also no relationships with depth, temperature, or dissolved oxygen content to explain these patterns. However, as bullies are bottom feeders, a possible explanation is that the green area of the lake bed (Fig. 9) has a naturally lower organic food content and thus lower numbers of resident bullies/m^2 than in the yellow area of the lake bed. The number of bullies in each trap would then reflect the ambient population adjacent to the trap as bullies have a known tendency to rest on elevated material on the lake bed. This concept implies that there is a natural focussing of organic matter into the yellow area of the lake bed of Lake Okaro. This may also have had some influence on the deposition of the applied Z2G1.

3.3.4 Chlorophyll *a*

Chlorophyll *a* concentrations in the surface waters (0 m) at trap site 11 on 20th and 21st August averaged 12.6 mg m^{-3} then suddenly increased to >50 mg m^{-3} on 24th August (Fig. 7). This change in concentration was too rapid for a natural growth and can be attributed to wind drift accumulation of algal material in the surface layer. In support of this, the chlorophyll *a* concentration was 22.0 mg m^{-3} at 5 m at trap site 11 on 24th August at the same time (Fig. 11).

Based on Redfield ratios (Redfield 1958), 1 mg chlorophyll *a* uses 1 mg P and 7.2 mg N. The reduction in DRP observed was around 10 mg m^{-3} and consequently, the maximum increase in chlorophyll *a* that might be expected would be 10 mg m^{-3}. Using

the N relationship, NH_4-N concentrations reduced by around 150 mg m^{-3} which equates to a potential chlorophyll *a* increase of around 20 mg m^{-3}. If the increase in chlorophyll *a* concentrations were due to growth, the increase would have caused reductions in the soluble N and P concentrations at a ratio of around 7:1.

Mean chlorophyll *a* concentrations at 5 m across the north-south axis of the lake increased from 20.9 mg m^{-3} on 24th August, at the beginning of the dosing, to 30.1 mg m^{-3} on 3rd September (excluding trap site 9) 6 days after dosing had finished. This increase over a period of 10 days is consistent with a slow but natural algal growth rate.

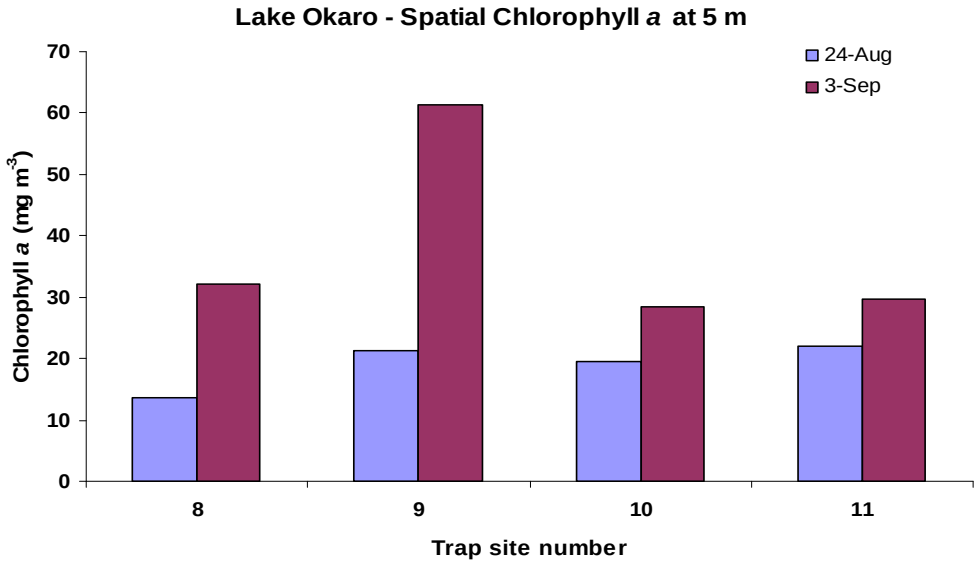

Figure 11: Sequential spatial chlorophyll *a* concentration data along the central north-south axis of Lake Okaro (site numbers refer to Fig.1). The elevated chlorophyll *a* concentration in the surface water at site 11 on 24th August was not present at 5 m depth.

The high value on 3rd September was excluded from the mean estimate as it correlated with a layer of dinoflagellates (*Peridinium sp.)* moving around the lake as a large patch. This layer was observed in the chlorophyll fluorescence data from the CTD profiler (Fig. 12). Time-series data indicate that the patch of algae moved across the lake from south to north and generally remained at the bottom of the euphotic zone (about 5 m) in a thin layer about 1 m thick.

