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Legacy impacts of acid sulfate soil runoff on mangrove sediments: Reactive iron accumulation, altered sulfur cycling and trace metal enrichment

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ABSTRACT

The off-site impacts of iron-rich, acidic runoff from drained acid sulfate soils (ASS) on the geochemistry of estuarine sediments are relatively poorly constrained. In this study, we examine the geochemistry of intertidal zone mangrove sediments and porewaters from an estuarine tributary that received ~15–20 years of acute ASS drainage, compared to adjacent control sites. Mixing of acidic, iron-rich ASS drainage waters with circumneutral pH estuarine waters drove precipitation of Fe(III) floc and has led to significant, localized accumulation of reactive-Fe species (Fe_R; Σ1 M HCl and citrate-buffered dithionite extracts; up to 4200 μmol g^{-1}) as well as significantly elevated porewater Fe^{2+} (>1000 μM) in ASS impacted sediments. X-ray diffraction indicates that goethite, lepidocrocite and ferrihydrite are important Fe(III) minerals in surficial sediments at ASS impacted sites. The abundant Fe_R is shifting the equilibrium of reduced inorganic sulfur (RIS) mineral-formation pathways towards accumulation of S(0) and acid volatile sulfide (AVS) species and is buffering porewater S(-II) to low concentrations. In contrast, RIS speciation at the control sites is dominated by pyrite (S_{CR}) and porewater S(-II) is present. Some porewater metals (i.e. Al, Mn, Cu, Cr) are significantly elevated at sites proximal to the source of ASS drainage compared to control sites. Abundant Fe_R also provides a substrate for sorption and accumulation of metals and correspondingly there is significant relative enrichment of reactive metal fractions (1 M HCl extractable) in sediments at the ASS impacted sites, with $Al \approx Mn \approx U > Cu > Cr > Ni$. This study demonstrates that ASS drainage, which causes accumulation of reactive Fe in mangrove environments, can substantially influence sediment biogeochemistry by altering reduced inorganic sulfur cycling and enhancing the availability of some trace metals.

1. Introduction

Over-drainage of coastal acid sulfate soils (CASS) in eastern Australia has left a legacy of degraded landscapes and environments (e.g. Johnston et al., 2003a; White et al., 1997). This environmental degradation can be broadly categorised as either a) on-site and proximal to the acidified soils themselves, or b) off-site and associated with the transport of aqueous products into adjacent receiving waters (Sullivan et al., 2011).

On-site environmental impacts are diverse and include acute acidification of soils (Dent and Pons, 1995; Lin and Melville, 1993; Walker, 1972); acute acidification of surface waters and groundwater (e.g. Green et al., 2006; Johnston et al., 2004a, 2004b, 2005a, 2011b; Van Oploo et al., 2008; White et al., 1997); salinisation of soil (e.g. Rosicky et al., 2006; Walker, 1972); soil toxicity from aluminum or trace metals/metalloids (e.g. Burton et al., 2008a; Johnston et al., 2010b; Van Breemen, 1973, 1993; Yvanes-Giuliani et al., 2014); vegetation community modification (Johnston et al., 2003b); vegetation loss and seasonal surface 'scalding' (Lin et al., 2001; Rosicky et al., 2004); irreversible changes in soil physical/hydrological properties (Dent, 1986; Johnston et al., 2009b); irreversible soil shrinkage and land subsidence (Dent and Pons, 1995; Smiles, 2009).

Studies documenting off-site environmental impacts of CASS tend to focus on estuarine receiving water quality (e.g. Åström, 2001; de Weys et al., 2011; Johnston et al., 2003c, 2004a; Österholm and Åström, 2008; Sammut et al., 1996; Santos et al., 2011; Wong et al., 2010) or aquatic biota (e.g. Amaral et al., 2012; Dove and Sammut, 2007; Russell and Helmke, 2002; Russell et al., 2011). CASS drainage impacts on receiving water quality are transitory and often seasonal, occurring in short-term (days to months) periodic pulses when local hydrological conditions are suitable to drive acid export (de Weys et al., 2011; Johnston et al., 2004a, 2005b; 2009a; Minh et al., 2002; Wilson et al., 1999).

