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Seawater-induced mobilization of trace metals from mackinawite-rich estuarine sediments

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ABSTRACT

Benthic sediments in coastal acid sulfate soil (CASS) drains can contain high concentrations (~1–5%) of acid volatile sulfide (AVS) as nano-particulate mackinawite. These sediments can sequester substantial quantities of trace metals. Because of their low elevation and the connectivity of drains to estuarine channels, these benthic sediments are vulnerable to rapid increases in ionic strength from seawater incursion by floodgate opening, floodgate failure, storm surge and seasonal migration of the estuarine salt wedge. This study examines the effect of increasing seawater concentration on trace metal mobilization from mackinawite-rich drain sediments (210–550 $\mu\text{mol g}^{-1}$ AVS) collected along an estuarine salinity gradient. Linear combination fitting of S K-edge XANES indicated mackinawite comprised 88–96% of sediment-bound S. Anoxic sediment suspensions were conducted with seawater concentrations ranging from 0% to 100%. We found that mobilization of some metals increased markedly with increasing ionic strength (Cu, Fe, Mn, Ni) whereas Al mobilization decreased. The largest proportion of metals mobilized from the labile metal pool, operationally defined as Σ exchangeable + acid-extractable + organically-bound metals, occurred in sediments from relatively fresh upstream sites (up to 39% mobilized) compared to sediments sourced from brackish downstream sites (0–11% mobilized). The extent of relative trace metal desorption generally followed the sequence $\text{Mn} > \text{Ni} \approx \text{Cu} > \text{Zn} > \text{Fe} > \text{Al}$. Trace metal mobilization from these mackinawite-rich sediments was attributed primarily to desorption of weakly-bound metals via competitive exchange with marine-derived cations and enhanced complexation with Cl^- and dissolved organic ligands. These results have important implications for trace metal mobilization from these sediments at near-neutral pH under current predicted sea-level rise and climate change scenarios.

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1. Introduction

Pyritic soils commonly underlie coastal floodplains globally (Andriesse and van Mensvoort, 2006; Sullivan et al., 2011).

Extensive drainage networks have been constructed on many coastal acid sulfate soil (CASS) floodplains for flood mitigation and to allow for year-round agriculture (Sammut et al., 1996). High concentrations of $\text{Fe}^{2+/3+}$ and SO_4^{2-} sourced from

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oxidized pyrite can be transported with surface water or shallow groundwater into drainage channels which have abundant accumulations of labile organic debris (Burton et al., 2006a; Johnston et al., 2004). This can lead to the formation of high concentrations of metastable iron sulfide minerals ($\sim 10\%$ w/w FeS) in benthic sediments of drainage channels as a result of microbially mediated SO_4^{2-} reduction (Burton et al., 2006b, 2009; Bush et al., 2004; Sullivan et al., 2002). These minerals include amorphous-FeS, nano-particulate mackinawite (FeS) and possibly greigite (Fe_3S_4), and can be operationally defined as acid volatile sulfides (AVS) (Rickard and Morse, 2005).

FeS-rich sediments can be an important sink for trace metals in anoxic systems and can regulate trace metal concentrations in surface and porewaters through dissolution or precipitation of metal sulfide minerals (Di Toro et al., 1992; Morse and Arakaki, 1993; Smith and Melville, 2004). Immobilization of metals can occur as a result of direct formation of metal sulfides, co-precipitation with Fe-sulfides, surface complexation with Fe monosulfides or organic complexation (Simpson et al., 2000). Sequestration of metals via these processes is an important control on trace metal bioavailability in surface and porewaters (eg. Burton et al., 2005b; Burton et al., 2006c, 2008a). The toxicity of trace metals in sulfidic sediments can be evaluated by comparing the ratio of the sum of simultaneously extracted metals (SEM), such as Ag, Cd, Cu, Ni, Pb and Zn, to AVS, determined by extraction with cold 1 M HCl (Simpson et al., 1998). It is generally assumed that trace metals are unlikely to be toxic when $\sum \text{SEM}/\text{AVS} < 1$ (eg. Di Toro et al., 1992). Other binding phases which control trace metal bioavailability can also occur in Fe–S-rich sediments, including organically-bound phases (Berry et al., 1996).

