

# Appendix C – Metal Speciation

# **SPECIATION MODELLING OF METALS IN SURFACE WATERS OF THE EDITH RIVER DURING WET SEASON DISCHARGE OF WASTEWATER FROM THE MOUNT TODD MINE**

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## SUMMARY

Geochemical speciation modelling was used to calculate the distributions, or physico-chemical forms, of dissolved (0.45 µm filtered) cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) in main wet season Edith River surface water (at control site SW2) receiving treated wastewater (retention pond 3) from the Mount Todd mine site. The free metal ion ( $M^{2+}$ ), generally considered to be a good predictor of the bioavailable metal fraction, was calculated to be the major proportion of dissolved Cd (84%), Co (91%), Mn (94%), Ni (84%), and Zn (91%), but accounted for only a relatively small proportion of Cu (8.4%). The speciation of dissolved Cu was dominated by binding with dissolved organic matter (DOM; 91%), in the form of humic substances (fulvic acid). In contrast, Cd, Co, Mn, Ni and Zn formed relatively weak complexes with DOM (i.e. 2.5-12%). After adjusting the dissolved concentrations of the selected metals for the percentage of the calculated free ion (i.e. the “bioavailable fraction”), Zn was the only metal likely to exceed its trigger value (by a factor of 1.7), based on an 80% species protection in freshwater ecosystems. These data should be interpreted in the context of an equilibrium model, and do not consider kinetic and/or biological processes, which may be important for some metals, such as Mn.

