Testing sediment capping agents: P-equilibrium, P-saturation, dispersion and settling velocities

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Contents

Executive Summary iv

1. Introduction 1

2. Phosphorus equilibration tests: 2
    - 2.1 Test conditions 2
    - 2.2 Sampling times: 3
    - 2.3 Observations: 3
    - 2.4 Results 4
    - 2.5 Summary 7

3. Phosphorus saturation test: 8
    - 3.1 Test conditions 8
    - 3.2 Sampling and analysis 8
    - 3.3 Observations 9
    - 3.4 Results 9
    - 3.5 Summary 12

4. Dispersion and settling 14
    - 4.1 Test conditions 14
    - 4.2 Measurement strategy 15
    - 4.3 Results 16
    - 4.3.1 5-m test 16
    - 4.3.2 10-m test 16
    - 4.3.3 15-m test 17
    - 4.3.4 Summary 17

5. Overview 19

6. Acknowledgements 19

7. References 19

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Executive Summary

Sediment capping techniques have the potential to manage phosphorus releases from the sediments of Lake Rotorua which will improve the water quality of the lake. Typically capping agents are applied at the lake surface and settle to the lake bed forming the active barrier against phosphorus release. However, preliminary data from hydrology studies on Lake Rotorua indicated that lake currents have the potential to move the capping material considerable distances from the point of application. To ensure that any capping agent applied to the lake can reach a specified target area on the lake bed, the capping agent needed to be formulated into a pellet (prill) that would fall rapidly through the water column before disaggregating near the lake bed and dispersing to form a thin layer on the sediment surface. Following a call for such formulations, NIWA was asked by Bay of Plenty Regional Council to test the products developed to assess (1) their P-equilibration (P-uptake) values at ambient lake dissolved reactive phosphorus concentrations, (2) their P-saturation (maximum P-binding) capacities, and (3) the settling rate and depth at which each product broke apart (disaggregated) and dispersed in Lake Rotorua water.

1. The P-equilibration tests showed that alum was the most efficient product for removing P from lake water at ambient lake water concentrations. Phoslock™ was almost as effective but appeared to have a threshold concentration of about 5 mg P m^{-3} below which it did not remove P. Aqual P (previously Z2G1) formulations were less effective at stripping P from the water column. These products were designed primarily as sediment capping agents. Some products released P into the water column indicating a diffusion process driven by concentration gradient. Some products did not disaggregate during this test.
2. The greatest mass-specific P-binding capacity was for alum and products containing alum. Comparisons of P-binding capacities of the new products with previous assessments of their powdered formulations showed substantial reductions for the Aqual P products and allophane and an increase for Phoslock™. The measured maximum P-saturation capacity of alum was 86 g P /kg which was slightly higher than the theoretical value from the literature.
3. Settling rates and dispersion specifications were met by the Aqual P slow release product which sank to a depth of around 12 m in about 3 minutes before disaggregating and dispersing. Aqual P fast release and Phoslock™ both disaggregated and dispersed in less than 5 m. However, while Phoslock™ appeared to remain as a fine suspension, Aqual P fast release fine granules settled to the lake bed over a period of about an hour. The other formulations did not disaggregate in the test and fell through the 15 m deep test water column in less than 5 minutes as intact pellets.

Of all the products tested, the most efficient at removing P was alum. However, further work is needed on application and buffering techniques to enable alum to be used in New Zealand’s soft water lakes.

1. Introduction

As part of the preparation for using sediment capping techniques for the restoration of Lake Rotorua, application techniques are being investigated for Bay of Plenty Regional Council. NIWA was asked to test several potential sediment capping agents (Table 1) that have been prepared by suppliers in formulations that should allow them to be applied to the lake surface as a granule which will settle rapidly to a mid water column depth before disaggregating and dispersing to produce a thin layer across the sediment. This report presents the results of a series of standardised procedures to assess:

- the P-equilibration and uptake characteristics of the capping agents at ambient lake dissolved reactive phosphorus (DRP) concentrations

- the maximum mass-specific P-saturation (P-binding) capacity of each product, and

- the settling rates and depth of disaggregation and dispersion of selected products in Lake Rotorua.

2. Phosphorus equilibration tests:

Objective: to determine the phosphorus (P) uptake rate of each product at the normal DRP concentrations found in Lake Rotorua during periods of stratification which result hypolimnetic anoxia.

Table 1: Products tested. (* original products retested; BPM = Blue Pacific Minerals).

Product	Code	Description
Aqual P FR	(AP-FR)	Aqual P fast release prill [BPM]
Aqual P SR	(AP-SR)	Aqual P slow release prill [BPM]
Aqual P +A	(AP+A)	Aqual P plus alum prill [BPM]
Aqual P (original)*	(AP)	Aqual P fine grain powder [BPM]
Phoslock™ granules	(Phos)	Commercial Phoslock™ pellets/granules
Allophane granules	(ALL)	Allophane bound with 2% lignin [Fertco]
Allophane (original)*	(ALL‡)	Allophane fine grain powder [LandCare]
Alum*	(A)	46% solution of aluminium sulphate
Alum/Lime granules	(A-L)	25% alum, 71% lime, 4% lignin [Fertco]
Virophos (small)	(VS)	Small balls [Virotech]
Virophos (large)	(VL)	Large balls [Virotech]
Bauxite (Andoom)	(BA)	powder
Bauxite (Weipa)	(BW)	powder

Most of the products tested (Table 1) were formulated specifically for this study. The manufacturer of the Virophos products had optimised their product formulation for depth dispersion rather than for P uptake (Graeme Colquhoun, Orica, pers. comm.).