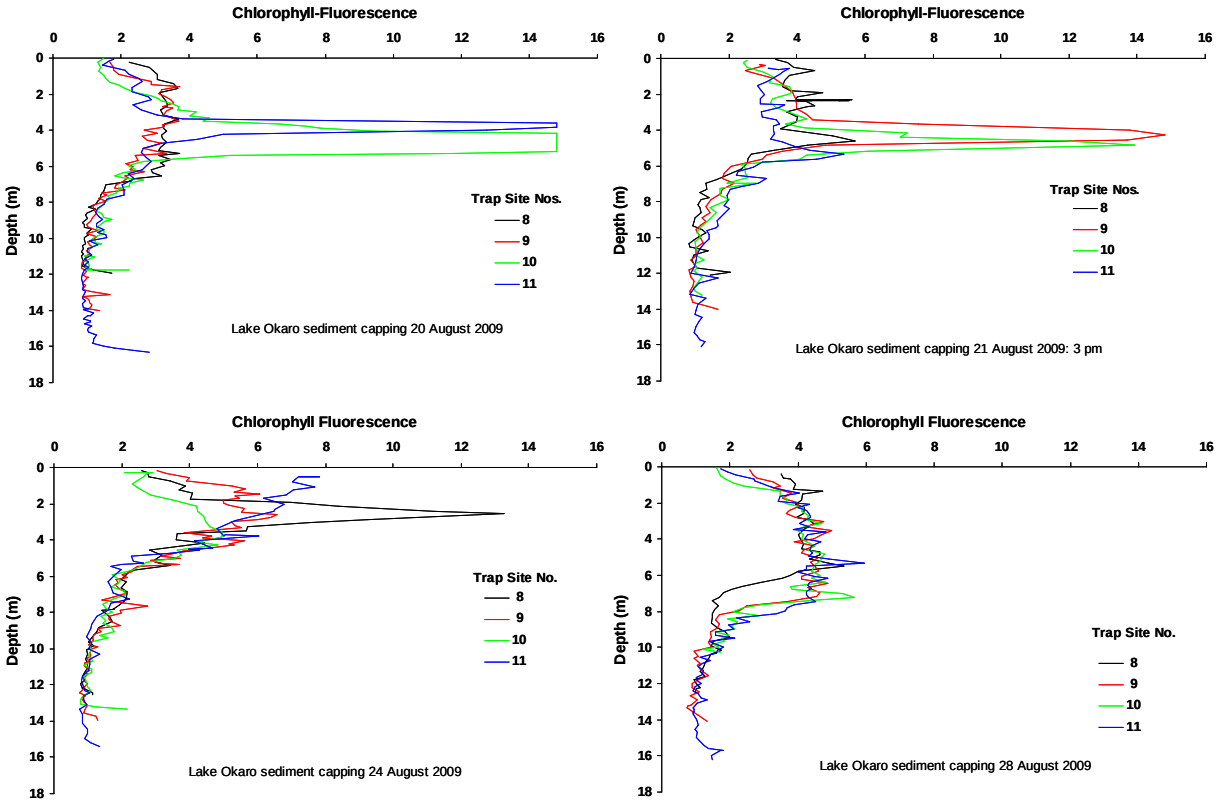

Figure 12: Spatial and time-series chlorophyll fluorescence data along the north-south axis of Lake Okaro on 20, 21, 24 and 28 August. On 20th August, the *Peridinium sp.* bloom was at 4 m depth at trap site 11 with a larger proportion at 5 m depth at trap site 10. On 21st August, the bloom patch had moved north with the layer covering trap sites 10 and 9 but being absent from trap sites 11 and 8. On 24th August the bloom was only present at trap site 8 and was not present at any site on 28th August.

The layer of dinoflagellates was present at trap site 8 only on the 24th August and was not found at any of the north-south axis trap sites on 28th August. The layer of *Peridinium sp*. was present again at trap site 9 only on the 3rd September (Fig. 13). Because the layer was not observed at all trap sites along the north-south axis on every occasion and was not seen at any of these trap sites on one occasion, it can be concluded that the patch of dinoflagellates occupied less than half the lake and possibly less than one third.

