Derivation of site-specific water quality objectives within a highly disturbed Tasmanian catchment

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Key Points

- The combination of metal speciation models and BLMs allows for a more in-depth understanding of the mechanisms responsible for bioavailability in river systems to inform management
- At Savage River, the assessment showed that only a fraction of the measured dissolved concentrations of contaminants in Savage River were bioavailable
- New site-specific water quality objectives were derived using verified BLM outputs

Abstract

At Savage River mine (Tasmania), historic acid mine drainage contributes important inputs of acidity, high sulphate concentrations and high dissolved metal concentrations (aluminium, cobalt, copper, iron, manganese, nickel and zinc). The high seasonality observed in contaminant concentrations along the river is associated with rainfall, driving concentrations of dissolved organic carbon (DOC) in the water as well as alkalinity and hardness. Seasonal variability of the contaminant mixture represents a challenge for management.

The combination of metal speciation model and biotic ligand models (BLMs) was used to provide a more in-depth understanding of the mechanisms responsible for bioavailability in the system to inform management. The speciation modelling provided estimates of the fraction of the element in the form of either free metal ion or charged inorganic complexes in solution which, together, form a “potentially bioavailable” fraction. BLMs use speciation data to further assess bioavailability by adding a “biotic ligand” representing typical aquatic organisms in the modelled system. This approach provided a more accurate estimate of bioavailability as it considered competitive binding of ions at the biotic ligand.

The key advantage of using a modelling approach in the case of Savage River was that it provided a long-term monitoring solution to address the large temporal variability of the metal mixture. This assessment showed that only a fraction of the measured dissolved concentrations of contaminants in Savage River were bioavailable, therefore new site-specific criteria could be developed. Appropriate water management strategies will need to be established to achieve these new water quality objectives.

Keywords

Speciation model, bioavailability, toxicity, biotic ligand model

Introduction

The Savage River mine is located in northwest Tasmania in steep mountainous terrain surrounded by areas of high wilderness values, including the Savage River National Park and the Pieman River catchment. The original open cut iron ore mine on Savage River was established in 1967. Operations during the first 30 years resulted in severe impacts to the water quality and the general condition of habitats in the Savage River and its tributaries. Consequently, the Savage River Rehabilitation Project (SRRP) was initiated in 1996 as a cooperative project between the Tasmanian Government (Environment Protection Authority) and the Savage

River Mine operator, Grange Resources (formerly Australian Bulk Minerals). Its objectives were to set out a strategic plan that focused on developing long-term solutions for mitigating historic pollution (1965 - 1996).

The main issue around mining operations identified in previous reports in the region is associated discharge of sulphates and metals (Koehnken, 1992; Koehnken, 2009; Koehnken 2014; Davies et al. 2001). The source of sulphate is the oxidation of sulphidic minerals, such as pyrite. The products of these reactions are collectively referred to as acid mine drainage (AMD). AMD may contain high concentrations of metals and sulphuric acid and can present a major risk to aquatic life, vegetation and water resources downstream. Once mining operations has ceased, poor water quality in the form of AMD may continue to impact the environment for decades or even centuries (Taylor & Pape 2007).

Key biological values and associated desirable targets have been identified under the SRRP and Pieman River Projects, they include:

- Sustainable populations of native fish species;
- Higher abundance, diversity and 'natural' taxonomic composition of benthic macroinvertebrates; and
- A diverse algal and macrophyte community.

In previous reports by Koehnken (2014) and Davies et al. (2001), as well as a further assessment of more recent water quality data (Hydrobiology 2015), it was evident that remediation options undertaken at Savage River resulted in reduced metal concentrations over time along with increased alkalinity downstream of the mine. However, concentrations of many metal contaminants reported in the surface waters downstream of the mine remained above ANZECC and ARMCANZ (2000) guidelines for the protection of 95% of aquatic organisms. Several toxicological studies have been carried out in regard to metal toxicity and acid mine drainage for the Savage River and Mt Lyell regions, with a main focus on copper and aluminium (Davies et al. 1996; Davies et al. 2001; Eriksen 2001; Eriksen 2002). These studies showed that the toxicity thresholds in this catchment were above ANZECC and ARMCANZ (2000), thus suggesting that the metals of concern were less bioavailable.