Two of the granular products in prill form, Aqual P and allophane, had previously been tested as fine grain formulations (Gibbs et al. 2008). The fine grain formulations of these two products were also tested for P-equilibration at natural DRP concentrations along side their prill formulations as reference materials. Aluminium sulphate (alum) was also tested.

2.1 Test conditions

The tests were conducted in a constant temperature room at 18ºC. Reaction vessels were new, clean, 5-litre plastic buckets with sealable lids. Approximately 50 mg of each product was suspended in 1 litre of filtered natural water [Waikato River] with phosphate P concentration amended to around 50 mg P m^{-3} and 100 mg P m^{-3} with constant agitation on a shaker table. The P addition solution was made by dissolving 0.50 g of sodium di-hydrogen phosphate ($NaH_2PO_4.2H_2O$) and 0.574 g of di-sodium hydrogen phosphate ($Na_2HPO_4.2H_2O$) in 1 litre of deionised water. This stock solution had a pH of 7.5 and a phosphate concentration of 212 mg l^{-1}. The addition of 2.5 ml or 5 ml of stock solution to 1 litre of filtered river water produced a concentration of about 52 mg P m^{-3} or 105 mg P m^{-3}, respectively.

The reaction mixture for alum was buffered to pH 7.0 using sodium bicarbonate solution during addition of the product.

2.2 Sampling times:

A 20 ml sample of the water was taken from each reaction vessel by syringe. The sample was pressure filtered through a 25 mm diameter Whatman GF/F glass fibre filter (nominal 0.7 µm filtration) in a Swinnex® filter holder immediately into a vial ready for analysis of DRP on a Lachat flow injection analysis (FIA) system. A sample of the starting water was used as the initial or time zero (T0) concentration. Subsequently, sequential samples were collected from each reaction vessel at 1 hr, 2 hr, 4 hr, 7 hr and 24 hr. Samples from day 1 were stored overnight at 4ºC and were analysed together with the 24 hr samples the next day.

2.3 Observations:

The product disaggregation time after addition to the aqueous mixture in the reaction vessels, was estimated for the test conditions (Table 2) as the time to change from the original "prill" shape to a dispersible finer powder or granule. The Aqual P products and Phoslock™ granules disaggregated rapidly in water while the other granular products remained as recognisable prills for at least 24 hours. Dispersion was interpreted as the spread of the product across the bottom of the reaction vessel after disaggregation. Settling was a comparative estimate of how fast the products reached the bottom of the reaction vessel and turbidity indicates whether there was a fine suspension left in the water after the bulk of the material had settled. The pH relative to the start pH of 7.50 was measured after 1 hour and again after 24 hours. The small increase in pH after 24 hours reflects a loss of CO_2 from the water.

Table 2: Summary of observations of general properties of the newly formulated products tested. (Product codes as per Table 1).

Effect	AP-FR	AP-SR	AP+A	Phos	All	A-L	VS	VL	BA	BW
Disaggregation	<1 min	~4 mins	~6 mins	<1 min	>24 hr	>24 hr	>24 hr	partial	N/A	N/A
Dispersion	even	even	even	even	lumps	lumps	lump	patchy	even	even
Settling	rapid	rapid	rapid	slow	fast	fast	fast	fast	slow	slow
Turbidity	nil	nil	nil	slow to clear	some fines	nil	nil	some fines	high turbidity	high turbidity
pH (1 hr)	7.50	7.50	7.13	7.51	7.54	7.56	7.55	7.56	7.49	7.49
pH (24 hr)	7.84	7.82	7.72	7.84	7.84	7.87	7.87	7.87	7.86	7.84

2.4 Results

The analytical results are listed in Table 3. With the notable exceptions of the allophane and small Virophos prills, all the new formulated products reduced the concentration of DRP in the reaction vessel water. However, with the exceptions of the alum, Aqual P and Phoslock™ product treatments, the reduction in DRP concentration in the reaction vessel water was small. The apparent greater DRP reductions associated with the Virophos treatments are most likely due to the larger amount of these products added to the reaction vessel because of the individual pellet size and the requirement for a minimum dose of 1 pellet rather than the crumbled powder from a pellet.

Table 3: Dissolved reactive phosphorus (DRP) concentrations (mg m^{-3}) in the overlying water in the reaction vessels after timed intervals. (Product codes as per Table 1; 50 and 100 are the DRP solution concentrations in mg m^{-3}; Weight is the amount of product added to the 1-litre reaction vessel; * = the weight of 1 pellet as the minimum dose rate). Note the different time sequence for the repeat Aqual P and Alum tests.

