Remediating coastal acid sulfate soils by tidal inundation: geochemical hysteresis of iron

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Abstract

The effects of restoring marine tidal inundation to a severely degraded acid sulfate soil landscape were investigated. Tidal inundation stimulated Fe and SO_4^{2-} reduction, leading to internal alkalinity generation and the reformation of considerable quantities of pyrite within former sulfuric horizons. After ~five years of regular tidal inundation the amount of acidity within former sulfuric horizons had decreased dramatically. However, the change in hydrology and geochemistry initiated by tidal inundation has had profound consequences for the fate, mobilisation, redistribution and transformation of Fe minerals in the landscape. The transition to mainly reductive pedogenesis has mobilised a store of previously immobile secondary Fe(III) minerals (e.g. jarosite). Tidal pumping is driving upward advection of mobile Fe^{2+}. Oxidation of Fe^{2+} near the soil-surface water interface leads to surficial accumulation of poorly-crystalline Fe(III) minerals, which display a mineralisation sequence related to tidal zonation. A conceptual representation of this hysteresis in iron geochemistry is presented.

Key Words

Acid sulfate soil; iron; sea-level rise; tidal marsh; East Trinity.

Introduction

An innovative technique to mitigate the negative environmental consequences of coastal acid sulfate soils (ASS) is the partial or complete inundation of ASS by tidal marine waters (Powell and Martens 2005; Johnston *et al.* 2009a, b). Tidal inundation ameliorates acute soil acidity by supplying bicarbonate alkalinity, and by stimulating upward migration of the redox boundary which generates an internal supply of bicarbonate alkalinity via iron and sulfate reduction (Johnston *et al.* 2009b).

ASS are typically rich in meta-stable, secondary Fe(III) minerals that formed after the oxidation of pyrite (e.g. jarosite, schwertmannite; Sullivan and Bush 2004). Re-establishing tidal inundation in an Fe(III)-rich ASS landscape generates considerable potential for reductive dissolution of Fe(III) mineral phases. Tidal pumping of shallow groundwater can be a powerful mechanism for porewater exchange and solute movement within intertidal zone sediments and its introduction may lead to subsequent mobilisation and redistribution of aqueous Fe. The biogeochemical cycling of Fe is closely linked with that of sulfur and a variety of important / toxic trace elements (e.g. arsenic), and thus changes in iron behaviour are likely to have consequences for these elements. We investigate and describe some of the effects of marine tidal inundation upon the behaviour and geochemistry of iron in ASS.

Methods

Study site

The study site, East Trinity, is situated in northern Australia near Cairns. It consists of an ~800 ha Holocene sedimentary coastal plain dissected by several estuarine creeks (145°47’ E, 16°56’ S). A tide-excluding sea wall was constructed around the site in the 1970’s (Powell and Martens 2005). Tide exclusion combined with intensive drainage caused the oxidation of iron-sulfides in mangrove sediments, leading to widespread formation of severe acid sulfate soils across the site (Powell and Martens 2005). A remediation program commenced in 2001–02, which has involved incrementally increasing tidal inundation of acid sulfate soils up to an elevation of ~0.5 m AHD (AHD is Australian Height Datum, 0 m AHD approximates mean sea level). Tides now regularly inundate most of the formerly acidified areas across the site.

Hydrology

Groundwater levels along each transect were measured at 30 minute intervals (±0.01 m) using submersible pressure transducers vented to the atmosphere (Odyssey, ODYPS05) housed in a series of four 50 mm diameter PVC piezometers.

Solid-phase sampling

Replicate soil cores were obtained by gouge-auger from selected sampling locations. Cores were immediately sectioned and sub-samples sealed in air-tight polyethylene bags, completely filled with soil and frozen after collection until analysis. Field pH (pH_F) and redox potential (Eh_F) were determined on additional duplicate cores by direct insertion of freshly calibrated electrodes. Fe-rich surficial sediment (0–0.01 m) was also sampled from a variety of locations within the study area and frozen. The elevation of all sample points was surveyed to AHD.