Metal contaminants are present in water in multiple different chemical forms that may be more or less toxic to organisms. The chemical forms (or speciation) and bioavailability of metals in freshwaters can be strongly influenced by a variety of physicochemical parameters. These include adsorption/desorption on suspended matter, complexation by Dissolved Organic Carbon (DOC), inorganic complexation related to water hardness, alkalinity, and pH, ion competition and other interactions with salinity, temperature, and redox potential. All of these parameters play a role in modifying the potential toxicity of some metals to biota.

The aim of this study was to assess metal speciation and bioavailability in Savage River and develop site-specific water quality objectives. While a number of techniques can be used to assess the toxicity of contaminants in a mixture, the marked seasonal variability of water characteristics at Savage River meant that a direct toxicity assessment would have offered limited applicability. The key advantage of the modelling approach is that it provides a long-term monitoring solution to address the large temporal variability of the metal mixture at Savage River. It also represents the most cost-effective method. The modelling approach adopted involved a two-step analysis comprised of speciation modelling and biotic ligand modelling (BLM).

Speciation modelling was used to determine the metal species partitioning and assess variations in ionic activity in the water at monitored Savage River sites. Speciation modelling represents a first step to the characterisation of bioavailability. It gives an indication of the likelihood of a metal to be in a form that could be taken up by aquatic organisms. However, it does not take into account interactions with organisms themselves. In particular, it does not consider the concept of competitive binding of ions which can have significant effects on the effective concentration of a metal that can be considered bioavailable. Biotic ligand modelling uses speciation data to further assess bioavailability by adding a "biotic ligand" representing typical aquatic organisms in the modelled system. This approach provides a more accurate estimate of bioavailability as it considers competitive binding of ions at the biotic ligand. BLMs have received substantial attention in a compliance-based regulatory framework in the United States Environmental Protection Agency (USEPA) and the European Union (EU) (Markich 2012).

Methods

Data collection

A dedicated sampling campaign was undertaken between July 2016 and June 2017. Water samples were collected once each month at key locations in the vicinity of the mine. For the purpose of this presentation, the data from three representative sites was selected (one upstream control site, one site directly downstream from the mine and one site 30 km downstream from the mine). All samples were analysed for a complete suite of analytes, including DOC. Additional parameters (including water temperature, pH and electrical conductivity) were measured in-situ.

Preliminary data analysis

Aluminium and copper were identified as the main contaminants of concern, although elevated concentrations of cobalt, manganese, nickel and zinc were also noted (based on comparisons with ANZECC & ARMCANZ (2000) guidelines).

A preliminary seasonal assessment of the dataset indicated that during higher flow periods, DOC concentrations downstream from Savage River Mine were generally higher, while alkalinity and hardness levels were lower. These variations in water quality parameters are expected to affect the bioavailability of metals in the river. Antagonistic effects would be expected to result from these changes in water chemistry as the increase in DOC would reduce metal bioavailability while the reduction of both alkalinity and hardness would be expected to increase it.

Modelling

For this assessment, data for each scenario and each location were entered into multiple recognised international modelling tools in order to mechanistically predict bioavailability and assess potential for associated toxicity. Outputs were compared between models.

Metal speciation

Speciation models utilise a comprehensive input of water chemistry parameters to determine the chemical assemblages within the system. The Windermere Humic Aqueous Model (WHAM7) version 7.0.5 was used for predicting metal speciation. This model has been specifically parameterised for chemical speciation in systems with significant influence from humic substances. Although WHAM7 was the main model used for speciation in this assessment, the data were also modelled in PHREEQC version 3.3.2 (May 2017) by US Geological Survey as a quality assurance and control tool. Results by PHREEQC were relatively comparable to WHAM7 albeit not including the organic fraction for metals other than copper.

