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RESEARCH PAPER

CONSIDERING BACKGROUND IONIC PROPORTIONS IN THE DEVELOPMENT OF SULFATE GUIDELINES FOR THE FITZROY RIVER BASIN

Jason E. Dunlop,[1,2*] Reinier M. Mann,[1,2] Dustin Hobbs,[3] Ross E.W. Smith,[3] Vinitha Nanjappa,[2] Suzanne Vardy[1] and Sue Vink[2]

[1] Queensland Department of Science, Information Technology and Innovation, Environmental Monitoring and Assessment Sciences, GPO Box 2454, Brisbane, QLD 4001, Australia

[2] The University of Queensland, Centre for Water in the Minerals Industry, Sustainable Minerals Institute, St Lucia, QLD 4072, Australia.

[3] Hydrobiology Qld Pty Ltd, PO Box 2151, Toowong, QLD 4066, Australia.

ABSTRACT

Sulfate (SO_4^{2-}) is commonly associated with saline mine water discharges to aquatic ecosystems. Despite the prevalence of sulfate in mine water releases around the world, there is a paucity of sulfate toxicity data describing its potential impacts on aquatic species and a lack of ecosystem protection guideline values relevant to Australia. The aim of this study was to evaluate the toxicity of sulfate using a test water representative of natural waters. An outcome of this study was the development of aquatic ecosystem protection guideline values for Na_2SO_4 using a test water and suite of test species relevant to the Fitzroy River basin in northeastern Australia where mine water releases are prevalent. Toxicity tests were undertaken on six species including a mayfly (*Atalophlebia* sp. AV 13), a ubiquitous freshwater alga (*Pseudokirchneriella subcapitata*), a plant (*Lemna disperma*), a zooplankton (*Ceriodaphnia dubia*), a fish (*Melanotaenia splendida*) and a shrimp (*Paratya australiensis*). Preliminary toxicant guidelines for sulfate (as Na_2SO_4) estimated to be protective of 80%, 90%, 95% and 99% of species in the receiving ecosystem and their upper 95th and lower 5th percentile confidence intervals were 936 (731-1548), 706 (525-1242), 545 (380-1103) and 307 (161-866) mg/L SO_4^{2-}, respectively, at a water hardness of 550 mg/L (as $CaCO_3$). Results were comparable to guideline values developed using species relevant to North America.

Key words: Salinity; Sulfate; Coal mining; Water quality guidelines.

* Author for Correspondence, e-mail: jason.dunlop@qld.gov.au

INTRODUCTION

Sulfate is a naturally occurring constituent of freshwater rivers and streams that is essential for the normal functioning of aquatic animals and plants (IDNR 2009). Sulfate has relatively low toxicity compared with other major ions (Mount et al.1997) yet it is known to be toxic to aquatic biota above certain thresholds (Elphick et al. 2011). A common source of elevated sulfate is the point source release of mine affected water from coal and metalliferous mines.

Although most mines seek to prevent water releases, episodic rainfall events can fill water storages beyond their capacity making it necessary to release water. Given the potential for sulfate rich water to be released from mines there is a need to ensure such releases can be managed effectively to prevent impacts on aquatic ecosystems. Toxicity based water quality guidelines (trigger values) provide a risk based approach to define thresholds for management. In Australia, guideline values are derived using a species sensitivity distribution approach (Warne et al. 2014). However, there are currently no toxicity-based water quality criteria for the protection of freshwater ecosystems from the toxic effects of sulfate adopted at the national level in Australia (ANZECC and ARMCANZ 2000) or Queensland (DEHP 2009). Likewise, there are no guidelines for sulfate at a national level in Canada or the United States of America. There are, however, regional scale guidelines that have been developed for sulfate in British Columbia (BC), Canada (Meays and Nordin 2013) and Illinois (IPCB 2013) as adopted by Iowa (IDNR 2009).

