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TECHNICAL ARTICLE

Is Dilution a Solution to Aluminium Toxicity in an Acid Mine Drainage Affected Stream on the Stockton Plateau, New Zealand?

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Abstract Acid mine drainage from open-cast coal mining has had detrimental effects on water quality and ecology in Herbert Stream, a low volume drainage on New Zealand's Stockton Plateau, due apparently to the low pH (3.19–3.39) and elevated Al (dissolved Al = 8.1–11.4 mg/L). The long-term management liability, difficulty of diverting flow to existing treatment facilities, lack of space, and ready access to a large volume of circumneutral water (the Mt Frederick (MF) Quarry Lake) made dilution of Herbert Stream a potentially attractive management option. Dilution experiments showed that to achieve a $pH > 4.5$ or a dissolved Al concentration of <1.0 mg/L, mixtures comprising 73 or 90 % by volume of MF water, respectively, are required. To achieve Al^{3+} <0.42 mg/L, a previously determined ecological threshold concentration above which macroinvertebrate richness is significantly reduced, a dilution of >85 % MF water is required. However, geochemical speciation modelling indicated that at about this dilution, small changes in dilution result in large changes in the proportion of dissolved Al present as Al^{+3}. In addition, while the proportion of Al^{3+} decreases significantly once the pH is sufficiently high to support the formation of Al hydroxide complexes (at >62 % MF water), precipitation of Al hydroxide and hydroxy-sulphate mineral phases also occurs at these dilutions. These precipitates and chemical species have established toxic effects. Negative ecological impacts across a range of dilutions, as well the difficulties of controlling dilution to the fine degree required within naturally variable streamflows, means that the use of simple dilution to manage Al toxicity in Herbert Stream is unlikely to be effective.

Keywords Water quality · Mine impacts · Aluminium speciation · Ecological impact · Geochemical modelling

Introduction

Acid mine drainage (AMD) is one of the most persistent point-source pollution problems affecting industrialised nations (Sengupta 1993), and commonly contains aluminium (Al) and other trace elements, many of which can be toxic to aquatic life (Soucek et al. 2003). Serious detrimental effects on aquatic ecology in receiving waters are reported due to the contaminants, the acidity, and habitat disruption by precipitates (e.g. Cravotta 2008).

AMD adversely affects water quality and ecology in the low volume streams of the Stockton Plateau, the site of New Zealand's largest open-cast coal mining operation (Black et al. 2005; Trumm et al. 2008). Fish, crayfish, and eels are virtually absent and macroinvertebrate taxonomic richness and abundance are severely reduced (PCE 2009; Trumm et al. 2008; Waters and Webster-Brown 2013). These effects have been partly attributed to Al concentrations (Black et al. 2005) that exceed the recommended guidelines for the protection of aquatic life in freshwater (ANZECC 2000). Al is a major contaminant in acid environments (Gensemer and Playle 1999) and presents a significant environmental problem on the Stockton Plateau.

AMD treatment may involve active or passive interventions, but these require long-term management and/or sufficient land area for infrastructure development. Where either of these factors are problematic and where a low-

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volume AMD drainage cannot be easily diverted into larger treatment systems, dilution may be an attractive management option, provided a source of circumneutral water exists. Dilution has traditionally been, and, in many jurisdictions is still, used as a management tool for disposal of effluent to aquatic environments (e.g. Cloutier et al. 2007) and is commonly relied on for the natural attenuation of contaminant plumes in groundwater (Young et al. 2014). Management guidelines for Al concentrations commonly focus on total dissolved Al ([diss Al]) (Waters and Webster-Brown 2013). Dilution will reduce this total concentration and hence may be attractive for reaching management guidelines, but where toxicity depends on the chemical form of the contaminant, caution is warranted. In an AMD-setting, dilution will alter stream chemistry and Al toxicity in complex ways, and the implications of such dilution need to be well understood.