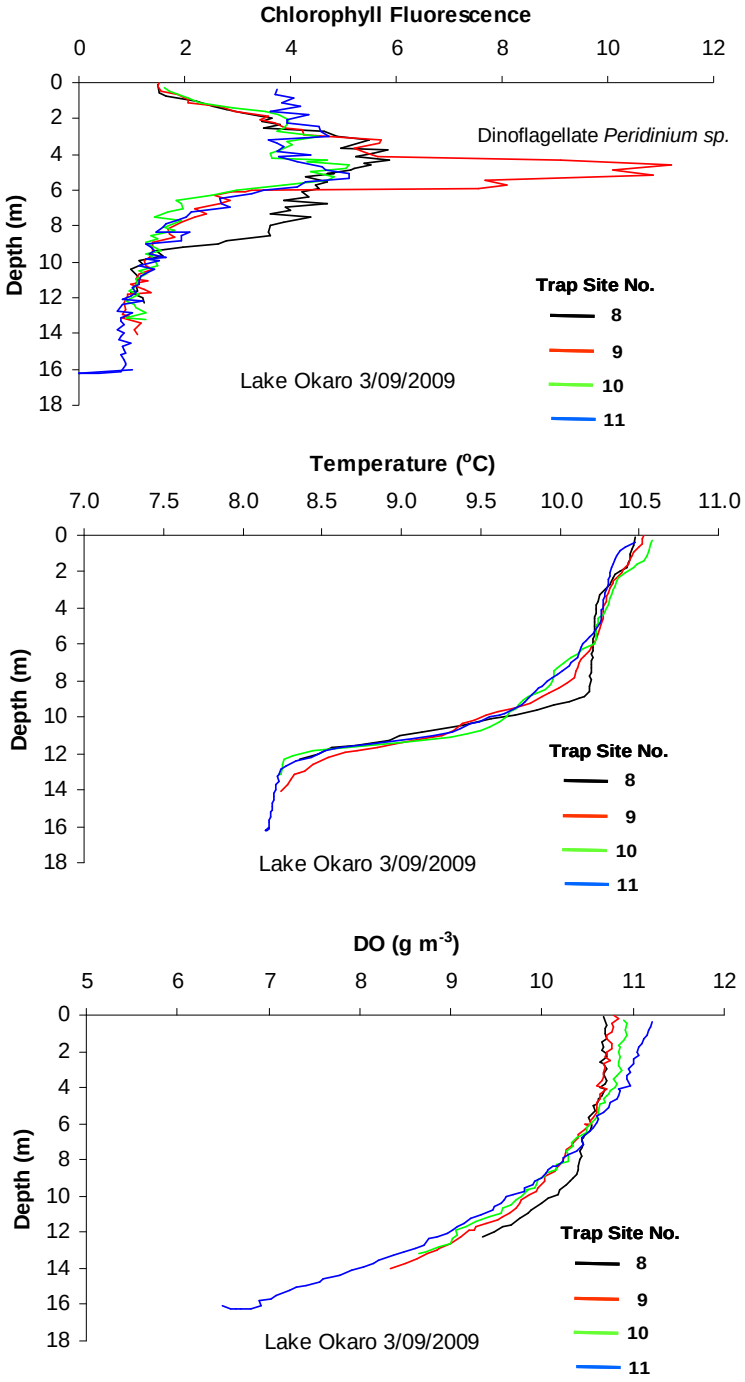

Figure 13: Spatial profile data for chlorophyll fluorescence, temperature, and dissolved oxygen (DO) along the north-south axis of Lake Okaro on 3rd September 2009.

Given the relatively small size of Lake Okaro, it would be reasonable to expect that the dinoflagellate bloom would extend across the whole lake, rather than exist as a large slowly moving patch. While the observed patchiness of the bloom may have

been natural, it could also have been caused by co-precipitation of the algal cells with the Z2G1 floc. The flocculation of pelagic algae may have been the source of material contributing to the higher organic content in some of the traps. Unfortunately, the sediment from the traps was not examined for algal cell content.

Data from the profiles at the four north-south axis trap sites on 3rd September (Fig. 13) show that the peak algal biomass was above the depth of the thermocline, indicating that the dinoflagellates were holding a depth position mostly for light.

The DO data in these profiles shows that the bottom waters of the lake were relatively well oxygenated indicating that there was unlikely to have been a release of nutrients from the sediment immediately before or during the dosing of the lake.

3.3.5 Argument for P adsorption rather than phytoplankton uptake

The assumption was made that the observed reductions in DRP and NH_4-N concentrations from the upper water at the time of Z2G1 application were due to adsorption by the Z2G1 treatment rather than uptake by phytoplankton which also peaked in the surface waters at that the same time. The reasoning behind this is as follows:

- The nutrient reduction did not include NO_3-N, which it should have if it was due to phytoplankton growth. Conversely, Z2G1 adsorbs both DRP and NH_4-N but not NO_3-N.

- The reduction was sudden (over 3 days) and coincided with the application of Z2G1. Nutrient changes did not occur before or after, as they should have if the reduction was due phytoplankton growth.

