ISSN 2463-6029 (Print),
ISSN 2350-3432 (Online).

Ecotoxicological Review of Alum Applications to the Rotorua Lakes: Supplementary Report

ERI Report Number 117

Client report prepared for Bay of Plenty Regional Council

By Grant Tempero

Environmental Research Institute
Faculty of Science and Engineering
University of Waikato, Private Bag 3105
Hamilton 3240, New Zealand

Cite report as:
Tempero, G.W. 2018. Ecotoxicological Review of Alum Applications to the Rotorua Lakes: Supplementary Report. ERI Report No. 117. Client report prepared for Bay of Plenty Regional Council. Environmental Research Institute, Faculty of Science and Engineering, University of Waikato, Hamilton, New Zealand. 17 pp.

Reviewed by:

Nick Ling

Associate Professor

Environmental Research Institute

University of Waikato

Approved for release by:

John Tyrrell

Acting Director

Environmental Research Institute

University of Waikato

Executive Summary

This report is intended to supplement the original 2015 report "Ecotoxicological Review of Alum Applications to the Rotorua Lakes" published as Environmental Institute Report Number 52 by the University of Waikato. A number of relevant studies published since 2015 regarding toxicological effects of aluminium (Al) are reviewed, and aspects specific to Lake Rotorua which were identified during the Plan Change 10 science review conducted by Professor Warwick Vincent for the Bay of Plenty Regional Council in 2018 including;

1) Are the aluminium concentrations used in toxicological testing relevant to the low concentration of aluminium measured in the water of Lake Rotorua?
2) Given Lake Rotorua has a low buffering capacity, are pH shifts driven by algal bloom photosynthesis likely to result in toxic aluminium complexes?
3) What is the potential for long-term chronic toxicological effects, particularly on down-stream receiving ecosystems?
4) What is the effect of natural geothermal sources of aluminium in Sulphur Bay?

Since 2015, significant advances have been made in determining toxic thresholds for Al, particularly chronic effects. The United States Environmental Protection Agency (USEPA) has recently published as series of studies (i.e., Cardwell et al. 2018, DeForest et al. 2018, Gensemer et al. 2018, Wang et al. 2018) covering acute and chronic toxicological testing on eight aquatic species under a wide range of environmental conditions and total aluminium concentrations, including those common to Lake Rotorua (i.e., water hardness 14 mg L^{-1} (as $CaCO_3$); dissolved organic matter 2 mg L^{-1}, pH 6.8; total Al ~0.020 mg L^{-1}. This work resulted in the publication of a multiple linear regression (MLR) model developed to predict chronic Al toxicity under varying conditions of dissolved organic matter (DOM), pH and water hardness (. The model predicts the likely total aluminium concentrations hazardous to 5% (HC5) of species or genera for a range of pH's. The HC5 value is a statistically derived value from sensitivity data of multiple species to a single toxicant, and is similar to the Predicted No-Effect Concentration (PNEC) reported for single species toxicological tests. The mean total Al concentration in Lake Rotorua (0.020 mg L^{-1}) was found to be well below the calculated threshold for chronic toxicity effects based on the modelled HC5 estimates (from 0.045 mg L^{-1} at pH 6.5 to 0.644 mg L^{-1} at pH 8, under typical DOM and hardness conditions). Therefore, chronic toxicological effects from Al exposure are unlikely to occur under typical pH conditions in Lake Rotorua. However, caution should be used in applying these values as the data is not based on New Zealand species.

In poorly buffered eutrophic systems such as Lake Rotorua, diel pH cycling of up to 3 pH units (i.e., pH 6.5 – 9.5) is common. When pH >8, $Al(OH)_3$ converts to the more toxic $Al(OH)_4^-$ species, resulting in a lowering of the toxic threshold concentration at pH levels >8. Compared to acidic conditions there is relatively little research examining toxic effects of Al under alkaline conditions. Most research indicates that toxicity increases above pH 8, with acute effects becoming more prevalent above pH 9. However, given the low total Al concentrations in Lake Rotorua and comparatively short exposure times to high pH during algal blooms, acute Al toxicological effects resulting from phytoplankton driven diel shifts in pH are unlikely. However, it is recommended that chronic effects of combined total aluminium and short-duration alkaline pH shifts be further investigated to determine the potential osmoregulatory impacts on key species for Lake Rotorua.

Currently, there is no requirement for monitoring of potential downstream impacts in the Kaituna River or Ōngātoro/Maketu Estuary from alum dosing to Lake Rotorua. A total Al concentration of 0.08 mg L^{-1} measured at the half-way point of the Kaituna River in May 2008 (following dosing to the Utuhina Stream but prior to Puarenga Stream dosing) has been reported, well below predicted HC5 toxicity threshold. Notably, tributaries to the Lower Kaituna River appear to make greater contributions to total Al loading of the Kaituna River, with inflow concentrations ranging from 0.14 – 0.52 mg L^{-1}, presumably associated with increased suspended sediment levels. The ultimate discharge point of Lake Rotorua is the Ōngātoro/Maketu Estuary. Golding et al. (2015) proposed a guideline value of 0.024 mg total Al L^{-1} for 95% species protection, based on chronic effect values from 11 species covering six taxonomic groups. This value is well above the mean total Al concentration for Lake Rotorua, therefore direct impacts of alum dosing on organisms in the downstream receiving environment are unlikely, however toxicological impacts may be occurring due to the contributing high total Al in some tributaries of the Kaituna River.

Concentrations of total aluminium in the Sulphur Bay area of Lake Rotorua are naturally high (>1 mg L^{-1}) due to geothermal fluid infiltration. This has produced an area of naturally low aquatic biodiversity due to the low pH (~3) and prevalence of highly toxic Al^{3+}. However, these effects are negated at the mouth of bay where the geothermally influenced waters mix with water from the main lake body. At this point normal lake diversity can be observed. No adverse effects have been observed from alum dosing of the Puarenga Stream.