The concentration of Al that is toxic depends not only on the type of organism but also, as with most trace metals, on the chemical form, or species, of the metal (Parent et al. 1996; Webster-Brown 2005). Of the dissolved Al (diss Al) species, very weak complexes and, in particular, the free ion Al^{3+}, are likely to be the most toxic (Roy and Campbell 1997). Ion-regulatory effects from Al^{3+} are the predominant toxicity mechanism at low pH (Gensemer and Playle 1999), while at moderate acidity (pH $\approx$ 5.0–6.0), respiratory effects predominate, particularly in fish, due to precipitation or polymerisation of Al on gill surfaces (Gensemer and Playle 1999; Poleo 1995). Previous work in Stockton's waterways has indicated that the Al^{3+} concentration is a greater determinant of ecological health than pH (Waters and Webster-Brown 2013). This is consistent with the research of Greig et al. (2010) on metal toxicity in fish in acidic streams in New Zealand. Organic or inorganic ligands that complex with the dissolved metal, or any change in chemistry that promotes Al complexation or adsorption to a solid surface, will reduce the concentration of the free ion, and hence Al toxicity.

The impact of Al on the ecology of Stockton's waterways is therefore highly dependent on its speciation (Parent et al. 1996), which is, in turn, dependent on water chemistry (Nordstrom and Ball 1986). Al speciation changes are rapid, and in-stream chemistry determines speciation rather than a metal's geochemical origin (Gensemer and Playle 1999). Speciation can rarely be measured directly, especially at trace Al levels (Markich and Brown 1999; Nordstrom and May 1996); however, geochemical modelling, using thermodynamic equilibrium constants, has been successful in predicting speciation (e.g. Cravotta 2008; Nordstrom and Ball 1986). This study used a mix of experimental and geochemical modelling approaches to investigate the effects on Al speciation and hence on Al toxicity, of diluting Herbert Stream (HS), a low-volume AMD-affected waterway on the Stockton Plateau, with circumneutral waters from a nearby quarry lake. The ramifications and practicalities of managing the AMD by dilution are considered.

Materials and Methods

The Stockton Plateau (Fig. 1) is an elevated area of approximately 35 km^2, between 600 and 1100 m above sea level. High rainfall makes it one of the wettest areas in New Zealand, with more than 6 m of rainfall annually (Lindsay et al. 2003) and the Plateau is characterised by stunted vegetation, shallow, poorly drained soils and the deeply incised, quartz sandstone pavements of the Brunner Coal Measures. Herbert Stream is at the southern end of the Plateau and drains south-east to the Waimangaro River via Cypress Stream (Figs. 1, 2). The upper drainage is buried beneath an overburden dam, which attempts to divert mine water north, away from the Waimangaro catchment towards the Ngakawau River into which most of the Stockton mine water drains. However, the dam is poorly sealed and an average of 5.3 L/s (Trumm et al. 2008) of AMD-impacted water flows from the base of the dam into the head of HS. Above the overburden dam lies the circumneutral Mt Frederick (MF) Quarry Lake (pH 6.64), which was excavated predominantly from basement rock. This lake is a large-volume potential source of water that could be used to dilute HS AMD.

Sampling Methods

Water was sampled in November and December (summer months) 2010, during stream baseflow conditions. In November, water samples were collected from the upper HS site ($HS\text{-}1_{NOV}$, Fig. 1) and the MF lake site (MF_{NOV}), in triple-washed polyethylene containers for use in dilution experiments. The pH, electrical conductivity (EC), dissolved oxygen (DO), and temperature were analysed at these sites and at a lower HS site ($HS\text{-}2_{NOV}$). In December, these sites ($HS\text{-}1_{DEC}$, $HS\text{-}2_{DEC}$, and MF_{DEC}) were revisited to collect samples for full water chemistry using 50 mL polypropylene centrifuge tubes. Field parameters were again measured, and unfiltered water samples were collected for general water chemistry (major ion concentrations). Samples for diss Al analysis were filtered on-site using sterile 0.45 µm MF-Millipore MCE membrane filters, and acidifed to pH < 1.5 with 8 N HNO_3. Samples for dissolved organic carbon (DOC) analysis were collected into 100 mL dark glass bottles.