All data provided through the 2016-2017 monitoring survey were deemed suitable for modelling, i.e. the ionic balance analysis estimated errors below 10%, which was considered an acceptable level of analytical variance.

Biotic Ligand models

BLMs require a less comprehensive suite of water quality parameters to be entered as input to determine bioavailability and potential for toxicity to aquatic species in the system. These models have been developed as user-friendly tools, and, as such, represent a potential ideal monitoring tool to use in cases like Savage River. To date, three international BLMs are available. The European BLMs (bio-met and m-BAT) require limited input. Key input parameters include the dissolved concentration of the element of concern, as well as DOC, calcium and pH. The North American BLM (Windward) takes into account additional parameters, including the percentage of humic acid, concentrations of all major ions, alkalinity and temperature. The European nickel BLMs have been validated for Australian freshwaters (Peters et al. 2016).

This assessment tested all three international BLMs, and compared the bioavailability outputs with those obtained through speciation modelling using more complex models to evaluate the potential for using BLMs in future assessment of monitoring data. Beyond the estimation of bioavailability, the BLMs are also parameterised to provide site-specific criteria for the protection of the aquatic ecosystem. Each of the three BLMs used in this assessment produced slightly different output criteria. These were compared, and the most conservative output was adopted.

Model assumptions

A number of assumptions were made in order to use the speciation models and BLMs:

- In the case where concentrations of key parameters were reported below the laboratory limits of reporting (LOR), they were replaced by half of the LOR. Any other non-essential parameters for which concentrations were reported < LOR were removed from the dataset. It is considered that concentrations <LOR would have had minor contributions to ion balance and as such, these modifications may have induced minor amelioration of the toxicity.
- Aquatic humic substances (i.e. humic and fulvic acids) are natural organic compounds capable of complexing with metal ions. Their presence as active organic ligands in the water is particularly important for the assessment of speciation and associated toxicity of metal contaminants. All BLMs assume that 50% of the DOC is fulvic acid (a fixed assumption that cannot be altered). Previous modelling work that was performed in the Pieman catchment suggest the use of 10% humic acid and 90% fulvic acid (Leenheer 1995 in Denney 2000). However, their findings indicated that the bioavailability of copper was largely overestimated for Savage River using these parameters and the reliability of speciation estimates were poor. In addition, recent unpublished work that quantified humic substances in north western Tasmanian waters (Dr Aleicia Holland, personal communication, 25/10/2017, unpublished data) showed that humic acids were dominating in the system which contradicted the assumption made by Denney (2000). Considering these latest data, the assumption of 50% fulvic acid was adopted for the speciation modelling, which was a conservative approach.
- In WHAM7, the data input requires the specification of iron species (i.e. Fe(II) or Fe(III)). The ferrous-ferric chemical equilibrium largely depends on pH and redox potentials. Redox potential measurements were not performed during the sampling campaign, however based on expected redox in flowing rivers (Garrels & Christ 1965) and in-situ pH measurements, it was estimated that the majority of iron in the Savage River catchment was in the Fe (III) form. As a result, dissolved iron concentrations were assumed to be 100% Fe (III).
- WHAM7 was set to prevent the precipitation of aluminium and iron hydroxides. The data entered in WHAM7 corresponded to dissolved ion concentrations measured in the field. Although it is possible

that some colloidal fractions of iron and aluminium may have gone through the filter, no precipitation of aluminium and iron were allowed for in the model run. This method represents a more conservative approach, but it is important to note that it may lead to the overestimation of the lability of some other metal species, including copper.

- Calcium concentrations measured at the upstream control site were below the lower end of the calibrated range for the bio-met and m-BAT BLMs. This adds uncertainty to the model outputs for the control site, but not the downstream sites.

Results and discussion

Although all potential contaminants of concern were investigated at Savage River, this paper concentrates on the results for copper only.

