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Geochemical processes following freshwater reflooding of acidified inland acid sulfate soils: An in situ mesocosm experiment

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ABSTRACT

In their oxidised form, inland acid sulfate soils (IASS) with sulfuric horizons (pH $\leq$ 3.5) contain substantial acidity and pose a number of threats to surrounding ecosystems. In their reduced form, IASS with sulfidic material are relatively benign. Freshwater reflooding has the potential to return oxidised IASS with sulfuric horizons to a reduced and benign state. This study uses mesocosms installed in situ to simulate reflooding in two sulfuric IASS profiles, one sandy textured and the other a cracking clay, and to document key geochemical consequences resulting from their reflooding. During the assessed period of 200 days of subaqueous conditions, reducing conditions were established in parts of the former sulfuric horizons in both the sandy textured and clayey textured IASS. In the permeable sandy IASS, acidity was removed from the sulfuric horizon and displaced downward in the profile by advective piston flow, and thus not completely neutralised. The removal of acidity away from the soil surface was critical in preventing surface water acidification. In contrast, solute transport in the less permeable clayey IASS was diffusion dominated and acidity was not removed from the sulfuric horizon following reflooding and no increase in pH was observed. In the absence of piston flow, a diffusive flux of acidity, from the soil to surface water, resulted in surface water acidification. In the acidic porewaters of the reflooded sulfuric horizons, results indicated dissolved aluminium was controlled by an aluminium species with stoichiometry Al:OH:SO_4 (e.g. jurbanite). In the same acidic porewaters, iron and sulfate activity appeared to be regulated by the dissolution of natrojarosite. Following the establishment of reducing conditions, the reductive dissolution of natrojarosite and schwertmannite was responsible for large increases in total dissolved iron. We did not observe any indirect evidence indicating the existence of sulfate reduction during the assessed period. It is likely that insufficiently reducing conditions, competitive exclusion by iron-reducing bacteria, and persisting low pH inhibited sulfate reduction during the assessed period. With insufficient in situ alkalinity generation, IASS are likely to continue to pose an environmental hazard following reflooding and remediation is likely to be slow. A number of geochemical processes involved in the remediation of sulfuric horizons were observed in this study. The key geochemical and physical processes affecting porewater chemistry, in particular Fe and Al, are summarised in a conceptual hydrogeochemical model, so that observations made in this study may be applied to other regions containing IASS with sulfuric horizons that are expected to be reflooded with freshwater.

1. Introduction

In Australia, inland acid sulfate soil (IASS) coverage is estimated at 157,000 km^2, which is substantially greater than the estimated 58,000 km^2 of acid sulfate soils located in Australia's coastal environments (Fitzpatrick et al., 2008a). Many of the IASS found in Australia are in the lakes, wetlands and river banks of the Murray–Darling Basin (MDB) (Creeper et al., 2013; Fitzpatrick et al., 2009). Inland acid sulfate soils are soils that contain, or are affected by transformations of sulfide minerals (e.g. pyrite, FeS_2) (Dent and Pons, 1995; Soil Survey Staff, 2014). In their reduced state, IASS consist of sulfidic materials (pH > 3.5) which contain iron sulfide minerals (e.g. pyrite, FeS_2), formed by the microbially catalysed reduction of Fe(III) and SO_4^{2-} (Eq. (1), overall reduction reaction). On exposure to air, the pyrite contained in sulfidic materials oxidizes, resulting in severe soil acidification and the formation of sulfuric horizons (pH $\leq$ 3.5), especially where the soils have limited acid neutralising capacity (Eq. (2), overall oxidation reaction). A sulfuric horizon comprises a soil material $\geq$15 cm thick, with a pH $\leq$ 3.5 and evidence that the low pH value is caused by sulfuric acid

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Abbreviations: AHD, Australian height datum; bgl, below ground level; CLLMM, Coorong, Lower Lakes and Murray Mouth; IASS, inland acid sulfate soils; MDB, Murray–Darling Basin; RIS, reduced inorganic sulfur; SI, saturation index; SWI, sediment–water interface; XRD, X-ray diffraction.

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from pyrite oxidation (Soil Survey Staff, 2014). A further consequence of severe soil acidification is the mobilisation of Fe, Al and other contaminants into porewaters, and often into nearby surface waters (Astrom, 2001). At the time of this study, drought conditions in the MDB of Australia had led to the decline of water levels in the Lower Lakes region, and the exposure of IASS that had previously been submerged for a continuous period of time, ~100 years. Once exposed, ca. 200 km^2 of IASS in the Lower Lakes severely acidified due to the oxidation of pyrite accumulated during this period and formed sulfuric horizons (Fitzpatrick et al., 2010).

$$15CH_2O + 8SO_4^{2-} + 4FeOOH + 16H^+ = 15CO_2 + 4FeS_2 + 15H_2O \quad (1)$$

$$FeS_2 + {}^{15}/_{4}O_2 + {}^{7}/_{2}H_2O = Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+. \quad (2)$$