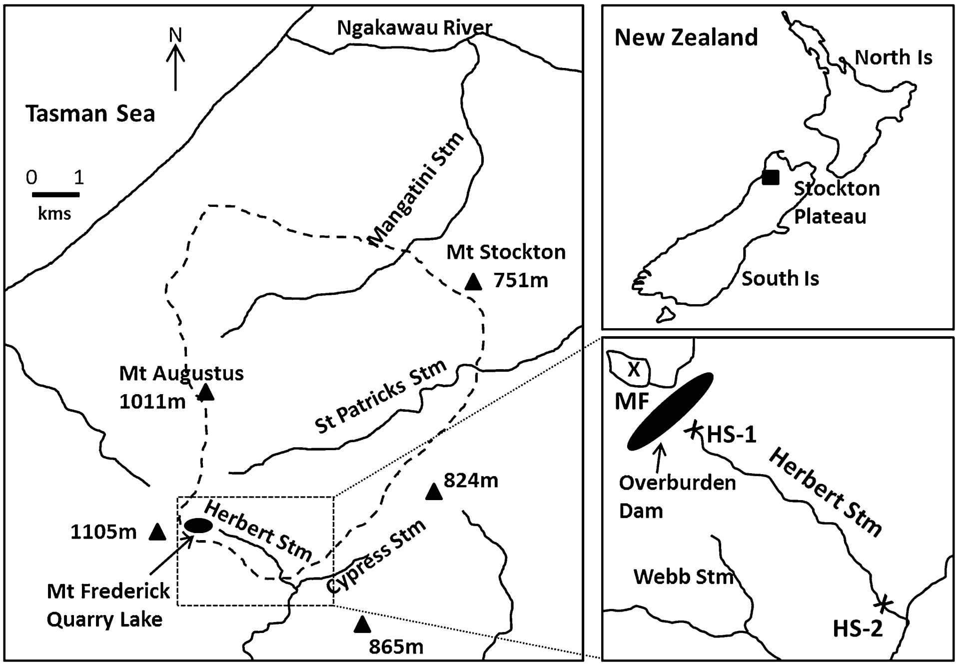

Fig. 1 Drainage systems on the Stockton Plateau, on the west coast of New Zealand, with Herbert Stream and the Mt Frederick Quarry Lake indicated. The *dashed line* approximately delineates the Plateau. Sample sites are indicated in the *lower inset* on the *right*

