Remediation of coastal acid sulfate soils by tidal inundation: Effectiveness and geochemical implications

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Abstract

The effects of restoring marine tidal inundation to a severely degraded acid sulfate soil landscape were investigated. Five years of regular tidal inundation led to substantial improvements in a range of key parameters used to assess soil and water quality. The pH of estuarine creeks improved dramatically following reintroduction of tidal inundation. Time series water quality and climatic data indicate a substantial decrease in the magnitude of creek acidification per given quantity of antecedent rainfall. The soil pH also increased by 2–3 units and titratable actual acidity (TAA) decreased by ~40–50 $\mu mol\ H^+\ g^{-1}$ within former sulfuric horizons. Tidal inundation stimulated Fe and SO_4^{2-} reduction within the landscape, leading to internal alkalinity generation and the reformation of considerable quantities of pyrite within former sulfuric horizons. In addition, there were large decreases in water-soluble and exchangeable Al fractions within former sulfuric horizons, which is an important finding from an eco-toxicology perspective.

However, the radical change in hydrology and geochemistry initiated by tidal inundation has had profound consequences for the fate, mobilisation, redistribution and transformation of Fe minerals and co-associated trace elements. There was substantial diagenetic enrichment of poorly crystalline Fe-oxides near the soil surface following tidal inundation. This was also associated with enrichment of some trace metals. High concentrations of arsenic were observed in porewaters (~300 $\mu g\ L^{-1}$) and were associated with reductive dissolution of secondary iron minerals, including jarosite, which had formed during the previous oxic / acidic phase. This study demonstrates that marine tidal inundation can be an effective method for remediating acid sulfate soils at a landscape-scale. However, there are a range of potential geochemical complexities which need to be considered prior to implementing this technique.
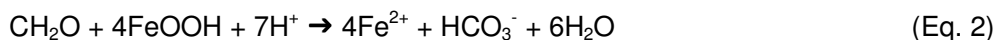
Introduction

Drainage of Holocene coastal floodplain sediments rich in iron sulfides (e.g. pyrite, FeS_2) can lead to the formation of acid sulfate soils (ASS; Dent, 1986). The soil and ground water in ASS can be severely acidic and develop similar geochemical characteristics to acid mine drainage environments (Bigham et al., 1996; Burton et al., 2006). ASS can cause considerable environmental degradation due to seasonal transport of aqueous acidity, Al, Fe and trace metals to adjacent estuarine waterways (Sammut et al., 1996; Sundstrom et al., 2002; Johnston et al., 2004).

An innovative technique to mitigate the negative environmental consequences of ASS is the partial or complete inundation of ASS by tidal marine waters (Powell and Martens, 2005; Johnston et al., 2009a, b). Tidal inundation of ASS is a potentially low-cost, landscape-scale remediation technique which has recently been trialled in far

north Queensland. It is well suited to situations where the site is close to a large marine source, where the elevation of ASS is close to mean sea level and conventional agricultural landuse has been abandoned.

Tidal inundation ameliorates acute acidity by several key processes. Tidal marine waters supply bicarbonate alkalinity, directly neutralising soil and surface water acidity. Tidal inundation also stimulates upward migration of the redox boundary, generating iron and sulfate reducing conditions, as well as curtailing further sulfide oxidation. When Fe(III) minerals and SO_4^{2-} are reduced as terminal electron acceptors during bacterially-mediated oxidation of organic matter, protons are consumed and bicarbonate alkalinity is generated. These reactions can be simplified as per Eqs. 1 and 2,

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad\qquad\qquad (Eq. 1)$$

$$CH_2O + 4FeOOH + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O \qquad\qquad (Eq. 2)$$

Although reduction of Fe(III) and SO_4^{2-} generate alkalinity, both reactions also generate potentially mobile aqueous ions that may re-oxidise and release acidity (i.e. Fe^{2+}). Therefore the incorporation of these ions into solid phase Fe(II)-sulfide minerals (e.g. FeS_2) is a key to long-term amelioration of acidity.