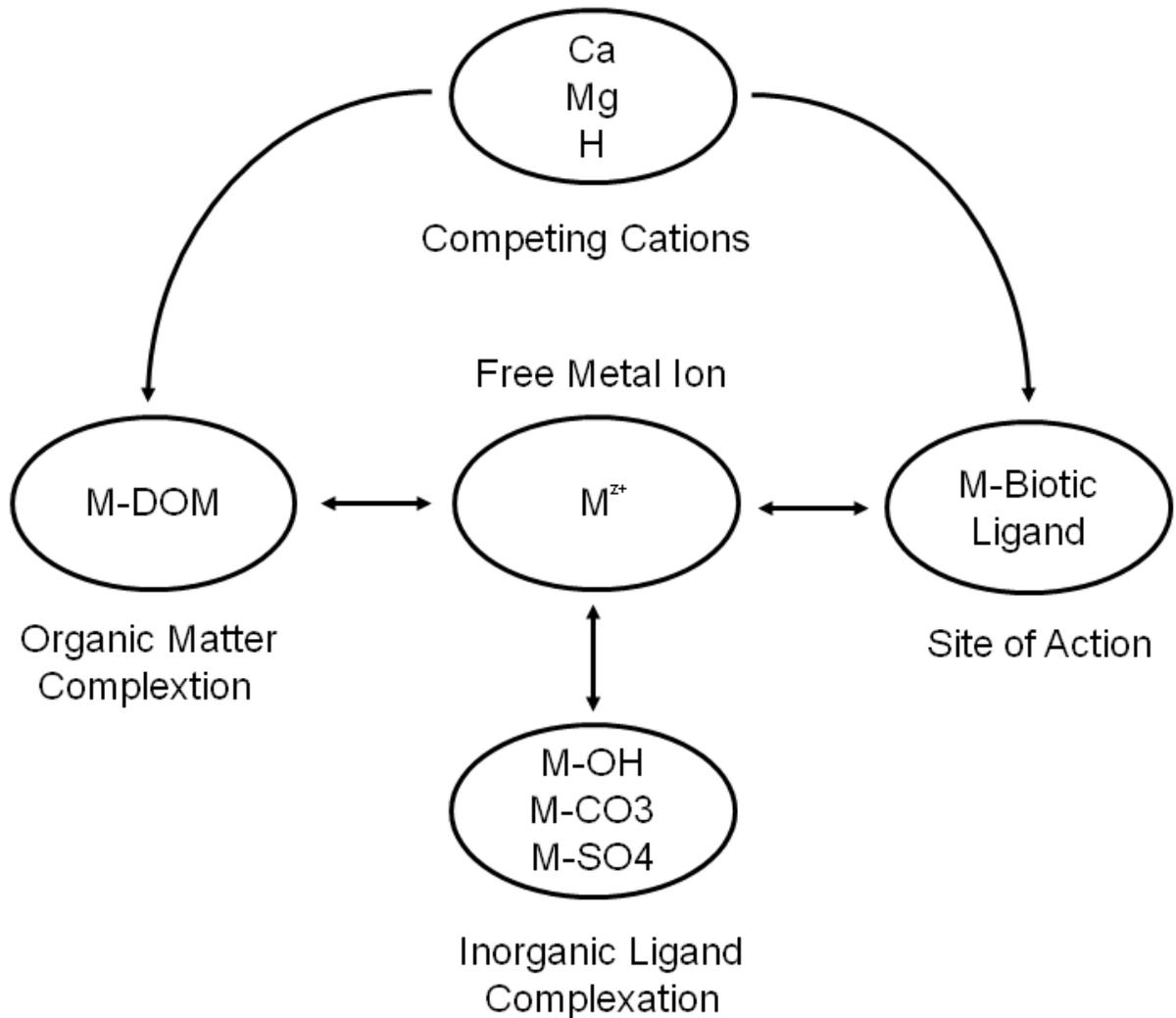
## INTRODUCTION

The speciation of trace metals in natural freshwaters plays a crucial role in determining their reactivity, mobility, bioavailability and toxicity (Markich et al., 2001). Trace metals in fresh surface waters are partitioned between different physico-chemical forms, such as dissolved, complexed or associated phases with colloids and particles (Ure and Davidson, 2001). The distribution between these physico-chemical forms determines potential metal bioavailability, and hence toxicity. Measurements of “dissolved” (e.g. typically following 0.45 µm filtration) metal concentrations provide little insight to potential ecotoxicological impacts in aquatic systems. A convincing body of experimental evidence supports the biotic ligand model (BLM; McGeer et al., 2010; Figure 1) - stemming from the free ion activity model and its extensions (Campbell, 1995; Brown and Markich, 2000) - which postulates that the bioavailability and toxicity of a dissolved trace metal is best predicted by the activity of the free ion (e.g.  $Zn^{2+}$ ), rather than the dissolved concentration. The use of BLMs in a compliance-based regulatory framework is an area which has received substantial attention. The United States Environmental Protection Agency (USEPA) and the European Union (EU) has either adopted, or are in the process of adopting, a BLM-based approach for Cu, Zn or Ni as part of a tiered approach for protecting freshwater organisms (USEPA, 2007; EU, 2008; DeForest and Van Genderen, 2012) – it accounts for metal speciation reactions and interactions with organisms under a wide range of water quality conditions. A BLM-based approach is being considered as part of the current revision of the Australian water quality guidelines for protecting freshwater organisms.

