

TOXICITY OF ACID WATER FROM MT MORGAN MINE SITE, CENTRAL QUEENSLAND, TO THE FRESHWATER SHRIMP *CARADINA INDISTINCTA*

Heather F Chapman^{1*} and Stuart L Simpson²

¹Australian School of Environmental Studies, Griffith University, Nathan, QLD 4111, Australia.

²Centre for Environmental Contaminants Research, CSIRO Energy Technology, Private Mail Bag 7, Bangor NSW 2234, Australia.

Manuscript received, 9/9/2003; resubmitted, 12/12/2004; accepted, 20/12/2004.

ABSTRACT

A combination of toxicity testing using the freshwater shrimp *Caradina indistincta* and modelling of metal speciation has been used to assess water quality requirements for mine pit water releases from the Mt Morgan gold and copper mine site in Central Queensland to the Dee River. Analysis of the mine pit water indicated concentrations of some metals (730 mg/L Al, 35 mg/L Cu, 25 mg/L Zn) were several orders of magnitude above the Australian water quality guideline trigger values. Dilution of the mine pit water (pH 2.9) with Fletchers Creek (pH 8.3) water (a tributary of the Dee River) resulted in neutralisation to pH 5.3 and pH 6.4 at 1.5% and 0.8% dilutions, respectively, and precipitate formation. At a dilution of 0.8% mine water, dissolved concentrations of Al, Cu and Zn were calculated to be approximately 300, 2.5 and 5 times the guideline trigger values, respectively. The acute toxicity of the diluted pit water to *C. indistincta* (96-h exposures) was observed to be very pH dependent and was least toxic at pH 6 and most toxic at pH 5. No toxicity was observed at dilutions of 0.8% mine water at pH 6 or 7. For waters of pH 4, 5, 6 and 7, LC50 values of 1.8, 5.7, 20.5 and 12.9% pit water were determined, respectively. Calculated metals concentrations indicated that dissolved aluminium would contribute most to the observed toxicity. Speciation modelling calculations indicated that the lowest concentrations of bioavailable aluminium would occur at pH 6, consistent with waters of this pH being least toxic. The study indicated that neutralisation of pit waters to pH 6 prior for discharge would minimise toxicity to *C. indistincta*. Further testing using species such as algae, water fleas and fish is suggested to better assess the impact of the metal-rich waters on metal-sensitive biota.

Key words: *Caradina* sp.; toxicity; acid mine water; Queensland.

INTRODUCTION

Gold and copper were mined at Mt Morgan in Central Queensland from 1882 until 1991 (Figure 1). A legacy of this activity is significant contamination at the mine site and in the adjacent Dee River (http://www.nrm.qld.gov.au/mines/environment/mt_morgan). The major sources of pollution are a significant amount of dissolved metals stored in the open-cut pit, various overburden heaps and the tailings deposits. Due to a groundwater pump-back system, installed to reduce impacts of contaminated water seepage from the open cut pit into the Dee River, the level of water in the open cut pit was rising and the likelihood of overflow to the Dee River during storms was increasing. If controlled discharges to the Dee River were not made, it was anticipated that the pit would eventually overflow, particularly during storms.

Screening of the water from the open cut pit at Mt Morgan identified 18 elements that were in excess of either the water quality trigger values (ANZECC & ARMCANZ 2000) or background concentrations at nearby Fletchers Creek. Aluminium, cobalt, copper, cadmium, nickel and zinc were the major contaminants in the pit water. The Al, Cu and Zn concentrations of 730, 35 and 25 mg/L, respectively, greatly exceed the Australian water quality trigger values for these metals (ANZECC & ARMCANZ 2000).

Controlled releases of pit water, with or without treatment, are a management strategy to reduce the likelihood of uncontrolled water releases during events such as storms. The dilution of the acidic (pH<3) Mt Morgan pit water with alkaline (pH 8) Fletchers Creek water, upstream of the mine, may occur during high flow conditions. The mixing of these waters will increase the pH of the pit water and result in precipitation of large amounts of aluminium and removal of trace metals by coprecipitation with, or adsorption onto, newly formed iron and aluminium oxide phases.

Chemical testing may be used to determine dilutions necessary to meet water quality guidelines (ANZECC & ARMCANZ 2000). However, for waters involving complex mixtures of contaminants, the trigger values for individual chemicals may not be appropriate. Interactions of toxicants in mixtures are not easily predicted, with both synergism and antagonism between chemicals observed (Franklin et al. 2002). Although chemical speciation analyses may benefit the development of cause-effect relationships, speciation analyses are often difficult to perform. For aluminium, speciation techniques that fully characterise the complex speciation are not available (Driscoll and Postek 1996; Simpson et al. 1997; Pyszynska et al. 2000), however Al speciation is believed to control the bioavailability and toxicity of Al (Witters et al. 1996; Gensemer and Playle 1999; Camilleri et al. 2003).