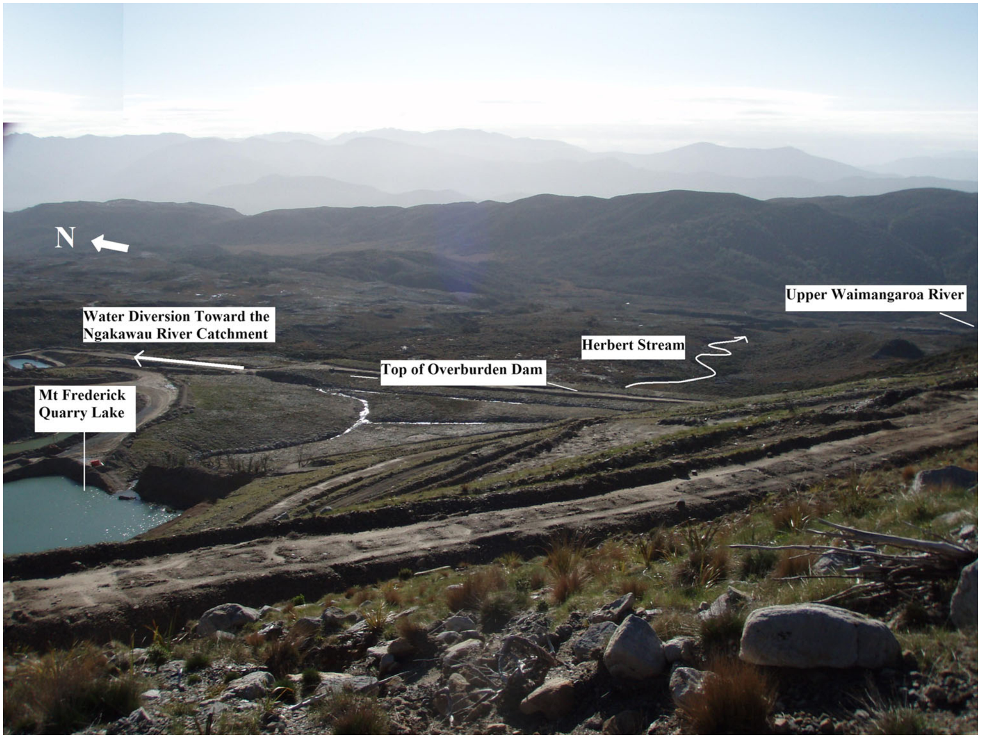

Fig. 2 The study area looking east from Mt Frederick. Water from above the overburden dam is diverted north to avoid contamination of the Waimangaroa River, but Herbert Stream, which rises from leakage of the overburden dam, is AMD affected

Dilution Experiment

250 g of the stream water (HS-1_{NOV}) was weighed out into 17 triple-washed polyethylene containers. The MF water (MF_{NOV}) was then added by weight in varying amounts (50–500 g) to achieve increasing dilution of the HS water (dilution factors ranging from 1 to 6, or 0 to 83 % MF water). Turbidity in agitated samples was measured after 1 h, while pH was measured and subsamples for dissolved Al analysis were taken after 24 days. The Al samples were

filtered through 0.45 µm membrane filters into 15 mL polypropylene centrifuge tubes and preserved by addition of two drops of 8 N HNO_3.

Analytical Methods

The pH, EC, and DO were measured using a portable HACH HQ40d multimeter. SO_4 concentration and turbidity were analysed using a HACH spectrophotometer by the HACH SulfaVer4 method 8051 and the HACH Absorptometric Method 8237, respectively. Turbidity was measured in formazin attenuation units (FAU), which are approximately equivalent to the more commonly used nephelometric turbidity units (NTU). Diss Al concentrations (hereafter denoted as [diss Al]) in the December water samples and in the dilution mixtures were determined by Hill Laboratories (Hamilton, New Zealand) using inductively coupled plasma-mass spectrometry (ICP-MS). The detection limit for Al was 0.003 mg/L.

Major ion, DOC, and silica concentrations must be known for speciation modelling. Analytical methods (and results) for these parameters in MF_{DEC}, $HS\text{-}1_{DEC}$, and $HS\text{-}2_{DEC}$ were reported in Waters and Webster-Brown (2013), together with those for other Stockton Plateau stream water samples. For the interpretation and geochemical modelling of the dilution experiment results, we assumed that MF_{NOV} had similar major ion, Al, DOC, and SO_4 chemistry to MF_{DEC}, based on their similar field EC and pH. The circumneutral pH waters of MF lake are AMD affected but, due to host rock neutralisation, have a much lower [diss Al], 0.034 mg/L, than local streams not impacted by AMD ([diss Al] = 0.129–0.260 mg/L; Waters and Webster-Brown 2013). Due to these low concentrations, we believe that any change in [diss Al] and geochemical modelling results between MF_{Nov} and MF_{Dec} would have been insignificant and inconsequential. Hence, the assumption of similar chemistries for the purposes of geochemical modelling is appropriate. The end-member [diss Al] in $HS\text{-}1_{Nov}$ was back-calculated from the analysed [diss Al] in the least diluted sample of the dilution experiment (17 % MF water), assuming conservative behaviour. This calculation indicated that the undiluted $HS\text{-}1_{NOV}$ [diss Al] was likely to have been 11.4 mg/L, rather than the concentration of 8.1 mg/L analysed in the $HS\text{-}1_{Dec}$. This, and the lower pH in the $HS\text{-}1_{NOV}$ sample, suggest a greater AMD contribution to HS during the November sampling than during December. Therefore, a correction based on the difference in [diss Al] was also made to the $HS\text{-}1_{NOV}$ Si and SO_4 concentrations (corrected to 8.38 and 224 mg/L, respectively). These corrections had little effect on the geochemical modelling. No correction to the assumed $HS\text{-}1_{NOV}$ DOC concentration (0.80 mg/L, same as for $HS\text{-}1_{DEC}$) was made, as this is not derived from AMD sources.