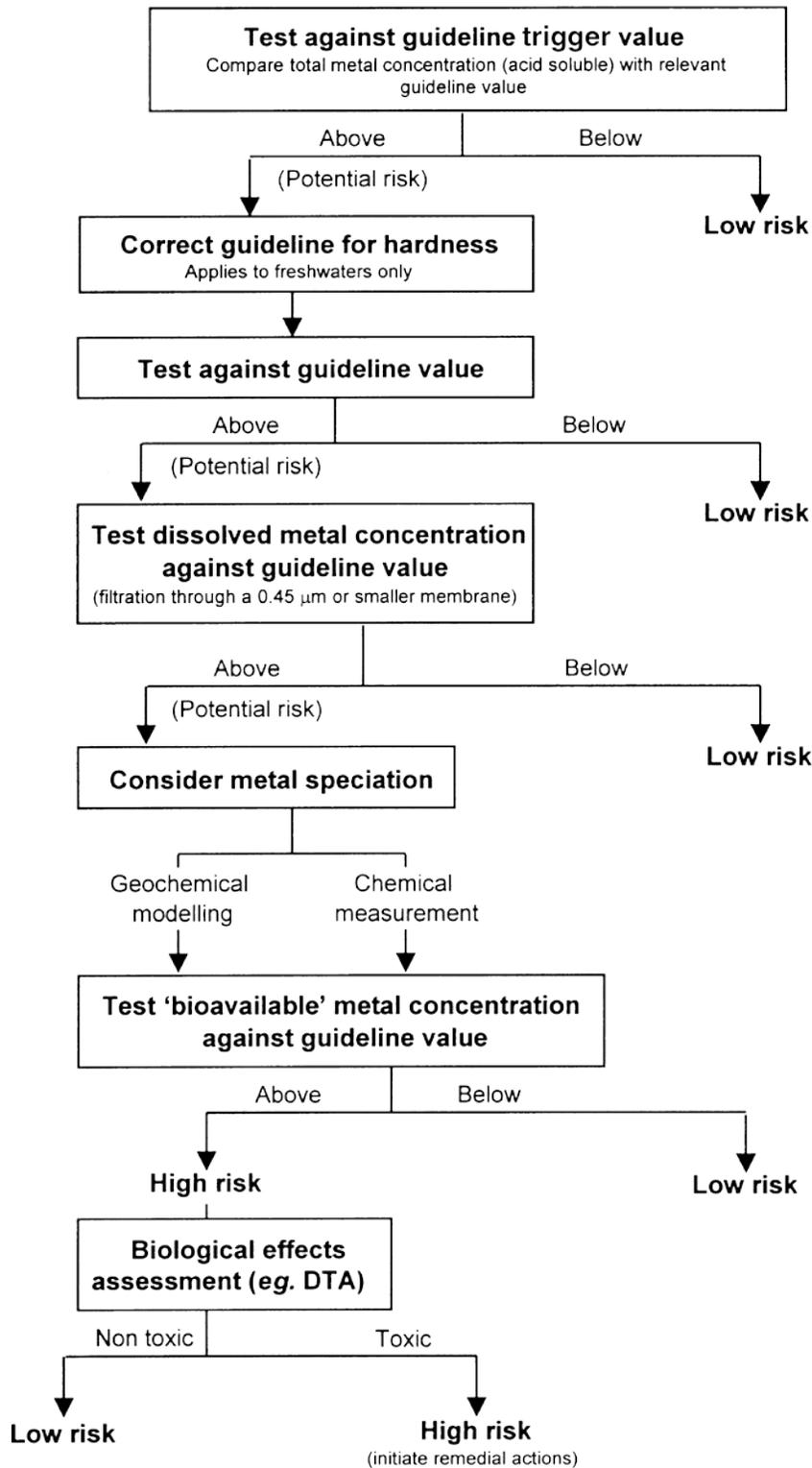
Many analytical techniques, both physical and chemical, are available to measure metal speciation in aquatic systems (Batley et al. 2004; Pesavento et al., 2009; Hamilton-Taylor et al., 2011), although rarely can a complete distribution of all species be determined. A complementary approach, which is more cost effective and time efficient, is the application of chemical speciation models, which estimate metal distributions on the basis of known or postulated chemical reactions. A number of chemical speciation models are currently available (Bethke, 2008), and are used to ascertain the speciation of a particular metal(s) in water under specified conditions (e.g. local measured ion concentrations, pH and temperature). Chemical speciation modelling may be employed as an integral part of a risk-based “decision-tree” approach (Figure 2) for determining metal bioavailability in freshwater ecosystems (ANZECC and ARM CANZ, 2000).

This study reports on speciation calculations for six key metals (Cd, Co, Cu, Mn, Ni and Zn) of potential ecotoxicological concern in the surface waters of the Edith River (control site