*Author for correspondence, email: H.Chapman@griffith.edu.au

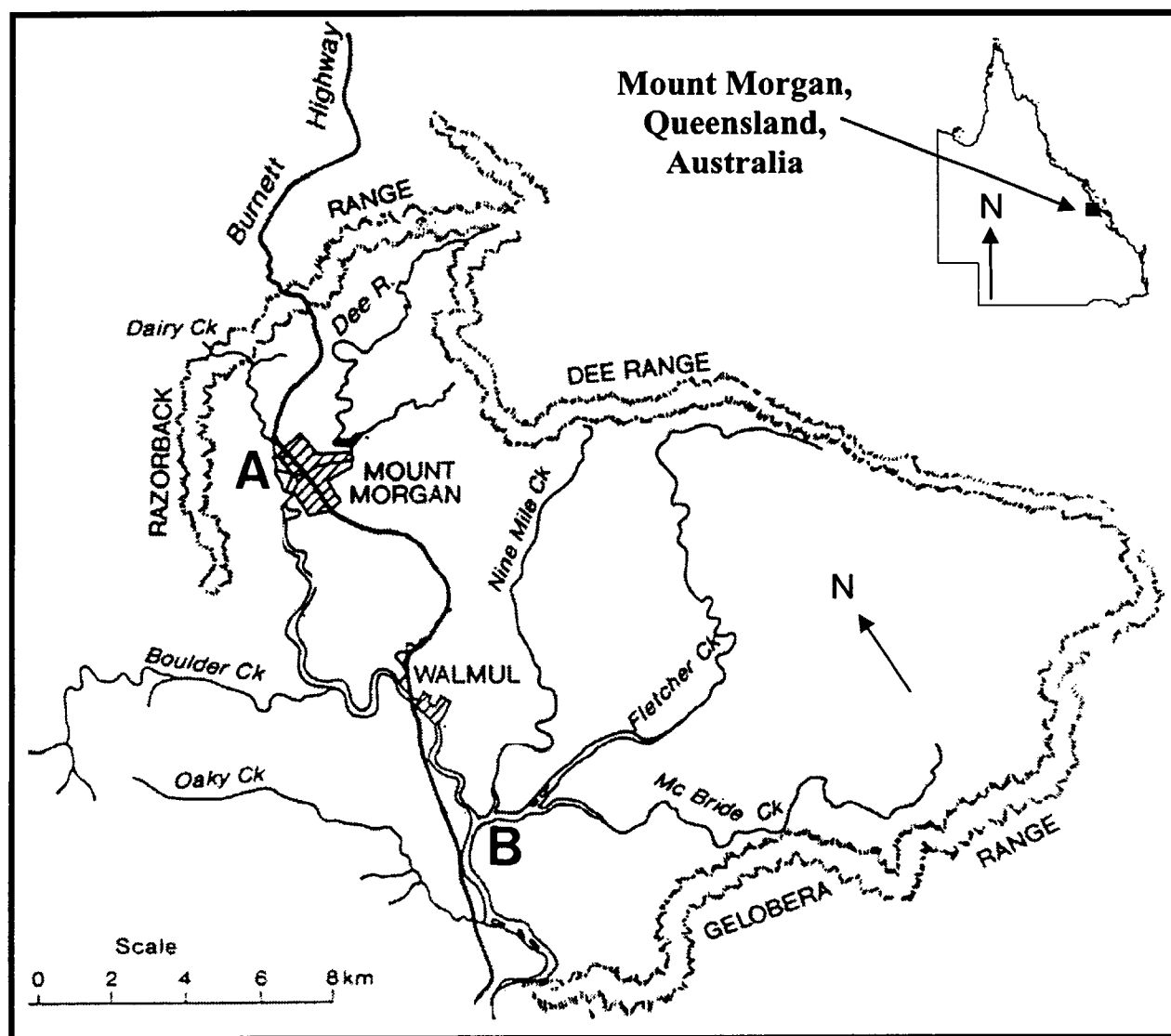


Figure 1. Mount Morgan Mine sampling site (A) and point of reference water collection in Fletchers Creek (B).