Previous studies demonstrate that oxic re-suspension of AVS-rich benthic sediments can result in severe acidification and mobilize trace metals (Boman et al., 2010; Burton et al., 2006c; Cantwell et al., 2008; Simpson et al., 1998; Sullivan et al., 2002). Metal mobilization from sediments to surface waters is highly dependent on the overlying water conditions, including salinity, dissolved oxygen concentrations and pH (Atkinson et al., 2007; Lu and Chen, 1977). Metals become increasingly bioavailable when released into the dissolved phase (Besser et al., 1996), impacting water quality, aquatic organisms and ecosystem health. Sulfidic sediments have the potential to be substantial sources of trace metals under rapidly changing environmental conditions (Burton et al., 2006c; Sundstrom et al., 2002).

Low-lying coastal floodplains are increasingly susceptible to enhanced seawater inundation due to sea-level rise and storm surge under current predicted climate change scenarios (Hennessy et al., 2004; IPCC, 2007). Higher sea-levels will result in an upstream shift of the intertidal plane and salt wedge, thereby increasing the area of estuarine benthic sediment exposed to increasingly saline surface water. Due to their low elevation and high connectivity to estuarine channels, AVS-rich benthic sediments in CASS drainage channels are highly susceptible to seawater ingress and rapid changes in ionic strength as a result of either perigean spring tides, storm surge, floodgate failure or floodgate opening (Johnston et al., 2005). These AVS-rich benthic sediments, therefore, have the potential to become significant sources of trace metals to the

water column due to metal desorption following rapid changes in ionic strength. However, the potential metal release from sulfidic sediments under neutral reducing conditions in response to changes in salinity is poorly understood. This study investigates the effects of increasing seawater concentrations on trace metal mobilization from natural mackinawite-rich sulfidic drain sediments from a CASS floodplain in eastern Australia.

2. Materials and methods

2.1. Sample collection

Benthic drain sediments were collected with a Van Veen grab sampler (approximately 0–20 cm depth) from an artificial drain in the Richmond River estuary ($28^{\circ}57'S$ $153^{\circ}23'E$) in the sub-tropical region of eastern Australia. Four sites (S1, S2, S3 and S4) were located along the artificially constructed 4.5 km Tuckean Main Drain, which ranges from approximately 3–5 m deep and up to 25 m wide (Fig. 1). S1 was located at the junction between the Tuckean Main Drain and the main channel of the Richmond River, approximately 4.00 km upstream from the river mouth. S2, S3 and S4 were located approximately 1.94, 3.70 and 5.66 km upstream of the junction, respectively. The sample sites are representative of an estuarine salinity gradient in which AVS-rich benthic sediments form in eastern Australia. S1 is representative of marine influenced sediments while S4 is representative of a typical site with a greater freshwater influence. Sites further upstream could not be sampled due to limited access.

Samples were placed on ice immediately following collection, purged with N_2 and frozen at -80°C until analysis. Surface water samples were also collected in acid-washed plastic bottles at the same sites. The bottles were rinsed three times in the surface waters prior to sample collection. Surface waters were collected at a depth of 10 cm. The bottles were filled, air expelled and kept cool at 4°C until analysis.

2.2. Solid-phase analyses

All glass and plastic-ware were cleaned by soaking in 5% HCl (v/v) for at least 24 h followed by repeated rinsing with deionized water (Milli-Q). All reagents used in analyses were analytical grade and all solutions were prepared with deionized water. Samples were thawed under a high purity N_2 atmosphere and homogenized prior to analysis. Sediment moisture content was determined by weight loss following drying a sub-sample at 105°C for 24 h. Sediment pH and EC were determined using calibrated probes. Reduced inorganic S (RIS) speciation was determined via a three step sequential extraction procedure to extract 1) monosulfides, operationally defined as AVS; 2) elemental S^0 , and 3) pyrite-S, operationally defined as Cr-reducible S (CRS) (Burton et al., 2008c). AVS was extracted using the cold diffusion method by Hsieh et al. (2002) and Burton et al. (2006a) by shaking sediment with 6 M HCl/0.1 M ascorbic acid for 18 h. The evolved H_2S was trapped in 3% Zn acetate in 1 M NaOH and analysed by iodometric titration. Elemental S^0 was extracted with methanol, with the S^0 quantified by high performance liquid

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