



Testing Geochemical Predictions of Trace Element Toxicity and Bioavailability at a Rehabilitated Mine Site

M. E. Fairgray¹ · J. G. Webster-Brown¹ · J. Pope²

Received: 10 April 2019 / Accepted: 31 October 2019 / Published online: 12 November 2019
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Abstract

The speciation, toxicity and bioavailability of trace elements in mine drainage environments can be readily predicted using geochemical modelling, and this is frequently the basis for assessing the likely impacts of mine effluents and efficacy of rehabilitation plans. However, such predictions are rarely validated against observed trace element characteristics after mine rehabilitation is complete. In this study of a former Pb–Zn mine in New Zealand, PHREEQC was used to predict dissolved trace element and sediment-bound speciation for the rehabilitated mine site, and the results were compared to the observed water and sediment quality. For Fe, Mn, Al, Cu, Pb, Zn, Cd, Ni, As, and Sb, it was predicted that only Zn²⁺ and Cd²⁺ concentrations would exceed recommended guideline values for ecosystem health. PHREEQC indicated that the pH would have to be raised to > 9.5 to reduce these toxicants to a level fit for ecosystem health. Modelling of potential mineral formation indicated that the waters were saturated with respect to a variety of Fe-, Mn- and Al (oxy)hydroxides at and immediately downstream of the mine site, but were not saturated with respect to any trace element-bearing minerals, or sulfide or carbonate phases. This was consistent with X-ray diffraction and scanning electron microscopy (SEM) observations of the sediment. Sequential extraction of the sediment showed strong associations of Zn, Cu, Pb, As and Sb with iron (oxy) hydroxides. Modelling trace element adsorption onto only hydrous ferric oxide surfaces accurately predicted the adsorption of Zn, Cd, Cu, and Ni, but predictions of Pb and As adsorption were less reliable. Additionally, a strong association between Zn and Mn oxyhydroxide was observed in SEM analysis.

Keywords Acid mine drainage · Attenuation processes · Metal speciation · Sequential extraction

Introduction

Mining can have severe impacts on the natural environment in the vicinity of a mineral resource (Bradshaw and Chadwick 1980; Cooke and Johnson 2002), including the contamination of local streams with acidic mine waters (Lottermoser 2003). The oxidation of iron sulfide minerals such as pyrite, pyrrhotite, marcasite, and mackinawite create

acidic conditions in weathering fluids (Lottermoser 2003; Nordstrom and Alpers 1999), which can then facilitate the dissolution of other minerals, releasing trace elements into downstream environments (Ziemkiewicz et al. 1997). The low pH, high sulfate, trace element-rich discharge can be referred to as acid rock drainage (ARD), if occurring naturally, or acid mine drainage (AMD), if associated with mining activities. This distinction is made because iron sulfide oxidation can be accelerated by mining activities when mineral surfaces are exposed to the atmosphere at a faster rate than would occur naturally (Akcil and Koldas 2006; Nordstrom and Alpers 1999). Neutral pH drainage can also occur where there is either low iron sulfide content in the ore or sufficient acid-neutralizing capacity in the host rock (Banks et al. 1997; Blowes et al. 2003; Warrender et al. 2011).

Freshly formed Fe-, Mn- and Al (oxy)hydroxides readily adsorb many trace elements (Johnson and Hallberg 2005; Watzlaf et al. 2004). Under favorable conditions, such (oxy) hydroxides will coagulate and settle into the sediment,

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10230-019-00644-y>) contains supplementary material, which is available to authorized users.

✉ M. E. Fairgray
marlese.fairgray@pg.canterbury.ac.nz

¹ Waterways Centre for Freshwater Management, University of Canterbury and Lincoln University, Christchurch, New Zealand

² CRL Energy, Christchurch, New Zealand

together with the associated trace elements, reducing the immediate toxicity of the water to aquatic life, but forming a reservoir of trace elements in the stream sediments. Spatial or temporal changes in pH, redox conditions, and water chemistry influence trace element adsorption and mineral precipitation processes. Reduced pH and redox conditions, for example, can lead to desorption of adsorbed cations or, if significant enough, the dissolution of oxide phases to which these ions had adsorbed. Additionally, pH and redox conditions when the oxide precipitate is forming can affect how effectively trace elements are scavenged from solution (Dale et al. 2015).

The presence and extent of these processes can be theoretically predicted using geochemical models based on thermodynamic equilibria, providing an indication of expected dissolved trace element speciation and adsorption, mineral precipitation under certain conditions and how this may change if conditions are altered. It is an important tool used in mine remediation planning to determine end points for different remediation techniques and to assess the ongoing toxicity and mobility of trace elements after rehabilitation, without having to carry out expensive and time-consuming field trials. However, there are few instances where geochemical model predictions have been validated against observations at a rehabilitated mine site.

The purpose of this research was therefore to compare geochemically modelled trace element speciation, adsorption, and precipitation to that observed at a rehabilitated

former Pb–Zn mine. PHREEQC (Parkhurst and Appelo 2013) was used to predict dissolved and sedimentary trace element speciation and trace element attenuation processes, which was then compared to observed trace element associations in the water and sediment of streams draining the mine site. The reliability of this approach for determining the ongoing environmental impacts of a rehabilitated mine site was then assessed.

The mine used in this research was the Tui Mine in New Zealand. The Tui mine is a former base metal mine located on the western slopes of Mt. Te Aroha in the Kaimai Ranges. It is 3 km northeast of the township of Te Aroha, at the base of the Coromandel Peninsula (Fig. 1). The mine sits at an altitude of between 300 and 400 m above mean sea level, is surrounded by native bush, and drained by two streams: the Tui Stream on the north side of the mine site and the Tunakohoa Stream on the south side. Both streams are tributaries of the Waihou River. The average rainfall is high, at around 2100 mm/year on Mt. Te Aroha (Harvey and Webster-Brown 2003).

The ore extracted at the Tui Mine came from two mineralized quartz reefs containing sphalerite (ZnS), galena (PbS), pyrite (FeS₂), and chalcopyrite (CuFeS₂) with minor amounts of cinnabar (HgS), marcasite (FeS₂), tetrahedrite [(Cu, Fe)₁₂Sb₄S₁₃], and tennantite [(Cu, Fe)₁₂As₄S₁₃] (Morrell 1997; Tay 1980; Wodzicki and Weissberg 1970). Although it was first mined for Pb, Au, and Ag in the 1880's to the early 1900's, the mine also provided Zn as a flux to

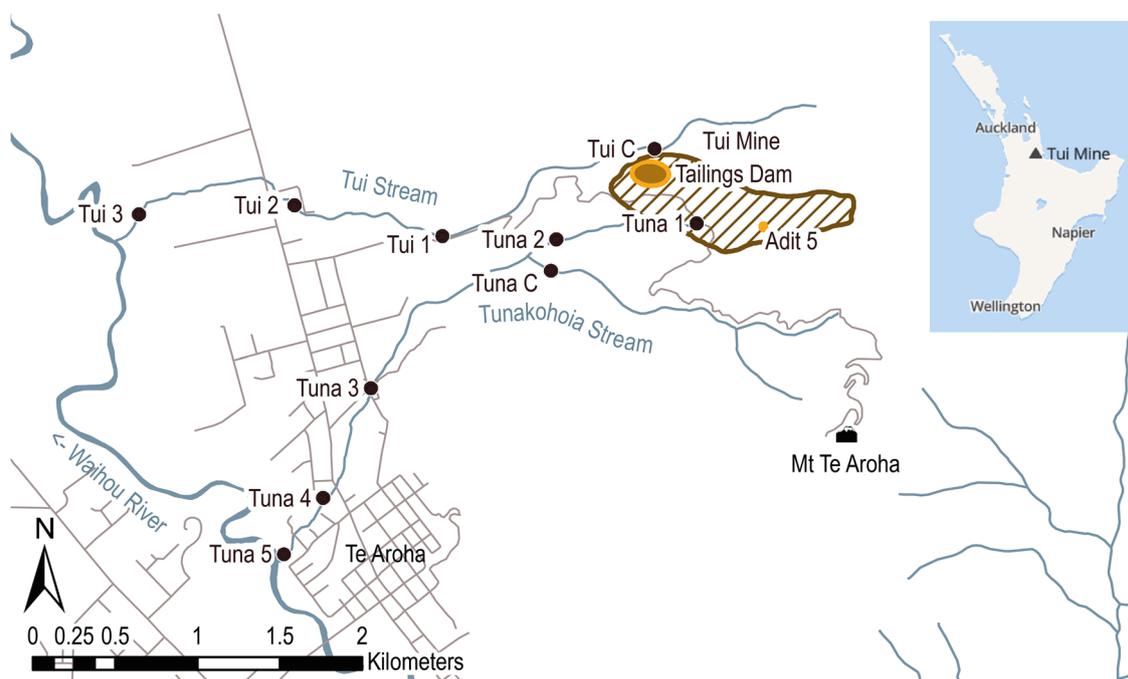


Fig. 1 Map of the study area near Te Aroha in Coromandel, New Zealand, showing the Tui Mine site (hatched) and sampling sites on the Tui and Tunakohoa streams

gold mining. However, due to primitive ore extraction technology, this early mining did not yield much ore of economic value (Morrell 1997; Tay 1980). In 1967, the mine was reopened by Norpac Mining Ltd to produce Cu, Pb, and Zn (Morrell 1997) but closed again in 1973 when levels of Hg found in the ore made it difficult to find a market (Morrell 1997; Tay 1980). The mine site was not rehabilitated but was left with waste rock dumps, an unstable tailings impoundment at risk of collapse, and contaminants leaching from the mine workings, tailings dam, and tailings impoundment. Load calculations by Harvey and Webster-Brown (2003) identified leachate from the tailings dam as the main source of contamination to Tui Stream, and Adit 5 as the main source of contamination to the Tunakohoa Stream. Consequently, the Tui Mine was recognized as New Zealand’s worst metal-contaminated site (Sabti et al. 2000) with high levels of metal contaminants in streams draining the site (Table 1). Partial site remediation—replacement of the sediment trap downstream of the tailings dam and the construction of a new spillway at the outlet of the sediment trap—was carried out in 2006 after heavy rain caused the former sediment trap to fail (Sharplin 2008). However, the ranking of most contaminated site in the country, along with perceived instability of the tailings dam in a major seismic or weather event, prompted the local regional and district councils to begin full rehabilitation of the site in 2010 (Fairgray et al. 2016). This project was completed in 2013.