ASS are typically rich in secondary Fe(III) minerals that formed after the oxidation of pyrite (e.g. jarosite, schwertmannite, goethite). Re-establishing tidal inundation in an Fe(III)-rich ASS landscape represents a radical change to the geochemical and hydrological regime. There is considerable potential for reductive dissolution of Fe(III) mineral phases. Tidal pumping of shallow groundwater can be a powerful mechanism for porewater forcing and solute exchange 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 outline the primary findings of a field-based study which investigates the effectiveness and geochemical implications of marine tidal inundation as a strategy for remediating coastal acid sulfate soils.

Materials and 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 (Figure 1; 145°47' E, 16 °56' S). It has a tropical monsoonal climate and annual rainfall of ~2200 mm. The study site originally contained large areas of intertidal mangrove sediments rich in iron-sulfides. A tide-excluding bund wall was constructed around the site in the 1970's to prevent tidal ingress, yet allow drainage waters to exit the site via one-way floodgates (Powell and Martens, 2005). Exclusion of tidal exchange combined with intensive drainage caused the oxidation of sulfidic sediments. This led to the widespread formation of severe ASS across the site and seasonal export of large quantities of acidity to the adjacent Trinity Inlet (Cook et al., 2000; Russell and Helmke, 2002).

This study focuses mainly on the Firewood Creek sub-catchment (Figure 1a). This sub-catchment contained severely acidic soils with extensive sulfuric horizons, mostly in areas with elevations less than 0.5 m AHD (AHD = Australian Height Datum; 0 m AHD approximates mean sea level). A remediation program is underway which mainly consists of incrementally increasing tidal exchange up to an elevation of ~0.5 m AHD via partial opening of the floodgates (see Powell and Martens, 2005). It also involves some treatment of residual acid drainage water with hydrated lime. This program began in 2001–02 and provides regular tidal inundation across most of the acidified areas within the Firewood Creek sub-catchment. Firewood Creek floodgates are located several kilometres from large marine bay and tidal inundation waters are highly saline (>40 dS m^{-1}) for most of the year (Johnston et al. 2009b).
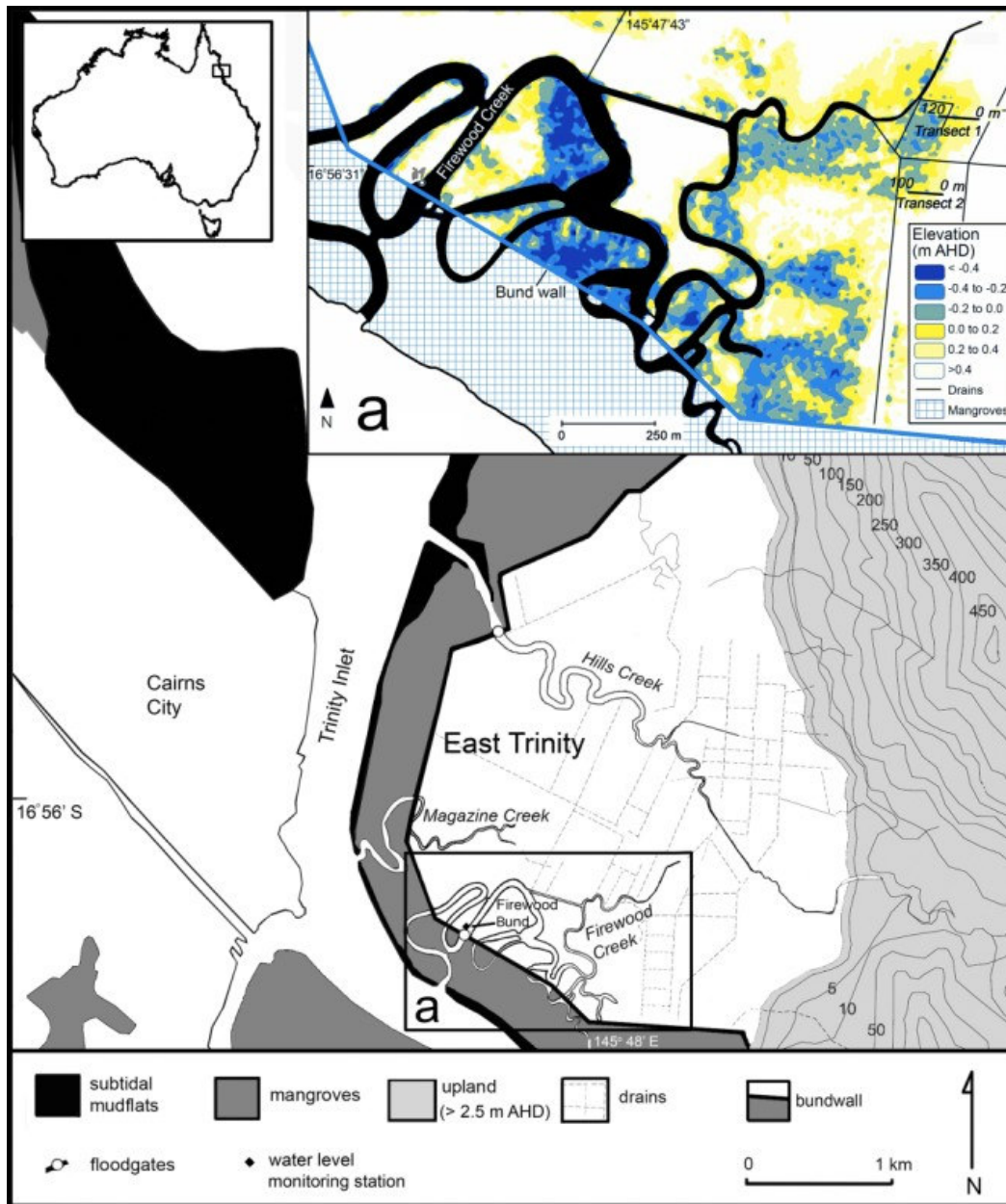