The cautious use of continuous low level alum dosing is an ecologically acceptable option for reducing phosphorus loading to Lake Rotorua. However, the low buffering capacity, soft water and low dissolved organic matter preclude bulk or widespread application of alum for phosphorus management. Under the present alum dosing regimen, impacts on downstream biota are unlikely due to low water column aluminium concentration. However, further evaluation of potential toxic effects during phytoplankton driven diel pH cycling is recommended.

Table of Contents

Introduction

The original report "Ecotoxicological Review of Alum Applications to the Rotorua Lakes" was published in 2015 (Tempero 2015. ERI Report number 52). That report concluded that the alum dosing programme for the Rotorua lakes was appropriately conservative due to the low buffering capacity of the lakes. The risk of acute aluminium (Al) toxicity was therefore minimal under the extant dosing regimen. It was also concluded that the risk of bioaccumulation and biomagnification were minimal provided pH levels are maintained above 6.0. However, the low buffering capacity of the lakes meant there was little capability to increase alum application rates. Finally, information examining the ecological effects of Al-floc formation and deposition was extremely limited, but dose rates to the Rotorua lakes were unlikely to form sufficient quantities of Al-floc to have a negative impact on lake biota.

Following the Plan Change 10 science review conducted by Professor Warwick Vincent for the Bay of Plenty Regional Council in 2018, several additional questions relevant to the renewal of alum dosing resource consents to Lake Rotorua in 2018 and 2019 were identified. A supplementary report was requested by the Bay of Plenty Regional Council to review relevant aluminium toxicity literature published since 2015, and to address the following questions specific to Lake Rotorua:

1) Are the aluminium concentrations used in toxicological testing relevant to the low concentration of aluminium measured in the main waters of Lake Rotorua?
2) Given the low buffering capacity of Lake Rotorua, are pH shifts driven by algal bloom photosynthesis likely to result in toxic aluminium complexes?
3) What is the potential for long-term chronic toxicological effects, particularly on down-stream receiving ecosystems?
4) What is the effect of natural geothermal sources of aluminium in Sulphur Bay?

Aluminium Toxicity Tests

Predicting aluminium (Al) toxicity in surface waters is an enduring and complex problem, in-part due to the interacting and potentially synergistic effects of pH, Al speciation, dissolved organic matter (DOM) and water hardness. Chemical forms of Al vary across the pH range of 3 to 10, resulting in changes in the toxicological mechanisms due to shifts in proportions of dissolved and precipitant Al species (Adams et al. 2018). For example, aluminium hydroxide $Al(OH)_3$ forms at around pH 7 and is more insoluble then Al species formed under acidic or alkaline pH values. At pH 7, toxicological effects are primarily due to accumulation and irritation of particulate $Al(OH)_3$ on gill surfaces, resulting excessive mucilage production and reduction of oxygen uptake (Sparling and Lowe 1996). In contrast, ionoregulatory effects predominate at higher (i.e., $Al(OH_4)^-$) and lower ($Al(OH_2)^+$) pH values and are synergistic with H^+ regulation (Gensemer and Playle 1999). A feature of these effects is that total aluminium concentrations must be significantly higher at near-neutral pH compared to acidic or alkaline pH's to elicit toxicological effects (Sparling and Lowe 1996, Gensemer et al. 2018). These dynamics compound the amount of testing required to determine Al toxicological thresholds, and result in differential thresholds dependent on a wide range of physical and chemical factors. For example, water hardness and DOM are two important modifying factors when evaluating Al toxicity. Increasing water hardness (calcium & magnesium as $CaCO_3$) is known to reduce aluminium toxicity to vertebrate and invertebrate species at neutral and acidic pH (Gundersen et al. 1994). Binding of calcium to the gill surface appears to be essential for proper maintenance of ionoregulatory systems (Gundersen et al. 1994, Gensemer and Playle 1999). The observed loss of electrolytes in fish and invertebrates exposed to low pH and Al may be due to the displacement of calcium from the gill surface by higher affinity Al and H^+ ions, and is mitigated by higher calcium concentrations in harder waters (McDonald et al. 1983, Sparling and Lowe 1996). Similarly, dissolved organic matter (DOM) decreases Al toxicity by acting as a complexing ligand: Al is bound by DOM and is kept in solution instead of accumulating on respiratory structures (Roy and Campbell 1997, Gensemer and Playle 1999, Winter et al. 2005).

To evaluate the relevance of Al concentrations used in toxicological testing to Lake Rotorua conditions, data collected by the Bay of Plenty Regional Council from two sites (Figure 1) for the period July 2011 – June 2017 were examined including pH, total Al, water hardness and DOM. Total Al and pH were sampled from surface water (0 – 6 m) and bottom water (>20 m), while water hardness and DOM were determined from 6 m vertically integrated surface water samples (Table 1). There was no significant difference (t-test; P>0.05) in total Al between surface waters (0 – 6 m) and bottom waters (>20 m) or between sites, therefore site data was pooled and summary statistics presented in (Table 1). There was no significant difference (t-test; P>0.05) in surface water and bottom water mean pH between sites, however, there was a significant difference (t-test; P<0.05) in mean pH between surface and bottom waters when site data was pooled (Table 1). Examination of total Al monitoring data for temporal trends from July 2011 – June 2017 found a seasonal increase in total Al during late winter – spring, likely associated with increased inflow, however, no significant change in Al concentration over time was observed (Seasonal Kendall Test; P<0.05) following deseasonalisation of the data (Figure 2).

Table 1. Descriptive statistics for total aluminium, pH, water hardness (as $CaCO_3$) and dissolved organic carbon measured at two Bay of Plenty Regional Council monitoring sites in Lake Rotorua from July 2011 – June 2017. There was no significant difference (P>0.05) in aluminium concentrations between sites and depths and data has been pooled. Mean pH was significantly different (P<0.05) between and surface and bottom waters (indicated by *).