The freshwater reflooding of IASS with sulfuric horizons (pH ≤ 3.5) can be natural (e.g. climate driven, such as the break of a drought) or management driven (e.g. for the purpose of remediation). The freshwater reflooding of severely acidified IASS has the potential to provide an effective means of remediation through (a) preventing further pyrite oxidation by minimising the ingress of oxygen into the soils via inundation (b) neutralising acidity by introducing an external source of alkalinity (i.e. surface water alkalinity), and (c) establishing the reducing conditions necessary to promote alkalinity generating geochemical reactions and the reformation of pyrite (Anderson and Schiff, 1987). However, many of these hypotheses originate from studies of coastal acid sulfate soils following marine tidal reflooding, which have demonstrated its success as a remediation method (Johnston et al., 2009a, 2009b; Portnoy and Giblin, 1997). Directly applying the conclusions of marine tidal reflooding, without caveats, to freshwater reflooding of IASS would be inappropriate due to differences in geochemical pathways and hydrological scenarios. For example, in the absence of a diurnal tidal cycle, freshwater systems do not have the same continuously regenerative external supply of anions such as HCO_3^- and SO_4^{2-}. A smaller number of studies have shown that freshwater reflooding shows promise as a viable remediation technique (Johnston et al., 2014; Virtanen et al., 2014). However, in the highly acidified IASS systems of the MDB, freshwater reflooding has led to surface water acidification and a heightened risk of ecological damage through persisting periods of low pH, increased metal mobilisation and off-site transportation of acidity and metal(loids) (Baker and Shand, 2014; Creeper et al., 2015; Hicks et al., 2009b; Mosley et al., 2014b; Shand et al., 2010). There remains considerable uncertainty in the rates of recovery and geochemical pathways taken following freshwater reflooding of IASS. The freshwater reflooding of severely acidified IASS has the potential to be a suitable remediation technique for use in ecologically significant wetlands and lakes, such as the Ramsar listed Lower Lakes region (Ramsar Convention, 1998). Many other existing techniques, such as the mechanical application of a neutralising agent, are either not practical or may cause environmental damage. Hence, the continued research of freshwater reflooded IASS is of high importance.

In this study, we used mesocosms installed in situ to monitor the response of IASS with sulfuric horizons, one sandy textured and the other a cracking clay, to freshwater reflooding. The main objectives were to: (i) examine the transport of existing acidity and identify key geochemical transformations of Fe and Al during the initial phase of reflooding, and (b) identify the key physical and geochemical processes that appear to be influencing the likely trajectory towards remediation under continued reflooded conditions. We aim to summarise the identified physical and geochemical processes in a conceptual hydrogeochemical model to explain changes in porewater chemistry, in particular Fe and Al, following freshwater reflooding, so that it can be applied to other regions containing IASS with sulfuric horizons that are expected to be reflooded with freshwater.

2. Materials and methods

2.1. Study site location, climate and hydrological history

Point Sturt and Boggy Creek study sites are located in Lake Alexandrina, a part of the Coorong, Lower Lakes and Murray Mouth (CLLMM) region of the MDB, South Australia (Fig. 1). The CLLMM region is a Ramsar listed wetland of international importance that provides habitat for internationally significant flora and fauna species, including migratory waterbirds and nationally threatened species of native fish (Ramsar Convention, 1998). Lake Alexandrina is a large (ca. 650 km^2), shallow freshwater lake that forms at the terminus of the River Murray. The Point Sturt study site was located on the then dry shoreline of Lake Alexandrina (lat. 35.499° S, long. 138.958° E), at an elevation ranging from −0.3 to −0.4 m Australian height datum ((AHD); 0 m AHD = mean sea level) (Fig. 1). The Boggy Creek study site was located in the dry bed of the Boggy Creek watercourse fringing Hindmarsh island (lat. 35.533° S, long. 138.917° E), at an elevation ranging from −0.05 to −0.4 m AHD (Fig. 1). Boggy Creek is connected at both ends to the Mundoo channel, which is connected to Lake Alexandrina.

The CLLMM region has a mediterranean climate, characterised by cool to mild wet winters and extended hot and dry summers. Median maximum and minimum air temperatures for days 0–100 (July–November) of the study period were 17 °C and 9 °C, respectively (Fig. S1a). Median, maximum and minimum air temperatures for days 100–200 (November–March) were 25 °C and 15 °C, respectively. At both study sites, median soil temperature 20 cm below ground level (bgl) was 13 °C for days 0–100 and 18 °C for days 100–200. Over the assessed period, total rainfall was 243 mm and total class A pan

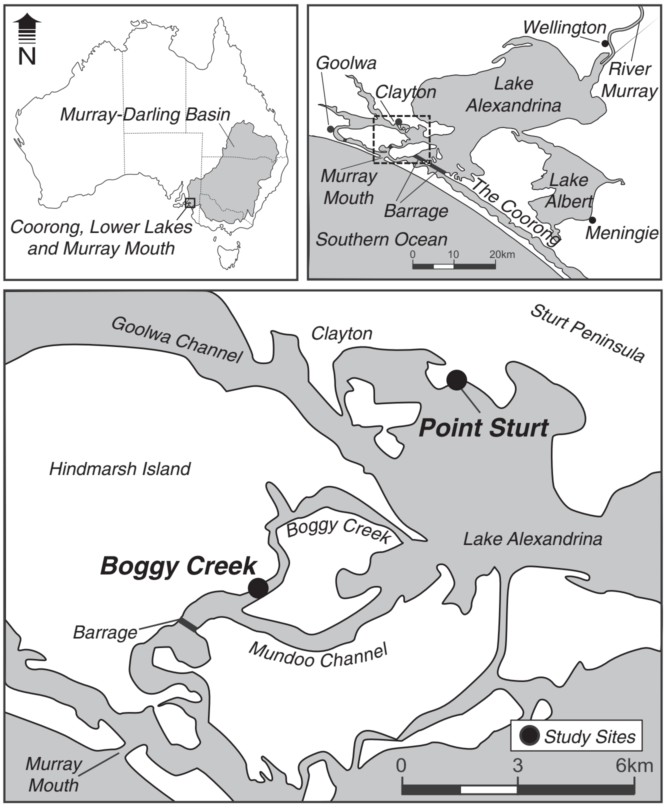

Fig. 1. Locality of Point Sturt and Boggy Creek study sites in Lake Alexandrina and in the CLLMM region and the locality of the CLLMM region within the MDB and Australia.