Although such guidelines are useful, there remains some uncertainty associated with their application to a range of scenarios. Because the toxicity of sulfate is known to be influenced by water hardness (Soucek and Kennedy 2005; Davies and Hall 2007), and the ratio of Ca:Mg (Davies and Hall 2007), there is a need to adjust guideline values to account for this. When evaluating the available toxicity data to derive a guideline for sulfate, Meays and Nordin (2013) found that although increasing water hardness was observed to reduce sulfate toxicity for a number of species, the relationship was not consistent between species. Inconsistencies were attributed to differences between the concentration ranges tested, organism sensitivity and the variation between endpoints investigated. Another consideration is that because hardness is a measure of the concentration of multivalent cations in water, waters with the same calculated hardness (such as calculated by the addition of Mg^{2+} and Ca^{2+} to represent hardness as $CaCO_3$) can contain significantly different ratios of ions (Soucek and Kennedy 2005).

Accordingly, the development of a standard technique to adjust sulfate toxicity to account for water hardness has proven problematic. As an alternative, this study assessed sulfate toxicity in a test water representative of the ion composition present in the Fitzroy River basin in northeastern Australia where mining is prevalent and water releases of sulfate-rich waters can occur. Although there is an increasing amount of data describing the aquatic toxicity of sulfate to freshwater taxa for North American species (e.g. Elphick et al. 2011; Soucek and Kennedy 2005), there remains a lack of data for species in northeastern Australia. This study assessed the toxicity of sulfate to six aquatic species relevant to northeastern Australia with the aim of developing water quality guidelines for sulfate. Test exposures were representative of the ionic composition of the Fitzroy River basin. Test species used were relevant to this region of subtropical Australia. The advantage of using a test water representative of natural waters is that such an approach allows the effect of sulfate to be determined when sulfate is added in a test solution that reflect the background concentrations of major ions present as a mixture. This adds greater environmental realism to test results and prevents the need for adjustment of toxicity data according to water hardness or the concentration of other ions present.

MATERIALS AND METHODS

Toxicity testing

Sodium sulfate (Na_2SO_4) was identified as a suitable salt to evaluate sulfate toxicity. Previous studies have demonstrated that Na^+ is not a major contributor to the toxicity of salt solutions (Mount et al. 1997), and preliminary studies that compared the relative toxicities of potassium, magnesium, calcium and sodium sulfate salts confirmed the relatively low contribution of the Na^+ ion to sulfate toxicity (Dunlop 2013). To account for background water hardness, Na_2SO_4 was added to a test solution with an ionic composition representative of surface water in the Fitzroy River basin. Test solutions were prepared by adding analytical grade dry salts to Milli-Q® water using approaches described in Dunlop et al. (2015). The concentration of Mg^{2+} was held below 2.5 mg/L to avoid the potential for Mg^{2+} related toxicity (van Dam et al. 2010). The relative proportions of major ions (as percentage of mEq/L) of the test water were: 23% Na^+, 21.1% Ca^{2+}, 5.4% Mg^{2+}, 0.6% K^+, 16.3% HCO_3^-, 28.1% Cl^-, and 5.6% SO_4^{2-}.

Toxicity test data were generated for six species that occur in subtropical Australia. Species tested included: *Pseudokirchneriella subcapitata* – a ubiquitous freshwater microalga universally used for toxicity testing; *Lemna disperma* – a freshwater plant found in Australian temperate and subtropical freshwater bodies; *Ceriodaphnia dubia* (occasionally referred to as *C.* cf. *dubia* or *C. dubia sensu stricto*) – a temperate zooplankton originally isolated from waters near Sydney, Australia, but with wide distribution throughout temperate and subtropical Australia; *Melanotaenia splendida* – an Australian fish found in northeastern and central Queensland including the Fitzroy River basin (Allen et al. 2003); *Paratya australiensis* – a common freshwater shrimp found extensively in parts of eastern Australia; and *Atalophlebia* sp. AV13 – a mayfly that is found in many parts of eastern Australia including in the Fitzroy River basin and southeast Queensland. The species *Atalophlebia* sp. AV13 (Dean 1999) has not been officially described. Baker et al. (2004) recognised it as a complex of at least 3 lineages while Dean (2011) noted at least five biological species have been recognised by molecular methods. To date, morphological methods only enable the taxon *Atalophlebia* sp. AV13 to be recognised.