Metal speciation

The WHAM7 model calculated the concentrations of free copper ions and inorganic and organic complexes in solution for each dissolved water sample. These can be divided into 4 categories that relate to bioavailability as follows:

- Free copper ions in solution are considered 100% bioavailable as they are in a form that can be readily taken up by aquatic organisms;
- Charged inorganic complexes in solution may be bioavailable. There is a possibility for the weak inorganic complexes to dissociate and induce toxicity or be taken up via charged ion uptake proteins on the cell surface.
- Uncharged inorganic complexes in solution are more stable and electrochemically inert, and likely not bioavailable.
- Organic complexes are formed from complexation of the metal with humic/fulvic substances. The copper bound to organic matter is considered 100% not bioavailable.

The first two fractions (free metal ions and charged inorganic complexes) can both be responsible for toxicity. Results of the speciation modelling for copper are presented in **Figure 1**. These graphs include a dash line representing the national water quality guideline (ANZECC & ARMCANZ 2000). Results indicate that DOC complexation (i.e. organic bound fraction) contributed to the decrease in copper bioavailability in Savage River. Substantial inorganic complexation was also observed. Although the concentrations of free copper ions (Cu^{2+}) in solution reflected a mine impact (higher concentration at sites impacted by mine activities compared with the upstream control), they remained below the guideline value for all samples. While copper was not a contaminant of concern at the upstream control site, the combination of free copper ion and charged inorganic complexes exceeded the guideline value at both sites located downstream from the mine. Therefore the risk of toxicity could not be ruled out. However, it is important to note that this is considering a worst-case scenario where WHAM7 did not allow the iron to precipitate in the system. There is the possibility that copper may have been less bioavailable than predicted as a result of co-precipitation with iron. In the case where precipitation of iron was allowed in WHAM7, the risk of copper toxicity was substantially reduced to a low risk for the site located 30 km downstream from the mine, however there was still a risk of toxicity at the site closer to the mine.

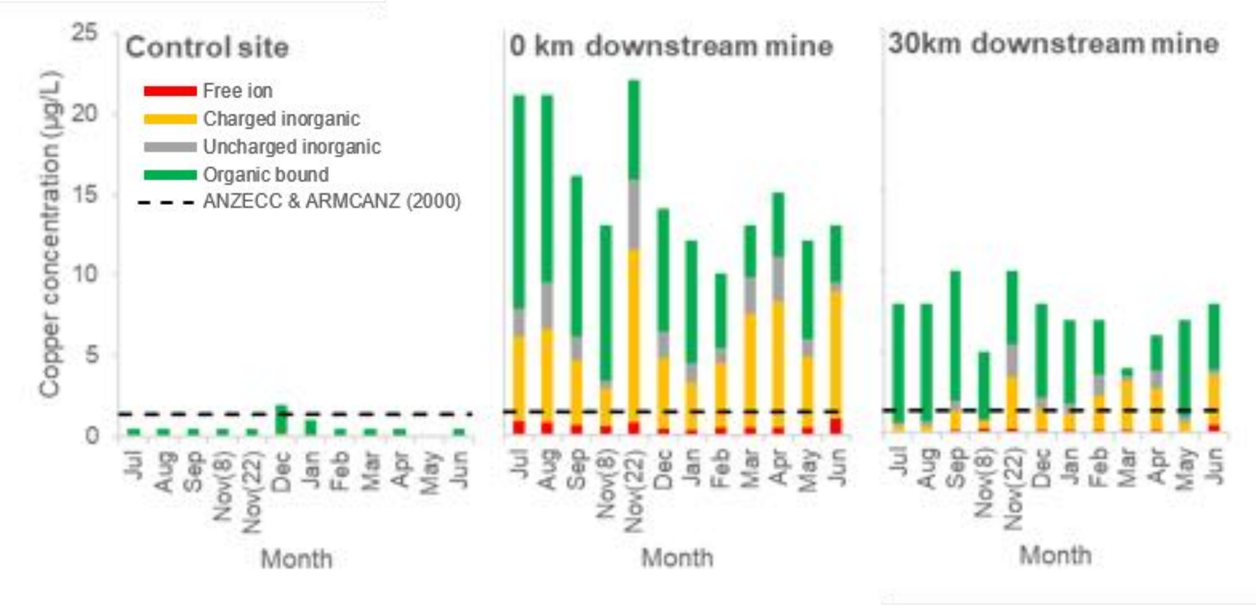

Figure 1. Copper speciation across sites corresponding to the samples collected in 2016 – 2017. The dashed line indicates the ANZECC & ARMCANZ (2000) guideline.