Figure 1: East Trinity study site and transect locations in Firewood Creek.

Soils and hydrology

Two transects were established in the upper reaches of Firewood Creek sub-catchment (Figure 1a) in order to span what is currently the supratidal / intertidal zone (0.6 m to 0 AHD). Both transects have similar stratigraphy and are comprised of clay-textured former ASS underlain by sulfidic estuarine muds. Prior to re-establishing tidal inundation, the soils in this vicinity were Hydraquentic Sulfaquepts (Johnston et al., 2009b). They had distinct sulfuric horizons in the upper 1 m with pedofeatures typical of ASS, including jarosite and Fe(III) oxides mottles (Johnston et al., 2009a). Soil profiles were described according to McDonald et al. (1990)

The extent of tidal inundation in Firewood Creek increased from 2003 to 2007 (Figure 2) due to incremental raising of the floodgates. Tidal maxima in 2007 were about 0.3 m AHD (Figure 2). The tidal range within Firewood Creek is substantially attenuated compared to outside the bund wall in Trinity Inlet, as the floodgate is only partially open and does not allow full propagation of the tidal signal into Firewood Creek.
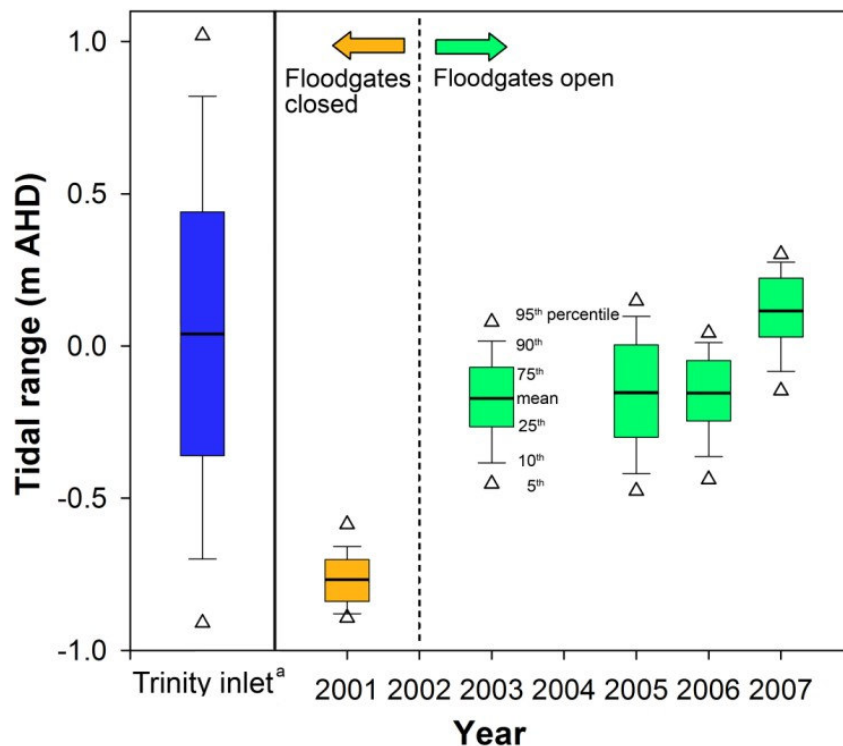

