



# Metal speciation and potential bioavailability changes during discharge and neutralisation of acidic drainage water



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## HIGHLIGHTS

- Discharge of acid drainage from farm irrigation areas represents a risk to ecosystem health.
- Rapid precipitation of Al and Fe increases removal of other metals from dissolved phase.
- Many dissolved metals in labile and potential bioavailability forms.
- Similar factors controlling the dissolved concentrations (pH, dilution and mixing time).
- Water quality guideline exceedance is unlikely for drainage waters dilution to 1%.

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## ABSTRACT

The discharge of acid drainage from the farm irrigation areas to the Murray River in South Australia represents a potential risk to water quality. The drainage waters have low pH (2.9–5.7), high acidity (up to 1190 mg L<sup>-1</sup> CaCO<sub>3</sub>), high dissolved organic carbon (10–40 mg L<sup>-1</sup>), and high dissolved Al, Co, Ni and Zn (up to 55, 1.25, 1.30 and 1.10 mg L<sup>-1</sup>, respectively) that represent the greatest concern relative to water quality guidelines (WQGs). To provide information on bioavailability, changes in metal speciation were assessed during mixing experiments using filtration (colloidal metals) and Chelex-lability (free metal ions and weak inorganic metal complexes) methods. Following mixing of drainage and river water, much of the dissolved aluminium and iron precipitated. The concentrations of other metals generally decreased conservatively in proportion to the dilution initially, but longer mixing periods caused increased precipitation or adsorption to particulate phases. Dissolved Co, Mn and Zn were typically 95–100% present in Chelex-labile forms, whereas 40–70% of the dissolved nickel was Chelex-labile and the remaining non-labile fraction of dissolved nickel was associated with fine colloids or complexed by organic ligands that increased with time. Despite the different kinetics of precipitation, adsorption and complexation reactions, the dissolved metal concentrations were generally highly correlated for the pooled data sets, indicating that the major factors controlling the concentrations were similar for each metal (pH, dilution, and time following mixing). For dilutions of the drainage waters of less than 1% with Murray River water, none of the metals should exceed the WQGs. However, the high concentrations of metals associated with fine precipitates within the receiving waters may represent a risk to some aquatic organisms.

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## 1. Introduction

Submerged soils and sediments are frequently observed to accumulate pyritic (FeS<sub>2</sub>) phases as a result of the sulfate reduction that occurs naturally through microbial respiration of organic carbon (Dent and Pons, 1995). When undisturbed and covered with

water, the pyrite poses little or no threat of acidification, however considerable oxidation and generation of acidity can occur when pyrite is exposed to the air (Bronswijk et al., 1993; Dent and Pons, 1995). The rewetting of oxidised acid sulfate soils may release significant quantities of metals to associated water (Cook et al., 2000; Simpson et al., 2010; Nystrand et al., 2012).

Drought conditions and long-term low inflows in the Murray-Darling Basin system from 2006 to 2010 led to unprecedented low water levels in the lower river reaches in South Australia

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(Mosley et al., 2012). During April 2009, the river water level fell to ~1.75 m below average long-term levels and exposed large areas of soils to prolonged drying and desiccation, which resulted in the oxidation and acidification of previously submerged acid sulfate soils in the Lower Murray Reclaimed Irrigation Area (LMRIA). Since late 2010, water levels have recovered in the Lower Murray, irrigation has recommenced in some areas, and the drought-affected soils have been rewetted. Acidic drainage waters with pH 2–5 are now being returned (via large drainage pumps) to the Murray River from a range of irrigation areas in the LMRIA (EPA, 2013). The low pH and high concentrations of soluble and potentially toxic metals within the drainage waters posed risks to aquatic ecosystems and drinking water off-takes in the river.

The risk posed by the acid drainage water discharges to the Murray River ecosystem will be strongly influenced by the form and fate of the metals and metalloids during mixing (Gundersen and Steinnes, 2003; Balistrieri et al., 2007; Nordstrom, 2011; Cresswell et al., 2013). Upon discharge and mixing with the river water alkalinity, pH neutralisation reactions can be expected to result in the flocculation and precipitation of a considerable portion of many of the metals, and adsorption of other metals or metalloids onto these new solid phases (Gundersen and Steinnes, 2003; Balistrieri et al., 2007; Lee and Faure, 2007; Schemel et al., 2007). Previous studies have observed a high degree of colloid formation, e.g. 75% for aluminium (Gundersen and Steinnes, 2003; Schemel et al., 2007) and ~40% for iron (Schemel et al., 2007) following mixing of acid-drainage waters with ambient waters. However, those studies were for acid-mine drainage, where the dissolved organic carbon (DOC) concentrations were much lower ( $0.2\text{--}2\text{ mg L}^{-1}$ ) than the  $10\text{--}40\text{ mg L}^{-1}$  range in the LMRIA acid drainage. It was unclear whether metals in the LMRIA acid drainage would show similar behaviour and potential bioavailability compared to acid-mine drainage sites.