Depth	Variable	N	Mean	Median	Minimum	Maximum	Standard deviation	95% Confidence interval
Surface (0-6 m depth)								
	Dissolved organic matter (mg L^{-1})	13	2.0	2.3	0.9	2.5	0.51	0.31
	Total water hardness (mg L^{-1})	13	14.0	14.6	12.5	15.0	0.91	0.55
	pH	259	6.9*	6.9	5.3	8.7	0.35	0.04
Bottom (>20 m depth)								
	pH	122	6.8*	6.8	6.1	7.7	0.24	0.04
Pooled data	Total aluminium (mg L^{-1})	262	0.020	0.018	0.004	0.013	0.011	0.001

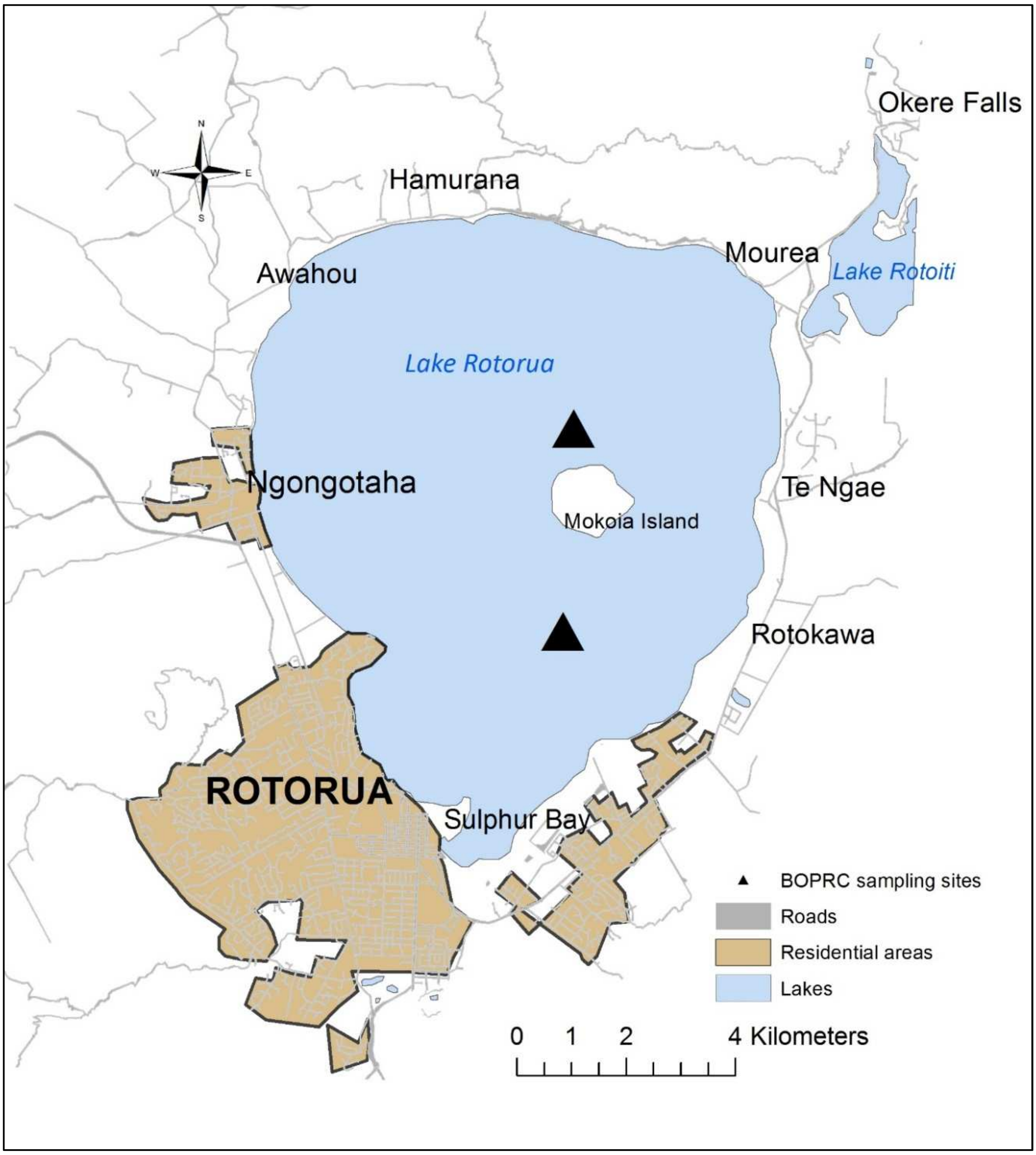
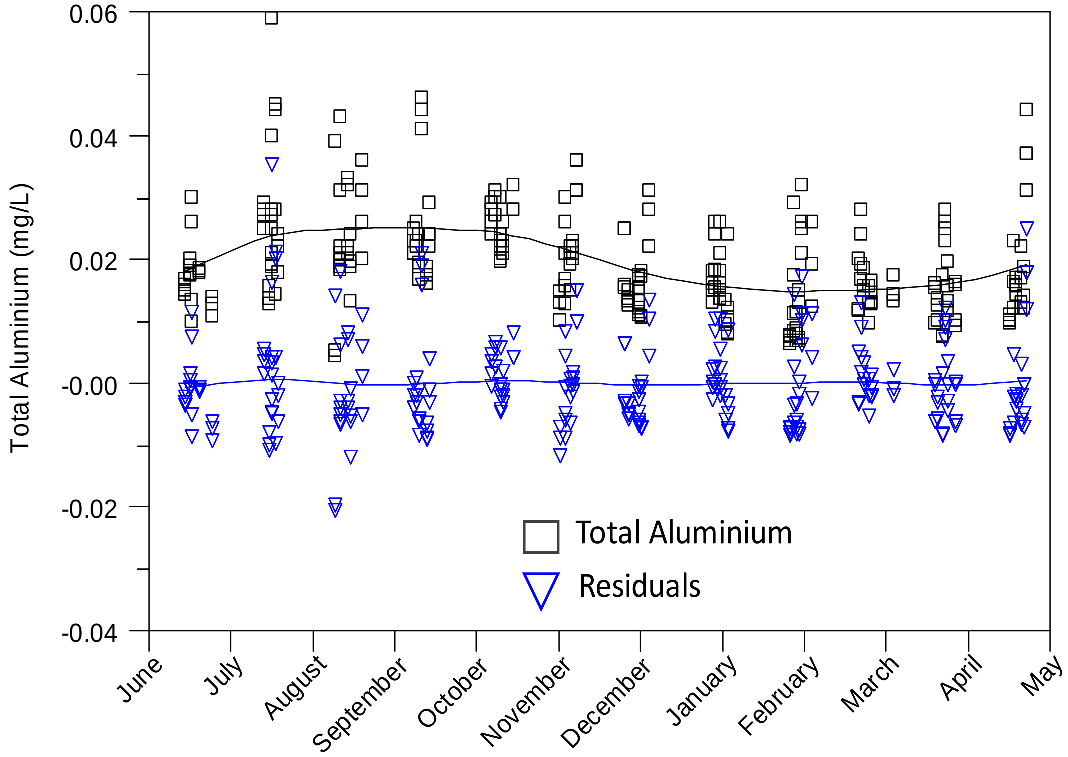