Biotic Ligand Models

The bioavailability of copper was further assessed through the use of the European and North American BLMs (bio-met, m-BAT and Windward). These BLMs are user-friendly tools that have been developed and verified for European and North American waters. In the case of the European BLMs, the input has been reduced to only a few parameters in order to provide a user-friendly interface. These parameters are the dissolved concentration of the metals of interest and calcium, DOC and pH. It was demonstrated that these water quality parameters were responsible for most of the variability observed on the calculated bioavailability estimates (Peters *et al.*, 2011; Rüdel *et al.*, 2015). While the concentration of calcium is a key parameter expected to play an important competitive binding role at the biotic ligand, the presence of other ions has also been shown to reduce the bioavailability of some metals in water. As such, the BLMs assume a given relationship between calcium and other ions in order to calculate the bioavailable concentration of a contaminant of concern. In freshwater systems, the concentrations of calcium and magnesium are generally linearly correlated. However, the calcium to magnesium (Ca:Mg) ratios observed in Savage River waters were lower compared with typical European waters. This suggests that Savage River is naturally richer in magnesium, but the effect at downstream sites is also associated with active neutralisation treatments (dolomite and magnesite) that are used in an effort to address acid rock drainage at Savage River (Hutchison and Brett, 2006). These neutralising materials are rich in magnesium, and their addition was found to significantly modify the Ca:Mg ratio in the river (**Figure 2**). Due to this important shift in water quality, the reliability of user-friendly European BLMs (which assume the relationship between ions is typical of European waters) in deriving new trigger values for Savage River was questionable.

In order to address this concern, a representative sample suite was analysed using the complete versions of the copper BLM. Outputs of the complete BLMs were compared with the user-friendly versions. The predicted no-effect concentration (PNEC) output values calculated through the complete BLM were generally lower than those obtained through the user-friendly BLM m-BAT and bio-met for downstream sites. This suggests that the user-friendly versions of the European BLMs underestimated the bioavailability of copper for Savage River, and therefore the trigger values calculated for copper through these tools may not be fully protective. This exceedance remained within a factor of 2 for m-BAT (**Error! Reference source not found.**), which is within the model's limitations (Peters *et al.*, 2011). The North American BLM (Windward) produced more conservative trigger values for copper, although some exceeded those derived using the complete European BLM. The larger differences observed between the Windward and complete European BLM results can be attributed to the difference in the toxicity database and the computational method used to derive the trigger values. In order to provide a conservative estimate of site-specific copper triggers, a factor of 2 (halving) was applied to the user-friendly m-BAT data. This was found to be the best compromise between all of the methods tested and provided conservative estimates for all samples investigated.

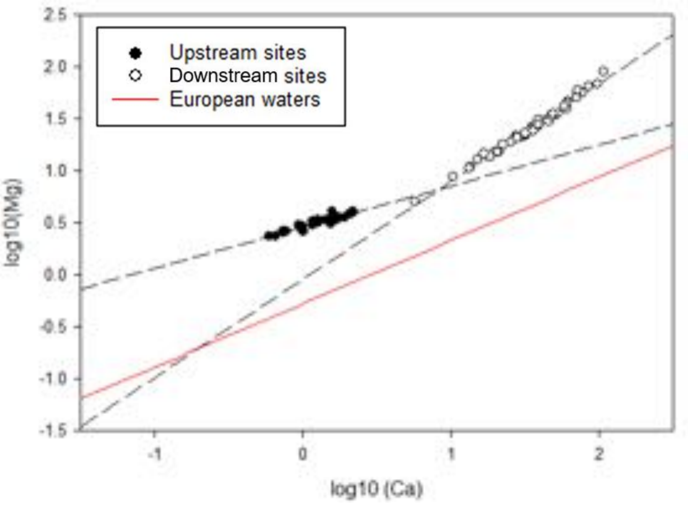

Figure 2. Relationship between calcium and magnesium concentrations at upstream sites and downstream sites compared with typical European waters.