Details of toxicity test methods are provided in Table 1. For the tests with *C. dubia*, the test water was diluted to 50% with dilute mineral water (DMW) because of reduced survival of *C. dubia* above this concentration. Dilute mineral water is typically 20% Perrier Water® (France) diluted with filtered Sydney tap water according to Bailey et al. (2000). Similarly, tests with *L. disperma* required dilution to 50% with Swedish Institute (SIS) medium (OECD 2006). To ensure survival of *M. splendida* (rainbowfish), and *P. australiensis* (freshwater shrimp), the dilution waters were adjusted by 50% with DMW. No dilution was necessary for the *P. subcapitata* (microalga) test. The 7-d chronic tests with *P. subcapitata,* and *C. dubia* required feeding and daily test water renewals. All other tests were conducted as static non-renewal tests.

Chemical analyses

For all tests, temperature, pH, dissolved oxygen (DO) and electrical conductivity (EC) were measured at test initiation. The concentration of sulfate was confirmed for all test solutions. The concentration of sulfate was calculated from the sulfur concentrations determined by inductively coupled plasma (ICP) method. Chemical analyses associated with mayfly tests were undertaken in the University of Queensland Waters Laboratory in accordance with the APHA 3120B and remaining analyses were undertaken at Envirolab Pty. Ltd., Chatswood, New South Wales (NATA accreditation number 2901) in accordance with APHA 21st Ed.

Table 1. Details of toxicity tests for six Australian freshwater species used to assess the toxicity of sodium sulfate.

Species	Test duration and type	Acceptability criteria for controls	Temperature, light intensity, photoperiod	Test medium	No. replicates (Individuals per replicate)	Static/daily renewals	Protocol
Pseudokirchneriella subcapitata	72-h growth inhibition (chronic)	>16.0x10^4 cells/mL	25±1°C; 4300 lux; 24 h light	Fitzroy composition	4 reps (10 000 cells/mL) and a blank	static	Based on U.S. EPA (2002), Stauber et al. (1994) and NIWA (1998)
Lemna disperma	7-d growth inhibition (chronic)	Frond doubling time <2.5 days	25±2°C; 4300 lux; 24 h light	Fitzroy composition amended with Swedish Institute medium (50%)	4 reps (3 fronds / replicate)	static	OECD (2006)
Ceriodaphnia dubia	48-h immobilisation (acute)	>90% survival	25±1°C	Fitzroy composition amended with DMW[a] (50%)	4 reps (5 neonates / replicate)	static	Modified from Bailey et al. (2000) and U.S. EPA (2002)
Ceriodaphnia dubia	7-d three brood survival and reproduction (chronic)	≥80% non-immobilised. An average of ≥15 young per non-immobilised female. 60% of non-immobilised cladocerans must produce ≥3 broods.	25±1°C	Fitzroy composition amended with DMW[a] (50%)	10 reps (1 neonate /replicate)	daily renewals	U.S. EPA (2002)
Melanotaenia splendida	96-h larval fish imbalance (acute)	>90% survival	25±1°C	Fitzroy composition amended with DMW[a] (50%)	4 reps (5 larval fish /replicate)	static	Based on U.S. EPA (2002)
Paratya australiensis	96-h juvenile shrimp survival (acute)	>80% survival	25±1°C	Fitzroy composition amended with DMW[a] (50%)	4 reps (5 shrimp / replicate)	static	Based on U.S. EPA (1996)
Atalophlebia sp. AV13	96-h survival (acute)	>90% survival	25 ±2°C.	Fitzroy composition	3 reps (10 mayfly nymphs / replicate)	static	Based on ASTM E729-96 (2007).

[a] *DMW: Dilute mineral water.*

Data analyses

For the purpose of deriving point estimates of toxicity (i.e. EC10 data), regression analyses were performed with ToxCalc™ (ver. 5.0.23F, Tidepool Scientific Software). The ToxCalc™ program uses Trimmed Spearman-Karber analysis (Hamilton et al. 1977), Maximum Likelihood Probit analysis (Finney 1971) or Log-Logit Interpolations (U.S. EPA 2002) as defined in ToxCalc. ECx values for *Atalophlebia* sp. AV 13 were determined from a logistic regression using R version 2.15.2 (Venables and Ripley 2002). In all instances, ECx values and associated 95% upper confidence limits were calculated on the basis of the measured concentrations of SO_4^{2-} at the commencement of toxicity tests.