Speciation Modelling

Geochemical modelling was conducted using the PHREEQC computer model (Parkhurst and Appelo 1999), an ion-association, aqueous model that is capable of speciation and saturation index calculations. It was used here to model equilibrium reactions between dissolved and mineral phases using the associated WATEQ4F thermodynamic database. Thermodynamic data was added for Al–silicate and Al–fulvate complexes from Pokrovski et al. (1996) and Markich and Brown (1999), respectively. Aluminium organic complexes are notoriously difficult to quantify due to the heterogeneous nature of humic and fulvic acids (Gensemer and Playle 1999), and so a number of assumptions were made based on the work of Markich and Brown (1999): that fulvate was the main complexing agent, as humate is mainly soluble at high pH levels; that 50 % of the DOC was present as fulvate; and that fulvate behaves as if it were citrate, a similar organic ligand in terms of its ability to complex Al. The stability constant input to PHREEQC is that of the strong Al-citrate complex, as reported by Markich and Brown (1999), which should produce a maximum estimate for organic complexing. HCO_3 was used in place of alkalinity in the modelling. Comparative analysis of alkalinity and HCO_3 (17 and 21 mg/L, respectively) in MF_{DEC} indicate that HCO_3 comprises the dominant species contributing to alkalinity in this water body. Finally, as [DO] indicated an oxidising environment in all streams sampled, a redox pe value of 13 was used for all modelled scenarios. For modelling purposes, the major ion, Si, and DOC concentrations of dilution mixtures were calculated from the end member chemistry, assuming conservative behaviour of these ions.

Results and Discussion

Water chemistry results (Table 1) indicate that upper HS (HS-1) is severely impacted by AMD. Although streams on the Stockton Plateau are naturally acidic (Black et al. 2005; Hughs et al. 2007; Waters and Webster-Brown 2013) the pH of 3.19–3.39 in upper HS was well below natural pH levels (≥4.7). This, together with the elevated [SO_4], is indicative of AMD contamination. [Diss Al] was elevated at HS-1 and the positive corrrelation observed between [diss Al] and [SO_4] in this and other Stockton streams (Waters and Webster-Brown 2013), was indicative of an AMD provenance for Al. HS-2 water chemistry (Table 1) indicated that natural dilution by the tributaries does not adequately reduce acidity or [diss Al] before HS discharges into Cypress Stream. Elevated SO_4 also indicated AMD contamination of the MF water; however, the quarry water had a circumneutral pH and a low [diss Al] due to acid

Table 1 Key measured water chemistry parameters for Herbert Stream (HS) and Mt Frederick Quarry Lake (MF) samples; concentrations in mg/L

Sample	Temp (°C)	pH	EC (μS/cm)	DO	SO_4	DOC	Si	Diss Al
HS-1_{NOV}	8.5	3.15	546	9.43				
HS-1_{DEC}	9.1	3.39	548	7.14	160	0.80	8.08	8.1
HS-2_{NOV}	8.5	3.27	439	10.48				
HS-2_{DEC}	13.9	3.79	215	9.09	39.4	1.30	3.68	3.19
MF_{NOV}	13.6	7.44	135	9.43				
MF_{DEC}	15.9	6.64	146	8.84	50.5	0.50	3.40	0.034