Figure 1. Location of Bay of Plenty Regional Council monitoring sites for total aluminium, pH, water hardness, nitrogen, phosphorus and dissolved organic matter in Lake Rotorua.

In 1988 the United States Environmental Protection Agency (USEPA) published water quality criteria for the protection of aquatic organisms from the toxic effects of Al (USEPA 1988). To provide protection from chronic toxicity the USEPA recommended that the 4-day mean concentration of aluminium not exceed 0.087 mg L^{-1} more than once every 3 years when ambient pH is between 6.5 – 9.0, and aluminium not exceed 0.750 mg L^{-1} for more than 1-hour when pH is 6.5 – 9.0 to avoid acute toxicity effects. This recommendation was based on acute toxicity data for 20 species of aquatic organisms and chronic toxicity data for five species (USEPA 1988). The majority of these toxicity tests were conducted under water hardness conditions of 47.4 mg L^{-1} (as $CaCO_3$) with a range of 14.9 – 220 mg L^{-1}, DOM was not reported.



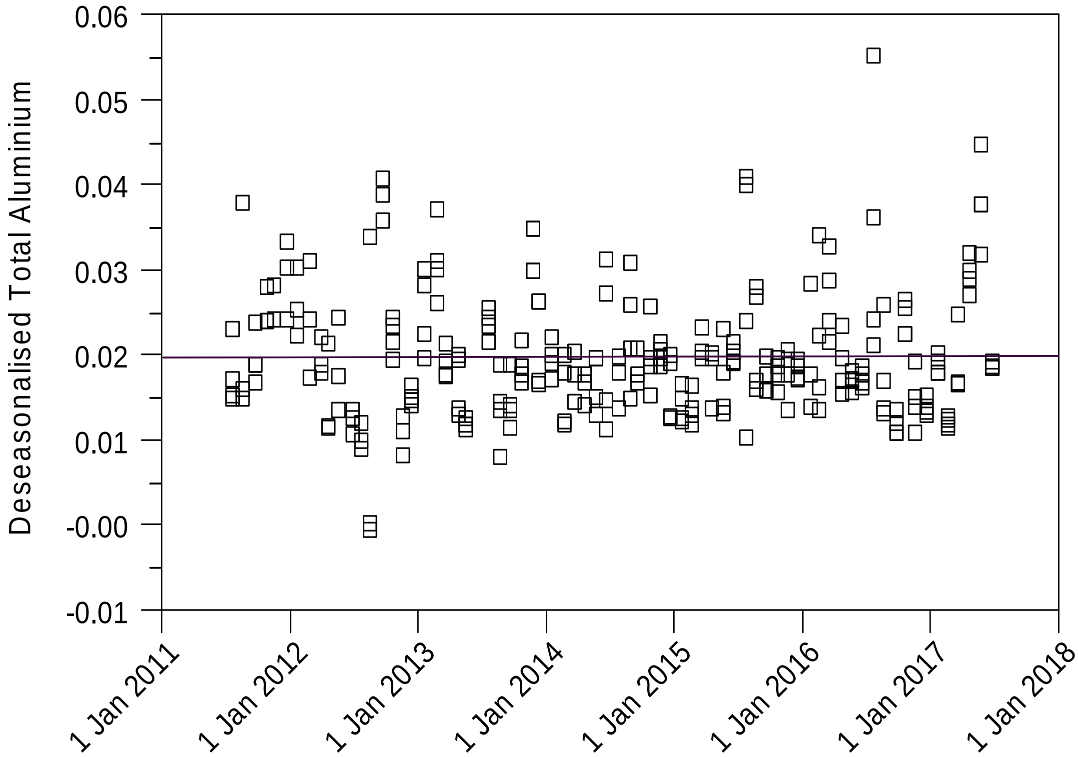


Figure 2. Top. Seasonal trend in water column total aluminium concentrations in Lake Rotorua from July 2011 – June 2017 and, Bottom. Deseasonalised total aluminium concentrations for the same period.

Further Al toxicological testing was conducted by the USEPA from 2009 – 2015 to address data gaps for pH ranges more representative of typical natural waters (pH 6 – 8) and to focus on chronic toxicological effects (i.e., survival and growth effects at low Al concentrations for longer periods of time) (Adams et al. 2018). Eight freshwater species, including two fish species, five invertebrate species and one plant species were included in the testing. Water hardness ranged from 54 – 117 mg L^{-1} (as $CaCO_3$), DOM was at or below 0.5 mg L^{-1} and Al concentration ranges varied from 0 – 0.45 mg L^{-1} for the amphipod *Hyalella azteca,* to 0 – 10 mg L^{-1} for duckweed (*Lemna minor*) (Cardwell et al. 2018). From these data and additional published data, species-sensitivity distributions (SSDs) were developed to derive concentrations protective of 95% of tested species. A generic hazard concentration (not adjusted for Al bioavailability) of 0.0744 mg total Al L^{-1} was estimated using the SSD (Cardwell et al. 2018).