Species Sensitivity Distribution (SSD)

Toxicity data were used to derive a toxicity guideline value based on a distribution of observed species sensitivities (Species Sensitivity Distribution (SSD)) in accordance with ANZECC and ARMCANZ (2000). For the construction of an SSD, EC10 data were used as they are considered statistically reliable estimates of the concentration at which no effect occurs (Warne and van Dam 2008; Warne et al. 2014). Because both acute and chronic data were obtained from the toxicity tests, it was necessary to convert the acute toxicity data to chronic data by applying an acute to chronic ratio (ACR). The ACR was obtained using the EC10 data generated for the acute cladoceran survival test and the EC10 data generated in the chronic 3-brood cladoceran reproduction test, and calculated as:

$$\text{ACR} = \frac{\text{EC10 (acute)}}{\text{EC10 (chronic)}}$$

Application of the ACR derived from a single species of invertebrate to determine chronic equivalent estimates for three species (fish, mayfly and shrimp) assumes that the ACRs observed between species will be largely similar.

The methods for deriving guidelines for toxicants in the Australian and New Zealand guidelines (ANZECC and ARMCANZ 2000) and revised by Warne et al. (2014; 2015) stipulate that at least five species from at least four taxonomic groups (at the level of phylum) be used to derive a guideline value. Where the number of test species used for the construction of an SSD is greater than eight, the ANZECC and ARMCANZ (2000) guidelines suggest using a Burr Type III distribution, and where the number of test species is less than eight, a log-logistic regression is appropriate. Given only six data points were available, an SSD was constructed using log-logistic regression but results must be treated with caution due to the low number of data available. The SSD and associated guideline values were calculated using Burrlioz 2.0 software (CSIRO 2015) in accordance with the ANZECC and ARMCANZ (2000) recommendations.

The SSD was used to derive toxicity guideline values at 80, 90, 95 and 99% species protection levels for sulfate in the Fitzroy River basin. This range of aquatic ecosystem protection values is recognised under the ANZECC and ARMCANZ (2000). Guideline values are reported with respective upper 95th and lower 5th percentile confidence intervals.

RESULTS AND DISCUSSION

Toxicity testing of sodium sulfate

The results of toxicity testing of Na_2SO_4 to the suite of species and end-points tested are shown in Table 2. Results showed that the chronic *C. dubia* test was the most sensitive. The concentration that caused reduced reproductive output (EC10) over three broods was 826 mg/L SO_4^{2-}. The least

sensitive test was the larval fish test, in which 8202 mg/L SO_4^{2-} was required to induce imbalance in 10% of larval fish. The ACR for *C. dubia* EC10 data (SO_4^{2-} concentrations) was EC10 acute/EC10 reproduction = 1124/826 = 1.36. The acute juvenile fish imbalance and prawn survival EC10 values were then converted to chronic equivalents by dividing the acute EC10 sulfate concentrations by 1.36. Chronic EC10 estimates of toxicity used to derive a sulfate guideline value are shown in Table 2. This ACR is comparable to ACR values derived from sulfate toxicity studies on *Ceriodaphnia dubia* and fathead minnow *Pimephales promelas* reported in Elphick et al. (2011). ACRs from that study were 1.17 for *P. promelas* and 1.92 for *C. dubia*. Both are also comparable to the ACR for *C. dubia* (1.7) derived as part of a site-specific study of sulfate toxicity for the McArthur River Mine (Hydrobiology 2012). As this ACR is based on observations of sulfate toxicity and aligns with reported ACR for fish, it was used in preference to the standard ACR of 10, which is recommended as the default approach in national guidelines for Australia (ANZECC and ARMCANZ 2000). However, the use of an ACR such as this is suboptimal and it is recommended that future studies evaluate chronic effects of sulfate. As the dataset used to derive the SSD is a mix of chronic and acute data converted to chronic, the resultant guideline values are deemed moderate reliability guideline values under national water quality guidelines (ANZECC and ARMCANZ 2000).