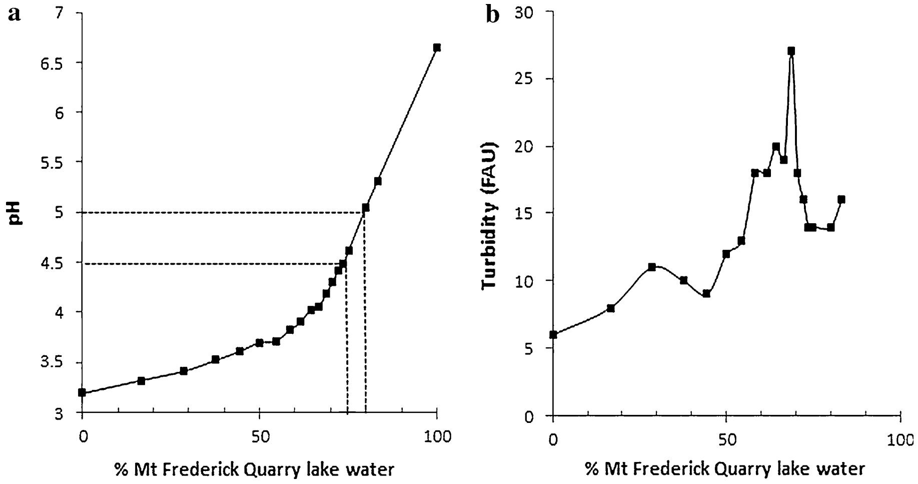

Fig. 3 The effect of increasing dilution of Herbert Stream water with Mt Frederick Quarry Water (as wt%) on: **a** pH, highlighting the dilutions required to achieve a pH in the range 4.5–5.0, and **b** turbidity

neutralisation by host rock minerals and the precipitation of Al minerals under these conditions (Waters and Webster-Brown 2013).

Dilution Effects on pH, Turbidity and [diss Al]

The operators of the Stockton mine, Solid Energy NZ Ltd, seek to achieve an environmental target of pH ≥ 4.7 in Stockton streams (Trumm et al. 2008). Figure 3a illustrates the pH effect of the dilution of HS-1_{NOV} water with MF_{NOV} water. To achieve a pH in the range of 4.5–5.0 requires a 73–80 % dilution. This would correspond to the addition of approximately 14–21 L/s of MF water to the average HS flow of 5.3 L/s. The main increases in turbidity occurred between 50 and 70 % dilution with MF water (Fig. 3), likely due to an increase in suspended precipitated particulates.

Solid Energy NZ Ltd also have an interim environmental target for [diss Al] of 1 mg/L (Trumm et al. 2008), which is subject to further refinement. A decrease in [diss Al] occurred with increasing dilution (Fig. 4) and greater decreases were seen in samples of ≥60 % MF dilution than had been anticipated, assuming conservative mixing (shown by the theoretical mixing line on Fig. 4). This indicated that Al was being actively precipitated (or otherwise removed) at dilutions >60 % MF. The turbidity increase observed between 54 and 70 % MF water may be due to this precipitation. The actual mixing line in Fig. 4 indicates that in order to achieve a target of [diss Al] <1.0 mg/L, a dilution of 90 % was required. This would correspond to adding 48 L/s of MF water to the average Herbert Stream flow (5.3 L/s).

Effects of Dilution on Dissolved Al Speciation and Toxicity

Environmental targets set in terms of [diss Al] can be problematic, because Al toxicity for susceptible organisms can vary widely for any given [diss Al], depending on Al speciation, which is, in turn, affected by water chemistry (Waters and Webster-Brown 2013). The [Al^{3+}] is the best indicator of eco-toxicity at pH < 5.0 (Gensemer and Playle 1991; Roy and Campbell 1997) and on the Stockton Plateau, streams with [Al^{3+}] ≥ 0.42 mg/L were observed to have a significantly reduced macroinvertebrate richness (Waters and Webster-Brown 2013). Modelled [Al^{3+}] for the dilution experiment are shown in Fig. 4. To acheive an [Al^{3+}] ≤ 0.42 mg/L requires an 85 % dilution, corresponding to the addition of 30 L/s MF water to the average Herbert Stream flow of 5.3 L/s. This would result in a pH of 5.4 (Fig. 3a).