The 2010–2013 rehabilitation included plugging the level 5 adit and modifying the level 4 adit to control the amount of mine drainage water discharged (Fairgray et al. 2016). The underground workings were allowed to flood and lime slurry was injected into the workings. The tailings dam was stabilized, mixed with lime, and capped with clean fill to prevent oxygen and water from entering the tailings. Recent monitoring has shown an apparent improvement in water quality (and ecological health) of the streams, although they do still receive some discharge from the adits and the tailings dam (Fairgray et al. 2016). In Tui Stream, for example, the pH is now circumneutral and dissolved Cu and Pb have been reduced to less than 20% of their previous concentrations. However, little is known about how the toxicity of dissolved trace elements has changed, and whether this reduction in concentration is sufficient to allow the recovery of a healthy

aquatic ecosystem. There is also concern that trace elements in the sediments may continue to be released from the sediment over time, providing an ongoing source of contamination. This has implications for the rate of recovery of this rehabilitated mine site.

Materials and Methods

Sampling and Analysis

Water and sediment samples were collected at ten sites in the Tui and Tunakohoa streams; four sites on Tui Stream, including a reference site (TuiC) upstream of the mine workings, and five sites on Tunakohoa Stream, and a reference site (TunaC) on the south branch of the Tunakohoa Stream, which is unaffected by mine drainage (Fig. 1). Samples were collected in spring (November 2015) to avoid the extremes of high rainfall and stream flow during winter, and low stream flow in summer.

Measurements of temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) were made in situ using a HACH HQ40d portable multi parameter meter. Water samples were collected in high density polyethylene (HDPE) centrifuge tubes. One water sample for major ions determination was collected, as well as two water samples for trace element analysis (one unfiltered, for “acid soluble” trace element analysis, and one filtered through a 0.45 µm membrane, for “dissolved” trace element analysis). Both samples were acidified to 1% HNO₃ with Aristar-grade concentrated nitric acid prior to analysis. Sediment samples were collected in HDPE bottles, from the top 5 cm of the stream sediment bed.

Water samples were analyzed for major cations and trace elements: Fe, Mn, Al, Cu, Pb, Zn, Cd, Ni, Hg, Sb, and As by inductively coupled plasma mass spectrometry (ICP-MS), with detection limits of 0.02 mg/L for major cations, 1.5 µg/L for Fe and Al, and 0.05 µg/L for all other trace elements except Zn (0.75 µg/L) and Sb (0.20 µg/L). Major anions were determined by high performance ion chromatography, with detection limits of 0.005 mg/L for Cl, 0.020 mg/L for NO₃ and 0.200 mg/L for SO₄. Dissolved inorganic carbon concentrations were determined by infra-red gas analysis,

Table 1 Dissolved trace element concentrations (mg/L) and pH in Tui and Tunakohoa Streams, downstream of the Tui mine workings, prior to full rehabilitation in 2010

Location	pH	Cu	Pb	Zn	Cd
Upper Tui Str	3.50–6.71	1.0–7.0	0.12–3	4.5–1460	0.7–6.0
Lower Tui Str	4.4–7.05	1.7–8.0	<0.1–1.04	4–590	0.1–2.0
Upper Tunakohoa Str	6.35–7.74	1–110	1–510	1590–16,200	10–140
Lower Tunakohoa Str	6.46–7.60	1–30	0.08–260	200–3790	1–100

References: (Tay 1980; HENDY 1981; Pang 1995; Webster 1995; Harvey and Webster-Brown 2003; Sharplin 2008)

then reported as HCO_3^- as all waters were of a neutral pH (DL = 5.9 mg/L).

Sediment samples were dried at 40 °C and sieved through a 67 µm nylon mesh, then digested in hot nitric acid; the digest was analyzed for trace elements by ICP-MS (as above). Sediment samples were also analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD was performed on a Philips 1130 diffractometer over a 2θ range from 2° to 62°. Clay separates were glycolated by exposure to ethylene glycol vapors for 48 h before being run from 2° to 22° 2θ. SEM was carried out on a JEOL JSM IT-300 variable pressure SEM with an Oxford Aztec SDD energy dispersive X-ray analysis system attached.

Sequential Extraction of Sediments

A sequential chemical extraction scheme based on that of Leleyter and Probst (1999), but including a final hot nitric acid step (Salvarredy-Aranguren et al. 2008), was used to identify the specific solid phases in the sediment that were binding trace elements. The extraction scheme is described in Table 2. A quantity of 0.1 g of sediment (dried and sieved as for total sediment digestion above) was used, with 10 mL of the extractant added to the sediment in most steps (volumes of 3–5 mL were used in steps 5 and 6). The trace element concentrations in fractions 1, 4a, 4b, 4c, 5, and 6 of the sequential extraction were analyzed by ICP-MS, and in fractions 2 and 3 were analyzed by ICP-OES (optical emission spectrometry).

As has been acknowledged in the literature, sequential extractions of this nature can be misleading due to the poor specificity of reagents for target mineral phases and the potential redistribution of elements to other phases during the sequential extraction process (Bacon and Davidson 2008). This has been taken into account when interpreting the results in this study. For example, the sodium acetate extractant (fraction 3) is often referred to as targeting the “carbonate” fraction, but has been renamed here as “low pH

leachable” fraction to acknowledge the potential for some trace element cations to desorb from mineral surfaces, as well as carbonates and minor Fe- and Mn-oxyhydroxides to dissolve in this step. The modified nomenclature for target fractions given in Table 2 is used throughout this paper. In addition to this, the sum of each trace element from the fractions in the sequential extraction was compared with the concentration determined by total sediment digest to ensure that redistribution of elements within the fractions was not occurring during the sequential extraction process.

Macroinvertebrate Sampling

Macroinvertebrate samples were collected in December 2014 according to the protocol of Stark et al. (2001). Samples were preserved in the field with 70% ethanol. Samples were then sieved through 500 µm mesh in the laboratory. Invertebrates were counted and identified to the lowest taxonomic level using the identification guides of Winterbourn et al. (2006).

Geochemical Modelling

Dissolved trace element speciation, mineral formation or dissolution, and adsorption reactions was predicted using PHREEQC version 3.3.2 with the WATEQ4F thermodynamic database (Parkhurst and Appelo 2013). PHREEQC is the most commonly used geochemical software for predicting mine effluent chemistry in New Zealand, and is commonly used in effluent chemistry prediction internationally (Rötting et al. 2008; Watten et al. 2005). In this study, PHREEQC was used in the two ways it is most commonly used to predict mine discharge chemistry by mining companies and their consultants;

1. To model current dissolved trace element speciation to determine free ion concentrations (to assess potential

Table 2 The sequential extraction scheme of Leleyter and Probst (1999) with an additional final step from Salvarredy-Aranguren et al. (2008)

Target Fraction	Reagent	Reaction time
1. Water soluble	Deionised water	30 min
2. Easily exchangeable	1 M magnesium nitrate	2 h
3. Low pH leachable	1 M sodium acetate at pH = 4.50	5 h
4a. Mn oxides	0.1 M hydroxylammonium chloride	30 min
4b. Amorphous Fe oxides	0.2 M ammonium oxalate + 0.2 M oxalic acid	4 h in dark
4c. Crystalline Fe oxides	0.2 M ammonium oxalate + 0.2 M oxalic acid + 0.1 M ascorbic acid	30 min
5. Organic matter	0.02 M HNO_3 + 35% H_2O_2	5 h
	3.2 M ammonium acetate in 20% v/v HNO_3	30 min
6. Residual (incl. sulfide)	8 M HNO_3	3 h

Extractions were undertaken at 20 °C, except for Fraction 4c (80 °C) and 5 and 6 (85 °C)

toxicity), and to determine speciation change under a regime of changing water quality.

- To predict dissolved trace element removal through mineral formation and adsorption onto freshly formed hydrous ferric oxide (HFO). For adsorption modelling in a mine remediation context, surface complexation using HFO as the only adsorbing surface is commonly used. This is based on the adsorption data of Dzombak and Morel (1990), which pertains to freshly-formed HFO, with 0.005 strong binding sites/mol Fe, 0.2 weak binding sites/mol Fe, and a specific surface area of 600 m²/g.

PHREEQC was used with the WATEQ4F database for dissolved speciation and adsorption. To model dissolved speciation changes following lime additions (e.g. to the tailings pile and inside Adit 5), 125 µmol of calcite was added stepwise to the stream water from July 2007, as reported by Sharplin (2008) until either the saturation limit (SI = 0.0) of calcite was reached or until CaCO₃ was no longer available. 125 µmol was used as it had been determined that this amount would result in the saturation index of calcite being reached but not exceeded.

Batch reactions were run initially to determine which trace element bearing phases were likely to be supersaturated in the solution, and therefore, which minerals were theoretically most likely to precipitate. The minerals that were unlikely to actually form in a low temperature, fresh-water environment were eliminated from consideration. This step discounted the formation of minerals such as hematite, cupric ferrite, and cuprous ferrite, which are only formed at high temperatures (Gholinejad et al. 2014; Kolta et al. 1981). The batch reactions were remodeled with the remaining minerals allowed to precipitate when saturated and the constituent dissolved ion concentrations reduced accordingly. The resulting pH change was calculated from the ion balance.