Time (hr)	AP-FR 50	AP-FR 100	AP-SR 50	AP-SR 100	AP+A 50	AP+A 100	AP 50	AP 100
Weight (mg)	53.7	53.7	51.6	59.5	53.7	53.7	50.6	52.4
0	52	105	52	105	52	105	56	106
1	41	89	57	96	17	20	43	83
2	44	88	49	95	14	20	41	81
4	40	84	45	88	14	22	40	78
7	43	85	45	96	16	27	39	75
24	38	77	41	81	15	27	38	74

Time (hr)	ALL 50	ALL 100	ALL‡ 100	Phos 50	Phos 100	A-L 50	A-L 100
Weight (mg)	54.6	54.2	54.6	53.4	53.4	55.0	52.4
0	52	105	106	52	105	52	105
1	52	101	102	33	68	49	93
2	55	105	100	12	43	56	96
4	58	106	96	7	30	49	95
7	61	110	92	4	16	53	96
24	62	110	81	3	5	47	85

Time (hr)	VS 50	VS 100	VL 50	VL 100	BA 50	BA 100	BW 50	BW 100
Weight (mg)	88.2	70.3	291.8	238.5	52.1	52.5	50.7	51.3
0	52	105	52	105	52	105	52	105
1	55	103	49	92	50	96	44	89
2	57	107	49	89	53	95	45	90
4	56	104	41	87	49	97	45	90
7	61	110	36	77	48	94	43	88
24	53	95	28	61	46	91	39	81

Time (hr)	AP 50	AP 100	Alum 50	Alum 100
Weight (mg)	50	50	25	25
0.0	51	101	52	102
1.5	35	87	0	1
3.0	37	79	1	2
5.0	37	75	3	3
21.0	33	73	6	5

The largest reduction in DRP concentration (P-uptake) was for alum which was almost 100% initially (Table 4). Subsequent sampling appeared to show a small release of DRP from the alum over the duration of the test. This was probably due to disaggregation of the initial floc and the passing of small amounts of the colloid through the filter. The colloidal material would dissolve in the acidic reagents used in the analysis.

The Phoslock™ treatments achieved almost 90% reduction after 24 hours (Table 4). Aqual P+A treatments achieved almost 70% reduction after 24 hours (Table 4). Aqual P FR was slightly more effective in removing DRP than Aqual P SR at around

25% and 20% reduction, respectively, in DRP concentration after 24 hours (Table 4). The natural bauxite mineral samples reduced DRP concentrations but with the material from Weipa, at 22-25% reduction, removing about twice as much as the material from Andoom at 11-13% reduction and being comparable with the removal efficiency of the Aqual P FR formulation (Table 4). Although natural bauxite has an aluminium assay of >60%, the aluminium appears to be in the wrong form to be an effective P binding agent. It was also very slow to settle (see below).

Table 4: Reduction (%) of dissolved reactive phosphorus (DRP) achieved by each product normalised to 50 mg product per 1-litre aqueous solution in the reaction vessel. (Product codes as per Table 1; 50 and 100 are the DRP solution concentrations in mg m^{-3}; negative values indicate DRP concentrations increased). Note the different time sequence for the repeat Aqual P and Alum tests.

Time (hr)	AP-FR 50	AP-FR 100	AP-SR 50	AP-SR 100	AP+A 50	AP+A 100	AP 50	AP 100
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	19.7	14.2	-9.3	7.2	62.7	75.4	22.9	20.7
2	14.3	15.1	5.6	8.0	68.0	75.4	26.5	22.5
4	21.5	18.6	13.0	13.6	68.0	73.6	28.2	25.2
7	16.1	17.7	13.0	7.2	64.5	69.2	30.0	27.9
24	25.1	24.8	20.5	19.2	66.3	69.2	31.8	28.8

Time (hr)	ALL 50	ALL 100	ALL‡ 100	Phos 50	Phos 100	A-L 50	A-L 100
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	3.5	3.5	34.2	33.0	5.2	10.9
2	-5.3	0.0	5.2	72.0	55.3	-7.0	8.2
4	-10.6	-0.9	8.6	81.0	66.9	5.2	9.1
7	-15.8	-4.4	12.1	86.4	79.4	-1.7	8.2
24	-17.6	-4.4	21.6	88.2	89.2	8.7	18.2

Time (hr)								
0	**VS 50**	**VS 100**	**VL 50**	**VL 100**	**BA 50**	**BA 100**	**BW 50**	**BW 100**
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	-3.3	1.4	1.0	2.6	3.7	8.2	15.2	14.9
4	-5.5	-1.4	1.0	3.2	-1.8	9.1	13.3	13.9
7	-4.4	0.7	3.6	3.6	5.5	7.3	13.3	13.9
24	-9.8	-3.4	5.3	5.6	7.4	10.0	17.1	15.8
	-1.1	6.8	7.9	8.8	11.1	12.7	24.7	22.3

Time (hr)				
Weight (mg)	**AP 50**	**AP 100**	**Alum 50**	**Alum 100**
0.0	0.0	0.0	0.0	0.0
1.5	31	14	100	99
3.0	27	22	98	98
5.0	27	26	95	97
21.0	34	28	89	95

Nested P-equilibration curves for allophane, alum, Aqual P and Phoslock™ are shown in Figure 1.