In this study the toxicity of diluted and undiluted pit water to the freshwater shrimp *Caradina indistincta* (Calman 1926) was investigated. Median lethal concentrations (LC50), no observable effect concentrations (NOEC) and lowest observable effect concentrations (LOEC) of the Mt Morgan pit water were calculated. Chemical speciation modelling was used to investigate the contaminants responsible for the toxicity measured for the diluted water compositions.

MATERIALS AND METHODS

Water samples

Mount Morgan is located in Central Queensland, Australia (Figure 1). In October 2001, a composite sample of the open cut pit water (P) was collected adjacent to the spillway by pumping water from 50 cm below the water-body surface (and from a maximum depth of 50 cm above the pit bottom). Reference water, used for dilutions, was collected from Fletchers Creek (F), upstream of the weir near the convergence with the Dee River. Test waters were stored

in black plastic containers to reduce biological activity and transported to the laboratory within 24 h.

Conductivity, pH, temperature and dissolved oxygen were measured *in situ* at the time of water collection using a water quality analyser calibrated prior to use. The composition of the waters was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or mass spectrometry (ICP-MS) (for cations and metals) and ion chromatography (major anions), calibrated for respective samples according to instrument instructions. Spike recoveries were undertaken to check the accuracy of analyses. Separate analyses were conducted for hardness (as CaCO₃) and dissolved organic carbon (DOC).

Test waters

Test waters were prepared by diluting the pit water (P) with Fletchers Creek water (F) to give waters compositions of 100, 33, 20, 11, 5.8, 3.0, 1.5, and 0.8% P. Control waters were 100% F (control F) and dechlorinated and oxygenated Brisbane tap water (control T). Test waters were aerated by

air bubbling to achieve O₂ saturation before use. In total, five separate toxicity tests were conducted, with the pH of the waters of each set of dilutions either not adjusted or adjusted to pH 4, pH 5, pH 6 and pH 7 by addition of dilute (0.1 M) NaOH or HCl (both analytical reagent grade). The pH was checked daily, throughout the four days of testing.

Bioassay procedure

The freshwater shrimp, *Caradina indistincta*, collected from South East Queensland, was used in the bioassays. *Caradina* spp are widespread and endemic to the Mt Morgan area, and therefore ecologically relevant to water quality in the Dee River.

Test methods used were in accordance with standard protocols for whole effluent toxicity testing (USEPA 2000) and the OECD Guidelines for aquatic toxicity testing (OECD 1995). Test containers for the bioassays were 1-litre poly methyl pentene (PMP) containers, which were thoroughly washed, sequentially, with phosphate-free detergent (2% Extran™), dilute HCl (AnalaR, BDH) and copious amounts of deionised water prior to use. Bioassays were carried out using static methods with 20 animals per dilution distributed between two test chambers per dilution to minimise crowding and including five dilutions per test plus two controls. Test species were not fed during testing. Test waters were kept oxygenated by a gentle stream of air bubbling in the top of the water throughout the tests. Observations were made each 24 h, until the tests were terminated at 96 h. An acute response (mortality) was used as the bioassay endpoint. The criteria for determining mortality were (i) no movement and (ii) no reaction to gentle touch. Temperature, pH, dissolved oxygen and conductivity were measured at commencement and daily throughout the tests.

Data analysis for the toxicity tests was carried out by using a probit transformation on the bioassay data, to enable the fit of a linear regression line to the bioassay results (Finney 1971). Median lethal concentrations and their fiducial limits were calculated using the statistical computer package SPSS V10 (Norusis 2000). No observable effect concentrations (NOEC) and lowest observable effect concentrations (LOEC) of the Mt Morgan pit water were estimated from the range of concentrations tested and the toxicological responses.

Modelling of metal speciation in test waters

The computer program MINEQL+ (version 4.5) (Schecher and McAvoy 1998) was used to calculate metal speciation in the bioassay test waters from measured concentrations in the source waters. The calculations included the formation of solid phases and adsorption of metals to hydrous iron oxide phases (Dzombak and Morel 1986). Metal ion adsorption to aluminium hydroxide precipitates was not considered in the modelling (Violante et al. 2003). The speciation focused on aluminium because the concentration of aluminium was over an order of magnitude higher than other potentially toxic metals and most elevated compared to water quality guidelines (ANZECC & ARMCANZ 2000). Concentrations of total dissolved aluminium and bioavailable aluminium (Al³⁺, AlOH⁺, Al(OH)₂⁺, Al(OH)₃, Al(OH)₄⁻, AlSO₄⁺,

Al(SO₄)₂⁻) were calculated. Polymeric aluminium species, e.g. Al₁₃(OH)₃₂⁷⁺ and solid phases were considered in the model (using stability constant data from NIST (1998)). The model included complexation of Al by organic matter (using the model described by Driscoll and Postek 1996) and sorption of metals onto hydrous iron oxides. For the data interpretation, aluminium fluoride and organic complexes were considered to be non bioavailable (non toxic) (Gensemer and Playle 1999).