Results

Dissolved Trace Element Concentration, Speciation and Toxicity

Observed Water Quality

Physiochemical water quality at the sampling sites during the November 2015 sampling survey is shown in Table 3. A more complete water chemistry (including all major cations and anions, as needed for speciation modelling) is given in Supplemental Tables A1 and A2 (which accompany the online version of this paper).

Remediation at the mine site has effectively raised Tui stream water pH to circumneutral, and lowered conductivity and sulfate concentrations. However, pH was already

Table 3 Physiochemical water quality parameters of relevance in determining water trace element speciation and assessing ecological impacts, in the Tui and Tunakohia streams in November 2015

Site	pH	Temp °C	DO (mg/L)	Conductivity (µS/cm)	SO ₄ (mg/L)
Tuna 1	7.42	13.7	9.69	666	285
Tuna 2	7.12	12.2	10.1	409	154
Tuna 3	6.84	13.8	9.88	308	93.6
Tuna 4	6.92	15.5	9.39	249	65.4
Tuna 5	7.52	19.6	10.1	252	65.6
Tuna C	7.07	12.1	9.85	102	14.6
Tui 1	7.40	11.9	10.3	150	29.2
Tui 2	7.23	12.9	9.94	150	29.6
Tui 3	7.31	15.9	8.98	149	28.6
Tui C	7.21	11.4	9.97	125	20.1

near neutral in Tunakohia Stream (Table 1) and the addition of lime in Adit 5 has only had a small effect on pH and little effect on EC or sulfate concentrations when compared with data of Sharplin (2008). Temperature and DO levels are sufficient to support a healthy ecology, with the possible exception of the elevated temperature at Tuna 5, a shallow section of this stream where it passes through open farm land.

Trace element concentrations are shown in Table 4 as both acid-soluble concentrations (in unfiltered, acidified water samples) and as the percentage of dissolved trace element. Acid soluble Hg was consistently below detectable levels, as was Sb at all sites except Tuna 1 (0.25 µg/L) and Tuna 2 (0.13 µg/L). The concentrations of trace elements were considerably higher in Tunakohia Stream, which still receives drainage from Adit 5, than in Tui Stream.

In New Zealand, any initial assessment of potential trace element toxicity to aquatic life compares acid-soluble concentrations with trigger values in the ANZECC (2000) water quality guidelines. For “moderately disturbed” streams, trigger values represent the highest trace element concentration that will still protect 95% of the aquatic species present. They are referred to as trigger values to indicate they are only the first stage of a toxicity assessment. If they are exceeded, further investigations, such as trace element speciation determination, are required to better assess the toxicity of the contaminant (ANZECC 2000).

Acid-soluble Zn and Cd exceeded ANZECC (2000) trigger values in both streams, but most significantly in Tunakohia Stream. Notably, the Zn trigger value was even exceeded (slightly) at the reference site (TuiC), upstream of any tailings drainage input, likely reflecting natural elevation due to the weathering of host rock. In addition, the dissolved fraction of these metals constituted 85–100% of the acid-soluble concentration at the contaminated sites, indicating that most of the element was bioavailable.

Table 4 Acid-soluble trace element concentrations ($\mu\text{g/L}$), together with percentage dissolved concentration (in parentheses) in the Tui and Tunakohoa Streams, as measured in November 2015

Site	Fe	Mn	Cu	Pb	Zn	Cd	Ni	As
Tuna 1	360 (1%)	453 (100%)	4.94 (56%)	16.5 (14%)	2440 (100%)	15.2 (100%)	7.79 (100%)	1.52 (73%)
Tuna 2	14.9 (21%)	75.3 (100%)	5.06 (76%)	5.04 (49%)	1860 (99%)	13.2 (100%)	3.73 (100%)	0.56 (100%)
Tuna 3	11.3 (82%)	1.85 (95%)	1.03 (89%)	0.19 (68%)	596 (100%)	6.11 (100%)	1.33 (100%)	0.41 (100%)
Tuna 4	31.3 (42%)	5.15 (78%)	0.94 (84%)	0.20 (50%)	352 (97%)	4.14 (94%)	0.88 (100%)	0.39 (100%)
Tuna 5	64.2 (41%)	20.9 (98%)	1.54 (74%)	0.68 (15%)	194 (93%)	2.67 (90%)	0.70 (93%)	0.47 (93%)
Tuna C	32.0 (26%)	3.58 (13%)	0.40 (82%)	0.17 (19%)	1.03 (79%)	<DL –	0.21 (80%)	0.26 (100%)
Tui 1	7.61 (38%)	1.13 (35%)	0.95 (89%)	0.23 (23%)	46.8 (98%)	0.37 (97%)	0.57 (100%)	0.44 (100%)
Tui 2	31.7 (64%)	11.8 (89%)	1.01 (89%)	0.11 (25%)	55.3 (97%)	0.43 (89%)	0.58 (96%)	0.49 (96%)
Tui 3	169 (39%)	51.3 (93%)	1.26 (75%)	0.41 (21%)	39.5 (95%)	0.27 (85%)	0.60 (99%)	0.91 (96%)
Tui C	38.2 (7%)	2.36 (9%)	0.29 (59%)	0.11 (8%)	11.0 (88%)	0.07 (94%)	0.21 (76%)	0.48 (93%)
ANZECC trigger value		1900	1.4	3.4	8.0	0.20	11	13

Values in bold exceed “ANZECC” trigger values, local water quality guidelines for the protection 95% of aquatic life present (ANZECC 2000)

Of the other trace elements tested, only Cu and Pb exceed trigger values, and then only in the upper reaches of the Tunakohoa Stream. The proportion of dissolved (bioavailable) Cu and Pb is also less than for Cd and Zn, with dissolved Cu constituting 56–89%, and Pb constituting 8–68% of their acid-soluble concentrations. Other trace elements (Fe, Mn, As, and Ni) did not exceed (ANZECC 2000) guidelines; therefore, further assessment of potential toxicity focuses on Zn, Cd, Cu and Pb.

Modelled Dissolved Trace Element Speciation

For dissolved trace element concentrations exceeding ANZECC (2000) trigger values, PHREEQC was used to determine the proportion of the trace element present in the free ion form. The free ion is assumed to be most toxic species to biota according to the free ion activity model (Campbell 1995).

Figure 2 shows PHREEQC predicted dissolved Cd, Cu, Pb, and Zn concentrations. The concentrations of free Cu^{2+} and Pb^{2+} ions are predicted to be well below ANZECC (2000) guidelines at all sites, including the upper Tunakohoa Stream, as these metals are complexed by hydroxyl ligands. Free Cu^{2+} ion constituted only up to 40% of the

dissolved Cu in Tunakohoa Stream, and up to 15% in the Tui Stream. Free Pb^{2+} ion constituted less than 35% of the dissolved Pb in the Tunakohoa Stream and up to 20% in the Tunakohoa Stream.

However, free Cd^{2+} and Zn^{2+} ions remained orders of magnitude higher than the ANZECC (2000) guidelines, for all except the reference sites. The main complexing ligand for Zn and Cd was the sulfate ion, although sulfate complexes made up < 25% of the dissolved Cd and Zn in the Tunakohoa and < 5% in Tui Stream.

Consistency with Ecological Monitoring Data

The modelled concentration of Zn^{2+} and Cd^{2+} ions were compared to the results of the ecological surveys carried out at these sites (Fig. 3). In Tunakohoa stream, there appears to be a reduction in ecological taxa at > 3.5 $\mu\text{g/L}$ free Cd ion and > 300 $\mu\text{g/L}$ free Zn ion. However, as high concentrations of Zn and Cd occur simultaneously, it is not possible to state with confidence which of these metals has the greatest detrimental effect on aquatic life. In Tui Stream, ecological effects appear to occur at much lower concentrations, and may be due to other factors, such as the long term low pH that occurred in this stream prior to mine remediation.