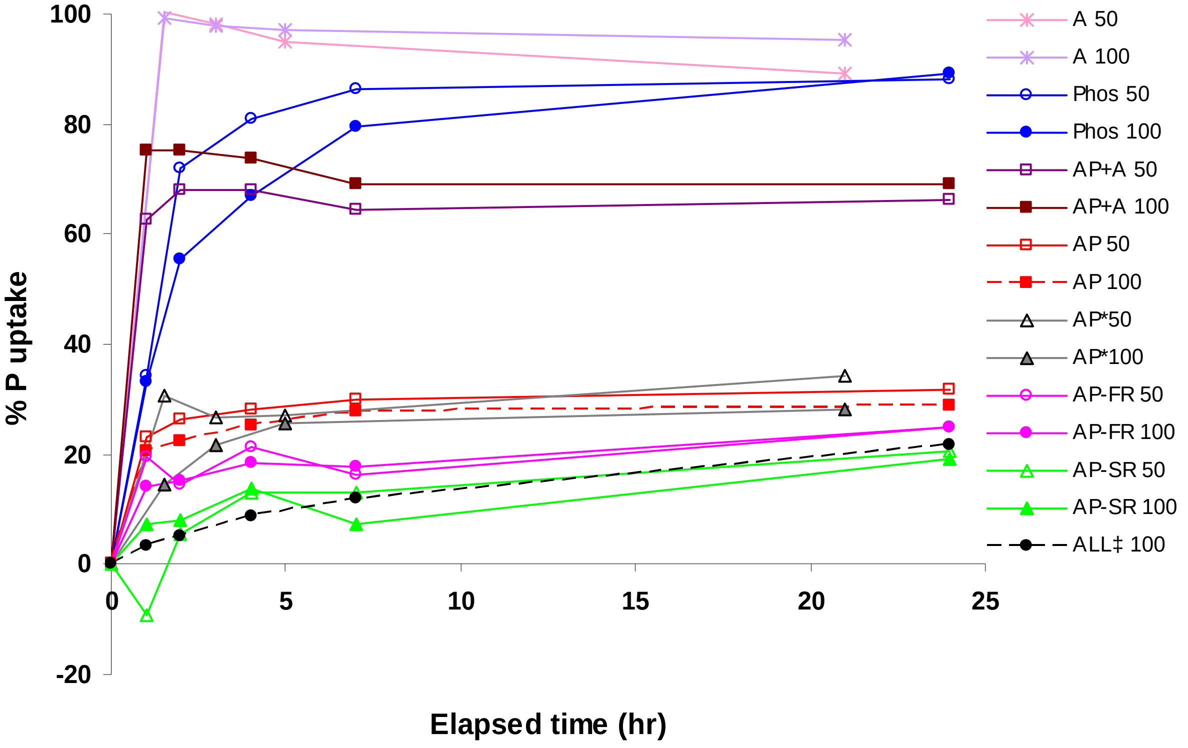

Figure 1: Nested P-equilibration curves for selected products normalised to 50 mg product per 1-litre aqueous mixture. (Product codes as per Table 1, AP* are repeated measurements of AP; 50 and 100 are the DRP solution concentrations in mg m^{-3}; negative values indicate DRP concentrations increased).

2.5 Summary

The Aqual P products were designed to disaggregate at different rates and performed as designed. Phoslock™ also disaggregated rapidly. The other products tested failed to disaggregate fast enough to be useful as capping agents in Lake Rotorua.

In terms of P-removal at lake concentrations, alum was the most effective product followed closely by Phoslock™. Sediment capping agents that previously worked well as a slurry [Aqual P (Z2G1) and allophane] had a substantial reduction in P-uptake efficiency on a weight-for-weight basis of final product when made into a pellet or prill. This is mostly due to the proportion of binding agent used to hold the fine particles together. Confirmation that this reduction in efficiency was not just an artefact of the test regime, was provided by the Phoslock™ product which retained it's previously measured high P-uptake efficacy. The Phoslock™ product was already in a pellet /granular formulation and was the same product as used in earlier tests.

3. Phosphorus saturation test:

Objective: to determine the maximum amount of phosphorus that could be bound by the product formulations tested.

Products tested were as for the P-equilibration tests (Table 1).

Two of the granular products, Aqual P and allophane have previously been tested as powdered formulations and were retested for maximum mass-specific P binding capacity along side the other products as reference materials. In addition, the maximum P binding of alum was measured. Previously the maximum P binding capacity of alum had been calculated from literature values. The results of the new tests were compared with previous estimates

3.1 Test conditions

About 2 g of each product was suspended in 200 ml of buffered phosphate solution (10 g P l^{-1}) in a 1 litre polyethylene bottle and the alum, Aqual P+A, and the alum/lime suspensions were adjusted to pH 7 with a few ml of sodium bicarbonate solution (since the buffer capacity of the test solution was exceeded by these products). The air gap in the bottles facilitated good mixing and the bottles were kept agitated on a shaker table at 18°C for 5 days. A separate transparent 100 ml container with 2 g of product in 100 ml water was also placed on the shaker table to assess disaggregation of the prills. Periodically, at least twice a day, each bottle and container was vigorously shaken for 1 minute and then returned to the shaker table.

3.2 Sampling and analysis

After 5 days the bottles were allowed to stand and the product settled over night (Fig. 2). The clear supernatant liquid was decanted and discarded. The solid residue was washed into a 50 ml plastic centrifuge tube and made up to 50 ml with deionised water. The tube was sealed and shaken before being centrifuged at 3000 rpm for 10 minutes. The clear liquid was decanted and discarded. The solid residue was rinsed with another 50 ml of deionised water and re-centrifuged. After decanting the liquid phase, the solid residue was smeared along the inside of the centrifuge tube which was then placed on its side, open, in an air fan oven at 102°C until dry.