Samples were thawed under N_2, homogenised and analysed sequentially in duplicate for reactive Fe fractions and speciation according to Kostka and Luther (1994). Poorly crystalline solid-phase Fe(II) and Fe(III) were extracted with 0.5M HCl on 1–2 g wet sub-samples [Fe_{HCl}]. The centrifuged residue was then extracted with a citrate-buffered dithionite solution [Fe_{DCb}]. The sum of Fe_{HCl} and Fe_{DCb} is reported as Fe_{Ex} and largely represents the Fe pool available for reductive transformations over biologically relevant timescales. A separate portion of sample was dried at 85 °C and crushed to pass a 0.5 mm sieve. These dried and crushed samples were digested for near-total Fe using hot aqua-regia (1:3 HNO_3:HCl, 110 °C, 1:60 soil:solution, 1 h digest) and filtered (0.45 μm) aliquots analysed for Fe by inductively coupled plasma mass spectroscopy (ICP-MS; APHA 1998) using a Perkin-Elmer ELAN-DRCe instrument. Selected samples were examined via XRD using a Bruker D4 Endeavor fitted with a Co X-ray source and Lynx-Eye detector. Samples were scanned from 15º– 80º 2θ with a 0.05º 2θ step-size and a 4 second count-time and analysed using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Karlsruhe, Germany).

Porewater geochemistry

Porewaters were sampled during April 2008 via equilibration dialysis using 1.5 m long peepers. This is described in detail by Johnston *et al*. (2009c). Porewater was analysed for Fe^{2+} and total Fe using the 1,10-phenanthroline method (APHA 1998).

Results and discussion

Soil pH increased substantially (2–3 units; Figure 1) in former sulfuric horizons subject to tidal inundation for approximately five years. Following tidal inundation there was a significant relationship between elevation and pH, with sites exposed to longer tidal inundation showing the greatest increases (Figure 1).

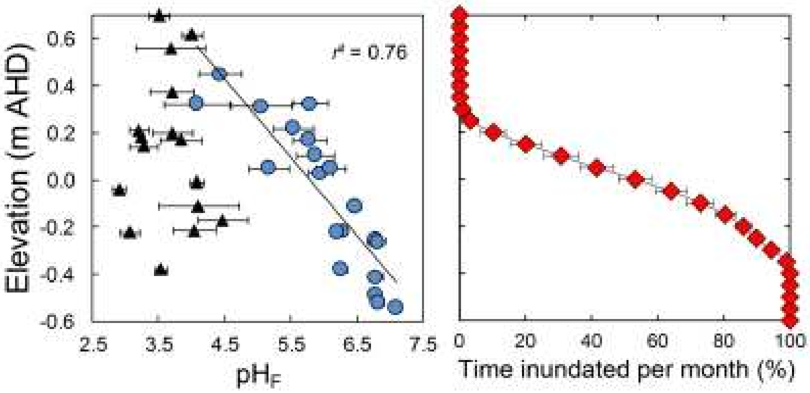

Figure 1. (a) Changes in the relationship between the mean (±std. error) soil pH_F of sulfuric horizons and surface elevation, prior to tidal inundation (2001-02; triangles), and after 5+ years of tidal inundation (2007-08; circles). (b) tidal inundation frequency relative to surface elevation during 2008.

The redox transition caused by tidal inundation has initiated extensive reductive dissolution of Fe(III) minerals, including jarosite. This has resulted in very high concentrations of porewater aqueous Fe^{2+} (>2000 mg L^{-1}) in former sulfuric horizons in the upper-intertidal zone (Figure 2).

This mobile Fe^{2+} is able to be re-distributed according to the prevailing tidally-influenced hydrology. Tidal pumping in the fringing aquifer generates oscillating hydraulic gradients which drive upward advection of Fe^{2+}-enriched porewater during the ebb-tide phase. This is followed by oxidation of Fe^{2+}, precipitation and subsequent accumulation of Fe(III) minerals in surficial tidal sediments (Figure 3a,b,c). Fe(III)-precipitates at the sediment surface-water interface are poorly crystalline and displayed a mineralisation sequence that is related to tidal zonation (Figure 3d). Schwertmannite ($Fe_8O_8(OH)_6SO_4$) was the dominant Fe mineral phase in the upper-intertidal zone at mainly low pH (3–4). This was followed by increasing lepidocrocite (γ-FeOOH) and goethite (α-FeOOH) at circumneutral pH within lower-intertidal and subtidal zones (Figure 3d).

