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## Seawater inundation of coastal floodplain sediments: Short-term changes in surface water and sediment geochemistry



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#### ABSTRACT

Coastal floodplains are highly vulnerable to seawater inundation as a result of storm surge and sea-level rise due to their low elevation and proximity to the coastline. Intact soil cores from a levee, acid-sulfate soil scald and four backswamp sites on a coastal floodplain in eastern Australia were inundated with artificial seawater treatments (0%, 50% and 100%) for 14 days to examine the short term consequences for surface water and floodplain sediment geochemistry. All sites displayed an initial decrease in surface water pH following inundation with 50% and 100% seawater. In addition, higher concentrations of trace metals (Al, Fe, Mn, Ni and Zn) were observed in most sites inundated with 50% or 100% seawater. This was generally attributed to competitive exchange and desorption of trace metals from sediments due to the higher ionic strength of the seawater solutions and upward diffusive flux of metals from the sediments to surface waters. At one backswamp site, reductive processes had established by day 7, which also resulted in elevated Fe<sup>2+</sup> concentrations in the overlying surface waters. Transmission electron microscopy (TEM) identified the presence of poorly crystalline ferrihydrite and schwertmannite, and goethite and jarosite. These meta-stable Fe(III) minerals can act as a source of metals for desorption and can also be readily reduced and act as a source of Fe<sup>2+</sup> to surface waters. Importantly, inundation with either 50% or 100% seawater resulted in a similar magnitude of acidity and trace metal mobilisation. The data suggest that an inundation event of ~0.2 m depth with either 50% or 100% seawater could cause a pulse mobilisation of up to 64.8 and 9.1 kg ha<sup>-1</sup> of Fe and Al, respectively – quantities of similar magnitude to previous estimates of annual drainage fluxes from similar backswamps. This study suggests that the short term inundation of coastal floodplain sediments by either brackish water or seawater will result in rapid declines in surface water quality as a result of increased liberation of acidity and trace metals.

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#### 1. Introduction

Coastal plains in many parts of the world, including Australia, southeast Asia and boreal Europe, contain acid sulfate soils (Andriesse and van Mensvoort, 2006). These are often referred to as coastal lowland acid sulfate soils (CLASSs). In eastern Australia, large areas of CLASS occur in low-elevation backswamp basins with elevations between 0 and 1 m above mean sea level (White et al., 1997). These backswamp basins are frequently underlain by sulfidic estuarine sediments which contain high concentrations of acidity and available trace metals (Pons, 1973; Pons and Van Breemen, 1982; Dent and Pons, 1995; Johnston et al., 2004; Sullivan et al., 2012). The estuarine sediments

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are usually capped by a thin layer of fluvial sediments, and hence, can have a strong influence on surface water, groundwater and drainage water geochemistry (Pons, 1973; Pons and Van Breemen, 1982; Sammut et al., 1996; Johnston et al., 2003; Johnston et al., 2005a). The watertable on coastal lowlands such as floodplains has been artificially lowered by extensive constructed drainage networks (Sammut et al., 1996; Minh et al., 1997; Boman et al., 2008). These drainage networks enhance oxidation of previously reduced sulfidic sediments which leads to degradation of soil and water as well as episodic acute and chronic transport of acidity and associated trace metals into adjacent estuarine receiving waters (van Breemen, 1975; Sammut et al., 1996; Johnston et al., 2004). In extreme cases, scalding of the soil surface occurs, resulting in bare areas without surface vegetation, very low pH and surface accumulations of Fe(III) minerals (Rosicky et al., 2004; Sullivan and Bush, 2004).