In contrast, benthic sediments in off-site environments receiving chronic CASS drainage are likely to be influenced over much longer-term time scales (years to decades) (Burton et al., 2007; Nath et al.,

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2013). Several studies have explored the impacts of CASS drainage on benthic sediment geochemistry in boreal environments (e.g. Nordmyr et al., 2008a; Nordmyr et al., 2008b). However, these boreal systems display relatively low mobility of iron (Fe) (Åström and Bjorklund, 1995; Boman et al., 2008), which contrasts sharply with Australian CASS drainage waters, in which Fe is often highly mobile (Burton et al., 2006c; Johnston et al., 2003c, 2004a, 2011a; Wong et al., 2010). Fe transported off-site by CASS drainage readily precipitates as poorly-crystalline Fe(III) oxyhydroxides when drainage waters mix with well-buffered estuarine waters of circumneutral pH. This process has the potential to cause substantial accumulation of Fe(III) precipitates within benthic sediments (Burton et al., 2006c; Johnston et al., 2011a).

The accumulation of poorly-crystalline Fe(III) oxyhydroxides in estuarine sediments can influence sulfur cycling and favor the formation of reactive reduced inorganic sulfur (RIS) species, including S(0) and acid volatile sulfur (AVS) (e.g. Burton et al., 2006a; Keene et al., 2011; Raiswell and Canfield, 2012; Rickard, 2012). Poorly-crystalline Fe(III) oxyhydroxides also provide surfaces that may enhance sorption and accumulation of various trace elements (Bigham et al., 1990; Johnston et al., 2010a, 2015; Keene et al., 2014; Macdonald et al., 2004; Morgan et al., 2012). Therefore, substantial accumulation of reactive Fe in estuarine sediments due to CASS drainage is likely to alter the cycling of RIS species and trace elements. However, in practice the consequences are poorly constrained, especially within sediments of intertidal mangrove environments.

In this study, we examine sediment and porewater geochemistry of an intertidal mangrove zone that has received acidic, Fe-rich drainage from a CASS wetland for ~15–20 years and compare this with adjacent, undisturbed control sites. We aim to determine if reactive Fe is accumulating in benthic sediments and, if so, explore what effect(s) this might be having on RIS speciation and trace metal accumulation/partitioning. The purpose of this study was to improve our fundamental understanding of the long-term legacy impacts of CASS drainage on estuarine intertidal sediments.

2. Methods

2.1. General methods

All laboratory glass-ware was soaked in 5% (*v*/*v*) HNO_3 for at least 24 h, followed by repeated rinsing with deionized water. All chemicals were analytical reagent grade. All reagent solutions were prepared with deionized water (MilliQ). Solid-phase samples were prepared and dried under oxygen-free conditions in an anaerobic chamber (1–5% H_2 in N_2), containing an O_2 consuming Pd catalyst.

2.2. Study site

The study site is located on the Hastings River in Eastern Australia (Fig. 1; lat. 31.426°S, long. 152.848°E). The climate is sub-tropical and average annual rainfall is ~1400 mm. The four sites impacted by CASS drainage (FC1–4) were situated in the intertidal pneumatophore zone of a fringing *Avicennia marina* mangrove forest in Fernbank Creek — a small tidal tributary of the Hastings River estuary (Fig 1b). Fernbank Creek received highly acidic (pH ~3–4) drainage water, rich in Fe and Al (Fig. 1a), from the adjacent Partridge Creek acid sulfate soil wetland drainage system for ~15–20 years from the late 1980s (Johnston et al., 2014). During this period, the flux of H^+ from the drained Partridge Creek ASS wetland was estimated to be ~800 t of H_2SO_4 equivalent for an average rainfall year (Aaso, 2004). Partridge Creek CASS wetland was subject to a remediation strategy commencing in 2004, which consisted of freshwater re-flooding. This involved retaining rainfall and shallow groundwater on-site by blocking the main drain outlet with a weir and has led to substantial increases in soil and water pH and a large decrease in acid export (Johnston et al., 2014).