To provide test organisms with trace elements necessary for survival, it was necessary to amend test solutions with culture medium to ensure test acceptability criteria in control treatments. This is likely to result in some variation in the ionic composition tested, though it is assumed that such variation would be small and unlikely to influence overall guideline values. To avoid the necessity of making these amendments, Mann et al. (2014) formulated test solutions such that the essential elements were included into the ion profile. Such an approach is recommended for future testing.

Species Sensitivity Distribution and guideline derivation

The SSD (Figure 1) was generated using actual and ACR-converted chronic EC10 data. Moderate reliability toxicity guideline values for SO_4^{2-} for six species at 80%, 95%, 90% and 99% species protection levels are shown in Table 3. The sulfate guideline for the protection of 95% of species was found to be 545 (380-1103) mg/L SO_4^{2-}.

Comparison with existing guidelines

The guideline values for sulfate derived in this study are applicable to waters with ionic compositions observed in the Fitzroy River basin. A comparison was made between the guideline values derived in

Table 2. Results (EC10s) of sulfate ecotoxicity testing presented as concentrations of sulfate. Chronic EC10 estimates were derived from acute test results using the acute to chronic ratio of 1.36 obtained from the *C. dubia* toxicity tests. NC = figure not calculated.

Test species, duration and end-point tested	Test	EC10 mg/L SO_4^{2-} (95% confidence limits)	Chronic EC10 estimates mg/L SO_4^{2-}
Paratya australiensis	acute	2805 (1894-3390)	2063
Melanotaenia splendida	acute	8202 (7503-8483)	6030
Atalophlebia sp. AV13	acute	1488 (421-2556)	1094
Lemna disperma	chronic	1250 (98-1373)	NC
Pseudokirchneriella subcapitata	chronic	1539 (1079-1602)	NC
Ceriodaphnia dubia	acute	1124 (806-1360)	NC
Ceriodaphnia dubia	chronic	826 (224-1137)	NC

this study and those previously derived in the Northern Hemisphere. This comparison was made using the same regression equations as used in the present study. Specifically, toxicity data from Elphick et al. (2011) were used to generate an SSD using the Burrlioz software version 2.0 (CSIRO 2015). The study by Elphick et al. (2011) reported five EC10 data points for four species at a hardness of 320 mg/L. The resultant log-logistic regression was used to calculate a 95% species protection value of 402 (182-1120) mg/L SO_4^{2-}. Although this value was slightly more conservative than the 95% species protection value derived in this study of 545 (380-1103) mg/L SO_4^{2-} at a higher hardness of 550 mg/L (as $CaCO_3$), estimates had overlapping confidence intervals. The guideline derived in the present study was also higher than the sulfate guideline of 429 mg/L SO_4^{2-} for very hard water (181-250 mg/L $CaCO_3$) derived for BC (Meays and Nordin 2013). However, the water hardness in the present study was again greater than the range for which the BC guideline applies. Where hardness is >250 mg/L SO_4^{2-} the BC guideline value would not apply, and site specific

Table 3. Moderate reliability toxicity trigger values (TVs) for sulfate at various levels of species protection (80-99%), based on chronic EC10 values for six species.

Level of species protection	Moderate reliability TVs mg/L SO_4^{2-} (95% confidence limits)
80%	936 (731-1548)
90%	706 (521-1242)
95%	545 (380-1103)
99%	307 (161-866)