Due to their low elevations and proximity to the ocean, coastal backswamp basins are highly susceptible to inundation by saline

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water, caused by saltwater intrusion, storm surge and rising sea levels (e.g. Johnston et al., 2005b). The construction of extensive drainage systems has increased the susceptibility of coastal backswamp basins to seawater inundation by increasing their connectivity to estuarine channels. This risk is likely to increase in the future due to predicted increases in sea level and extreme events associated with climate change. Recent rises in sea level have resulted in an upstream shift of the tidal plane, altering Fe-S-C cycling in estuarine sediments due to changes in salinity (Roy et al., 2010; Wong et al., 2010; Wong et al., 2013). Similarly, saltwater intrusion into previously freshwater tidal environments has been previously shown to impact biogeochemical processes, increasing carbon mineralisation by altering rates of both methanogenesis and sulfate reduction (Weston et al., 2006; Weston et al., 2011). Seawater inundation of tidal freshwater ecosystems has also resulted in substantial changes in nutrient cycling, resulting in higher concentrations of N released to overlying waters, which may lead to eutrophication (Jun et al., 2012).

In previously drained coastal floodplain environments, long-term tidal inundation by seawater has been used as an effective, low cost method to remediate CLASS at a landscape scale (e.g. Johnston et al., 2012; Powell and Martens, 2005). Water quality improvements have also been demonstrated as a result of controlled tidal exchange in drains with estuarine water (Indraratna et al., 2002; Johnston et al., 2005b). Regular long-term tidal inundation can result in decreases in soil acidity and increasing alkalinity due to the addition of marine-derived bicarbonate alkalinity and the promotion of reducing conditions (Johnston et al., 2009a; Johnston et al., 2009b; Johnston et al., 2012). Over longer time periods (i.e. months to years), this process can result in substantial decreases in soluble trace metal concentrations, including Al, in surface waters *via* increases in pH and the formation of reduced Fe and sulfide minerals (Johnston et al., 2010; Keene et al., 2010; Burton et al., 2011).

Therefore, it is possible that long-term seawater inundation of CLASS, as a result of higher sea levels, will eventually neutralise the acidity produced in oxidised CLASS floodplains. Neutralisation will occur both as a result of inputs from the carbonate/bicarbonate alkalinity contained within seawater and from alkalinity generated in situ via Fe and  $SO_4^{2-}$  reduction. If current sea level rise scenarios eventuate, it is possible the resulting inundation will restore reducing conditions and mimic processes similar to the reintroduction of tidal inundation. Conversely, previous studies have suggested that rapid trace metal desorption from CLASS can occur with increasing salinity (Wong et al., 2010). Hence, there is a need to further investigate the effects of seawater inundation on surface water and sediment geochemistry over shorter time periods. This study employs intact soil core mesocosms to explore the short term surface water-sediment interactions and geochemical changes following inundation of coastal floodplain sediments by brackish water and seawater.

#### 2. Materials and methods

### 2.1. Site description and field sampling

Intact soil cores were collected from the Rocky Mouth Creek floodplain, a CLASS backswamp basin underlain by estuarine Holocene sediments, situated in the sub-tropical region of eastern Australia (153°19′2.28″E 29°6′33.48″S; Fig. 1). The Rocky Mouth Creek floodplain forms part of the lower Richmond River floodplain, both of which are susceptible to variations in sea level due to large areas at low elevation. Specifically, in the lower Richmond River floodplain there is 175 km<sup>2</sup> of land <0 m AHD (m Australian Height Datum; AHD, where 0 m AHD is approximately sea level); and 177 km<sup>2</sup> of land between 0 and 1 m AHD. The elevation classes were derived from a high resolution digital elevation model (DEM) with a vertical accuracy of 0.26 m and pixel size of 5 m.

