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Near shore groundwater acidification during and after a hydrological drought in the Lower Lakes, South Australia

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ABSTRACT

An extreme hydrological drought in the Lower Lakes of the Murray–Darling Basin (Ramsar listed site) resulted in exposure of large areas of lake bed (25% of pre-drought lake area), containing the reduced iron (Fe) sulfide mineral pyrite. The pyrite oxidised and the resulting acidification ($pH < 4$) posed risks of acid and metals entering shallow groundwater and potentially discharging to the remaining lake water body. Piezometer transects were installed at four locations and monitoring of the groundwater levels and quality was undertaken for six years from 2009 (drought) to 2014 (4 years post-reinundation). Acidic (pH 3–5) groundwater was recorded at three of the four piezometer locations and included sites close to the lake water. The acidic groundwater (0.5–2 m below lake bed) at these sites is likely to have originated from the transport of acid from the upper oxidised sediment layer formed during the drought. High soluble metal (Fe, Al, Mn) levels were also recorded at acidic locations. Acidic shallow groundwater has persisted at many sites for over 4 years following reinundation post-drought, and is likely due to slow diffusion and limited sulfate reduction. Increases in dissolved Fe and Mn with decreases in redox potential suggest that reductive dissolution of Fe and Mn hydrous oxides and Fe oxy-hydroxysulfate minerals (e.g. jarosite) occurred post-drought. Groundwater hydraulic head gradients were low, indicating there was limited potential for groundwater to discharge to the lake. The hydraulic gradients at all locations were dynamic with complex relationships along the near-shore environment. The results highlight the long lasting and severe effects on groundwater that can occur following hydrological drought in aquatic environments with sulfidic sediments.

1. Introduction

It is predicted that the frequency and intensity of droughts will increase, especially in arid and semi-arid areas, as climate change affects patterns of rainfall and the availability of water across different environments (IPCC, 2008, 2011; Vörösmarty et al., 2000; Sahagian, 2000; Vörösmarty and Sahagian, 2000). Droughts can place extreme stress upon river and lake environments and have been shown to result in negative and long lasting water quality impacts (Hipsey et al., 2014; Hopkin, 2007; Tweed et al., 2009, 2011; Mosley et al., 2012; van Vliet and Zwolsman, 2008). Often the negative water quality impacts of drought are exacerbated when the system is already experiencing stress from long-term, catchment-wide unsustainable water uses (Mosley et al., 2012).

Australia's largest river catchment system, the Murray–Darling Basin, experienced a major hydrological drought from 2006–2010. The system recorded the lowest flows in 100 years, due to the combination of decreased rainfall and a long-term

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over allocation of water resources in the river system, with the water levels of Lake Alexandrina and Lake Albert in South Australia (known collectively as the Lower Lakes — Fig. 1) retreating to their lowest levels in over 90 years of records (Fig. 2).

From 2007 to 2009 the water level in Lake Alexandrina declined approximately 2 m from a pre-drought average of +0.7 m AHD, to the lowest recorded level of −1.2 m AHD and −0.5 m AHD in Lake Albert in April 2009. The degree of water level drop was less severe in Lake Albert due to the construction of an artificial bund at the entrance to Lake Albert at Narrung. As the lakes receded, approximately 209 km^2 of marginal shoreline and embayments dried out completely (Mosley et al., 2014a). The exposure of the shoreline and lake beds presented a severe risk to the local environment due to the widespread presence of acid sulfate soils. Acid sulfate soils are those soils which have accumulated iron sulfide minerals (predominantly pyrite) and may acidify (pH < 4) if they are exposed to air and insufficient neutralising capacity (carbonates) is present (Fitzpatrick et al., 2010). These soils occur naturally when sulfate is reduced by heterotrophic bacteria to sulfide which reacts with metals (usually Fe) to form sulfide minerals (Fitzpatrick et al., 2010). Soils with high pyrite content are harmless when submerged and undisturbed, but when exposed to oxygen react to form sulfuric species with pH < 4, via the following overall general reaction (Dent, 1986):

$$FeS_{2(s)} + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_{3(s)} + 2SO_4^{-2} + 4H^+ . (1)$$

There were concerns that Lake Alexandrina and Lake Albert would experience severe and catastrophic acidification events resulting from the discharge of the sediment acidity to the remaining lake water (see conceptual model — Fig. 3). Indeed, there was severe and rapid surface water acidification of many localised areas on the lake margins when re-inundation occurred (Mosley et al., 2014a). While there have been a few reports of groundwater acidification following sulfide oxidation during drought (Appleyard and Cook, 2009; Mosley et al., 2014b,c), direct acidification of groundwater and associated risks under a drying lake bed has, to our knowledge, not been previously reported.