The dry solid was ground and digested in aqua rega before being analysed for elemental content on an ICP-Mass spectrometer.

3.3 Observations

The visual appearance of the products after 5 days shaking and then settling was very different (Fig. 2). Aqual P FR and Aqual P SR both formed a fine sediment layer on the bottom of the container, although the Aqual P SR was visibly courser than the Aqual P FR. Aqual P+A separated into two layers with a white floc (presumably aluminium hydroxide) on top of the pale yellow zeolite powder. The zeolite powder appeared to have the same granular structure as in the Aqual P SR container. Phoslock™ produced a thick flocculent layer, whereas allophane and the alum/lime mixture prills remained as well defined granules despite repeated vigorous shaking (Fig. 2). The small Virophos pellets were still apparent in the settled layer but the large Virophos pellets has disaggregated to a finer particle size. Both bauxite samples formed a fine layer across the bottom of the container but had a substantial amount of very fine particles left in suspension (Fig. 2).

Figure 2: Products (2 g/100ml) as settled for 24 hours after 5 days of agitation and periodic vigorous shaking. Both bauxite samples remained highly turbid (only one shown).

3.4 Results

The analytical results of elements in the solid products before and after exposure to the high concentration P solution are listed in Table 5. The P-saturation values from this P-saturation test were compared with those from an earlier P-saturation tests

(Fig. 3). Because part of the prill formulation may have dissolved or have been lost relative to the starting material during test, P-saturation values were normalised to the aluminium content of the starting material. The “Allophane fine” was the original material previously tested. The “Aqual-P fine” was made by grinding the granular product previously tested to a fine powder. This powder was used in the Aqual P prill formulations. The Phoslock™ was the same product previously tested.

Table 5: Comparison of elemental concentrations (mg kg^{-1} dry weight) in the products tested before and after being exposed to high concentration phosphate solution for 5 days. P-uptake is the difference between the untreated and P-saturation results normalised to the start material using the aluminium content. (Results are rounded). Elemental Al content of alum is nominal as the sample was not diluted to resolve the “off scale” peak.

Untreated	**P**		**Al**	**Fe**	**Mn**	**Na**	**K**	**Mg**	**Ca**	**La**
Aqual P fine grain	110		18100	3180	202	10200	6560	1570	8410	
Aqual-P FR	45		18300	5810	214	46300	9850	1140	6750	
Aqual-P SR	43		17300	5540	201	10000	9480	985	5190	
Aqual-P +A	42		34800	5530	197	10100	9280	900	5480	
Phoslock	287		13700	7980	175	4630	833	5700	11500	42500
Allophane-granule	837		68075	30610	675	280	170	1008	972	
Allophane prill	837		43425	28800	529	1810	208	1600	20700	
Alum+Lime	164		20000	1690	60	2750	238	3120	230000	
Virophos small	406		75800	149000	37	38300	545	2790	12200	
Virophos large	403		76700	150000	54	38400	534	2770	11400	
Bauxite Andoom	54		75500	76800	386	20	8	44	84	
Bauxite Weipa	25		92300	37000	20	2	5	40	81	
P-saturated		**P-uptake**								
Alum	86368	86368	O/S	236.6	1.5	96543	53	105	653	1.0
Aqual P fine grain	14016	14083	17874	3860	181	12600	4140	1010	8470	10.2
Aqual-P FR	12952	10728	22000	7490	265	13300	9690	672	4800	9.6
Aqual-P SR	11479	8667	22800	7210	244	9760	11500	704	5280	9.2
Aqual-P +A	36505	48631	26100	6940	218	8580	10400	426	2430	8.2
Phoslock	16540	12372	17900	9670	186	5880	929	6570	13200	26840
Allophane-granule	19460	17211	73399	29355	665	6232	221	805	1073	16.3
Allophane-prill	16086	11786	55337	41400	681	1650	446	2600	19000	18.7
Alum+Lime	66086	45729	28800	2980	87	226	283	3540	289000	5.8
Virophos small	7220	5635	90600	187000	60	33200	463	2750	12400	1.0
Virophos large	8100	6402	91300	180000	46	34000	466	2930	13700	1.0
Bauxite Andoom	1270	1403	65800	72100	369	326	6	39	68	1.0
Bauxite Weipa	1150	1490	70100	30600	17	339	3	35	72	1.0

Unlike Phoslock™, which had essentially the same P-saturation value as measured in earlier studies, the P-saturation values for the prill formulations of Aqual P and Allophane were substantially lower than for the original fine grain size of these products. The alum-lime and “Aqual P +A” mixtures had P-saturation values around 3 to 4 times greater than Phoslock™ while the Virophos formulations had P-saturation values around half that of Phoslock™. The two different bauxite minerals, although nominally containing 60% Al, had the lowest P-saturation values of all the products tested, indicating that the aluminium was probably in the wrong form and thus not able to bind the P. Of interest, the treated Phoslock™ lost >30% of its lanthanum content during the 5 days of the P-saturation test.