The conditions under which Al toxicological testing was conducted by the USEPA are similar to the prevailing conditions in Lake Rotorua. Water hardness levels in the USEPA testing can be primarily classified as slightly hard (17 – 60 mg L^{-1}) compared to the soft (0 – 16 mg L^{-1}) waters of Lake Rotorua (WHO 2009). Dissolved organic matter concentrations tested were minimal (≤ 2 mg L^{-1}), similar to reported levels for Lake Rotorua (Table 1). Tested Al and pH levels were also coincident with the ranges observed in the monitoring data for Lake Rotorua. The resulting USEPA recommended toxicological thresholds are higher than the observed mean total aluminium concentrations in both the surface and bottom waters of Lake Rotorua (Table 1). Therefore, it can reasonably be concluded that there is sufficient toxicological testing appropriate to Lake Rotorua conditions to evaluate the likely risk of Al toxicity from alum dosing.

Algal Bloom Driven Shifts in pH

Lake Rotorua has a limited buffering capacity resulting in reduced resistance to pH changes. In poorly buffered eutrophic systems, diel pH cycling is common as uptake of CO_2 for photosynthetic processes during the day drives pH up, followed by respiratory CO_2 release during the night pushing the pH down through the formation of carbonic acid (Maberly 1996, Heini et al. 2014). During these events, diurnal pH shifts of up to three units have been observed (Heini et al. 2014). An example of pH variability in relation to algal bloom formation in Lake Rotorua can be observed in data from the BOPRC monitoring buoy from 4 March – 14 April 2017 (Figure 3). Significant diel variation up to 3 pH units can be observed from 15 March – 30 March 2017, coinciding with an increase in chlorophyll as determined by fluorescence measurements.

Below pH 9.5, chronic toxicological effects (i.e., increased blood glucose concentration and about 30% increase in blood haematocrit after 3 weeks) from $Al(OH)_4^-$ have been reported for Atlantic salmon (*Salmo salar*) at total Al concentrations of 0.35 mg Al L^{-1} but no acute effects were observed (Poléo and Hytterød 2003). Recent Al toxicological testing conducted at pH 8 by Gensemer et al. (2018) for the cladoceran *Ceriodaphnia dubia*, green alga *Pseudokirchneriella subcapitata* and fathead minnow (*Pimephales promelas*) found low acute mortality for *C. dubia* and *P. subcapitata* at concentrations above 1.5 mg Al L^{-1} and the 10% effect concentration (EC10) for growth in fathead minnow was 4.67 mg Al L^{-1}. Despite this, Al toxicity under alkaline conditions remains comparatively unexplored, primarily due to the low number of alkaline freshwater systems with low Ca^{2+} concentrations, and the apparent higher acute toxicity thresholds for Al above pH 8. In addition, determination of toxicological effects above pH 9 is further complicated by osmoregulatory disruption by pH alone (Winter et al. 2005).

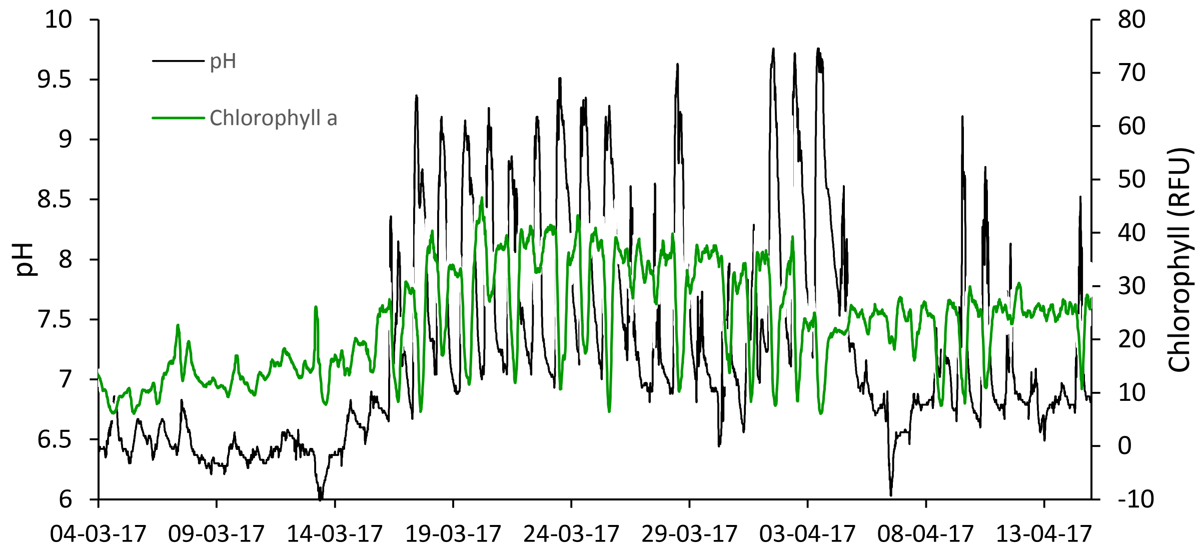


Figure 3. Example of pH variation in Lake Rotorua surface water (0.5 m) in response to algal bloom formation. 15-minute interval data obtained from the Bay of Plenty Regional Council Lake Rotorua automated monitoring buoy.

Given the low total Al concentrations in Lake Rotorua and comparatively short exposure times to high pH during algal blooms, acute Al toxicological effects resulting from diel shifts in pH are unlikely. However, it is possible that such diel shifts in pH could impact the osmoregulation of aquatic fauna resulting in chronic effects due to osmoregulatory stressors such as $Al(OH)_4^-$ (Shaw 1981, West et al. 1997, Barile et al. 2016, Garcia-Garcia et al. 2017). It is recommended that chronic effects of combined total aluminium and short-duration alkaline pH shifts be further investigated to determine the potential osmoregulatory impacts on key species.

Chronic Toxicological Effects

The primary objective of toxicological testing is to determine thresholds for toxicological impacts through variations in concentration and duration of exposure for a given substance. Chronic toxicological testing of aquatic organisms is not widely carried out due to logistical considerations and the potential for confounding effects from captivity stress (Eggen et al. 2004). Chronic effects of Al exposure were reviewed in the Tempero (2015, p.22) report focusing on the potential for bioaccumulation of Al. It was concluded that there was a low risk of bioaccumulation as trophic transfer rates were relatively limited and direct uptake from water minimal, however a conservative approach was recommended as chronic exposure to Al had not been widely investigated.

