Appendix For 28 April 2010 Meeting notes.

Alum use on Lake Rotorua

Max Gibbs, NIWA 12 May 2010

Lake Rotorua is a low alkalinity lake; alkalinity = $12.5 \text{ mg CaCO}_3/L$

Alum $(Al_2(SO_4)_3.18H_2O)$ dissociation in water is pH dependent, as is its capacity to adsorb phosphate (chapter 8 in Cooke et al., 2005; Kennedy & Cooke, 1982; Peterson et al., 1976).

- Between pH 6.0 and 8.0, most will be in the insoluble form as Al(OH)₃
- As the pH falls below pH 6.0, other soluble forms including Al(OH)₂⁺ andAl³⁺ become increasingly important. These forms are toxic in varying degrees, particularly Al³⁺.
- Toxic levels of Al^{3+} should not occur if the pH remains between 6.0 and 8.0
- The dissolution of alum in water tends to lower the pH.

The nomogram (Fig.1) can be used to estimate the maximum amount of unbuffered alum that can be added to lake water with different levels of alkalinity and different initial pH values before the pH will fall below 6.0.



Aluminum dose (mgAl/ ℓ) to obtain pH 6.0

Figure 1. Estimated aluminium sulphate dose (mg Al/L) required to obtain pH 6 in treated water of varying initial alkalinity and pH. (From Kennedy, R.H. and G.D. Cooke, 1982. Water Resource Bulletin 18: 389-395).

With an initial pH of 7.2 and a total alkalinity of 12.5 mg CaCO₃ /L, the suggested minimum alum dose rate of 75 g alum/m² (= 3 mg Al/L) would reduce the pH of Lake Rotorua water to just below pH 6.0 which is on the edge of the danger zone. In lab tests a treatment dose of 75 g alum/m² was sufficient to bind the sediment P in the top 4 cm of the Lake Rotorua sediments (i.e., 3 g P/m²). This treatment dose represents an Al:P ratio 1:1 which is OK for the sediment capping but the literature (Cooke et al., 2005) suggest a higher ratio (up to 8:1) would be needed in the water column, because the adsorption of P into the floc is concentration dependent.

The minimum estimated dose rate of 75 g alum/m² determined in the laboratory study does not allow for the water column P, which will be bound and removed during the precipitation phase of the treatment. A dose rate higher than 75 g alum/m² will be required to ensure the P-binding capacity of the floc, when it reaches the sediment, is still sufficient to inactivate the P released from the sediment. How much higher depends on how much P is in the water column at the time of treating the lake.

Because the dose rate of 75 g alum/m² in Lake Rotorua would take the surficial lake water dangerously close to the pH 6.0 limit, I would strongly recommend that buffered alum was used, if alum is the treatment of choice. Increasing the dose rate of alum to accommodate the water column P will cause the pH to fall well below pH 6.0 and the addition of a buffer would be mandatory.

Worked example using Lake Okaro data to estimate how much buffer would be required if a full single dose treatment of alum had been used in 2003/04:

When alum was used on Lake Okaro (December 2003), the water column DRP concentrations in the hypolimnion were around 0.5 g/m^3 and the thermocline depth was 3 m. With a mean lake depth of 12 m, the hypolimnion thickness was 9 m. Therefore, on an areal basis, the hypolimnion contained up to 4.5 g P/m², (ignore any residual P in the sediment).

Assuming the Al:P ratio required for total removal of P in the water column is 8:1, the alum dose rate needed would be 36 g Al/m². When first applied (by spray application), the alum representing these 36 g Al will become mixed into the top 1 m depth giving an initial concentration of 36 mg Al/L. To accommodate that treatment within the pH range of 6.0 to 8.0, from figure 1, the alkalinity would need to be very much greater than 250 mg CaCO₃/L. The alkalinity of Lake Okaro is 28 mg CaCO₃/L, so a buffer application in the order of 300 mg CaCO₃/L (i.e., 300 g CaCO₃/m²) would be needed at the time of application.