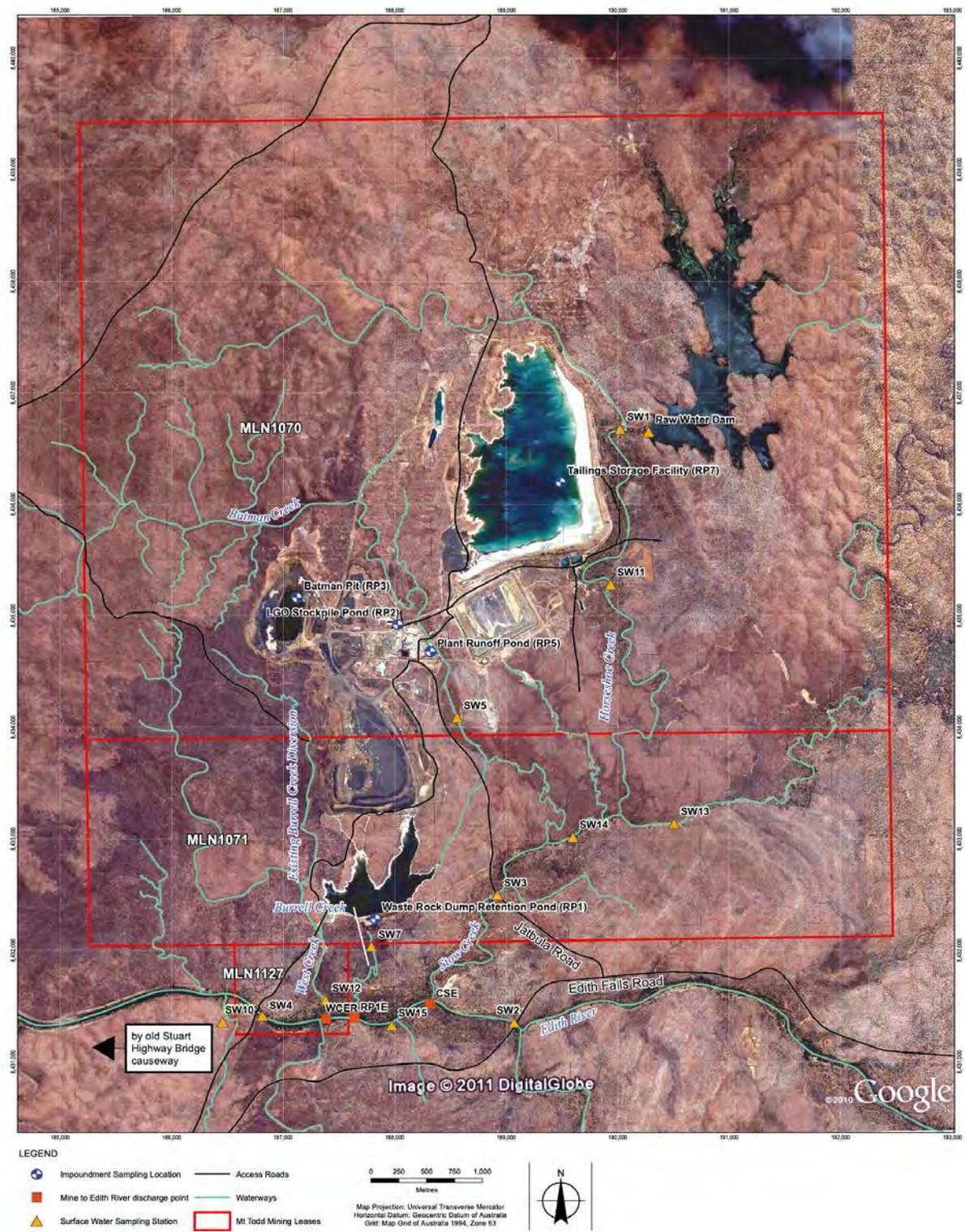
SW2; Figure 3) that may receive wastewaters (Retention Pond (RP) 3; Figure 3) from the Mount (Mt) Todd mine site during the wet season, via controlled discharge. The calculated “bioavailable fraction” of the dissolved concentrations of Cd, Co, Cu, Mn, Ni and Zn is also compared with trigger values at 80% protection for local freshwater species inhabiting the Edith River.



**Figure 1.** Schematic diagram of the biotic ligand model (BLM).



**Figure 2.** Risk-based decision-tree approach (ANZECC and ARMCANZ, 2000), incorporating metal speciation (modelling) for adjusting dissolved metal concentrations.



**Figure 3.** Location map of the Mount Todd mine site in relation to the Edith River – showing the RP3 and SW2 sampling sites.