RESULTS AND DISCUSSION

Chemical characteristics of waters

Water quality parameters and chemical concentrations of major ions and metal contaminants in the Mount Morgan mine pit and Fletchers Creek waters are shown in Table 1. The pit water had very high hardness and sulfate concentrations and low pH reflecting acid mine drainage inputs. Concentrations of Al, Cd, Co, Cu, Ni and Zn in the pit water were generally several orders of magnitude above water quality guideline trigger values (ANZECC & ARMCANZ 2000). The concentration of Ag, Hg, Pb and Sb were less than 1 µg/L in the pit water. The Fletchers Creek water had low metal concentrations and was of high hardness (155 mg/L CaCO₃).

Total concentrations of the potentially toxic metals in the test water dilution series and their associated water quality guideline trigger values for disturbed freshwater systems (90% protection level; ANZECC & ARMCANZ 2000) are shown in Table 2. Increasing water hardness has been found to alleviate the toxic effects of trace metals due to increased competition from Ca and Mg for binding sites where toxic effects occur (Gensemer and Playle 1999; Markich et al. 2001). The guideline trigger values shown in Table 2 are for a very hard water (200 mg/L CaCO₃, i.e. 1.5% mine water). According the hardness-dependent algorithms of the guidelines, multiplier factors of 5.4 for Cd and 5.0 for Cu, Ni and Zn are applied to the trigger values. No hardness adjustment is made for Al, Co and Mn. The guideline value for Al is pH dependent (0.001 µg/L for pH <6.5, 0.08 µg/L for pH >6.5) and is considered to be of low reliability (ANZECC & ARMCANZ 2000).

Following dilution of the acidic (pH 3) pit water with alkaline (pH 8.3) Fletchers Creek water, the pH of the waters increased significantly (Table 2). At a dilution of 0.8% mine water, total concentrations of Al, Cu and Zn were >1000, 60 and 5 times the guideline trigger values, respectively. While the undiluted pit water was clear and a light amber colour, visible precipitates formed in the diluted and pH-adjusted waters prepared for the bioassays. The water above the precipitates was clear and colourless.

Toxicity of the test waters to *C. indistincta*

Throughout the 96-h bioassay test period, the test water temperatures were 21.5 ± 0.5°C and dissolved oxygen (checked every 24 h) remained within acceptable limits (OECD 1995). One hundred percent survival of shrimps was observed in laboratory controls.

Table 1. Water quality parameters and composition of Mount Morgan mine pit and Fletchers Creek waters.

Water quality parameters									
Water	Temperature °C	pH	Conductivity mS/cm	DO ^a mg/L	DOC ^b mg/L	Hardness mg/L CaCO ₃			
Mine Pit	19.2	2.7	12.9	4.5	5.3	6200			
Fletchers Creek	25.3	8.6	0.58	6.2	2	155			
Major ions, mg/L									
Water	Na	K	Ca	Mg	SO ₄	Cl	F	Fe	Si
Mine Pit	780	8	450	1250	11500	330	0.08	250	35
Fletchers Creek	60	<1	20	25	30	-	-	0.3	4
Potentially toxic metals, mg/L									
Water	Al	Cd	Co	Cu	Mn	Ni	Zn		
Mine Pit	730	0.15	2.3	35	80	0.71	25		
Fletchers Creek	<0.05	<0.001	0.001	0.002	0.1	<0.001	0.003		

^a DO = dissolved oxygen, ^b DOC = dissolved organic carbon. Concentrations of Ag, Hg, Pb and Sb were <1 µg/L.

Table 2. Calculated total metal, DOC and hardness concentrations (mg/L) and measured pH in test waters.