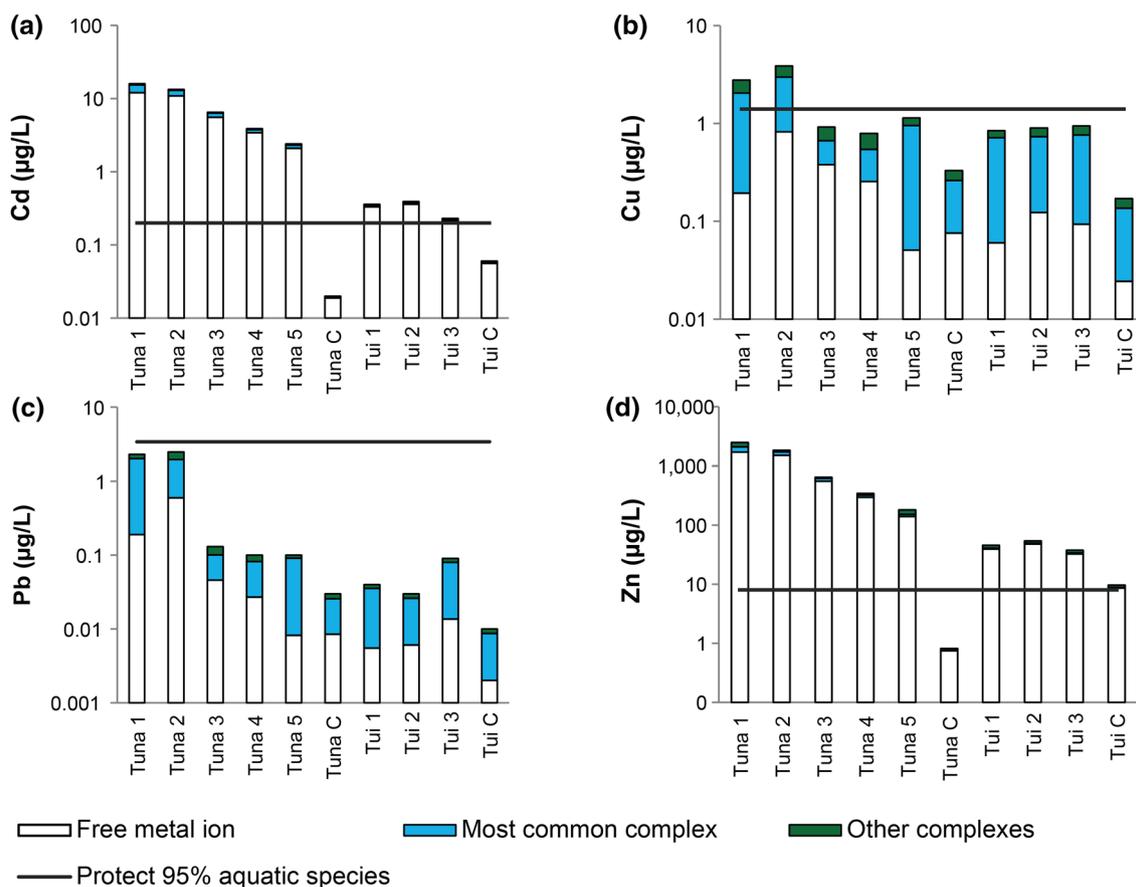


Fig. 2 Speciation of elements exceeding ANZECC (2000) trigger values in Tui and Tunakohioa streams, showing the relevant water quality guideline to protect 95% of aquatic life

Sediment-bound Trace Element Speciation

Observed Sediment Mineralogy and Chemistry

XRD analysis showed that the sediment minerals were predominantly quartz and plagioclase, with chlorite, smectite, illite, and kaolinite clays present as weathering products. No major trace element bearing minerals were identified by XRD. SEM analysis revealed a residual Zn-sulfide particle in Tuna1 sediment just below Adit 5 drainage (Fig. 4), but no other sulfide minerals. No residual carbonates (such as limestone fragments from the remediation activities) or secondary carbonate phases were observed in the sediments. However, strong mineralogical associations between Fe, Pb, and Cu, and between Mn and Zn were observed (examples shown in Fig. 4).

Sediment-bound trace element concentrations are shown in Table 5. ANZECC (2000) interim sediment quality guidelines (ISQG) for aquatic life protection are also shown; ISQG-High is the guideline above which an adverse biological effect is frequently observed, and ISQG-Low is the guideline below which adverse effects rarely occur. For

values between these two guidelines, adverse effects occur occasionally (ANZECC 2000; Long et al. 1995). ANZECC (2000) sediment quality guidelines are not available for Fe, Mn, or Al.

Fe concentrations were most elevated in the upper reaches of the streams, closest to the mine discharges, up to 11.4% in Tunakohioa Stream (Tuna 1) and 7.1% in Tui Stream (Tui 1 and 2), but close to background levels elsewhere (3.3–5.2%). Mn was similarly elevated below Adit 5 (3.3%) at Tuna 1 and high immediately below the tailings dam at Tui 1 and 2 (0.34–0.43%), but not significantly elevated downstream. Copious brown Fe oxyhydroxide floc was evident in the upper reaches of both streams; however, the dissolved Fe concentration appeared to increase particularly in Tui Stream. This may, however, be a result of the filtration method as, in the lower reaches, Fe oxide flocs were not as visible, and presumably present as smaller particulates, of which some could have passed through a 0.45 µm filter to register as “dissolved” Fe in the stream.

The Tunakohioa and Tui stream sediments were severely contaminated with Zn, Pb, and Cd, particularly in the upper reaches where concentrations were well above ANZECC

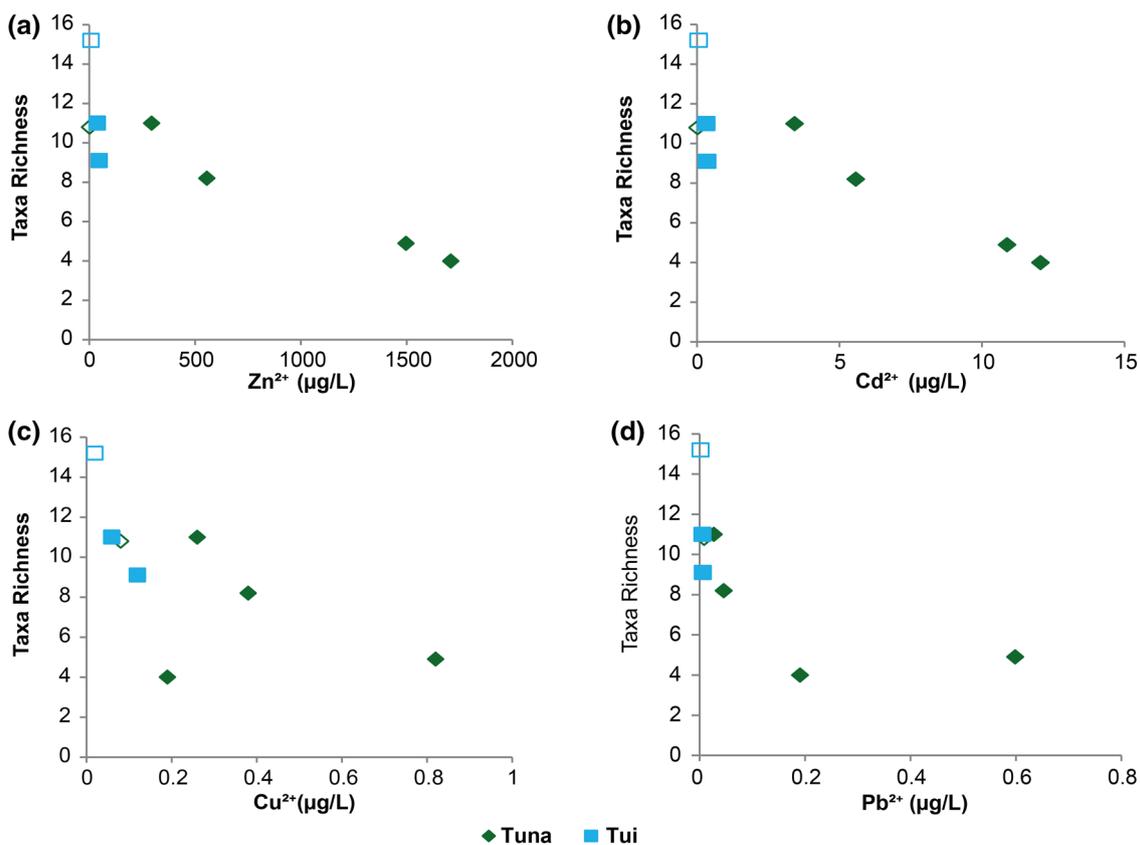


Fig. 3 Ecological taxa richness compared to free Zn and Cd ion activity in Tunakoioia and Tui streams. Reference sites are shown as open symbols

(2000) ISQG-High guideline values. Concentrations of up to 4.5% Zn and 1.2% Pb were present in the sediments immediately below Adit 5 drainage (Tuna 1 site) and these sediments also showed high concentrations of Cu, Ni, As, Sb, and Hg. Ni was also high immediately below the tailings dam drainage in Tui Stream and, unexpectedly, at the reference site TunaC.

Modelled Trace Element Precipitation

Modelling carried out using dissolved trace element concentrations showed that once high-temperature phases were discounted, the only trace element-bearing phases that were saturated were oxides of Fe, Mn, and Al. No carbonate minerals of trace elements, such as calcite (CaCO_3), rhodochrosite (MnCO_3), smithsonite (ZnCO_3), otavite (CdCO_3), cerussite (PbCO_3), CuCO_3 , or mixed hydroxycarbonates, such as malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$] and azurite [$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$] were saturated at the site. Sulfides of the trace elements, such as sphalerite (ZnS), chalcopyrite (CuFeS_2), or galena (PbS), were also not saturated in the stream waters due to the redox state of the water favoring SO_4 over HS. This indicates that the removal of trace elements from the water column is not

likely due to mineral precipitation for Zn, Cd, Cu, or Pb. This also highlights the importance of HFO or ferrihydrite as a key to trace element removal in these streams due to the adsorption of trace elements to the HFO surface.

Sequential Extraction of Sediments

Sequential extraction results confirmed that Fe and Mn were predominantly bound in their respective hydrous oxide phases (Fig. 5a and b). For Mn, this was especially notable at Tuna 1 and Tuna 2 where the total Mn content was very high. A higher proportion of Mn was extracted from the Fe oxide fractions for the Tui stream and Tuna 3 sediment samples. 10–15% of the Fe in the Tui sediments appears to have been in a residual sulfide fraction.

As and Sb were principally extracted from the Fe oxide fractions (Fig. 5g, h), almost to the exclusion of all other fractions. Most of the Zn, Cu, and Pb was extracted in either the low pH leachable, or Fe oxide fractions (Fig. 5c–e). The Fe oxide fraction was of greatest importance downstream in the both streams. Pb and Zn also showed some (less) affinity for the Mn oxide fraction, and Cu and Zn for the “organic” fraction. However, Cu, Zn and Pb in the sulfide and residual

fraction was < 3% for all sites, indicating that residual sulfide minerals such as chalcopyrite, sphalerite, and galena make an insignificant contribution to sediment chemistry, despite sphalerite being observed with SEM (Fig. 4a).

In contrast, Cd showed little affiliation with the Fe oxide fractions (Fig. 5f). Cd was instead mainly extracted from the low pH leachable fraction in the upper Tunakohoa Stream sediments, and from the low pH leachable and exchangeable fractions at Tuna 3 and in the Tui Stream sediments. We note that low pH leachable can include leaching from Fe oxide mineral surfaces at pH 4.5.