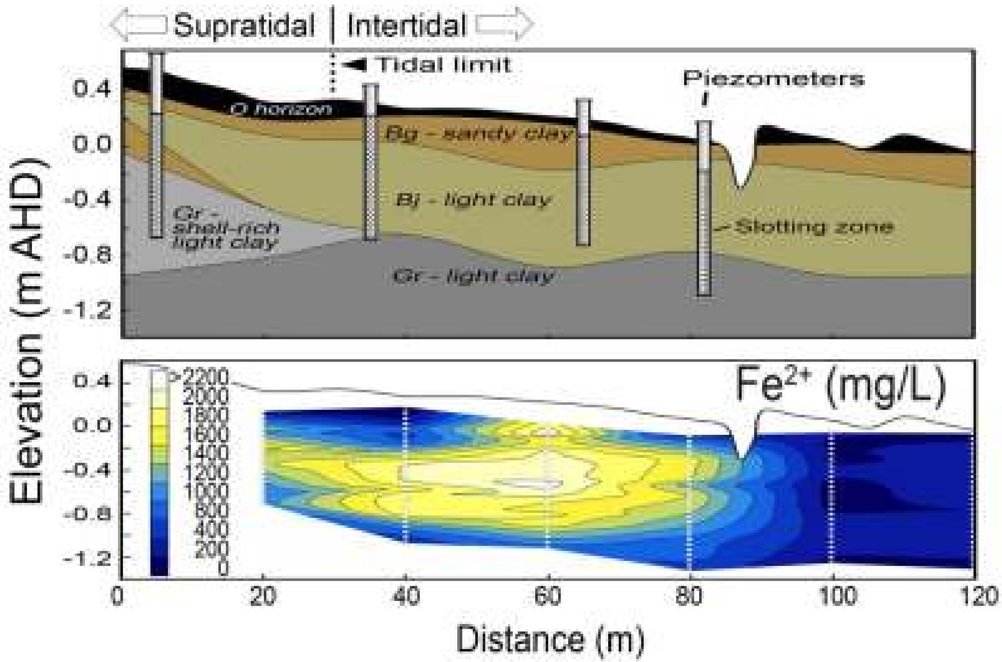

Figure 2. Stratigraphy and porewater Fe^{2+} concentrations across a tidally inundated acid sulfate soil toposequence.

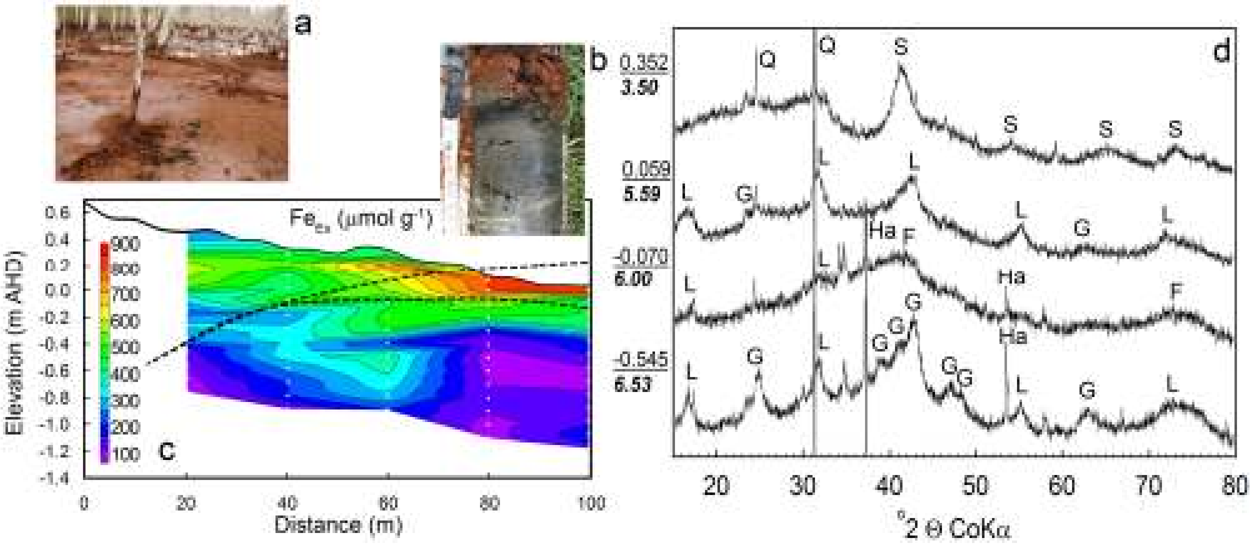

Figure 3. Surface accumulations (a), (b) of poorly crystalline Fe(III) minerals; (c) surface enrichment of poorly crystalline reactive Fe fractions (Fe_{Ex}) within the intertidal zone at Transect 2. Dashed lines represent tidal water table minima and maxima at time of sampling; (d) representative X-ray diffractograms of Fe-rich surficial (0-1 cm) accumulations. Underline text on y-axis is surface elevation (m AHD) at the point of sample collection and bold italic is pH_F. S, schwertmannite; Q, quartz; G, goethite; L, lepidocrocite; F, ferrihydrite; Ha, halite.