The speciation of the metals in the dissolved phase will influence their bioavailability and the hazard posed. This may be mediated by other cations that compete for metal binding sites, by metal complexation by organic ligands, and by metals in colloidal forms (van Dam et al., 2008; Fortin et al., 2010; Gandhi et al., 2011). Australia's water quality guidelines (WQGs) for the protection of aquatic ecosystem health were derived using species sensitivity distributions of chronic no observed effects concentrations (NOECs) or 10% chronic effect concentrations (EC10's) derived predominantly from laboratory-based bioassays on solutions of metals in highly labile and bioavailable forms, e.g. predominantly as free metal ions (e.g.  $\text{M}^{2+}$ ) or weak and labile inorganic metal complexes, with negligible strong metal–ligand complexes that are kinetically non-labile such as metal complexes with humic or fulvic acids (ANZECC/ARMCANZ, 2000). In the application of the WQGs, when there is evidence that, in the test waters, a significant portion of the total dissolved concentration is present in forms that are not considered bioavailable (e.g. non-labile strong metal–ligand complexes that occur with humic and fulvic acids and or colloid-associated metals), it is appropriate to make the WQG comparison with just the labile fraction (determined either by measurement or modelling). In the case of acidic drainage waters entering the Murray River, the proportions of dissolved metals in bioavailable forms are expected to vary both spatially and temporally. Under acid conditions, free metal ion concentrations are higher, but under more neutral conditions, complexation becomes important as does the association with precipitating iron oxyhydroxides, reducing bioavailability.

The persistence and severity of the acid drainage in the LMRIA has created considerable challenges to management agencies. To address these risks, this study investigated the fate and forms of metals and metalloids following dilution and neutralisation of the drainage water with river water. The changes in metal concentrations and speciation (e.g. complexed or colloidal forms) as acidic

drainage waters undergo neutralisation with river water were investigated and the potential for ecological effects assessed.

## 2. Material and methods

### 2.1. Study area

The LMRIA comprises approximately 5200 hectares of flood irrigated agriculture protected by a levee bank system on the former floodplain of the Murray River in South Australia, between the townships of Mannum and Wellington (Fig. 1). The irrigation channels are typically 1.0–1.5 m below the normal river pool level (+0.75 m Australian Height Datum), enabling gravity fed flood irrigation. The drainage waters within the channels are returned to the river using large pumps (Mosley and Fleming, 2010) (see conceptual model in Fig. S1 of the Supplementary information). The region contains important aquatic ecosystems and is immediately upstream of Coorong-Lower Lakes system which is collectively recognised as one of Australia's most significant ecological assets and a wetland of international importance (Ramsar-listed).

### 2.2. Sample collection

The LMRIA sites chosen for analysis were Toora, Mobilong, Long Flat, Woods Point and Wellington (at the ends of Jervois) (Fig. 1). Murray River water was collected from the Thiele Reserve in Murray Bridge to be used as the diluent in for drainage water dilutions. The Supplementary information section provides GPS coordinates of the sites (Table S1). The water pH, temperature, specific electrical conductivity (EC), redox potential (ORP), dissolved oxygen (DO) concentration, total dissolved solids (TDS) were measured at the time of sampling using a calibrated water quality probe (YSI 556). Alkalinity and acidity ( $\text{mg L}^{-1}\text{ CaCO}_3$ ) were measured in the field using a test kit (HACH Model AL/AC-DT,  $\text{mg L}^{-1}\text{ CaCO}_3$  can be converted to  $\text{meq L}^{-1}$  by dividing by 50).

Water samples for analyses of trace metals and metalloids were collected from all locations on March 22, 2012, using strict protocols to avoid sample contamination (Ahlers et al., 1990). Deionised water (18 M $\Omega$  cm, Milli-Q, Millipore) and high-purity acids (Tracepur, Merck, Darmstadt, Germany) were used for washing of bottles (Nalgene, LDPE) and filters and for sample acidification. All plastic ware was acid-washed by soaking for >24 h in 10% v/v  $\text{HNO}_3$ , then rinsing with copious amounts of deionised water (Milli-Q) before drying in a laminar-flow cabinet (Clyde-Apac, HWS Series) prior to use.

All samples were collected in acid-washed low-density polyethylene (Nalgene) bottles (1 L bottles and 5 L carboys). Field duplicates and field blanks were included as part of the water sampling program. Following collection, the water samples were transported to the laboratory in ice-filled cooler boxes and then stored at 4 °C. Water filtration through 0.45- $\mu\text{m}$  membrane filters was undertaken in a Class-100 cleanroom laboratory as described in Cresswell et al. (2013). This involved the use of acid-washed 0.45  $\mu\text{m}$  membrane filters (Millipore HA, mixed cellulose esters) and polycarbonate filter unit (Sartorius). Samples for dissolved metals or metalloid analyses were preserved in 0.2%  $\text{HNO}_3$ , dissolved organic carbon (DOC) preserved in 0.4%  $\text{H}_2\text{SO}_4$ , and samples for alkalinity, major ions and labile metal analyses contained no preservatives. All sample bottles and containers were stored in plastic bags and refrigerated in the dark.

### 2.3. General methods

All glass and plasticware for analyses were usually new and were cleaned by soaking in 10% (v/v)  $\text{HNO}_3$  (BDH, Analytical

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