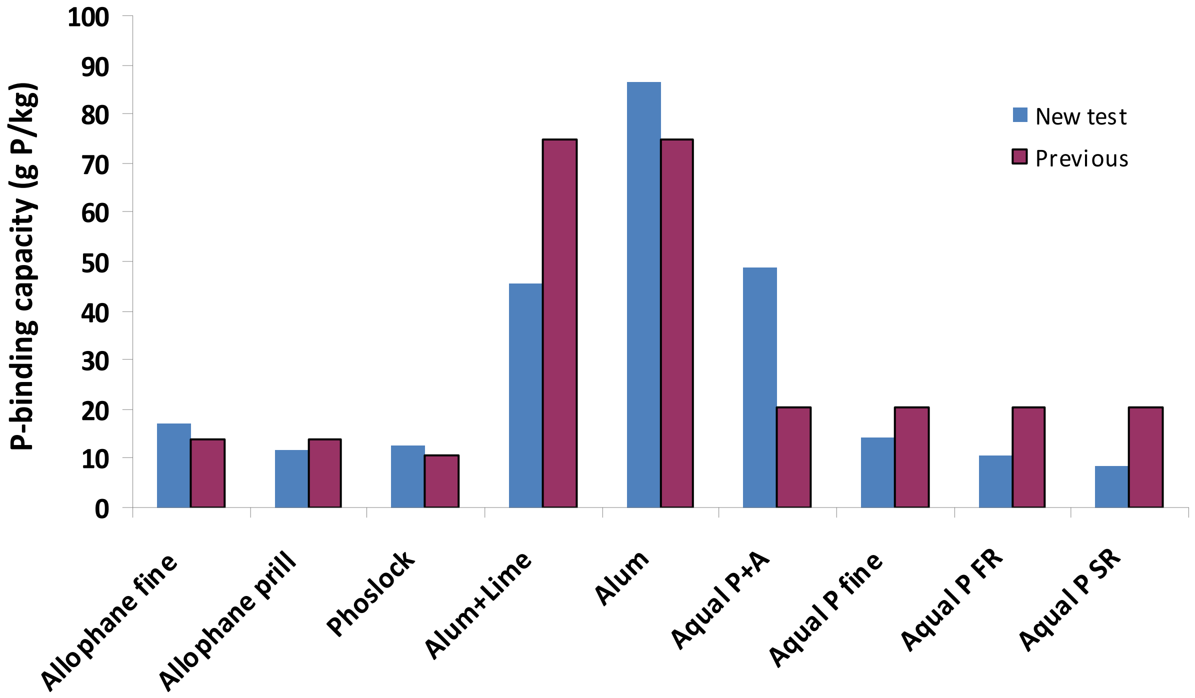

Figure 3: Comparison of maximum P-binding capacity of the pelletized products (blue) with the original fine granular products previously tested (red) (Gibbs et al. 2008). P-binding capacities have been normalised to the aluminium content of the raw product (see text). The previous estimate of P-binding capacity for alum was calculated from literature values. This value is used for the comparison with alum+lime product and the alum as measured.

Table 6: Comparison between original granular material and the pelletized form of that material for Aqual P (AP formulations), allophane, and Phoslock™. AP fine is the finely ground powder form of the granular product previously tested (Gibbs et al. 2008). Fine grain allophane is from a different source to that used in the original test. The same Phoslock™ material was used in the previous and current testing. Uptake data from Table 5 and Gibbs et al. 2008.

Formulation	AP fine	AP FR	AP SR	AP +A	Allophane	Allophane	Phoslock
Original	20490				13680		10689
Fine grain	14080	14080	14080	14080	17211	17211	
Prill/pellet		10730	8670	48630		11786	12372
Change (%)	-31	-24	-38	245	26	-32	16

The comparison between the original material and the prill formulation of that material indicates that the grinding of granular material and the addition of a binder to form the prill, has reduced the nominal P-binding capacity of the Aqual P formulations (Table 6). The ~30% reduction in P-binding capacity following grinding to a fine powder was unexpected and may be due to exposing the inner, non-activated part of the granular material. The pelletized formulations of Aqual P are compared against this starting material, not the original material. These ~24% and ~38% apparent reductions in P-binding capacity are on a weight-for-weight basis and do not allow for the weight of binder added to formulate the prill. There will be proportionally more binder in the slow release (Aqual P SR) than in the fast release (Aqual P FR) formulation. This means that proportionally more of these products needs to be added per unit area than the original product to achieve the specified P-removal. Note that the incorporation of alum into the Aqual P prill dramatically increased the P-binding capacity by ~250%, raising it to about half that of alum alone.

A similar effect is seen with the allophane and the alum+lime mixture, the latter being compared with alum. The new source of allophane has a higher P-binding capacity than the original material. This may be due to the more recent supply of allophane coming from a different source or depth strata. The comparisons of prills with the starting material of both allophane and the alum+lime mixture are on a weight-for-weight basis so the reduction in P-binding capacity is most likely due to the proportion of binding material added to make these prills.

In contrast the same granular Phoslock™ material was used in this study as in the original tests. The small increase in P-binding capacity may be within the range of experimental error in the test procedure or it may be associated with the much higher DRP concentration in the test solutions used in this study.