Waters	Al	Cd	Co	Cu	Mn	Ni	Zn	DOC	Hardness	pH
100% Mine Pit (P)	730	0.15	2.3	35	80	0.71	25	5.3	6340	2.91
33% P ^a	243	0.051	0.76	12	27	0.24	8.3	3.1	2220	3.35
20% P	146	0.030	0.45	7.1	16	0.14	5.0	2.6	1390	4.06
11% P	81	0.017	0.25	3.9	9.0	0.079	2.8	2.4	842	4.35
5.9% P	43	0.009	0.13	2.1	4.8	0.042	1.5	2.2	518	4.62
3% P	22	0.005	0.070	1.1	2.5	0.021	0.77	2.1	342	4.93
1.5% P	11	0.002	0.036	0.56	1.3	0.011	0.40	2.1	250	5.32
0.08% P	5.9	0.001	0.019	0.30	0.73	0.005	0.21	2.0	203	6.42
Fletchers Creek (F)	<0.05	<0.001	0.001	0.002	0.1	<0.001	0.003	2.0	155	8.32
Trigger Value ^b	0.001 ^{d,e}	0.002 ^c	0.02 ^e	0.009 ^c	0.44	0.065 ^c	0.075 ^c	-	-	-

^a Diluted with Fletchers Creek water. ^b ANZECC & ARMCANZ (2000) water quality trigger values for 90% protection level in freshwaters (appropriate for disturbed systems). ^c Adjusted for water hardness of 200 mg/L. Metal concentrations shown in bold exceed trigger values. ^d Al trigger value if for waters of pH <6.5. ^e Trigger values considered to be of low reliability.

The lethality of the test waters to *C. indistincta* increased with increasing exposure time. The toxicity of the pit water decreased with increasing dilution and was least toxic at pH 6. Test water pH had the greatest effect on water toxicity. Table 3 shows the LC50 values, expressed as percentage of pit water (diluted with Fletchers Creek reference water). Test waters of the same dilution were most toxic at pH 4 and least toxic at pH 6 (highest LC50 value) (Figure 2). At pH 6 the calculated LC50, LOEC and NOEC values were 21, 11 and 5.9 percent pit water, for 48-96-h exposures, respectively. The toxicity of the dilution series with no pH adjustment (pH values given in Table 2) was similar to that observed for the dilution series adjusted to pH 4 based on overlap of the confidence intervals for both time periods (Table 2). At pH 4 and 5 significant toxicity was observed at the most dilute (0.08%) pit water.

Speciation calculations

The speciation calculations predicted that precipitation would occur of iron and manganese at pH>3 (as oxyhydroxide phases, e.g. FeOOH, MnO(OH)₂), aluminium at pH>5 (as

Al(OH)₃), and of copper at pH>6 (as Cu(OH)₂, Cu₂CO₃(OH)₂ or Cu₄SO₄(OH)₆). Table 4 shows the predicted speciation of aluminium and copper in the test waters at pH 5, 6 and 7. These calculations predicted that the majority of the aluminium would precipitate in the waters at pH 6 and 7, however for all dilutions, the concentrations of dissolved aluminium remained above the guideline trigger value of 0.08 mg/L (90% protection of waters pH>6.5). The speciation calculations predicted that complexation of aluminium by DOC in the waters was greatest at pH 6, but decreased at higher pH due to the increased formation of Al(OH)₄⁻. Model calculations that included polymeric aluminium species (Al₂(OH)₂⁴⁺, Al₃(OH)₄⁵⁺ and Al₁₃(OH)₃₂⁷⁺) predicted that the Al₁₃ species would dominate aluminium speciation for pH>5. However, it is generally believed that polymeric species are transient intermediates in the formation of Al(OH)_{3(s)}, and at equilibrium only mononuclear Al and Al(OH)_{3(s)} will exist (Gensemer and Playle 1999; Witters et al. 1996). Polymeric aluminium species were not included in the calculations shown in Table 4. However, transient Al₁₃ may have contributed to the higher toxicity of the pH 5 test

Table 3. Cumulative toxicity to *Caradina indistincta*. LC50s, NOECs and LOECs ^{a, b} as percentage of pit water.

Test	Time Interval (h)	LC50 (fiducial limits)	LOEC	NOEC
No pH adjustment	24	8.1 (5.1 - 13.6)	1.5	0.8
	48	4.6 (2.9 - 7.4)	1.5	0.8
	72	2.9 (2.5 - 3.7)	0.8	<0.8 ^b
	96	2.7 (2.0 - 3.7)	0.8	<0.8 ^b
pH 4	24	15.3 (11.6 - 20.8)	1.5	0.8
	48	5.9 (4.1 - 9.1)	<0.8 ^b	<0.8 ^b
	72	2.8 (2.1 - 3.9)	<0.8 ^b	<0.8 ^b
	96	1.8 (1.5 - 2.1)	<0.8 ^b	11
pH 5	24	11.7 (9.1 - 15.4)	0.8	<0.8 ^b
	48	9.5 (7.1 - 13.3)	0.8	<0.8 ^b
	72	6.3 (4.9 - 8.2)	0.8	<0.8 ^b
	96	5.7 (4.1 - 7.9)	0.8	<0.8 ^b
pH 6	24	89.3 (58.4 - 220.8)	20	11
	48	21.4 (20.2 - 22.8)	11	5.9
	72	20.6 (18.0 - 23.6)	11	5.9
	96	20.5 (18.0 - 23.6)	11	5.9
pH 7	24	22.1 (14.6 - 35.0)	11	5.9
	48	28.9 (13.0 - 23.2)	11	5.9
	72	13.5 (12.6 - 14.4)	5.9	3.0
	96	12.9 (12.0 - 13.8)	5.9	3.0