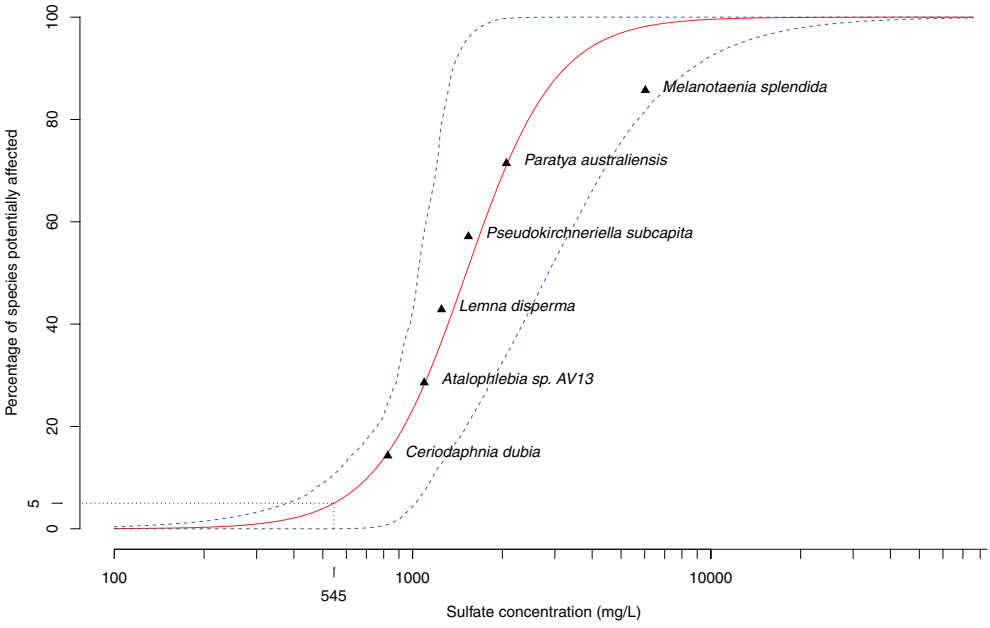

Fig. 1. Species Sensitivity Distribution (SSD) generated using BurrliOZ as a log logistic regression (r^2 = 0.88, slope = 3, df = 4) for sulfate using chronic EC10 estimates of toxicity for six species. The curve shows the cumulative percentage of species affected in response to increasing sulfate concentration. The y axis shows the percent of species affected; the solid line is the SSD; and the dashed lines are the upper and lower 95th and 5th percentile confidence intervals.

guidelines would need to be derived (Meays and Nordin 2013). Lastly, compared with the sulfate guideline from the U.S. State of Iowa (IDNR 2009) of 2000 mg/L (for a water hardness of greater than 500 mg/L and a chloride concentration of waters greater than or equal to 5 mg/L) the sulfate guideline presented here for the Fitzroy River basin is considerably more conservative.

CONCLUSIONS

The literature suggests that hardness affects sulfate toxicity. It has also been suggested that calcium and chloride may influence its toxicity. Although the mechanisms behind these interactions are not well understood, there is a clear need to account for water hardness and the presence of other ions when deriving guidelines. Observed differences between the responses of different species to sulfate under conditions of varying water hardness have made it difficult to account for ionic composition. The approach used here to define toxicity test exposures according to observed surface water ion composition allows the background water hardness, calcium concentration and concentration of other major ions to be built into toxicity tests. Such an approach provides environmentally realistic test conditions and the resultant data accounts for potential toxicity modification from background ionic composition. However, a disadvantage of this approach is that resultant guideline values relate only to the surface water used to define them at the catchment scale and they are not likely to be applicable to other water types, although, considering that the species tested have distributions wider than the Fitzroy River basin, the study has implications that extend outside this catchment to areas where the ionic composition is similar. For exposure scenarios with differing water hardness and ionic composition, further testing to evaluate the potential interactive effects of anions and cations in solution to assess toxicity is recommended. Such testing should evaluate sulfate toxicity in a greater range of natural waters where sulfate rich water releases occur. The data set used to derive the guidelines presented here was limited to six species and an ACR derived from a single species was assumed to be representative of three taxa. This was considered valid as this ACR was similar to those observed in comparable studies. As an ACR provides an estimate of likely chronic response, it is recommended that further data collection be undertaken using chronic test end-points to support the derivation of high reliability guidelines. Such testing should evaluate the toxicity of sulfate to a wide range of taxa using chronic end-points and, of course, where site-specific guidelines are required, there remains a need to undertake local studies using site water and sensitive endemic test organisms.

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