## **METHODS**

### ***Water Chemistry***

Baseline surface water chemistry of the Edith River (site SW2) during the 2011-2012 main wet season (Table 1; excluding “first flush” events) was compiled from water monitoring data made available by Vista Gold Australia and the Northern Territory Department of Natural Resources, Environment, Arts and Sport. Surface water chemistry for treated RP3 water from the Mt Todd mine was based on two samples (8/7/2011 and 24/8/2011; Table 1). Dissolved (operationally defined as 0.45 µm filtered) concentrations of trace metals (Al, Cd, Co, Cu, Fe, Ni, Mn and Zn) were used for all speciation modelling calculations. A 1:58 dilution ratio of baseline Edith River / treated RP3 water was used to calculate the likely surface water chemistry of the Edith River during controlled discharge of RP3 water during the main wet season (Table 1) - if required, as part of the water management strategy at the Mt Todd mine site. Mean (and standard deviation) values were calculated for the above waters using Statistica (version 7).

### ***Chemical Speciation Modelling***

The speciation of Cd, Co, Cu, Mn, Ni and Zn in the Edith River (at discharge) was calculated using both WHAM (version 7.0; Tipping et al., 2011) and Visual MINTEQ (version 3.0; Gustafsson, 2011). The inorganic equilibrium constants used in both models were derived from Markich (2012). Metal binding with dissolved organic matter (DOM) was calculated using three independent sub-models (Humic Ion-Binding Model VII (HIBM) – incorporated into WHAM, the Stockholm Humic Model (SHM) and the NICA Donnan Model (NICA) – both incorporated into Visual MINTEQ). The HIBM and SHM use a discrete-site approach for calculating proton- and metal-binding; however, there are important technical differences in their calculations. In contrast, the NICA uses a bimodal continuous distribution of affinities approach for calculating proton- and metal-binding. A more detailed description of each model is available within the references given above.

It was assumed that the ratio of active DOM / DOC was 1.4 and that 100% of the active DOM was fulvic acid (which forms ~90% of freshwater humic substances) – this is based on DOM containing 50% carbon (DOC) by mass with a 70% fulvic acid composition (a mean value based on reviews by Bryan et al. (2002) and Sjostedt et al. (2010)). The generic acid-base properties and proton binding constants of fulvic acid used in the NICA model were

**Table 1.** Water chemistry for the Edith River (baseline), Retention Pond (RP) 3, the Edith River at time of RP3 discharge and the calculated bioavailable concentrations of selected metals relative to water quality guideline trigger values for ecosystem protection.

	Edith River (baseline) <sup>a</sup>	Treated RP3 <sup>b</sup>	Edith River (discharge) <sup>c</sup>	Bioavailable Metal <sup>d</sup>	WQG <sup>e</sup>
pH	6.0 (0.5)	7.8	6.1	—	—
Conductivity (µS/cm)	18 (1.0)	2700 (140)	62	—	—
Suspended solids (mg/L)	5.1 (4.5)	< 5	5	—	—
Hardness (mg/L as CaCO <sub>3</sub> )	3.6 (1.0)	1775 (25)	34	—	—
Na (mg/L)	1.3 (0.4)	44 (2)	2.0	—	—
K (mg/L)	0.2 (0.1)	6.8 (0.2)	0.31	—	—
Ca (mg/L)	0.45 (0.11)	385 (7)	7.1	—	—
Mg (mg/L)	0.60 (0.15)	200 (2)	4.0	—	—
Fe (µg/L)	195 (85)	10 (2)	192	—	—
Al (µg/L)	60 (31)	15 (7)	59	—	—
Mn (µg/L)	5.4 (3.3)	15500 (2100)	270	253	3600
Cu (µg/L)	0.3 (0.1)	24 (15)	0.70	0.06	2.8 <sup>f</sup>
Zn (µg/L)	0.3 (0.1)	3700 (420)	64	58	34 <sup>f</sup>
Ni (µg/L)	0.3 (0.1)	390 (140)	7.0	5.9	19 <sup>f</sup>
Co (µg/L)	0.3 (0.1)	535 (100)	9.5	8.7	—
Cd (µg/L)	0.035 (0.02)	52 (6)	0.93	0.78	0.89 <sup>f</sup>
HCO <sub>3</sub> (mg/L)	7.2 (2.7)	159 (2)	9.8	—	—
Si(OH) <sub>4</sub> (mg/L)	19 (4)	—	19	—	—
Cl (mg/L)	1.2 (0.4)	5.5 (1)	1.3	—	—
SO <sub>4</sub> (mg/L)	0.2 (0.1)	1550 (210)	27	—	—
NO <sub>3</sub> (µg/L)	10 (3)	—	10	—	—
PO <sub>4</sub> (µg/L)	5 (2)	—	5	—	—
Organic carbon (mg/L)	3 (1)	2 (1)	3	—	—