Since 2015 a more substantial body of chronic toxicity testing has been carried by Cardwell et al. (2018) on eight freshwater species including two fish species (*Pimephales promelas* and *Danio rerio*), an oligochaete worm (*Aeolosoma* sp.), a rotifer (*Brachionus calyciflorus*), a snail (*Lymnaea stagnalis*), an amphipod (*Hyalella azteca*), a midge (*Chironomus riparius*), and an aquatic plant (*Lemna minor*). Sub-chronic and chronic Al toxicity testing has also been carried out by Gensemer et al. (2018) for fathead minnow, two invertebrate species (*Ceriodaphnia dubia* and *Daphnia magna*) and the alga *Pseudokirchneriella subcapitata*. Wang et al. (2018) also tested chronic and acute toxicity for the unionid mussel (*Lampsilis siliquoidea*) and *Hyalella azteca*. Collectively, these data provide a significant advance in assessing potential Al toxicity under a range of conditions including DOM, water hardness and pH.

Utilising the data from the above studies, DeForest et al. (2018) developed a multiple linear regression (MLR) model to predict chronic Al toxicity under varying conditions of DOM, pH and water hardness. Hazardous concentrations to 5% (HC5) of species or genera were then derived using the methodology described in Stephan et al. (1985). The HC5 is a statistically derived value from species sensitivity data of multiple species to a single toxicant, and is analogous to the Predicted No-Effect Concentration (PNEC) for a single species. Using the DOM and water hardness values provided in Table 1 for Lake Rotorua, the MLR model of DeForest et al. (2018) was used to calculate HC5 values for a range of pH values (Figure 4). When compared to both the ANZECC 2000 trigger value for dissolved Al (0.055 mg L^{-1}) and mean total Al concentration in Lake Rotorua (0.020 mg L^{-1}), chronic toxicological effects from Al exposure are unlikely to result under typical pH conditions in Lake Rotorua.

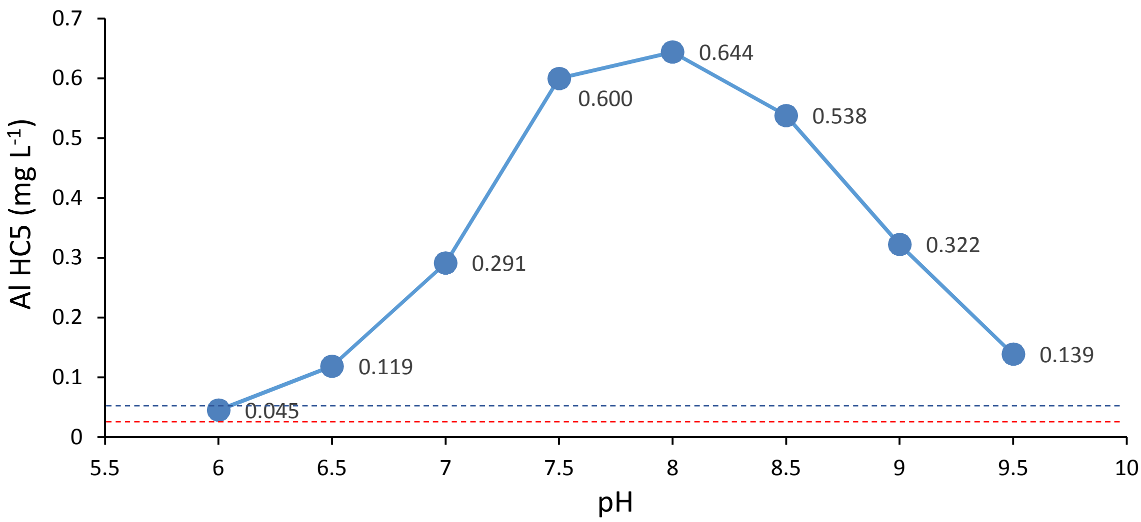


Figure 4. Total aluminium 5% hazardous concentrations (HC5) for Lake Rotorua under differing pH values based on mean dissolved organic matter concentration of 2 mg L^{-1} and mean water hardness of 14 mg L^{-1} (as $CaCO_3$). HC5 values were calculated using DeForest et al. (2018) multiple linear regression models. The blue dashed line indicates ANZECC 200O trigger value for dissolved aluminium in freshwater systems, and the red dashed line indicates mean total aluminium concentration for Lake Rotorua.

Although Al is not specifically monitored, chronic toxicity in receiving environments downstream of Lake Rotorua is also unlikely. Dissolved and suspended Al in the discharge from Lake Rotorua (mean discharge 17.8 m^3 s^{-1} (Fish 1975)) is assumed to be further diluted by combination of flow from Lake Rotoiti (mean discharge 4.83 m^3 s^{-1} CLUES (Semadeni-Davies et al. 2016)) before entering the Kaituna River and discharging (mean 39 m^3 s^{-1} (Jensen et al. 2011)) at the Ōngātoro/Maketu Estuary where further dilution likely occurs due to tidal exchange. A total Al concentration of 0.08 mg L^{-1} was measured in May 2008 (i.e., following initiation of dosing to the Utuhina Stream, but prior to Puarenga Stream dosing) approximately half-way down the Kaituna River (Park 2010), well below likely toxicity threshold concentrations for total Al. It should be noted that significant loading of Al to the Lower Kaituna River likely occurs from tributaries to the Kaituna River, with reported tributary concentrations ranging from 0.14–0.52 mg L^{-1} (Park 2010). These higher total Al tributaries are likely to make ascertaining impacts on the downstream receiving environment difficult, particularly given a lack of monitoring data prior to the start of alum dosing. It is recommended that a longitudinal study of water column and sediment Al concentrations be undertaken to further determine the likelihood of Al impacts on the Kaituna River.