The most abundant Al-species making up the total [diss Al], as modelled by PHREEQC, are shown in Fig. 5. During dilution to approximately 60 % MF water, the

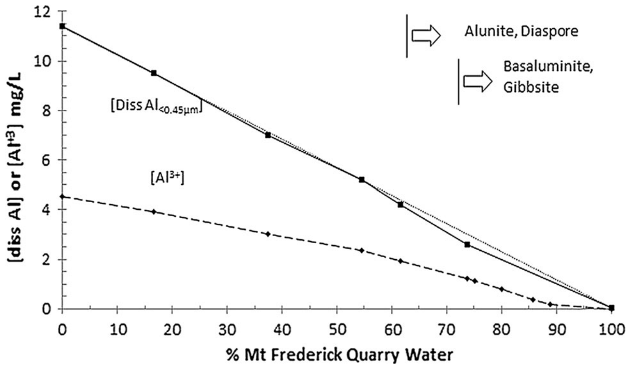

Fig. 4 Changes in measured [diss Al] and modelled [Al^{3+}] with increasing dilution. The *dotted line* is a theoretical, conservative mixing line for [diss Al]. Dilutions resulting in saturation with respect to the denoted Al mineral phases are indicated by the *arrows*

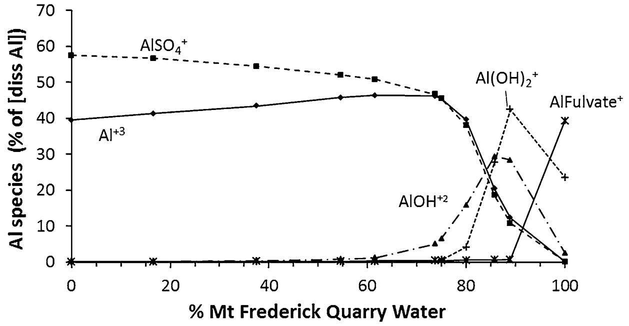

Fig. 5 Significant Al species as a percentage of [diss Al] versus increased dilution of Herbert Stream with Mt Frederick Quarry water

proportion of dissolved Al present as the toxic free ion, Al^{3+}, increases slightly (from 40 to 45 %), as the most abundant species, $AlSO_4^+$, becomes less stable. Modelling on other waterways in the Stockton area has indicated that at pH < 3.9 (dilutions of <60 %, Fig. 3a), the concentrations of $AlSO_4^+$ and the free ion Al^{+3} are inversely correlated (Waters 2011). Hence, as increasing dilution increases the pH and decreases the stability of $AlSO_4^+$, the proportion of diss Al present as Al^{+3} is increased. However, between 75 and 100 % MF water, the abundance of both species declines rapidly with [Al^{3+}] decreasing from 45 to 10 % of [diss Al] over this dilution range. The rapid increase in Al-hydroxide complex stability is responsible for this steep decline in the proportion of Al^{3+}, and is consistent with the hydrolysis of Al expected at pH > 4.6 (Nordstrom and Alpers 1999). This rapid decline in [Al^{3+}] during dilution of between 75 and 100 % MF water means that Al toxicity is very sensitive to small changes in dilution, and small additions of MF or Hebert Stream water greatly change the proportion of diss Al present as Al^{3+}.

Managing Al^{3+} toxicity in HS by dilution, would therefore be a challenging undertaking. A high degree of dilution with MF water (>80 %) would be required to achieve pH and [diss Al] environmental targets, but as just discussed, at these dilutions, the [Al^{3+}] would be very sensitive to minor variations in the degree of dilution. In addition, HS has a variable flow regime. Trumm et al. (2008) report short-lived fluctuations in HS between 2.6 and 25 L/s. Data for [diss Al] during high flows is unavailable; however, pH 3.5 has been recorded at flows of 20 L/s, indicating that high flow events do not result in significant natural dilution of AMD effects. Even if constant volumes of MF can be delivered (e.g. via a siphon pipe) to upper HS, natural fluctuations in the flow of HS could result in major fluctuations in [diss Al] and [Al^{3+}] in the resulting stream flows. Table 2 presents modelled results for such a scenario in which a constant volume of MF (the volume required to achieve [Al^{3+}] <0.42 mg/L for an average HS flow of 5.3 L/s), is added to variable HS flows. A constant [diss Al] was assumed for the different flows. Both [diss Al] and [Al^{3+}] vary widely, with [Al^{3+}] varying from nearly a third, to more than five times the environmental target of 0.42 mg/L. Hence, if MF flows are not adjusted to maintain a relatively constant dilution of 85 % MF water, there is a risk of significant spikes occurring in [diss Al] and [Al^{3+}]. The ecological effect of short term pulses of Al^{3+} under high flow conditions is uncertain, as is the effect of high flows on [diss Al].