^a LC50 = median lethal concentration, LOEC = lowest observable effect concentration and NOEC = no observable effect concentration. ^b LOEC or NOEC could not be determined due to a response at the highest dilution.

waters for shorter (24-h, 48-h) exposure times compared to longer exposure periods and to waters of pH 4 in which Al₁₃ is not predicted to form.

The calculations predicted that dissolved copper concentrations were above the guideline trigger value of 9 µg/L (hardness adjusted, ANZECC & ARMCANZ 2000) for all dilutions and all pH values. Although dissolved copper may have contributed to the observed toxicity, aluminium was expected to have caused a greater portion of the toxic effects.

Total manganese concentrations were also above guideline concentrations (Table 2), however dissolved manganese concentrations were predicted to be low due to precipitation of manganese oxyhydroxide phases. In the test waters comprising 0.8% mine water (pH 6.4), dissolved concentrations of Al, Cu and Zn were predicted to be 300, 2.5 and 5 times the guideline trigger values, respectively (Table 4).

Factors controlling aluminium-induced water toxicity

Toxicity of aluminium is known to vary considerably depending on the physical and chemical properties of the test water (Markich et al. 2001). Conductivity, pH, temperature, dissolved oxygen, dissolved organic carbon and the presence of substances such as fluoride and silica, have been observed to alter the toxic effect of aluminium (Camilleri et al. 2001; Parent and Campbell 1994). Aluminium has been observed to be most toxic over the pH range 4.4 – 5.4, with a maximum toxicity occurring around pH 5.0 – 5.2 (Parent and Campbell 1994). The inorganic monomeric aluminium species (Al(OH)₂⁺) is thought to be the most toxic (Driscoll et al. 1980). Polymeric aluminium species form quickly in solution, particularly when acidic solutions containing high aluminium concentrations are neutralised (Gensemer and Playle 1999). Al₁₃ has a high affinity for gill tissue in aquatic organisms (particularly fish) and could be indirectly lethal due to smothering effects rather than direct toxicity (Witters et al. 1996; Gensemer and Playle 1999).

Figure 3 shows the LC50 values calculated for the 96-h bioassay exposures, and dissolved aluminium concentrations in the most dilute (0.8%) pit water, as a function of water pH. The speciation calculations predicted that total dissolved aluminium concentrations decrease rapidly to a minimum near pH 6. The toxicity of the pH 7 waters was greater than the pH 6 waters. This is consistent with the model calculations which show increased formation of the monomeric aluminium species Al(OH)₄⁻ with increasing pH (comprising <10% and >80% of monomeric aluminium at pH 6 and 7, respectively). The decrease in aluminium toxicity to a minimum at pH 6 is consistent with the free (Al³⁺) hydroxy aluminium species (Al(OH)_n⁽³⁻ⁿ⁾⁺) being the main contributors to aluminium toxicity.

Table 4. Speciation of aluminium and copper in waters predicted from modelling calculations.

Water ^a	Bioavailable Al, mg/L ^b			Al-Org, % ^c			Total dissolved Cu, mg/L		
	pH 5	pH 6	pH 7	pH 5	pH 6	pH 7	pH 5	pH 6	pH 7
100% P	360	0.75	0.53	0.07	4.2	0.01	8.6	0.29	0.29
33% P	194	0.53	0.50	0.10	8.5	0.01	6.7	0.23	0.23
20% P	131	0.44	0.48	0.10	9.6	0.02	5.8	0.21	0.21
11% P	81	0.37	0.46	0.15	12	0.03	3.9	0.18	0.18
5.9% P	43	0.32	0.45	0.26	14	0.04	2.1	0.16	0.16
3% P	22	0.29	0.45	0.49	15	0.03	1.1	0.094	0.094
1.5% P	11	0.27	0.44	0.93	16	0.05	0.56	0.056	0.056
0.08% P	5.6	0.25	0.43	1.8	18	0.10	0.30	0.023	0.023
100% F	<0.05	<0.05	<0.05	36	26	0.12	0.002	0.002	0.002

^a Percent mine pit (P) water diluted with Fletchers Creek (F) water.