The alum P-binding capacity was measured as slightly higher than the literature values. In this study, the P-binding capacity was measured at pH 7.0. A small shift to a higher pH (e.g., 7.5) would be sufficient to reduce the P-binding capacity by the amount estimated.

3.5 Summary

In contrast to the P-equilibration testing results, all products removed P. However, the sediment capping agent that previously worked well as a slurry [Aqual P (Z2G1)] had a substantial reduction in maximum P-binding capacity when made into a pellet or prill. This is attributable to the amount of binding agent used to hold the fine particles together and the comparison of original material with the pelletized product on a weight-for-weight basis. It is possible that the binding agent has blocked the exchange sites on the modified zeolite crystal structure. Phoslock™, on the other hand, increased it's P-binding capacity, indicating that the reduction in P-binding capacity for Aqual P was not just an artefact of the test regime.

Part of the assessment of these products was to find a product that would settle through the water column and disaggregate into a fine grain material which would disperse near the lake bed. While the Alum+Lime pellet from Fertco showed a high P-binding capacity, its failure to disaggregate to a dispersible powder makes that formulation unsuitable as a capping agent. Similarly allophane and the Virophos formulations failed to disaggregate rapidly making those formulations unsuitable as capping agents.

In contrast, Phoslock™ and the Aqual P prills all disaggregated to a finer material within an appropriately short time. These products were subsequently tested to determine how far they settled through the water column before disaggregation and dispersion.

4. Dispersion and settling

Objective: to determine the settling rates of the products and determine the depth at which they disaggregated and dispersed in Lake Rotorua.

Products tested were Aqual P-FR, Aqual P-SR, Phoslock™, allophane prills, alum/lime prills and Virophos balls (Table 1).

4.1 Test conditions

A deep settling chamber was constructed by installing a 1.6-m diameter mesocosm tube in Lake Rotorua under calm conditions. The resultant settling chamber tube extended to a depth of 15 m and was suspended from surface floats tethered to the research vessel (Fig. 4).

Figure 4: The 15 m deep settling chamber tube suspended from surface floats and tethered to the research vessel which used a 2-point mooring to hold position in the light breeze.

The bottom of the settling chamber was about 2 m above the lake bed and the tube was closed with an internal sediment catcher. The sediment catcher was designed to open as a cone and seal against the wall of the tube when lowered into the settling chamber, and to close on lifting to allow retrieval of the sediment applied to the settling chamber for disposal off lake.

The resulting settling chamber was large enough to allow unimpeded operation of a submersible video camera or “drop cam” and target within the settling chamber. The results were observed with a surface monitor fitted with a recorder (Fig.5). The drop-cam could be positioned at any depth to time the arrival of and observe the state of the products being tested. The drop cam was focused on a black target and the depth of the target was referenced to the lake surface using the fibre measuring tape. Initial testing showed that the target was clearly visible down to 15 m under natural light. A black target was used because the products being tested were pale coloured. Additional lights were available if required.

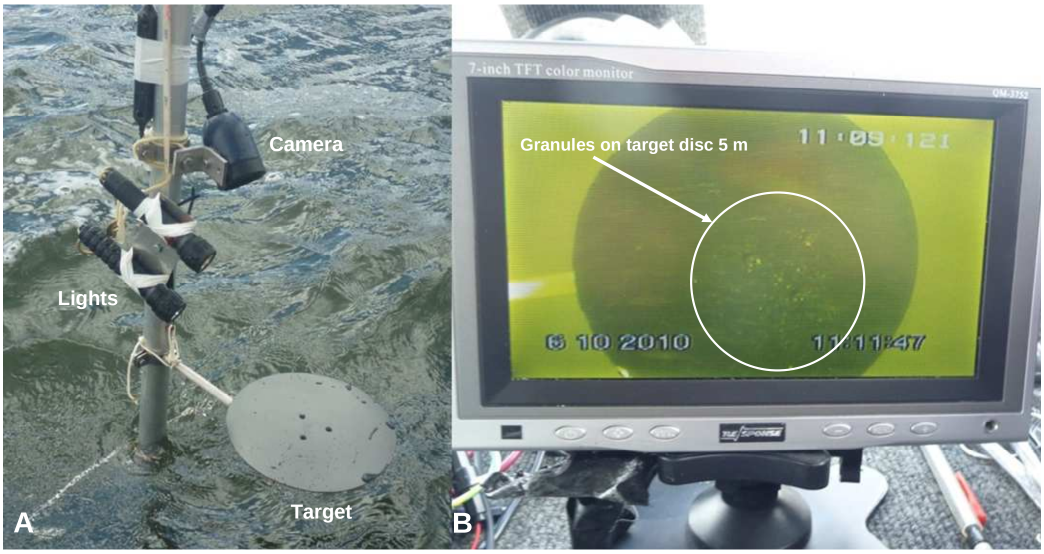

Figure 5: **A**) Drop-cam assembly showing the camera and black disc target plus the auxiliary lighting (xenon torches). **B**) The arrival of the product being tested on the target disc was very obvious and the degree of disaggregation was clearly visible. (Test product Aqual P FR at 5 m shown).