Golding et al. (2015) proposed a marine water quality guideline of 0.024 mg total Al L^{-1}. This value is based on chronic 10% inhibition or effect concentrations (IC10 or EC10) and no-observed-effect concentrations (NOECs) from 11 species (two literature values and nine species tested including temperate and tropical species) representing six taxonomic groups (Golding et al. 2015). The proposed guideline concentration is above the current mean water column concentration for Lake Rotorua (0.020 mg total Al L^{-1}), however further data should be collected to determine Lake Rotorua's contribution to the total of Al loading to the Ōngātoro/Maketu Estuary and the exposure levels of biota in the estuary.

Geothermal Sources of Aluminium

Sulphur Bay is a continuously active geothermal area and a designated wildlife reserve on the southern shores of Lake Rotorua (Figure 1). Total Al concentration within the Sulphur Bay water column is naturally elevated (1 mg L^{-1} prior to Al dosing) due to geothermal fluid infiltration (Martin et al. 2000, Landman and Ling 2009). In addition, pH within the Bay is very low (~pH 2.5 – 3.0) resulting in the formation of highly toxic monomeric Al species (Al^{3+}) (Sparling and Lowe 1996, Ling 2017). The toxic conditions within the bay restrict species diversity to highly tolerant species, primarily *Chironomus* spp..

Near the mouth of the bay the geothermally derived water mixes with water from the main body of the lake and pH increases to ~ pH 7, resulting in the formation of less toxic $Al(OH)_3$ precipitate, and chironomids, aquatic plants (*Eleocharis* spp.) and kakahi (*Echyridella menziesi*) can be found. However, plumes of cloudy white, lower pH, water can often be observed flowing from the bay along the south-western shore of the lake, likely driven by prevailing westerly winds and currents. These plumes appear to be highly variable, resulting in stochastic impacts on the local biota, likely due to low pH and geothermally derived elements, and producing abrupt changes in the abundance of less mobile organisms (Landman and Ling 2009, Ling 2017). Ecological monitoring initiated prior to alum dosing of the Puarenga Stream has found no adverse effects to Lake Rotorua shoreline biota nor caused any apparent increase in aluminium bioaccumulation in lake biota in the vicinity of Sulphur Bay (Ling 2017). It is recommend that regular monitoring for impacts is continued and potentially expanded to provide more insight into the extent of the impacts from plumes flowing from Sulphur Bay and the likely mechanisms for these impacts.

Conclusions

Following the publication of the original ERI report "Ecotoxicological Review of Alum Applications to the Rotorua Lakes" in 2015, a number of studies investigating the toxicological effects of Al have been published. Notable advances in the understanding of chronic effects and mediating (DOM and water hardness) factors have been achieved. From reviewing this literature the following conclusions can be made:

1. Total Al concentration in the water column of Lake Rotorua is at the lower end of concentrations used in toxicological testing, but the results of such studies are still applicable to Lake Rotorua. Recent studies examining chronic low level effects support the previous assessment that toxic effects from alum dosing in Lake Rotorua are unlikely.
2. Formation of algal blooms in Lake Rotorua can cause diel shifts in water column pH of up to 3 pH units (6.5 – 9.5). Laboratory studies have demonstrated toxicological effects at the alkaline end of this shift. However, these extreme pH values are highly transient, limiting the exposure time, and when coupled with low average Al concentration in the water column it is reasonable to conclude algal blooms are unlikely to promote acute Al toxicity. However, it is recommended that chronic effects of combined total aluminium and short-duration alkaline pH shifts be further investigated to determine the potential for negative osmoregulatory impacts on key species.
3. Significant advances have been made in determining thresholds values for chronic Al exposure. Using MLR models developed by the USEPA, statistically derived threshold values (HC5) can be produced for a range of pH conditions under specified concentrations of DOM and water hardness. When calculated for Lake Rotorua these threshold values indicate that chronic effects from alum dosing are unlikely. However, caution should be used in applying these values as the data is not based on New Zealand species.
4. Due to active geothermal activity, Al concentrations are significantly higher (1 mg L^{-1}) and pH lower (~pH 3) in Sulphur Bay compared to the rest of Lake Rotorua. This has produced an area naturally depauperate in freshwater biota but at the mouth of the bay mixing with waters from the main lake body negates these effects and normal lake diversity can be observed. No adverse effects have been observed from alum dosing of the Puarenga Stream. However, plumes of low pH, geothermally derived water often flow from Sulphur Bay along the south-eastern shoreline producing abrupt changes in the abundance of biota. It is recommend that regular monitoring for impacts is continued and potentially expanded to provide more insight into the extent of the impacts from plumes flowing from Sulphur Bay and the likely mechanisms for these impacts

This review supports previous findings that the cautious use of continuous low level alum dosing is an ecologically acceptable option for reducing phosphorus loading to Lake Rotorua. The low water hardness, low dissolved organic matter concentration and low buffering capacity of Lake Rotorua caution against the bulk or widespread application of alum for phosphorus management. Under the present alum dosing regimen, impacts on downstream biota are unlikely due to low lake concentration, however, it is recommended that a longitudinal study of water column and sediment Al concentrations be undertaken to further determine the likelihood of Al impacts on biota in the Kaituna River and Ōngātoro/Maketu Estuary.

Acknowledgements

Review of this report was provided by Warwick Vincent, Nick Ling and John Tyrrell. Funding was provided by the Bay of Plenty Regional Council as part of the Plan Change 10 science review in 2018 for Lake Rotorua.

References

Adams WJ, Cardwell AS, DeForest DK, Gensemer RW, Santore RC, Wang N and Nordheim E (2018). Aluminum bioavailability and toxicity to aquatic organisms: Introduction to the special section. *Environmental Toxicology and Chemistry* **37**: 34-35.

Barile J, Escudero M and Jara L (2016). Effect of pH on embryonic survival, embryonic and hatching period of Galaxias maculatus. *Revista De Biologia Marina Y Oceanografia* **51**: 181-185.

Cardwell AS, Adams WJ, Gensemer RW, Nordheim E, Santore RC, Ryan AC and Stubblefield WA (2018). Chronic toxicity of aluminum, at a pH of 6, to freshwater organisms: Empirical data for the development of international regulatory standards/criteria. *Environmental Toxicology and Chemistry* **37**: 36-48.