The aim of this paper is to describe the changes in hydrogeochemical processes in shallow groundwater that occurred during and following a drought induced exposure of acid sulfate soils in the Lower Lakes of the Murray–Darling Basin. The results are widely applicable to other shallow lake systems where sulfidic sediments have accumulated and highlight the

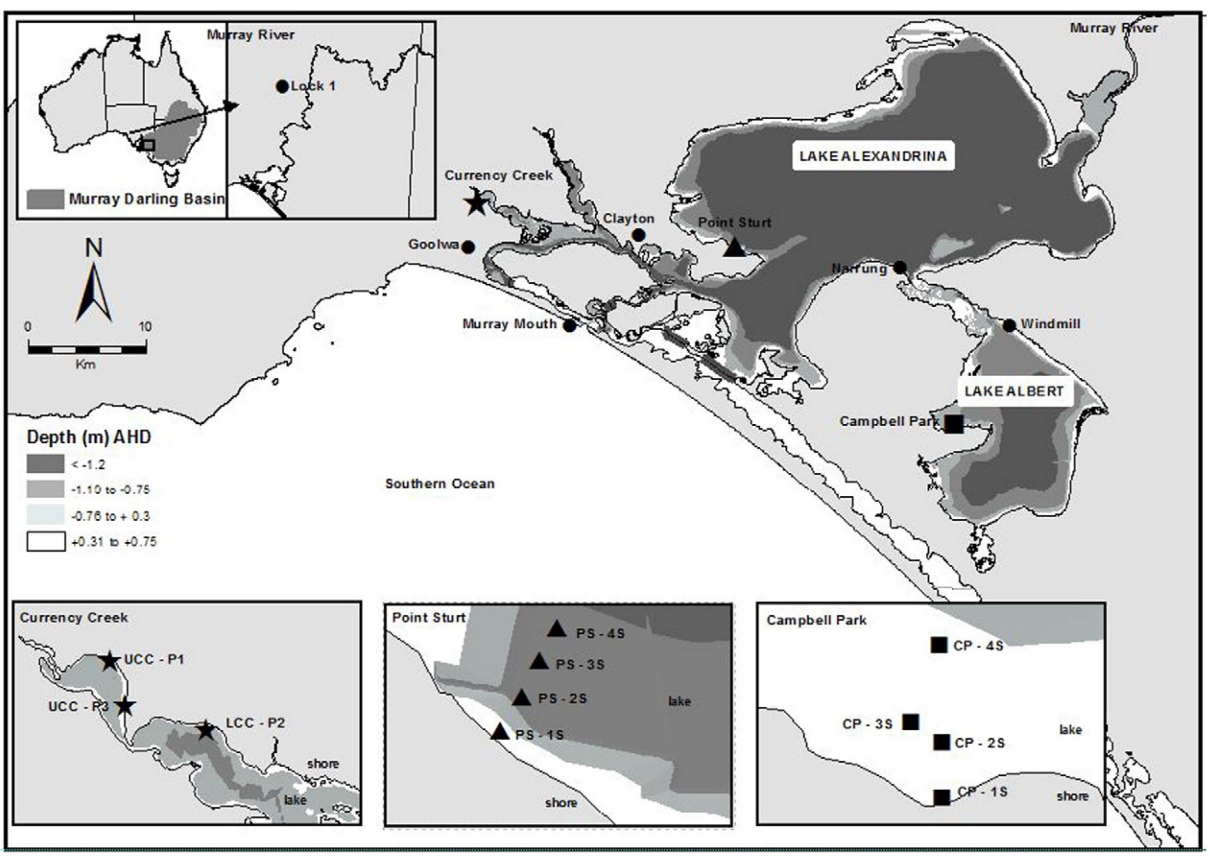

Fig. 1. Study site locations showing regional location, and piezometers sites. Piezometers are spaced 75 m apart a transect perpendicular to the shoreline at Point Sturt, and 50 m apart at Campbell Park. Currency Creek consists of 3 single piezometers positioned along the shoreline. The bathymetry at each site is shown in the site boxes in order to indicate the shoreline during the drought (Lake Alexandrina was at −1.3 m AHD, Lake Albert was at −0.75 m AHD and Currency Creek was at +0.3 m AHD) and post drought (Lower Lake summer water level (2016) is +0.56).