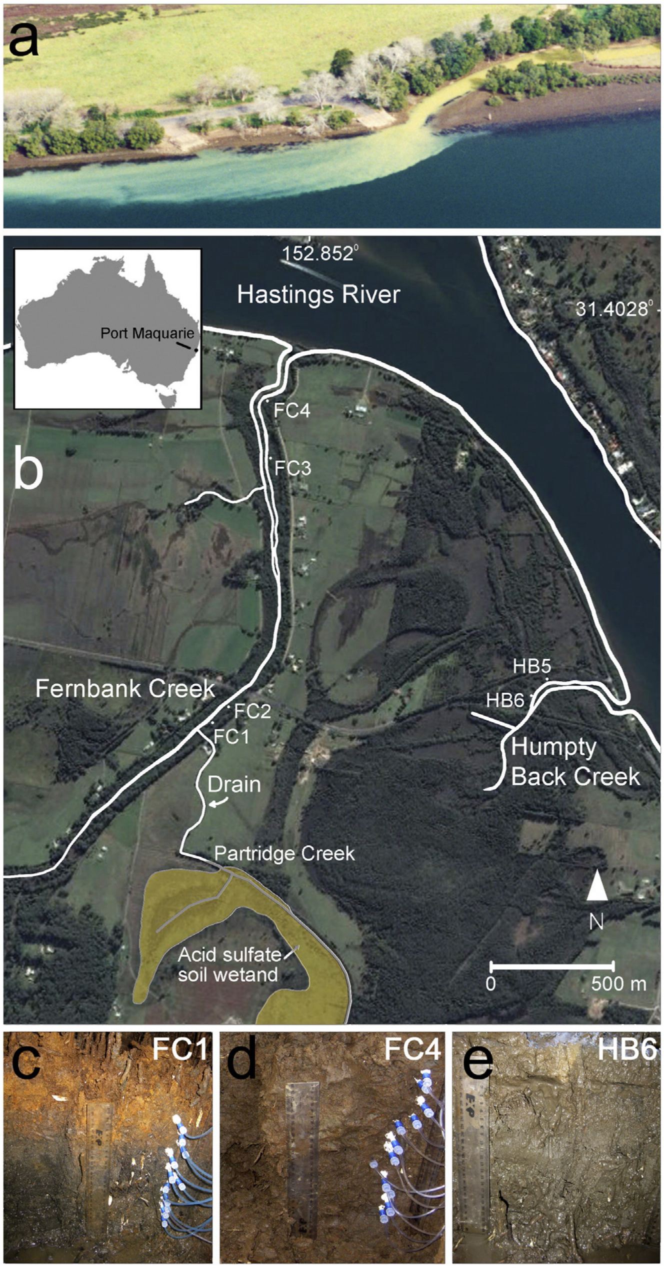

Fig. 1. Study site location map with a) an acidic plume rich in Fe and Al species discharging from the confluence of Fernbank Creek into the Hastings River and b) mangrove sediment sample locations (FC1–4; HB5–6) and Partridge Creek acid sulfate soil wetland boundary and drain, c), d) and e) are examples of contrasting sediment profiles at sites FC1, FC4 and HB6.

The two locations selected as control sites (HB5–6) were situated in an adjacent small tidal tributary of the Hastings River estuary, Humpty Back Creek (Fig. 1b). Humpty Back Creek has a very small floodplain catchment that does not receive direct inputs of CASS drainage water. Sample sites in Humpty Back Creek were also situated in the intertidal pneumatophore zone of a fringing *A. marina* mangrove forest.

2.3. Sample collection

Sampling was conducted during low tide. Shallow pits were constructed using a stainless steel shovel. The sides of the pit were scrapped clean using a plastic spatula and approximately 300 g of sediment collected from the side of each pit at 2 cm increments to a depth of 24 cm below the surface. Samples were sealed in polyethylene bags