The sum of trace elements from the fractions extracted was within 30% of the concentration determined by total sediment digest for all samples except for Tuna 2, which had a significantly greater amount of Mn, Cu, Pb, Zn, and Cd for the sequential extraction process. This is more likely due to a non-homogeneous sample than an error in the sequential extraction process.

Modelled Adsorption of Trace Elements onto HFO

PHREEQC was used to characterize the degree of adsorption onto fresh HFO present in the water column and surface sediment. We assumed that the concentration of fresh HFO was equal to the amount of particulate Fe in each water sample, as calculated from the difference between the dissolved and acid soluble Fe concentrations. PHREEQC dissolved trace element concentrations are compared to observed concentrations in Fig. 6.

PHREEQC reliably predicted the dissolved proportion of Zn, Cd, Ni, which were all predominantly dissolved. It also predicted the proportion of dissolved Cu reasonably well (within 20% of observed dissolved concentrations, generally overestimated). PHREEQC overestimated dissolved concentrations to a greater extent at the control sites and the lower catchment waters, indicating additional binding processes (unrelated to HFO adsorption) may be more important for Cu in these waters.

However, PHREEQC was less reliable when predicting the proportion of dissolved Pb and As. For Pb, PHREEQC overestimated the proportion of dissolved Pb for all sites except for the control sites and Tui 3. Although little of the Zn was predicted to adsorb to the HFO, the very high concentration of this trace element in the stream water meant that it still occupied a large portion of the HFO binding sites, inhibiting the adsorption of other trace elements. When Zn adsorption was completely excluded, more Pb bound to the strong binding sites on HFO and the amount of dissolved Pb therefore decreased. The reliability of Pb modelling is therefore likely to be sensitive to competition for binding sites when there are such high concentrations of Zn present.

For As, PHREEQC consistently predicted a high degree of adsorption to the HFO present, which was clearly not

occurring as dissolved As was observed to constitute 73–100% of the acid-soluble As. Using only 2–3% of the HFO surface actually available in the model provided a better estimate of the amount of As adsorbed, as was also noted when modelling geothermal As adsorption in lowland rivers (Webster-Brown and Lane 2005).

Modelling Speciation Change with Limestone Addition

The remediation of Tui mine included the addition of crushed limestone to both the tailings pile and Adit 5 to increase pH. This was anticipated to reduce trace element toxicity by complexation, and to facilitate the removal of dissolved trace elements by precipitation and adsorption. If these changes in trace element speciation can be collectively and reliably modelled, this can be used to support remediation decisions.

Where the mineral formed is HFO, the adsorption of cationic trace elements, such as Cu, Pb, Zn, and Cd, is expected to increase with pH, while the adsorption of anionic trace elements such as As decreases under the same conditions. Figure 7 demonstrates this trend for Cu, Pb, Zn, and As adsorption under a regime of increasing pH, for the temperature and HFO concentration present at the Tuna1 site. This shows that where both cationic and anionic trace elements are present at toxic concentrations, modelling can be used to find the stream pH that will result in the optimum cationic and anionic trace elements adsorption onto HFO.

In terms of mineral precipitation, PHREEQC was used to add calcite (CaCO_3) stepwise to pre-remediation stream waters, until saturation with respect to calcite was reached. The pre-remediation composition of water at the Tuna1 and Tui1 sites, as reported for July 2007 (Sharplin 2008), was used and the electron potential (pe) was set to 12, to reflect the fast-flowing, fully-oxygenated stream waters. The results are shown in Fig. 8 for pre-remediation Tui 1 stream water, and Fig. 9 for pre-remediation Tuna 1 stream water. The same amount of limestone (125 μmol of CaCO_3) added to each stream water yielded quite different results: Tui 1, which had a starting pH of 6.5, could be raised to 9.0 before the solution became saturated with CaCO_3 , whereas Tuna 1, which had a starting pH of 7.16, could only be raised to 7.67 with the same amount of CaCO_3 , and did not reach saturation with respect to CaCO_3 . This shows the diminished return of trying to achieve a pH increase with limestone in a near-neutral, well buffered stream such as Tunakohoa Stream, compared to Tui Stream. The pH actually measured in the streams during this study was around 7.4 for both streams, indicating that the reaction had progressed approximately halfway along these projected trajectory paths.

In both examples, the predicted concentrations of dissolved Fe were well below the measured concentrations, with the solution being saturated with respect to HFO. This

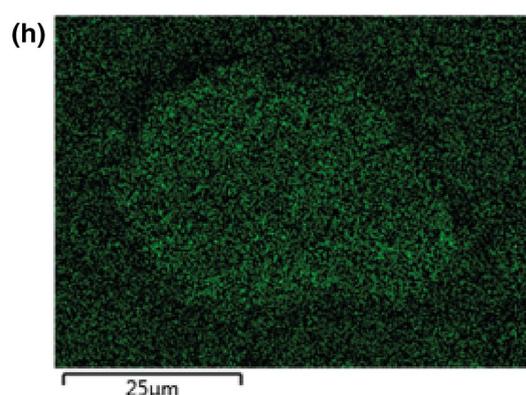
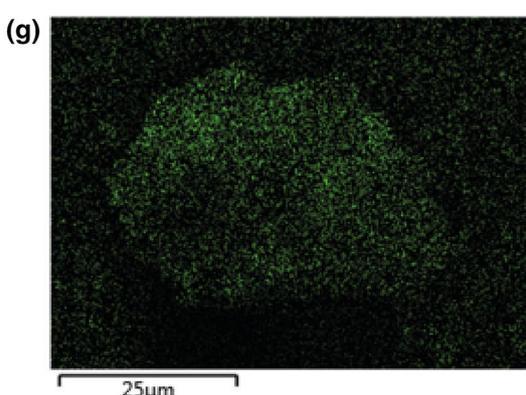
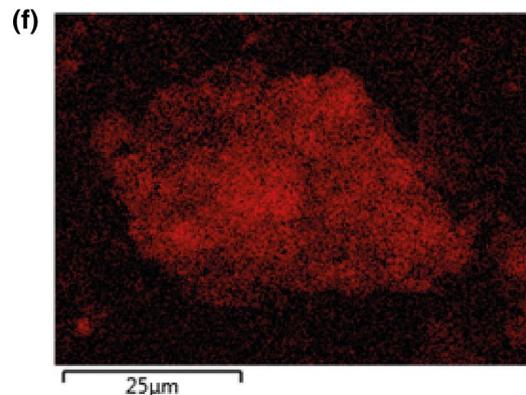
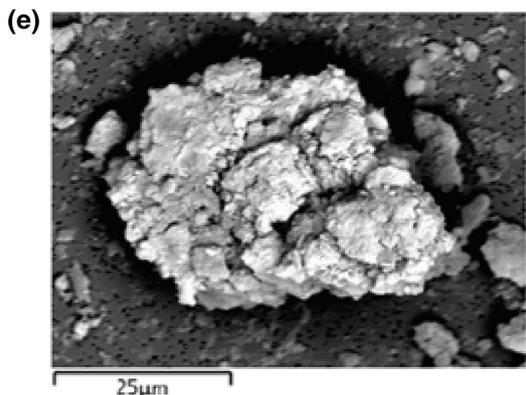
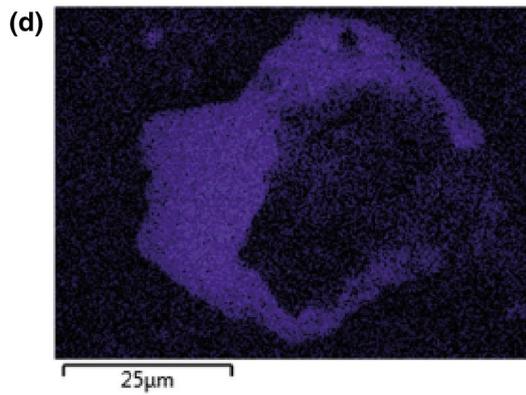
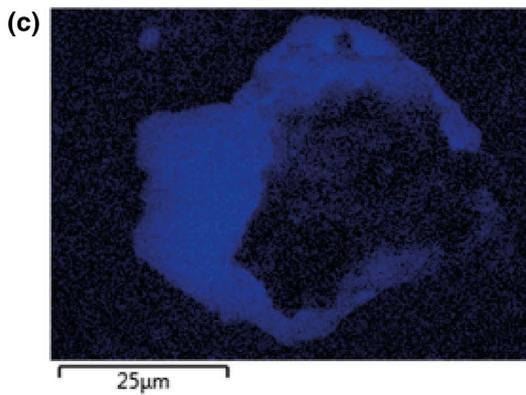
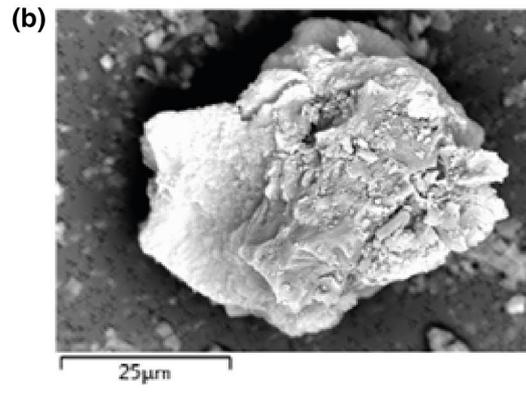
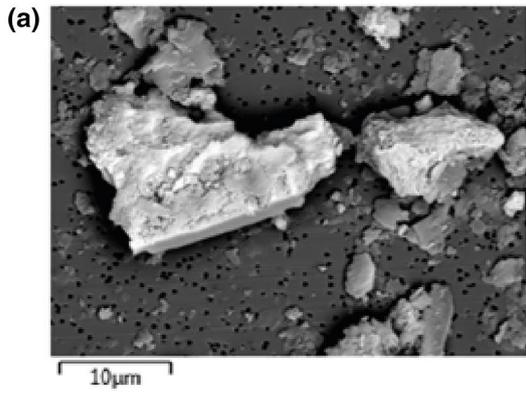


Fig. 4 Scanning electron microscope images of; **a** a sphalerite particle (Zn 35.4% and S 17.2%) from site Tuna1; **b** a particle showing a strong Mn-Zn association, with high Mn density (**c**) and high Zn density (**d**); **e** a particle showing an Fe–Pb–Cu association, with high Fe density (**f**), high Pb density (**g**), and high Cu density (**h**)

effect became more pronounced at higher pH. The discrepancy between predicted and measured dissolved Fe concentrations in commonly reported and attributed to the ability of fine HFO colloids to pass through 0.45 μm filters and be included in “dissolved” Fe concentrations. Dissolved Fe decreased markedly with increased pH, and was predominantly complexed with hydroxide.