DeForest DK, Brix KV, Tear LM and Adams WJ (2018). Multiple linear regression models for predicting chronic aluminum toxicity to freshwater aquatic organisms and developing water quality guidelines. *Environmental Toxicology and Chemistry* **37**: 80-90.

Eggen RI, Behra R, Burkhardt-Holm P, Escher BI and Schweigert N (2004). Challenges in ecotoxicology. *Environmental Science and Technology* **February**: 59A-64A.

Fish GR (1975). Lake Rotorua and Rotoiti, North Island, New Zealand: their trophic status and studies for a nutrient budget. Wellington, New Zealand, New Zealand Ministry of Agriculture and Fisheries**:** 71.

Garcia-Garcia G, Jimenez-Contreras J, Vargas-Hernandez AA, Nandini S and Sarma SSS (2017). Is aluminum innocuous to zooplankton at pH below 6? *Bulletin of Environmental Contamination and Toxicology* **98**: 489-495.

Gensemer RW, Gondek JC, Rodriquez PH, Arbildua JJ, Stubblefield WA, Cardwell AS, Santore RC, Ryan AC, Adams WJ and Nordheim E (2018). Evaluating the effects of pH, hardness, and dissolved organic carbon on the toxicity of aluminum to freshwater aquatic organisms under circumneutral conditions. *Environmental Toxicology and Chemistry* **37**: 49-60.

Gensemer RW and Playle RC (1999). The bioavailability and toxicity of aluminum in aquatic environments. *Critical Reviews in Environmental Science and Technology* **29**: 315-450.

Golding LA, Angel BM, Batley GE, Apte SC, Krassoi R and Doyle CJ (2015). Derivation of a water quality guideline for aluminium in marine waters. *Environmental Toxicology and Chemistry* **34**: 141-151.

Gundersen DT, Bustaman S, Seim WK and Curtis LR (1994). pH, hardness, and humic acid influence aluminum toxicity to rainbow trout (*Oncorhynchus mykiss*) in weakly alkaline waters. *Canadian Journal of Fisheries and Aquatic Sciences* **51**: 1345-1355.

Heini A, Puustinen I, Tikka M, Jokiniemi A, Lepparanta M and Arvola L (2014). Strong dependence between phytoplankton and water chemistry in a large temperate lake: spatial and temporal perspective. *Hydrobiologia* **731**: 139-150.

Jensen JK, Tuckey B and Gasc A (2011). Lower Kaituna River – Maketu Estuary Initial Water Quality Modelling: Final report. Massey University, Albany, DHI Water and Environment**:** 44.

Landman MJ and Ling N (2009). Sulphur Bay Baseline Monitoring for the Puarenga Stream Alum Discharge. Rotorua, Scion**:** 10.

Ling N (2017). Puarenga Stream alum dosing – effects on Lake Rotorua/Sulphur Bay biota 2016. The University of Waikato, Hamilton, New Zealand., Environmental Research Institute, Faculty of Science and Engineering**:** 12.

Maberly SC (1996). Diel, episodic and seasonal changes in pH and concentrations of inorganic carbon in a productive lake. *Freshwater Biology* **35**: 579-598.

Martin R, Rodgers K and Browne P (2000). Aspects of the distribution and movement of aluminium in the surface of the Te Kopia geothermal field, Taupo Volcanic Zone, New Zealand. *Applied Geochemistry* **15**: 1121-1136.

McDonald D, Walker R and Wilkes P (1983). The interaction of environmental calcium and low pH on the physiology of the rainbow trout, *Salmo gairdneri*: II. Branchial ionoregulatory mechanisms. *Journal of Experimental Biology* **102**: 141-155.

Park S (2010). Water Quality Survey of the Lower Kaituna Catchment 2007 - 2008. Environmental Publication 2010/01. Whakatane, New Zealand, Bay of Plenty Regional Council**:** 82.

Poléo ABS and Hytterød S (2003). The effect of aluminium in Atlantic salmon (*Salmo salar*) with special emphasis on alkaline water. *Journal of Inorganic Biochemistry* **97**: 89-96.

Roy RL and Campbell PG (1997). Decreased toxicity of Al to juvenile Atlantic salmon (*Salmo salar*) in acidic soft water containing natural organic matter: A test of the free-ion model. *Environmental Toxicology and Chemistry* **16**: 1962-1969.

Semadeni-Davies A, Elliot S and Shankar U (2016). CLUES - Catchment Land Use for Environmental Stability. Auckland, NIWA.

Shaw TL (1981). Acute toxicity of increased pH to the fresh-water shrimp *Paratya curvirostris*. *New Zealand Journal of Marine and Freshwater Research* **15**: 91-93.

Sparling DW and Lowe TP (1996). Environmental hazards of aluminum to plants, invertebrates, fish, and wildlife, Springer. New York.

Stephan CE, Mount DI, Hansen DJ, Gentile J, Chapman GA and Brungs WA (1985). Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses, US Environmental Protection Agency Duluth, MN.

USEPA (1988). Ambient water quality criteria for aluminum. EPA 440/5-86/008. United States Environmental Protection Agency. Washington, DC.

Wang N, Ivey CD, Brunson EL, Cleveland D, Ingersoll CG, Stubblefield WA and Cardwell AS (2018). Acute and chronic toxicity of aluminum to a Unionid mussel (*Lampsilis Siliquoidea*) and an Amphipod (*Hyalella Azteca*) in water-only exposures. *Environmental Toxicology and Chemistry* **37**: 61-69.

West DW, Boubee JAT and Barrier RFG (1997). Responses to pH of nine fishes and one shrimp native to New Zealand freshwaters. *New Zealand Journal of Marine and Freshwater Research* **31**: 461-468.

WHO (2009). Calcium and magnesium in drinking-water: public health significance. Spain, World Health Organization.

Winter AR, Nichols JW and Playle RC (2005). Influence of acidic to basic water pH and natural organic matter on aluminum accumulation by gills of rainbow trout (Oncorhynchus mykiss). *Canadian Journal of Fisheries and Aquatic Sciences* **62**: 2303-2311.