4.2 Measurement strategy

To enable rapid testing within the weather window, and armed with the knowledge of poor disaggregation of some of the products, the drop cam target was set at a depth of 5 m and the products that disaggregated rapidly (Table 2) were tested first. The drop cam and target were then lowered to a depth of 10 m and the tests repeated. The drop cam and target were finally lowered to 15 m and the tests were repeated with all products.

Product application was manual - a small handful of granular product was scattered across the water surface above the drop cam. Timing was by stopwatch and on-screen clock.

4.3 Results

4.3.1 5-m test

Both Aqual P-FR and Phoslock™ disaggregated before reaching the 5 m target depth. Phoslock™ disaggregation was slightly faster than for Aqual P FR although an occasional larger particle of both products was observed to reach the target plate. The Phoslock™ particles arrived as streamers with the fine product forming a "smoke" trail behind the particle. Both of these products left a dispersing cloud in the water column about 2-3 m below the surface. However, while the Aqual P FR granules landed on the target plate as a fine powder (Fig. 4B), the Phoslock™ material appeared to hang in the water column and slowly move past the target rather than settle. This movement is consistent with a floc–like cloud and the slight movement of the target due to boat movement.

Settling times for these two products were consistently 55 seconds to travel 5 m. Aqual-P SR landed on the target plate as intact prills after 35 seconds.

4.3.2 10-m test

With both Aqual P-FR and Phoslock™ having disaggregated by 5 m, only Aqual P SR was tested at a depth of 10 m. The Aqual P-SR arrived as intact prills although these were beginning to disaggregate on the target plate. Settling time was 3 minutes to travel 10 m.

Settling times for the Allophane and alum/lime prills were also checked on the 10 m target depth. Large particles arrived at the target plate after 1 min 35 seconds and the smaller particles arrived after about 3 minutes.

During the 10-m test the cloud of fine particles from the Aqual P-FR tested at 5 m began to arrive. Settling time for this cloud was about 30 minutes.

4.3.3 15-m test

Aqual P SR disaggregated to fine granules which spread across the target plate at 15 m. These particles were easily dislodged from the target plate by movement of the drop-cam assembly due to the boat motion.

Settling time to 15 m for Aqual P SR was between 6 and 7 minutes with the disaggregation cloud arriving shortly after indicating that most of the disaggregation had probably occurred about the just above the target at 15 m depth.

Fine particles from the earlier Aqual P FR tests arrived at the 15 m depth about an hour after the initial application to the settling chamber. Allophane and alum/lime prills reached the target in about 5 minutes. The Virophos small balls took 2 minutes 45 seconds to reach the target plate at 15 m.

4.3.4 Summary

The disaggregation of the products tested followed the pattern observed during the P-equilibration and P-saturation tests. Phoslock™ was the fastest product to disaggregate followed by Aqual P FR and then Aqual P SR (Table 7). There was no indication that the allophane, alum/lime and Virophos pellets/prills disaggregated significantly in the 15 m water depth.

Table 7: Settling times, disaggregation depths and dispersion settling times for the products tested in the settling chamber. (NT = not tested; Nil = did not disaggregate; - do data).

	Prill time to depth (min)			Break-up depth	Cloud time to depth (min)		
Product	**5 m**	**10 m**	**15 m**	**(m)**	**5 m**	**10 m**	**15 m**
Aqual P FR	0:55	NT	NT	4-5	1:30	~30	~60
Aqual P SR	0:35	3	6-7	11-13	-	-	7-15
Phoslock™	0:55	NT	NT	~4	1:30	-	-
Allophane	NT	1:30	~5	Nil	-	-	-
Alum/lime	NT	1:30	~5	Nil	-	-	-
Virophos	NT	NT	2:45	Nil	-	-	-

From these measurements it is apparent that only one product, Aqual P SR, met the desired specification of settling to around 10 m before disaggregation and dispersion. Not withstanding this, the disaggregation of Aqual P FR occurred higher in the water column and produced a fine granular product which slowly settled to 15 m depth over the following hour. Conversely, Phoslock™ formed a cloud of very fine particles which did not appear to settle. Rather, they became indistinguishable from the natural fine detritus in the water column and presumably remained in the water column. This would be consistent with a recent overseas report (unpublished manuscript under review for scientific journal) noting that it took 47 days for the water to clear after a lake was treated with Phoslock™.

5. Overview

Testing of the pelletized sediment capping agents showed that it was possible to design a product that, when applied to the lake surface would sink to a mid-water column depth before disaggregating and dispersing across the lake bed. Unfortunately, the process of pelletizing the product substantially reduced its P-binding capacity rendering it less efficient that the original material previously tested. It is not certain whether, in contact with sediment, the P-binding capacity would increase back to the initial capacity as that has not been tested. This means that further refinement is required on the pelletizing of these products before they are ready to use in a lake application, and that adjustments to the product dose will be required when a formulated product is used.

Bottom line: Of all the products tested, the most efficient at removing P was alum. Further work is needed on application and buffering techniques to enable the use of alum in New Zealand’s soft water lakes, such as the Te Arawa / Rotorua lakes. Refinement of the Alum+lime prills would be required before these would be suitable for surface application to lakes.

Recommendation for the plot trials on Lake Rotorua is that all products be applied to the 30 m x 30 m plots as a slurry of the un-pelletized material. This will eliminate bias between products for the plot trial tests and will allow suppliers further time to develop and test appropriate prill formulations.

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7. References

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