<sup>a</sup> Mean (and standard deviation) measured values for surface waters of the Edith River during the 2011/2012 main wet season 2011/2012 (n=6–45). Values represent dissolved (0.45 µm filtered) concentrations for trace metals.

<sup>b</sup> Mean (and standard deviation) measured values (n=2) for treated water. Values represent dissolved (0.45 µm filtered) concentrations for trace metals.

<sup>c</sup> Calculated values based on a 1:58 dilution of RP3 water with baseline Edith River water. Values represent dissolved (0.45 µm filtered) concentrations for trace metals.

<sup>d</sup> Calculated values based on results from geochemical speciation modelling (see Table 2), where the free metal ion (e.g. Cd<sup>2+</sup>) is a proxy for the bioavailable metal fraction (e.g. Cd: 0.93 x 0.844 [84.4% as Cd<sup>2+</sup> from Table 2] = 0.78).

<sup>e</sup> Water quality guideline (WQG) trigger values for disturbed freshwater ecosystems (80% protection level) ANZECC and ARMCANZ, 2000).

<sup>f</sup> Corrected for a water hardness of 34 mg/L as CaCO<sub>3</sub> (using the algorithms given in ANZECC and ARMCANZ, 2000).

**Table 2.** Speciation calculations for selected metals in surface waters of the Edith River, receiving RP3 discharge.

Metal species <sup>a</sup>	Distribution (%) <sup>b</sup>
<b>Cadmium</b>	
Cd <sup>2+</sup>	84.4 (4.3)
CdSO <sub>4</sub>	3.8 (0.2)
Cd-DOM <sup>c</sup>	11.5 (3.8)
<b>Cobalt</b>	
Co <sup>2+</sup>	91.3 (1.9)
CuSO <sub>4</sub>	4.1 (0.1)
Co-DOM	4.5 (2.1)
<b>Copper</b>	
Cu <sup>2+</sup>	8.4 (2.2)
CuSO <sub>4</sub>	0.4 (0.1)
Cu-DOM	90.8 (6.2)
<b>Manganese</b>	
Mn <sup>2+</sup>	93.8 (1.2)
MnSO <sub>4</sub>	3.3 (0.1)
Mn-DOM	2.5 (0.8)
<b>Nickel</b>	
Ni <sup>2+</sup>	84.4 (5.0)
NiSO <sub>4</sub>	3.5 (0.2)
Ni-DOM	12.0 (4.8)
<b>Zinc</b>	
Zn <sup>2+</sup>	91.0 (2.7)
ZnSO <sub>4</sub>	3.3 (0.1)
Zn-DOM	5.1 (2.2)

<sup>a</sup> Each metal species is shown as a percentage of its measured dissolved (0.45 µm filtered) concentration. Metal species comprising <0.2% were excluded for clarity.

<sup>b</sup> Mean (and standard deviation).

<sup>c</sup> DOM, Dissolved organic matter.

revised according to Lenoir et al. (2010). In addition, revised binding constants of Mn and Zn with fulvic acid were used in the WHAM model, based on “in house” research and development work. The speciation models also account for any minerals that may precipitate or any metal binding/adsorption to iron and/or aluminium (oxy)hydroxides, if applicable. The

input parameters for both speciation models were based on measured water chemistry data (pH and ion concentrations) given in Table 1. Mean (and standard deviation) values were calculated (using Statistica, version 7), based on the results of the three different metal-DOM binding sub-models.