Triplicate intact cores were collected to a depth of 0.2 m with 100 mm diameter polyvinyl chloride (PVC) pipe from six sites on the floodplain; natural levee (termed levee), scald (termed scald) and four backswamp sites (termed BS1, BS2, BS3 and BS4, respectively). The estimated elevations of each sample site, derived from the DEM, are as follows: levee, 1.7 m AHD; scald, 0.1 m AHD; BS1, -0.1 m AHD; BS2, 0.4 m AHD; BS3, 0.3 m AHD, and; BS4, 0.4 m AHD. Bulk soil samples were also collected at each location for geochemical characterisation (Table 1). The overlying vegetation was clipped to the level of the surface prior to sampling. The soil types were sulfuric/sulfidic oxyaquic Hydrosols (Isbell, 1996) or hydraquentic Sulfaquepts (U.S. Soil Survey Staff, 1998) in the backswamp and scald and brown Dermosols (Isbell, 1996) or fluvaquentic Epiaquolls (U.S. Soil Survey Staff, 1998) on the levee. Sampling occurred during an extensive dry period, with low watertables and oxic upper soil layer conditions. The intact cores were stored at 4 °C prior to inundation.

#### 2.2. Sample preparation

Intact soil cores from each site were inundated, in triplicate, for 14 days with either 50% or 100% artificial seawater, prepared according to Cavanaugh (1975) and diluted in deionised water. The synthetic seawater had a pH  $\approx$  8, EC  $\approx$  46 dS m<sup>-1</sup> and consisted of the major cations (i.e.  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$ ) and anions (i.e.  $Cl^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ ) found in natural seawater. The concentration of salts (mmol  $L^{-1}$ ) in 100% synthetic seawater were as follows: NaCl, 422; KCl, 8.99; CaCl<sub>2</sub>·2H<sub>2</sub>O, 9.25; MgCl<sub>2</sub>·6H<sub>2</sub>O, 37.8; MgSO<sub>4</sub>·7H<sub>2</sub>O, 41.8, and; NaHCO<sub>3</sub>, 2.14. One control treatment consisting of de-ionised water (0% seawater) was also examined for each site. 0.2 m of overlying surface water was added to each soil core. Surface waters were sampled via a port approximately 0.05 m above the soil surface. Surface waters were sampled at days 0 (2 h after inundation), 1, 2, 7 and 14. The soil cores were maintained at a constant temperature of 20 °C during the 14 day experimental period. The pH, EC and dissolved oxygen were determined in situ in the surface waters using freshly calibrated probes. The soil cores were destructively sampled at the end of the sampling period for sediment characterisation. Sediments were analysed from the 0-5, 5-10 and 10-20 cm depth layers.

#### 2.3. Aqueous-phase temporal analysis

Surface waters were passed through a 0.45  $\mu$ m filter prior to analysis. The samples were analysed for alkalinity, trace metals (Al, Fe and speciation, Mn, Ni, Zn) and major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>). Alkalinity was determined spectrophotometrically according to Sarazin et al. (1999). Soluble Fe speciation was determined using 1,10-phenanthroline (APHA 3500; APHA, 2005). Fe<sup>3+</sup> was determined from the difference between Fe<sup>2+</sup> and total Fe following reduction with hydroxylammonium chloride. Samples analysed for trace metals and major cations were preserved with HNO<sub>3</sub> and stored at 4 °C prior to analysis by inductively coupled plasma-mass spectrometry (ICP-MS) on a Perkin Elmer Elan DRC-e inductively coupled mass spectrometer.

#### 2.4. Solid-phase analysis

Bulk soil samples were characterised prior to inundation. Sediments from within the cores were also characterised at the end of the 14 day experimental period. Moisture content was determined by weight loss following oven drying at 105 °C for 24 h. The samples were ovendried at 40 °C for 48 h and lightly crushed to pass through a 2 mm sieve. Soil pH, EC and soluble cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>) and metals (Al, Fe, Mn, Ni, Zn) were determined on 1:5 soil:water extracts (Rayment and Lyons, 2011). Exchangeable cations and metals were extracted with 0.1 M BaCl<sub>2</sub>/NH<sub>4</sub>Cl extracts (Rayment and Lyons, 2011). Where the EC<sub>1:5</sub>  $\geq$  0.3 dS/m, soluble salts were removed by washing three times with an ethanol/glycerol solution as described in Rayment and Lyons (2011). Acid-extractable metals were determined on the Download English Version:

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