- The 40 mg m^{-3} increase in chlorophyll *a* concentration associated with the 10 mg m^{-3} reduction in DRP concentration was 4 times more than would be expected based on Redfield ratios which show 1 mg chlorophyll *a* uses 1 mg P. Redfield ratios also show that 1 mg of chlorophyll *a* uses 7.2 mg N. Consequently, the 150 mg m^{-3} reduction in NH_4-N concentrations at the same time is only about half the amount of N required to support the observed increase in chlorophyll *a*.

- To achieve that increase in 3 days would require a high doubling rate which is unlikely in August with low ambient light and water temperatures around 10ºC.

- The increase in chlorophyll *a* on the 24th August can be explained as a surface effect caused by a wind-drift accumulation of algae near trap site 11. The chlorophyll fluorescence data (Fig. 12) hint at the higher surface concentrations at trap site 11 but do not show the expected high concentrations deeper in the water column that would have occurred if the algae were growing in the surface mixed zone. There were no elevated chlorophyll fluorescence values at any of the other sites on that day, apart from the deep layer of dinoflagellates at the other end of the lake.

Undoubtedly there would have been some algal growth in the lake at that time, but the majority of the reduction in DRP and NH_4-N can reasonably be attributed to adsorption into the Z2G1 suspension in the water column before it settled.

4. Conclusions

- The Z2G1 was successfully applied across the bottom of the lake below 5 m depth at a mean areal loading of 178 g m^{-2}. This compares favourably with the expected coverage of 166 g m^{-2} from the 44 tonnes applied.

- The minimum coverage achieved was at least 100 g m^{-2} across the deep lake bed, an areal loading more than sufficient to take up the estimated potential phosphorus release from the sediment of around 1.5 g P m^{-2}.

- The coverage was uneven and ranged from around 100 g m^{-2} up to 245 g m^{-2}, and there was substantial amounts of Z2G1 in shallow lake edge zones <5 m deep. Much of this variability can be attributed to slow settling of the fine grain material and lake currents causing drift. This indicates that there is still work to be done to devise a formulation that will settle quickly and yet give the coverage required in the target area.

- The fine grain size product appears to have some degree of nutrient uptake capacity in the surface waters before it settles to the sediment surface. This is likely to be a function of contact time. This contact time did not appear to extend to the deeper waters, possibly due to flocculation effects.

- The fine grain size formulation of Z2G1 also appears to have a flocculation capability and caused co-precipitation of organic matter from the lake water column. There was a statistically significant relationship ($P << 0.001$, $r^2 = 0.77$, $n = 13$) between the amount of organic matter and the Z2G1 in each of the deep (>5 m) traps. Once the Z2G1 began to clump during flocculation, the particles would rapidly fall to the sediments and have less contact time to adsorb nutrients in the lower water column.

- It is possible that some of the organic matter caught in the floc came from the dinoflagellate bloom in the lake at that time. This bloom was detected by chlorophyll fluorescence profiles as a large patch about 1 m thick, moving around the lake at a depth of 5 m, rather than being a coherent layer covering the whole lake, as might be expected in a relatively small lake the size of Lake Okaro.

- Because of the mobile nature of the dinoflagellate patch in Lake Okaro, there is a possibility that time-series chlorophyll *a* data from single site samplings may be misleading.

- Mean chlorophyll *a* concentrations at 5 m across the lake (excluding the dinoflagellate influence) showed a slow increase from 20.9 mg m^{-3} to 30.1 mg m^{-3} over a 10 day period consistent with natural growth without stimulation by the Z2G1 dosing.

- Evidence from the P analyses of the Z2G1 from the 2007 application recovered from the top 4 cm of the sediment cores taken before the 2009 application, confirmed that the Z2G1 adsorbs P from the lake sediment. Although there are potentially large errors in the data due to the large spatial variability of the 2007 application and loss of key sediment traps at that time, only about 10% the P-binding capacity of the large Z2G1 granules was used. This was most likely due to the large granules sinking into the sediments and becoming isolated from P released in the sediment between the granules but not in contact with them.

- The finer grain-size Z2G1 applied in the 2009 application is not expected to sink into the sediment and thus should remain effective as a sediment cap blocking P release.

5. Acknowledgements

I would like to thank Eddie Bowman for taking the additional profile and water samples that enabled an understanding of the movement of the dinoflagellate patch in the lake, Deniz Özkundakci for the analysis of the P in the Z2G1 granules recovered from the 2007 application, and Dave Rowe for the interpretation of the bully data in the sediment traps.

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