If the application were made in the winter mixed period, however, most of the P would be bound in the sediment and the binding ratio would be 1:1. The residual DRP in the water column has been ignored. Assuming that the P is loosely bound to iron in the sediment or bound in precipitated organic matter on the sediment, a capping layer of alum would need to be equivalent to 4.5 g Al/m^2 . At application, the required alkalinity in the top 1 m depth would be about 45 mg CaCO₃/L. With an alkalinity of 28 mg CaCO₃/L, the required amount of buffer would be around 17 g CaCO₃/m² at the time of application. These are minimum amounts of buffer that should be applied. However, larger amounts may be needed depending on the method of application.

Kinetics of application:

The actual alum application made in Lake Okaro in December 2003 was equivalent to 1.5 g Al/m^2 in the top 3 m depth or 0.5 mg Al/L, which should not have needed a buffer (Fig.1). However, the 0.5 mg/L assumes the alum was evenly mixed through the top 3 m. As it was applied by surface spray, it obviously wasn't and probably spent several minutes as a thin layer on the surface before mixing down. When first applied, assume it mixed into the top 0.1 m immediately before dispersing. The aluminium dose at that stage would have been 15 mg Al/L requiring an alkalinity of well over 100 mg CaCO₃/L. At that time the local pH was probably well below 6.0 and thus conducive to toxic Al(OH)₂⁺ andAl³⁺ formation rather than floc formation. The measured 0.6 g Al/m³ concentration in the 3 m-thick epilimnion at that time suggests that, essentially, the whole of the 1.5 g Al/m² dose was still in solution, which is consistent with the lack of flocculation.

These calculations demonstrate that the kinetics of application must also be considered, not just the stoichiometry. A similar kinetic consideration was applied to the Z2G1 treatment where the mass applied was right but the grain size was wrong and the treatment was less effective than it should have been.

While in theory, multiple smaller doses of alum could be used to treat a lake in order to reduce the need for adding a buffer, Cooke et al., (2005) state that long-term control of internal P loading will not be achieved with low doses.

Way forward.

Alum is a valid product to treat any lake to control internal P loads. It works well in high alkalinity lakes but not so well in soft-water lakes with alkalinity below 30 mg $CaCO_3/m^3$. When the alkalinity is low, a buffer has to be included in the application to make the alum form a floc. Lime (CaO) forms $Ca(OH)_2$ in water. This hydroxide will raise the pH but has no buffer capacity and is therefore not suitable as a buffer. Soda ash (sodium bicarbonate) is a suitable buffer, and sodium aluminate is another.

To be comparable with the other products considered, the costing for alum must include the cost of the buffer <u>AND</u> the mechanism for applying the buffer at the same time as the alum – the two cannot be mixed because the floc would form in the mixing tank and clog the application gear.

The key factors with alum are;

- 1. Alum needs a buffer if used in the Rotorua Lakes;
- 2. Alum floc has unknown settling velocity in a real lake situation so could drift
- 3. Lab indications are that the alum floc may be disturbed by lake currents when it first settles. The worst case scenario would be for the alum floc to roll into hollows leaving large areas of sediment uncovered.

Actions:

Measurement equipment for lake currents is being prepared to answer questions related to drift – direction and how far.

Further study is needed to determine how fast the floc settles in natural lake water and whether it forms a cohesive layer on the lake bed or rolls into the hollows with lake currents.

NIWA has a 2-m tall settling chamber for in-lab measurements or could use in-lake mesocosms to 10 m depth or greater for testing

- 1. the amount of buffer required to cause the alum to floc in Lake Rotorua water,
- 2. the rate the floc settles once formed, and
- 3. whether the floc forms a coherent layer on the lake bed once it settles.

References:

- Cooke, G.D.; Welch, E.B.; Peterson, S.A.; Nicols, S.A. (2005). Restoration and management of lakes and reservoirs (3rd Edition). Taylor and Francis. Boca Raton.
- Kennedy, R.H. and G.D. Cooke, (1982). Control of lake phosphorus with aluminum sulfate: dose determination and application techniques. Water Resource Bulletin 18: 389-395.
- Peterson, S.A.; Sanville, W.D.; Stay, E.S.; Powers, C.F. (1976). Laboratory evaluation of nutrient inactivation compounds for lake restoration. *Journal of the Water Pollution Control Federation* 48: 817-831.