All estimated site-specific criteria for copper were above the ANZECC & ARMCANZ (2000) guideline value of 1.4 µg/L (**Figure 3**), indicating that the chemical characteristics of the surface waters in Savage River were expected to reduce the bioavailability of copper to organisms, thereby reducing the potential for toxicity. While no exceedances were noted upstream of the mine site, measured dissolved concentrations exceeded the modelled criteria for most of the year at the site directly downstream from the mine. Occasional exceedances were also noted further downstream, indicating a potential risk for toxicity to be carried downstream.

This assessment showed that only a fraction of the measured dissolved concentrations of contaminants in Savage River were bioavailable, therefore new site-specific criteria could be developed. The available BLMs provided revised water quality criteria for copper for each sample over the 2016 – 2017 campaign. Due to the large seasonal variations in water quality, the derivation of a single water quality objective for copper was not a viable option, and its applicability would not be realistic. Instead, the BLM method offers the option of an adaptative trigger value by providing water quality criteria for any surface water sample collected.

Together, the speciation model and BLM provide complementary information on the potential for toxicity of copper in the river. The BLM results suggested that only a portion of the charged inorganic copper complexes estimated by WHAM7 were bioavailable and contributed to the toxicity. Adjusted trigger values were derived and provide more realistic objectives for management.

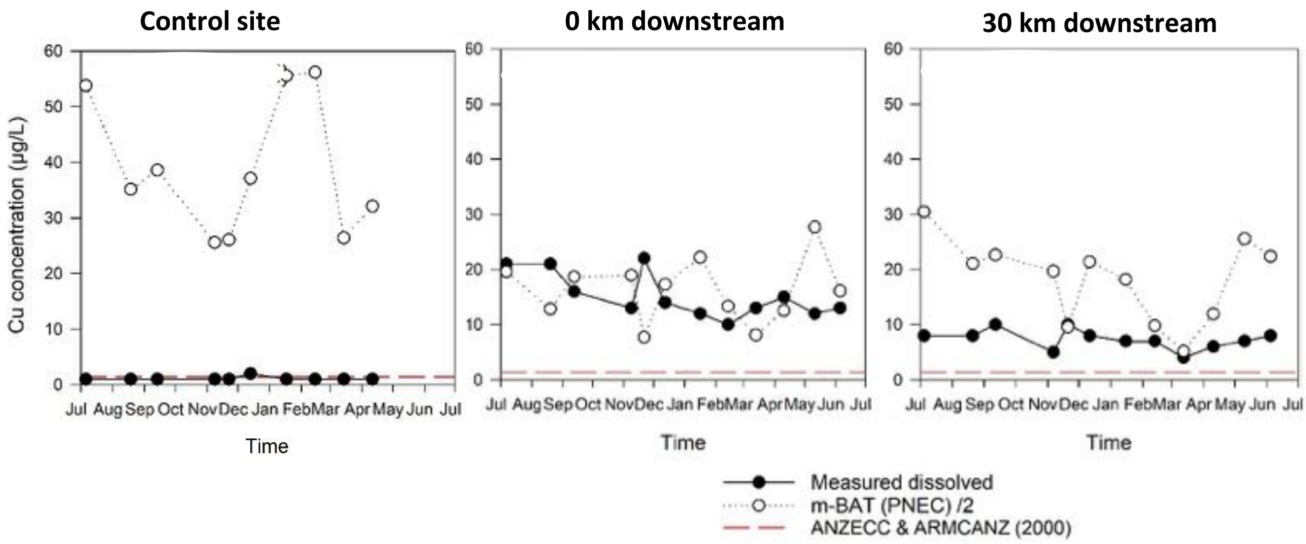

Figure 3. Comparison of calculated copper (Cu) trigger values to the ANZECC & ARMCANZ (2000) guideline value and corresponding measured dissolved concentrations at sites along Savage River (the correction factor of 2 was not applied to the control site trigger values)