## RESULTS AND DISCUSSION

A summary of the surface water chemistry for (i) the Edith River (baseline), (ii) treated RP3 water and (iii) the Edith River (at discharge), is presented in Table 1. The results of speciation calculations (i.e. distribution of species) for Cd, Co, Cu, Mn, Ni and Zn are reported in Table 2. The free metal ion, generally considered to be a good predictor of the bioavailable metal fraction, was calculated to be the major proportion of dissolved (0.45  $\mu\text{m}$ ) Cd (84%), Co (91%), Mn (94%), Ni (84%), and Zn (91%), but accounted for only a relatively small proportion of Cu (8.4%). The speciation of dissolved Cu was dominated by binding with dissolved organic matter (91%), whereas Cd, Co, Mn, Ni and Zn formed relatively weak complexes with DOM (i.e. 2.5-12.0%). Given that sulphate is a major anion, by concentration, in the Edith River during discharge of RP3 water from the mine site (Table 1), metal sulphate complexes make-up the ionic charge balance / proportion for Cd, Co, Mn, Ni and Zn (i.e. 3.3-4.1%; Table 2).

Following the current risk-based decision-tree approach of ANZECC and ARMCANZ (2000), the dissolved (0.45  $\mu\text{m}$  filtered) concentrations of Cd, Co, Cu, Mn, Ni and Zn in the Edith River (discharge; Table 1) were adjusted for their respective percentage of calculated free ion (i.e. the best predictor of the “bioavailable fraction”; Table 1). In addition, the default trigger values for Cd, Cu, Ni and Zn, based on an 80% species protection in freshwater ecosystems (ANZECC and ARMCANZ, 2000), were corrected for water hardness (i.e. 34 mg/L as  $\text{CaCO}_3$  in Edith River (discharge)) using established algorithms (ANZECC and ARMCANZ, 2000). The results indicate that the “bioavailable fraction” of Cd, Cu, Mn and Ni is less than their respective trigger values (Table 1) - there is no reliable trigger value for Co. However, the “bioavailable fraction” of Zn exceeds the corrected trigger value by a factor of 1.7 (Table 1). Based on this result, ecotoxicological testing with Zn is warranted using relevant freshwater organisms, as the next stage in the decision-tree approach (Figure 2).

While there are limitations in using geochemical speciation models, the general consensus is that they can provide useful results if applied correctly with an understanding of the differences between simulated and real systems (Bethke, 2008). Speciation modelling typically assumes chemical (pseudo-) equilibrium exists in the system. However, due to

biological and geochemical processes in natural waters, chemical equilibrium may not always be attained (Millero, 2000). Of the trace metals most relevant to this study, only Mn has a more complex aquatic chemistry than the equilibrium calculations suggest, due to kinetically slow redox reactions, where soluble  $Mn^{2+}$  is oxidised to  $Mn^{4+}$ , as insoluble oxides ( $MnO_2$ ) and oxyhydroxides ( $MnOOH$ ), which form colloidal suspensions, coatings on other minerals and amorphous solid particles mixed with iron oxides (WHO, 2004). Transition between these two forms occurs via oxidation and reduction reactions that may be abiotic or microbially mediated (WHO, 2004). Based on results of the present study, the bioavailability of soluble  $Mn^{2+}$  is expected to be high, whereas the bioavailability of insoluble  $Mn^{4+}$  is expected to be very low.

On-going water chemistry monitoring of both the Edith River and RP3 may benefit from routine analyses of nitrate ( $NO_3$ ), phosphate ( $PO_4$ ) and dissolved organic carbon (filtered with 0.4  $\mu m$  polysulfone membrane filters). Of these,  $PO_4$  and DOC may bind strongly to trace metals, where the proportion of complexed metal-phosphate or metal-DOM increases with increasing  $PO_4$  or DOC concentration, and thus, a decrease in the proportion of the free metal ion (or the “bioavailable fraction”).