Dissolved Mn and Zn were also predicted to decrease significantly, but only above pH 8 (i.e. in Tui Stream), when water became saturated with respect to rhodochrosite (MnCO₃), ZnO, and Zn(OH)₂. Free Mn²⁺ and Zn²⁺ remained the dominant species. Saturation with respect to rhodochrosite was also achieved in the Tuna1 model, but did not significantly reduce the concentration of Mn or Mn²⁺. The Mn and Zn concentrations measured in both streams were much less than predicted, indicating that additional precipitation or adsorption reactions were occurring.

For both streams, no change in dissolved Cd, Cu, or Pb concentrations were predicted to occur over the pH range investigated, as no Cd, Cu, or Pb-bearing minerals were predicted to reach saturation. However, the concentrations of Cu²⁺ and Pb²⁺ were predicted to decrease in the Tui1 water, as Cu(OH)₂⁰ and PbCO₃⁰ became the dominant dissolved species. In the Tuna1 solution, Cu²⁺ and Pb²⁺ were already low as Cu(OH)₂⁰ and PbCO₃⁰ were the dominant species at the starting pH. Neither the concentration nor percentage of Cd²⁺ was predicted to decrease significantly in either water. The concentrations of Cd, Cu, and Pb were measured to be much lower at Tui 1, indicating additional precipitation or

adsorption reactions occurring. Cd was measured to be much less at Tuna 1, but Cu and Pb concentrations were slightly higher, although similar, to those measured in 2007.

Discussion

The full characterization of the stream water and sediment geochemistry revealed that, even following the rehabilitation of the Tui mine site in 2013, there are still very high concentrations of some trace elements in the water and sediment of Tunakohoa Stream and upper reaches of the Tui stream. In November 2015, dissolved Zn and Cd concentrations were still above guidelines for the protection of aquatic life at all sites except the control site on Tunakohoa Stream, and the dissolved Cu concentration was still above these guidelines in the upper reaches of the stream. The addition of lime slurry to the adits draining to Tunakohoa Stream has not reduced the concentration of either Cd or Zn significantly, and certainly not enough to restore a healthy aquatic ecosystem. Nor has lime addition raised the pH of the adit drainage, which has always been high (circumneutral) relative to the more acidic drainage from the tailings dam (Hendy 1981; Sharplin 2008; Tay 1980; Webster 1995). The rehabilitation of the tailings dam has, however, been more effective, increasing pH to near-neutral and decreasing the concentration of trace elements, such that only Cd and Zn remain above guideline values. Ecological surveys have shown an improvement in Tui Stream health, but overall a strong negative correlation between macroinvertebrate taxa richness and the concentration of Zn²⁺ and Cd²⁺ (Fairgray et al. 2016).

Additionally, the concentrations of Cu, Pb, Zn, Cd, Ni, As, Sb, and Hg in the sediment of these streams is elevated and at a level likely impacting aquatic life. In the sediment, strong associations with Mn- or Fe-oxide phases were

Table 5 Trace element concentrations (mg/kg, except for Fe, Mn and Al in %) in fine sediment (<0.67 μm fraction) in streams receiving Tui Mine drainage, as measured in November 2015

Site	Fe	Mn	Al	Cu	Pb	Zn	Cd	Ni	As	Sb	Hg
Tuna 1	11.4	3.31	3.34	2160	11,600	45,600	254	112	221	5.91	6.14
Tuna 2	4.69	0.206	5.60	168	611	4280	22.8	49.0	26.6	0.46	<0.01
Tuna 3	4.83	0.210	5.89	149	599	4230	21.8	50.3	26.2	0.56	0.974
Tuna 4	4.24	0.150	4.08	103	397	3290	14.4	45.7	17.3	0.47	<0.01
Tuna 5	3.34	0.119	5.53	29.4	26.7	91.0	0.505	39.7	14.5	0.22	<0.01
Tuna C	4.83	0.175	4.22	46.2	38.0	120	0.553	53.7	16.7	0.10	<0.01
Tui 1	7.14	0.338	6.95	249	434	3460	16.6	88.8	54.1	0.78	0.071
Tui 2	7.14	0.430	5.76	277	521	3320	23.5	90.4	62.3	0.71	0.57
Tui 3	4.05	0.145	4.00	85.2	145	767	4.34	38.1	22.5	0.16	<0.01
Tui C	5.18	0.0946	5.63	43.9	35.9	402	1.58	49.5	30.6	0.10	<0.01
ISQG-H	–	–	–	270	220	410	10	52	70	25	1.0
ISQG-L	–	–	–	60	50	200	1.5	21	20	2	0.15

Concentrations are in italics if significantly exceeding ISQG-low, or bold italics if significantly exceeding ISQG-high sediment quality guidelines (ANZECC 2000)

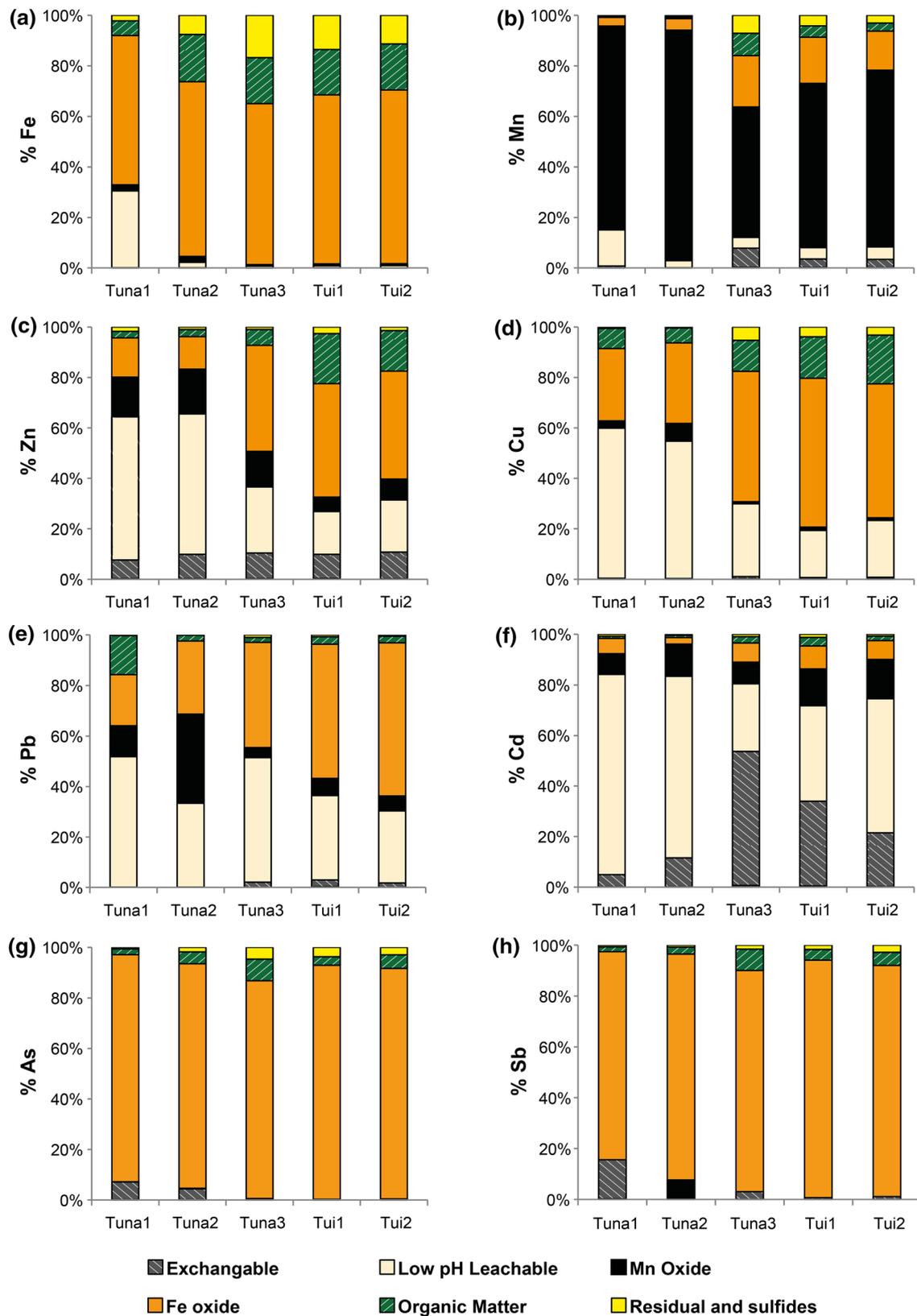


Fig. 5 The percentage of elements extracted from each fraction during the sequential extraction process for sediments in the upper Tunakohoia and Tui stream catchments