Table 2 Approximate [Diss Al] and [Al^{3+}] produced by diluting varying Herbert Stream flows with a constant volume of water from the Mt Frederick Quarry Lake; flows in L/s; concentrations in mg/L

MF-1	Herbert stream	Dilution (% MF)	[Diss Al]	[Al^{3+}]
30	2.6	93	0.7	0.15
30	5	85	1.8	0.42
30	10	75	2.5	1.0
30	25	54	5.2	2.1

Dilution Effects on Al Mineral Precipitation

The departure of [diss Al] from the theoretical mixing line (TML), and the increased turbidity observed at dilutions of >60 % MF water in the dilution experiment (Figs. 3, 4), suggest the formation of an suspended Al-bearing mineral, as previously noted. PHREEQC predicts saturation with respect to the minerals diaspore (AlOOH) and alunite ($KAl_3(SO_4)_2(OH)_6$ at 62 % MF water, and further saturation with respect to gibbsite ($Al(OH)_3$) and basaluminite ($Al_4(OH)_{10}SO_4$) at >72 % MF, with a correspondingly higher pH (Fig. 4).

Brown precipitates were observed at dilutions >50 % MF water, but the close agreement of [diss Al] and TML at 55 % MF (Fig. 4) suggest that this precipitate did not contain Al. The colour and the fact that a dilution of 50 %

MF water had a pH of 3.7, the minimum pH observed for Fe-oxide staining in these streams (Harding and Boothroyd 2004), suggest that Fe-oxyhydroxides probably began to precipitate.

Al-hydroxide mineral precipitates would have a detrimental effect on stream communities in higher pH waters ($pH > 5.9$) at Stockton (Waters and Webster-Brown 2013), due to the previously reported mechanisms of physical change to habitats (Cravotta 2008; Harding and Boothroyd 2004) or direct precipitation and accumulation on biological surfaces (Gensemer and Playle 1999; Soucek et al. 2003). Additionally, in mixing zones where acid waters are neutralised, a rapid rise of pH to 5.0 or 6.0, may induce hypoxia in fish when Al polymerisation occurs at negatively-charged sites on gill surfaces. However, toxicity by this mechanism is progressively reduced over a short time period (seconds/minutes) after mixing (Gensemer and Playle 1999; Poleo 1995; Poleo et al. 1994). Such adverse effects from the precipitation of Al-hydroxide minerals, and/or Al polymerisation, resulting from the dilution of HS with MF water, are likely to occur at dilutions below those required to increase pH and decrease [Al^{3+}] to ecological threshold levels.

Conclusions

Long-term management of acidity and Al toxicity in HS by a simple dilution system using MF lake water does not appear feasible. Al toxicity in susceptible organisms is highly dependent on speciation, which is affected by the changing water chemistry during dilution. During normal flow in HS, the required pH increase and [Al^{+3}] and [diss Al] decreases can be achieved by diluting HS water to 75, 85, and 90 % MF respectively, but at these dilutions, increased toxicity due to the precipitation of Al-hydroxide minerals and/or polymerisation of Al, are predicted. In addition, the dilutions required to achieve environmental pH, [diss Al], and [Al^{3+}] targets would be very difficult to maintain consistently in a natural stream with significant flow variations. These flow variations, with the resulting dilution and speciation changes, would likely result in potentially toxic spikes of [diss Al] and [Al^{+3}]. Hence, although dilution is still relied on in some juridictions as a management tool for the discharge of effluent to aquatic bodies, and can be effective in reducing total contaminant concentrations, for contaminants such as Al in AMD, the toxic effects of which are dependent on speciation, dilution is unlikely to be a satisfactory mangement solution.

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