^b Bioavailable Al = Σ(Al³⁺, AlOH²⁺, Al(OH)₂⁺, Al(OH)₃, Al(OH)₄⁻, AlSO₄⁺, Al(SO₄)₂⁻).

^c Al-Org = organically complexed Al / total dissolved Al, %.

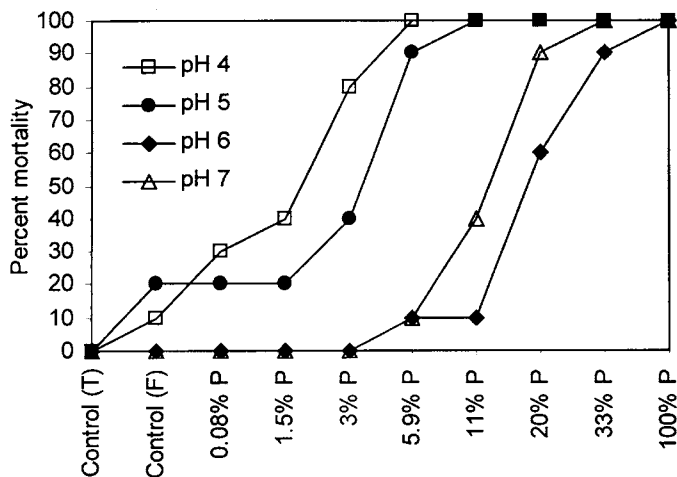


Figure 2. Percentage mortality for *Caradina indistincta* after 96-h exposure to pH-adjusted test waters expressed as % mine pit water (P) diluted with control water from Fletchers Creek (F). Control (T) was tap water.

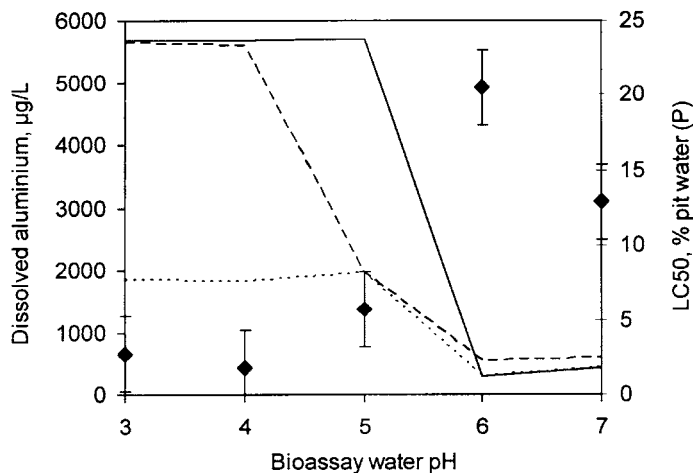


Figure 3. LC50 values calculated for the 96 h bioassay exposures (u) and dissolved aluminium concentrations in the 0.8% mine pit water are shown as a function of water pH. The three lines represent the sum of (i) all dissolved aluminium species, including $Al_{13}(OH)_{32}^{7+}$ (solid line), (ii) $Al(OH)_n^{(3-n)+}$ and $Al(SO_4)_n^{(3-2n)+}$ (dashed line), and (iii) $Al(OH)_n^{(3-n)+}$ (dotted line).

Greater interpretation of the toxicity data in terms of aluminium speciation is impeded by the transient existence of many of the aluminium complexes. The toxic Al_{13} complex is thermodynamically unstable with respect to solid phases (e.g. $Al(OH)_{3(s)}$), and the toxicity due to polymeric aluminium species have been observed to decrease with time as species such as Al_{13} precipitate from solution (Witters et al. 1996; Gensemer and Playle 1999). Al_{13} may have contributed to the toxicity for some water, but only for the shorter time periods. All test waters contained considerable amounts of aluminium precipitate (e.g. $Al(OH)_{3(s)}$). The effect of this solid phase on the observed toxic effects is unknown, however fine precipitates may cause disruption of gill function in *C. indistincta*.

CONCLUSIONS

Bioassays using the freshwater shrimp, *C. indistincta*, appeared to be promising for determining the toxicity to crustaceans of acid mine drainage waters. The toxicity of the diluted pit water was observed to be very pH-dependent and was least toxic at pH 6 and most toxic at pH 5. The toxicity was attributed to the high dissolved aluminium concentrations. The study indicated that the toxicity of the Mount Morgan mine pit waters to *C. indistincta* would be minimised if diluted to <5% and neutralised (by dilution or otherwise) to $pH \geq 6$. For pit waters of $pH < 6$, dilutions to <1% would be required to minimise toxicity. Metal speciation calculations indicated that dissolved aluminium and copper would contribute most to the observed toxicity. Further testing using species such as algae, water fleas and fish is suggested to better assess the impact of the metal-rich waters on metal-sensitive biota.