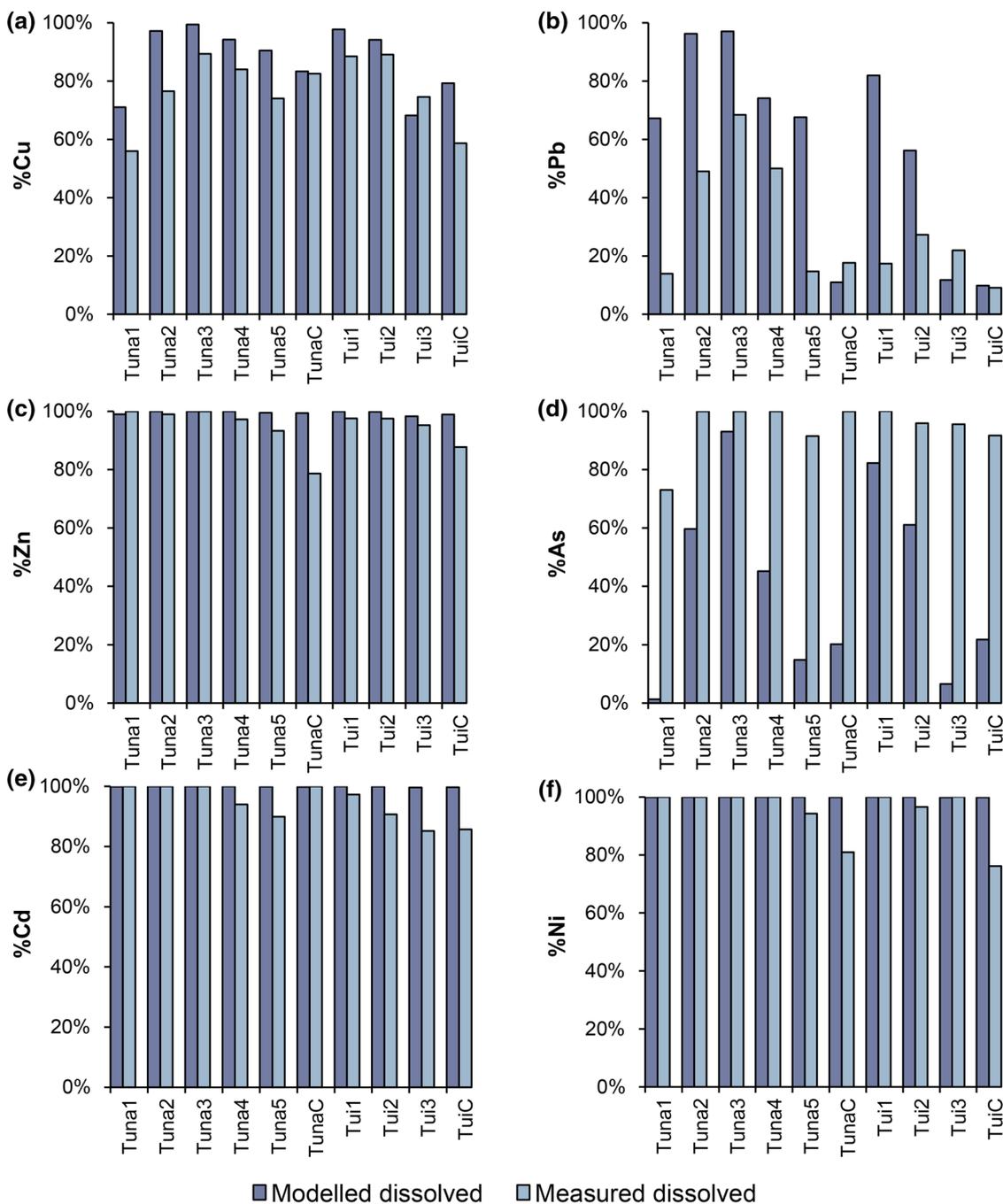


Fig. 6 The modelled percentage of dissolved trace element in the water column, after adsorption onto available freshly-formed HFO, compared to the measured percentage of dissolved trace element at each site

observed for Zn, Cu, Pb, and Cd, but associations for As and Sb were more exclusively associated with Fe-oxides. The association of Fe, Cu, and Pb was confirmed by SEM elemental mapping while evidence of a Mn–Zn association was also seen. No discrete carbonate minerals were observed by SEM. Additionally, although only a small portion of trace

elements in the sediment are currently “exchangeable”, and therefore readily released in a bioavailable form, the sediment is acting as a reservoir for large quantities of trace elements, which could be released should the geochemical conditions (pH or redox) change (Fairgray and Webster-Brown 2017).

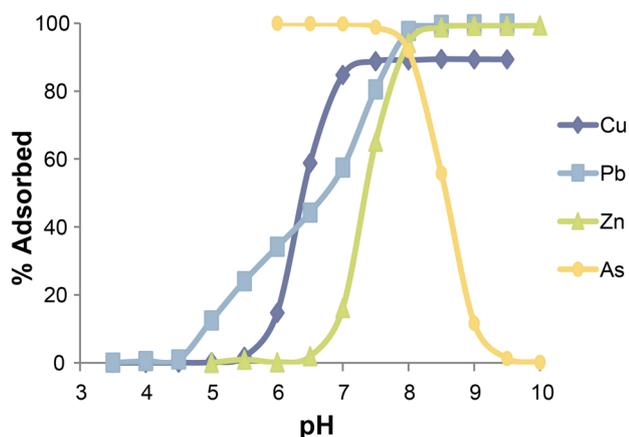


Fig. 7 Adsorption edges for Cu, Pb, Zn, and As onto HFO, under the following conditions: temperature 13.7 °C (Tuna 1), element concentration of 0.01 mg/L with no competing ions and HFO concentration of 355 mg/L (Tuna1)

It was reasoned that the trace elements extracted in step three of the sequential extraction process included elements that were released at pH 4.5 [and may also include the dissolution of Fe- and Mn- (oxy)hydroxides] but were not strictly associated with carbonate minerals. This is why step three of the sequential extraction was renamed “low pH leachable,” as opposed to “bound to carbonates,” per Leleyter and Probst (1999).

Modelling of Dissolved Trace Element Speciation

PHREEQC was used to assess the toxicity of trace elements to aquatic life by determining the proportion of the element present as the free ion in a similar method to Waters and Webster-Brown (2013). This predicted that most of the dissolved Zn and Cd would be present as free ion and therefore toxic to aquatic life, while the free ion Cu concentration would be below aquatic protection guidelines. This was supported by ecological data showing that taxa richness is reduced at sites with high Zn^{2+} and Cd^{2+} concentrations (Fairgray et al. 2016), indicating that PHREEQC could be reliably used to predict the toxicity of Zn and Cd in these environments.

Modelling of Trace Element Speciation in Sediment

PHREEQC has previously been used extensively to understand mine remediation processes and predict efficacy (Bäckström and Sartz 2011; Rötting et al. 2008; Watten et al. 2005). The ability of a geochemical program to predict the precipitation and dissolution behavior of trace elements has been tested by comparing observed sediment characteristics,

with predictions based on processes that could control trace element concentrations and mobility in this catchment system. PHREEQC predicted the precipitation of Fe, Mn, and Al oxides, but no trace element bearing minerals under the current water quality conditions. This is consistent with the lack of trace element minerals phases, other than very minor residual primary ZnS (sphalerite) in the sediments. This also supports the conclusion that the Pb, Cu, Zn, and Cd extracted in step three of the sequential extraction were not actually associated with carbonate minerals. PHREEQC also indicated that increasing pH by the addition of more calcite would not significantly change this scenario for Tunakohoa Stream. In Tui Stream, Zn oxide and Mn carbonate precipitation may occur if calcite addition can be used to achieve a high enough pH (> 8.0). Enhanced Fe precipitation could be expected in both catchments. Secondary mineral precipitation is therefore not significantly reducing dissolved trace element concentrations except by adsorption onto the freshly formed secondary Fe, Mn, and Al oxides.

Our results showed that PHREEQC could be used to predict adsorption of trace elements onto HFO by surface complexation, indicating that this was likely an important removal mechanism for Cu, Pb, and As, but less so for Zn, Cd, or Ni. However, removal of Pb (and to a lesser extent Cu) was underestimated and As removal was overestimated; using < 5% of the available HFO better simulated the actual amount of adsorption. This indicates that for Cu and Pb, adsorption to HFO is not the only process binding these metals to the sediment, particularly where HFO concentrations were lower, at the control sites and in the lower reaches of the catchments.

The precipitation of Mn oxides was predicted to be currently occurring in the streams, despite the fact that particulate Mn concentrations (particulate Mn = total acid soluble Mn—dissolved Mn) in the water samples collected were low. However, moderate proportions of Mn, Pb, and Zn were sequentially extracted from the sediment in the Mn oxide fraction. This, combined with the strong association between Mn and Zn observed with SEM, supports the presence of Mn oxide phases, perhaps too fine or only in the sediment where Fe oxides can facilitate their formation (Davies and Morgan 1989). It also indicates that adsorption onto and/or co-precipitation with Mn oxides may be an important metal removal process for Zn and Pb. However, formation of Mn oxides and attenuation of trace elements to Mn oxides is likely to be of less overall importance than formation of and adsorption to Fe (oxy) hydroxides, given their relative abundance.