The surficial enrichment of poorly crystalline Fe(III)-minerals has a range of geochemical consequences. Poorly crystalline Fe(III)-minerals provide an effective substrate for adsorption / co-precipitation of trace metals and is likely to influence their long-term accumulation. In addition, poorly crystalline Fe can promote the formation of elemental sulfur (S^0) and acid volatile sulfides (AVS) in surficial sediments at the expense of pyrite formation (Burton *et al.* 2007).

The onset of mass reductive dissolution of Fe in combination with tidal pumping has effectively mobilised a large store of previously immobile secondary Fe(III) minerals. Whilst the neutralisation of acidity has caused the soil pH to return to a status similar to the original, pre-drainage condition, there is a hysteresis in the geochemical trajectory of remediation with respect to Fe. This can be represented conceptually (Figure 4a) where, **(1)** corresponds to a natural, pyrite-rich, anoxic, inter-tidal mangrove environment with circumneutral pH and a low proportion of reactive Fe (Fe_R:Fe_{Tot}). The exclusion of tides and drainage of sediment leads to **(2)**, where the oxidation of pyrite and formation of secondary Fe (III) minerals was associated with increased

H^+ and some increase in reactive Fe. The reintroduction of tidal inundation **(3)**, has caused the neutralisation of acidity, but surficial enrichment of reactive-Fe. Increasing pyritisation of this reactive Fe pool is likely over time, but the kinetics of this process are uncertain. Corresponding field data from the East Trinity site is shown in Figure 4b, for surficial sediments (0–0.1 m) under natural **(1)** and drained **(2)** conditions and after the reintroduction of tidal inundation **(3)**.

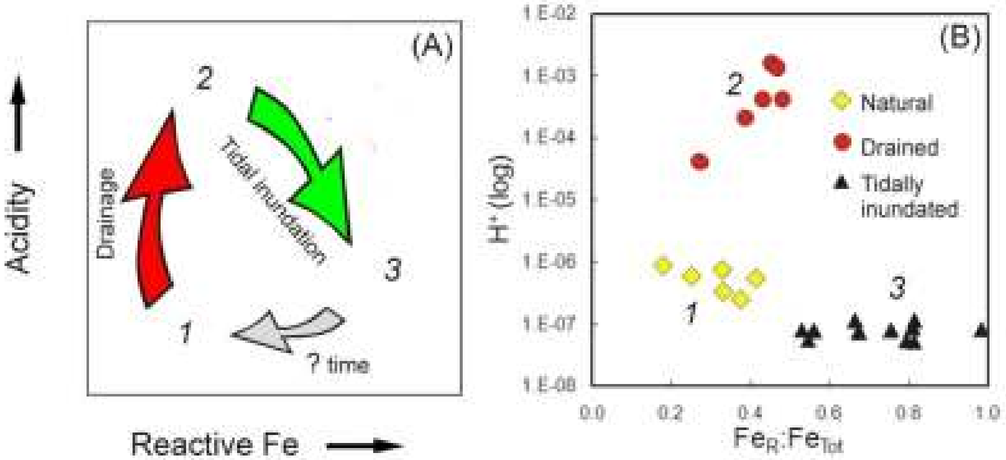

Figure 4. Conceptual representation of hysteresis in tidal remediation of ASS with respect to changes in acidity and the reactive-Fe fraction in surficial sediments

Conclusion

This study demonstrates that marine tidal inundation can be effective at raising the pH of soils through internal generation of alkalinity via Fe / S reduction. However, interactions between topography and tides exert a fundamental hydrological control on the geochemical zonation, redistribution and subsequent mineralogical transformations of Fe within the landscape. These transformations involving Fe underpin important aspects of the geochemical trajectory of remediation, including the behaviour of co-associated trace elements and the formation of reduced inorganic sulfur species. A clear understanding of the behaviour of Fe is critical in evaluating the transferability of this remediation technique.

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