ACKNOWLEDGEMENTS

We wish to acknowledge Tania Laurent, Rudi Cepon, Steve Dobos and Matt Courtney for assistance in the field and David Jones who provided feedback on the initial report. This work was funded by the Department of Natural Resources and Mines, Central Regional Office, Rockhampton, Qld.

REFERENCES

ANZECC & ARMCANZ. 2000. *Australian and New Zealand guidelines for fresh and marine water quality*. Australia and New Zealand Environment and Conservation Council/ Agricultural and Resource Management Council of Australia and New Zealand, Canberra, Australia.

Camilleri C, Markich SJ, Noller BN, Turley CJ, Parker G and van Dam R. 2003. Silica reduces the toxicity of aluminium to a tropical freshwater fish (*Mogurnda mogurnda*). *Chemosphere* **50**, 355-364.

Driscoll CT, Baker JP, Bisogni JJ and Schofield CL. 1980. Effects of aluminium speciation in dilute acidified waters. *Nature* **284**, 16-164.

Driscoll CT and Postek KM. 1996. The chemistry of aluminium in surface waters. In *The Environmental Chemistry of Aluminium* (2nd ed.), Sposito G. (Ed), Lewis Publishers, New York, pp 363-418.

Dzombak DA and Morel FMM. 1986. Sorption of cadmium on hydrous ferric oxide at high sorbate/sorbent ratios: equilibrium, kinetics, and modelling. *Journal of Colloid and Interface Science* **112**, 588-598.

Finney DJ. 1971. *Probit Analysis 3rd Edition*, Cambridge University Press, Cambridge, UK.

Franklin NM, Stauber JL, Lim RP and Petocz P. 2002. Toxicity of metal mixtures to a tropical freshwater alga (*Chlorella* sp.): The effect of interactions between copper, cadmium, and zinc on metal cell binding and uptake. *Environmental Toxicology and Chemistry* **21**, 2412-2422.

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

- Markich SJ, Brown PL, Batley GE, Apte SC and Stauber J. 2001. Incorporation of metal speciation and bioavailability into water quality guidelines for protecting aquatic ecosystems. *Australasian Journal of Ecotoxicology* **7**,109-121.
- NIST. 1998. *NIST Standard Reference Database 46, Version 5.0*. National Institute of Science and Technology (NIST), Standard Reference Data Program, Gaithersburg, MD, USA.
- Norusis MJ. 2000. *SPSS 10.0 Guide to Data Analysis*. Prentice Hall, New Jersey, USA.
- OECD. 1995. *Guidance Document for Aquatic Effects Assessment*. OECD Environment Monograph Series No. 92. Organisation for Economic Cooperation and Development, Environmental Health and Safety Division, France.
- Parent L and Campbell PGC. 1994. Aluminium bioavailability to the green alga *Chlorella pyrenoidosa* in acidified synthetic soft water. *Environmental Toxicology and Chemistry* **13**, 587-598.
- Pyrzyska K, Gucer S and Bulska E. 2000. Flow injection speciation of aluminium, review paper. *Water Research* **34**, 359-365.
- Schecher WD and McAvoy DC. 1998. *MINEQL+ : A chemical equilibrium modelling system, version 4 for Windows Users Manual*. Environmental Research Software.
- Simpson SL, Powell KJ and Nilsson NHS. 1997. Flow injection determination of Al^{3+} and $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ species using a 1.3-s reaction with 8-quinolinol-derivatised Fractogel. *Analytica Chimica Acta* **343**, 19-32.
- USEPA 2000. *Method Guidance and Recommendations for Whole Effluent Toxicity (WET) Testing (40 CFR Part 136)*, United States Environmental Protection Agency – Office of Water (4303) EPA 821-B-00-004.
- Violante A, Ricciardella M and Pigna M. 2003. Adsorption of metals on mixed Fe-Al oxides in the absence and presence of organic ligands. *Water Air and Soil Pollution* **145**, 289-306.
- Witters HE, Puymbroeck SV, Stouthart AJHX and Wendelaar Bonga SE. 1996. Physicochemical changes of aluminium in mixing zones: mortality and physiological disturbances in brown trout (*Salmo trutta* L.). *Environmental Toxicology and Chemistry* **15**, 986-996.