PHREEQC reliably predicted the formation of secondary Fe and Mn oxide phases and the adsorption of Zn, Cd, and Ni, and to a lesser extent Cu, onto HFO. It under and overestimated the adsorption of Pb and As, respectively. We note that a significant limitation of PHREEQC is that

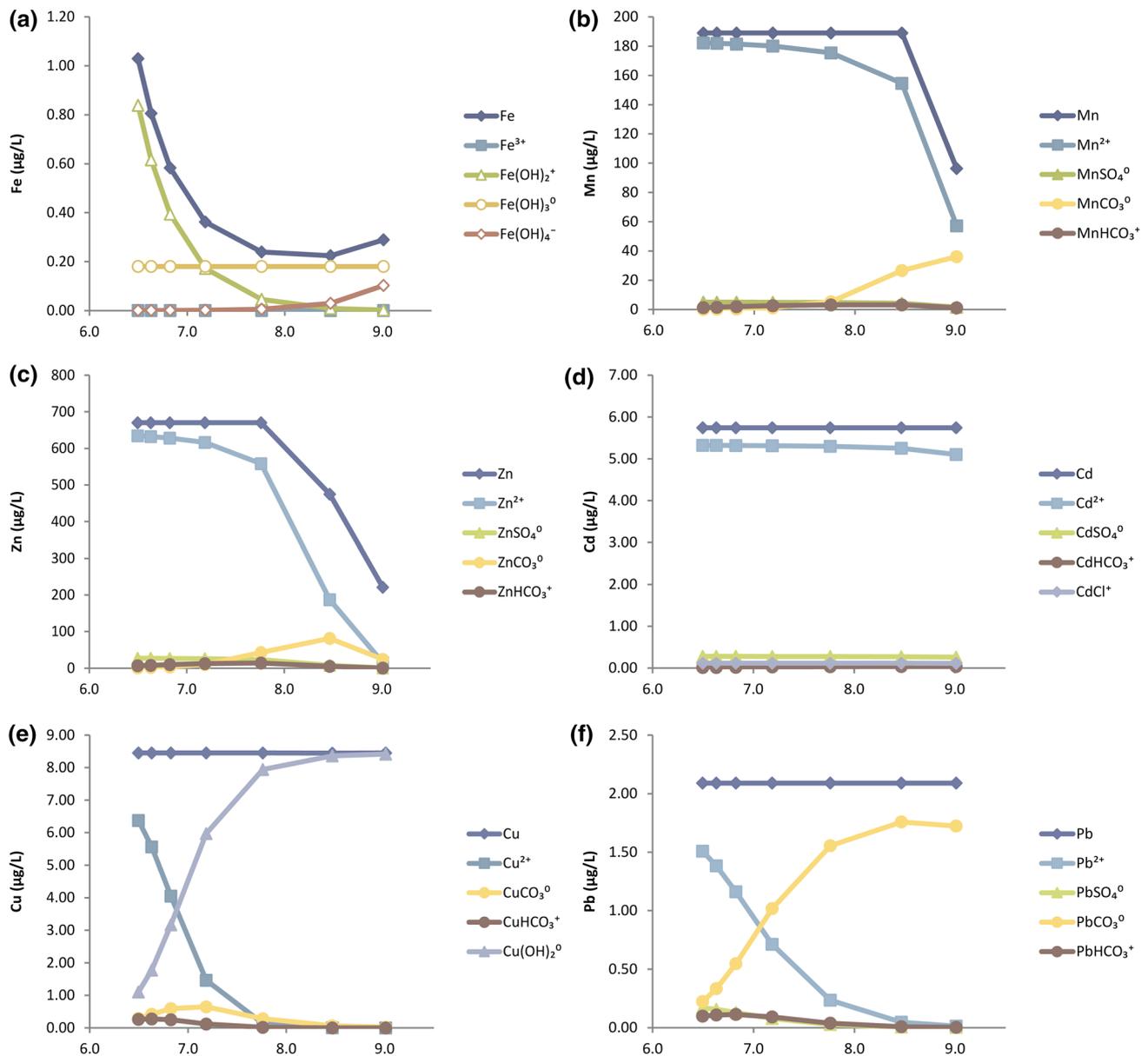


Fig. 8 Modelled changes in dissolved element speciation when a water from Tui 1 (2007 chemistry; Sharplin 2008) is mixed with calcite, simulating the remediation works carried out at the mine site between 2010 and 2013

it assumes that the system is at thermodynamic equilibrium. This may not always be the case when fast moving mine drainage streams allow little time for sediment–water interactions to take place. However, if water and sediment chemistry are constant with time, such programs can still provide useful predictions of AMD effects on impacted aquatic environments. In the case of the Tui Mine, for example, modelling of geochemical processes indicates that further mine remediation through calcite addition alone is unlikely to be more effective.

Conclusions

The extent to which mine site restoration has been achieved has been evaluated by geochemical assessments, measurements, and modelling. Mineral precipitate formation is identified as an important metal removal process for Fe and Mn. Adsorption onto these precipitates and the formation of complexes has reduced Cu, Pb, and As concentrations, such that these elements now meet aquatic health guideline values.

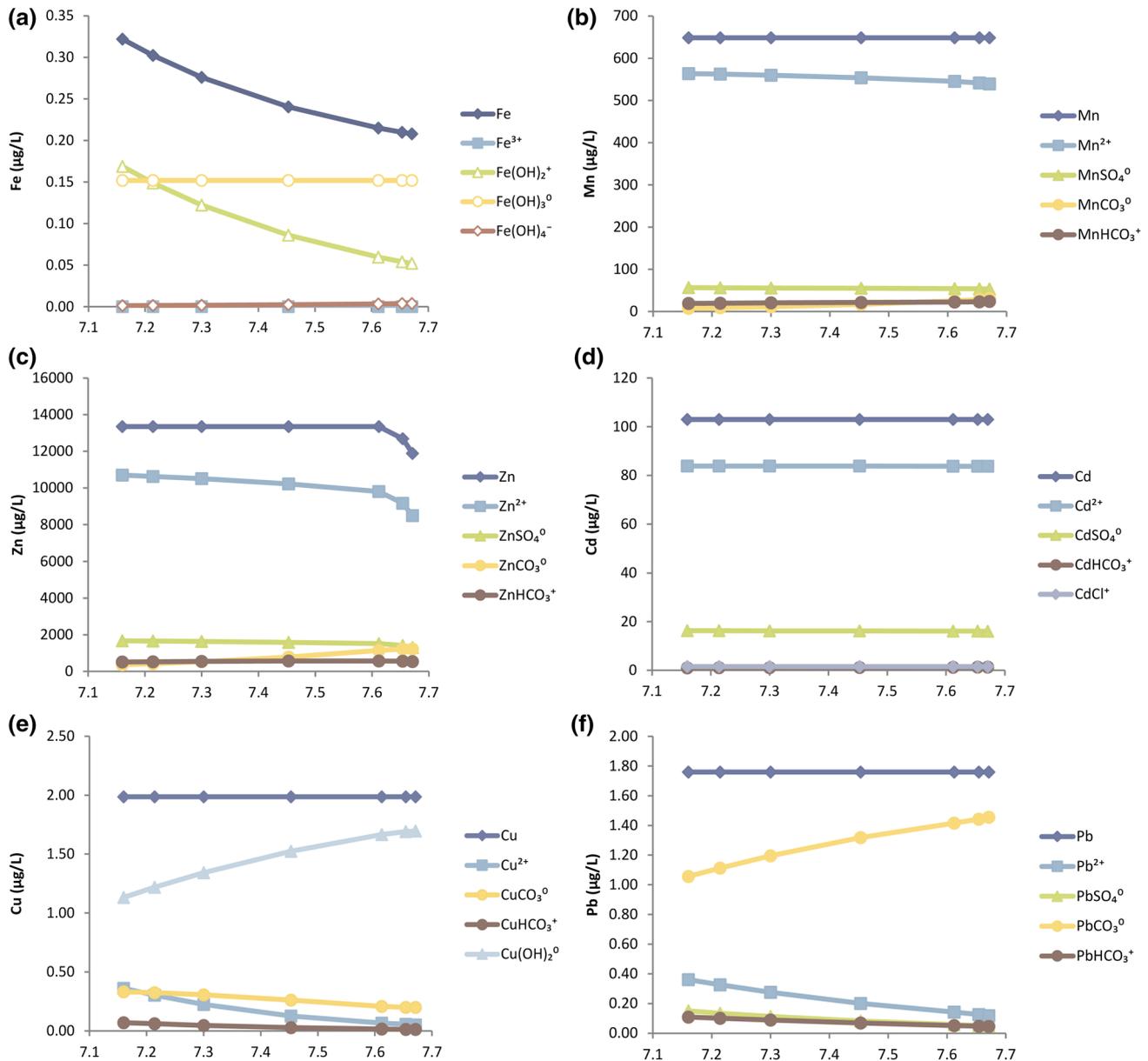


Fig. 9 Modelled changes in dissolved element speciation when a water from Tuna 1 (2007 chemistry; Sharplin 2008) is mixed with calcite, simulating the remediation works carried out at the mine site between 2010 and 2013

Neither the formation of mineral precipitates nor sorption to freshly formed mineral precipitates has reduced Zn and Cd concentrations enough to meet water quality guidelines. Modelling has shown that this is unlikely to be achieved by more of the same rehabilitation methods [i.e. addition of limestone $[\text{CaCO}_3]$].

PHREEQC proved to be reliable for predicting Cu, Zn, and Cd concentrations when HFO was determined by the difference between acid soluble and dissolved Fe concentrations, but was less reliable for As and Pb. Modelling also

indicated where further characterization of the water and the sediment binding phases was required.

Acknowledgements The authors thank: the Ministry of Business, Innovation and Employment (MBIE) for funding this research (CRLE 1403 contract); the laboratory staff at Lincoln University (John Revell, Roger Cresswell, and Lynne Clucas) and the University of Canterbury (Rob Stainthorpe) who carried out sample analysis; Mike Flaws (UC) for assistance with SEM imaging; Phil White (Panda Geosciences) for XRD analysis; Prof. Jon Harding, Justin Pomeranz, Dr. Kevin Simon, and Rose Gregersen who accompanied the authors during field work and carried out sampling and identification of macroinvertebrate

samples; the Waikato Regional Council for access to the site; and the Iwi Advisory Group for their cultural guidance.

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