## REFERENCES

- ANZECC, ARMCANZ. 2000. *Australian Water Quality Guidelines for Fresh and Marine Waters*. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- Batley, G.E., Apte, S.C., Stauber, J.L. 2004. Speciation and bioavailability of trace metals in water: Progress since 1982. *Aust. J. Chem.* 57, 903–919.
- Bethke, C.M. 2008. *Geochemical and Biogeochemical Reaction Modeling*. Cambridge University Press, London.
- Brown, P.L., Markich, S.J. 2000. Evaluation of the free ion activity model of metal-organism interaction: Extension of the conceptual model. *Aquat. Toxicol.* 51, 177–194.
- Bryan, S.E., Tipping, E., Hamilton-Taylor, J. 2002. Comparison of measured and modelled copper binding by natural organic matter in freshwater. *Comp. Biochem. Physiol.* 133C, 37–49.
- Campbell, P.G.C. 1995. Interactions between trace metals and aquatic organisms: A critique of the free-ion activity model. In: Tessier, A., Turner, D.R. (Eds), *Metal Speciation and Bioavailability in Aquatic Systems*. John Wiley and Sons, Chichester. pp. 45–102.

- DeForest, D.K., Van Genderen, E.J. 2012. Application of U.S. EPA guidelines in a bioavailability-based assessment of ambient water quality criteria for zinc in freshwater. *Environ. Toxicol. Chem.* 31, 1264–1272.
- EC. 2008. EU Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy, amending and subsequently repealing council directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. *Off. J. European Union* 348, 84–97.
- Gustafsson, J.P. 2011. Visual MINTEQ (Version 3.0): A Windows version of MINTEQA2. <http://www2.lwr.kth.se/English/OurSoftware/vminteq/>
- Hamilton-Taylor, J., Ahmed, I.A., Davison, W., Zhang, H. 2011. How well can we predict and measure metal speciation in freshwaters. *Environ. Chem.* 8, 461–465.
- Lenoir, T., Matynia, A., Manceau, A. 2010. Convergence-optimised procedure for applying the NICA-Donnan model to potentiometric titrations of humic substances. *Environ. Sci. Technol.* 44, 6221–6227.
- Markich, S.J. 2012. *Thermochemical Data (log K) for Environmentally-Relevant Elements*, 2<sup>nd</sup> Ed. ASI C1/12. Aquatic Solutions International, Sydney.
- Markich, S.J., Brown, P.L., Batley, G.E., Apte, S.C., Stauber, J.L. 2001. Incorporating metal speciation and bioavailability into water quality guidelines for protecting aquatic ecosystems. *Australas. J. Ecotoxicol.* 7, 109–122.
- McGeer, J.C., Clifford, M., Janssen, C.R., De Schampelaere, K.A. 2010. Modeling the toxicity of metals to aquatic biota using the biotic ligand approach. In: Bury, N.R., Handy, R.D. (Eds), *Surface Chemistry, Bioavailability and Metal Homeostasis in Aquatic Organisms: An Integrated Approach*. SEB Press, London, pp. 205–231.
- Millero, F. 2000. *The Physical Chemistry of Natural Waters*. Wiley, New York.
- Pesavento, M., Albertini, G., Biesuz, R. 2009. Analytical methods for the determination of free metal ion concentration, labile species fraction and metal complexation capacity of environmental waters: A review. *Anal. Chim. Acta* 631, 129–141.
- Sjöstedt, C.S., Gustafsson, J.P., Kohler, S.J. 2010. Chemical equilibrium modelling of organic acids, Ph, aluminium and iron in Swedish surface waters. *Environ. Sci. Technol.* 44, 8587–8593.
- Tipping, E., Lofts, S., Sonke, J.E. 2011. Humic ion-binding model VII: A revised paramaterisation of cation-binding by humic substances. *Environ. Chem.* 8, 225–235.

- Ure, A.M., Davidson, C.M. 2001. *Chemical Speciation in the Environment*. 2<sup>nd</sup> Ed. Blackwell Science, London.
- USEPA. 2007. *Aquatic Life Ambient Freshwater Quality Criteria – Copper*. EPA-822-R-07-001. United States Environmental Protection Agency, Washington DC.
- WHO. 2004. *Manganese and its Compounds: Environmental Aspects*. World Health Organisation, Geneva.