Conclusion

The combination of metal speciation models and BLMs allows for a more in-depth understanding of the mechanisms responsible for bioavailability in the system to inform management. These methods provide more realistic objectives for management, thus they are proposed for the future assessment of monitoring data collected at Savage River.

This paper presented the modelling approach adopted for the derivation of site-specific water quality objectives for copper in Savage River. This method was also applied for other contaminants of concern, including aluminium, manganese, nickel and zinc. In the case of cobalt and iron (other identified contaminants of concern in Savage River), no BLM was available at this time. For these contaminants, it is possible to adopt alternative methods to assess the potential bioavailability based on the results from the speciation modelling.

Based on the 2016-2017 data used in this report, ongoing remediation effort of AMD sources will be required if management is to meet the bioavailability-based triggers derived for the contaminants of concern in Savage River.

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References

ANZECC & ARMCANZ. (2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality - Aquatic Ecosystems, Rationale and Background Information (Chapter 8), National Water Quality Management Strategy 2 (4), 678 pp.

Davies, P., Mitchell, N., Barmuta, L. (1996). Mount Lyell Remediation: The impact of historical mining operations at Mount Lyell on the water quality and biological health of the King and Queen River catchments, western Tasmania.

Davies, P., Eriksen, R., Cook, L.S.J., Risdon, M.L. (2001). Toxicological evaluation of acid drainage waters and treatment options at Savage River, western Tasmania. Savage River Rehabilitation Program. Report to Department of Primary Industries, Water and Environment, Tasmania.

Denney, S. (2000). Trace metal speciation in the Pieman River catchment, Western Tasmania. Deakin University.

Eriksen, R. (2001). Savage River Rehabilitation Project Toxicity Testing Program.

Eriksen, R. (2002). Savage River Rehabilitation Program Toxicity Testing Project: The effect of hardness and alkalinity on copper toxicity using invertebrate toxicity tests.

Hutchison, B.J., Brett, D. (2006). Savage River Mine - Practical Remediation works, 7th International Conference on Acid Rock Drainage (ICARD), 810–820.

Hydrobiology. (2015). Savage River Stage 1: Literature Review and Assessment of Contaminant Toxicity in Savage River, Hydrobiology Pty Ltd.

Koehnken, L. (1992). Pieman River Environmental Monitoring Programme.

Koehnken, L. (2009). Water quality review 2009, report to the SRRP.

Koehnken, L. (2014). Water quality review 2014. Report to the SRRP.

Markich, S.J. (2012). Speciation modelling of metals in surface waters of the Edith River during wet season discharge of wastewater from the Mount Todd mine (Appendix C – Metal Speciation).

Peters, A., Merrington, G., De Schamphelaere, K., Delbeke, K. (2011). Regulatory consideration of bioavailability for metals: simplification of input parameters for the chronic copper biotic ligand model, Integrated Environmental Assessment and Management 7(3), 437–444.

Rüdel, H., Díaz Muñiz, C., Garelick, H., Kandile, N.G., Miller, B.W., Pantoja Munoz, L., Peijnenburg, W.J.G.M., Purchase, D., Shevah, Y., van Sprang, P., Vijver, M., Vink, J.P.M. (2015). Consideration of the bioavailability of metal/metalloid species in freshwaters: experiences regarding the implementation of biotic ligand model-based approaches in risk assessment frameworks, Environmental Science and Pollution Research, 22(10), 7405–7421.

Taylor, J., Pape, S. (2007). Managing Acid and Metalliferous Drainage. In Leading Practice Sustainable Development Program for the Mining Industry - Department of Industry Tourism and resources; Australian Government, 28–40.