Figure 2: Tidal water level dynamics within Firewood Creek during a period of floodgate closure compared to periods after partial floodgate opening. [a]Tidal range in Trinity Inlet is also shown.

Water quality

The pH, EC and temperature were logged at 10 to 15 minute intervals using either TPS 90FL or Hydrolab Quanta multi-parameter sondes in combination with Campbell Scientific CR10X loggers. Sensor probes were situated in the upper 1 m of the water column and were maintained and serviced regularly with intervals between calibration ranging from 1 to 2 weeks. Whilst pH can only be regarded as an indicator of the total acidity within waterways located in ASS landscapes (Cook et al., 2000), it is

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nonetheless a very useful proxy due to the primary control it exerts over trace metal mobility, solubility, speciation and bio-toxicity.

Transect hydrology

Groundwater levels were measured in a series of four 50 mm diameter PVC piezometers installed along each transect. Each piezometer housed a submersible pressure transducer vented to the atmosphere (Odyssey, ODYPS05) which recorded relative groundwater levels (±0.01 m) at 30 minute intervals. Screened intervals ranged from 0.8 to 1.2 m in length.

Solid-phase properties

Four replicate soil cores were obtained by gouge-auger from each sampling location. Cores were sectioned and sub-samples from equivalent depths were combined in approximately equal quantities to decrease variability arising from spatial heterogeneity. Samples were sealed in air-tight polyethylene bags, completely filled with soil and frozen after collection until analysis. Field pH and redox potential were determined on additional duplicate cores by inserting freshly calibrated electrodes directly into soil. Samples of Fe-rich surficial sediment (0–1 cm) were also collected from a variety of locations within the Firewood Creek sub-catchment and frozen. The elevation of all sample points was surveyed to AHD.

Solid-phase Fe fractions and reduced inorganic sulfur species were extracted from sediments using procedures outlined in Johnston et al. (2009b). Scanning electron microscopy (SEM; Leica 440) was used to examine the micro-morphology of selected samples. Material was mounted on aluminium stubs and coated in carbon. The elemental composition of these samples was determined with an ISIS energy dispersive X-ray (EDX) microanalysis system.

Porewater geochemistry

Porewater was sampled at both transects during April 2008 using an equilibration dialysis method as described in detail by Johnston et al. (2009c). Briefly, duplicate peepers 1.5 m long with removable 25 mL dialysis cells (cell vertical spacing = 0.05 m) were installed at selected intervals along each transect and allowed to equilibrate for up to 38 days. After peeper retrieval, removable dialysis cells were retained in an N_2 atmosphere to prevent alteration of redox sensitive species.

Redox potential and pH were measured immediately using freshly calibrated probes. All redox data presented here has been corrected to the standard hydrogen electrode (SHE). Aliquots of filtrate (0.45 μm) were preserved for colorimetric determination of redox sensitive species. The 1,10-phenanthroline method was used for Fe^{2+} and total Fe (APHA, 1998). Alkalinity (HCO_3^-) was determined by spectrophotometry. The remaining filtrate was preserved with HNO_3 and stored at 4 ^oC stored in the dark for subsequent analysis ICP-AES (Perkin-Elmer DV4300). Total As was determined by ICP-MS (Perkin-Elmer ELAN-DRCe), operated in DRC mode to optimize interference removal. Five percent of samples analysed in duplicate had a precision within 6%.

Results and discussion

Decreased acidity in surface waters

Tidal dynamics in Firewood Creek changed substantially following floodgate opening (Figure 2). Time series water quality data collected over 5 consecutive annual wet seasons were analysed to assess changes in water quality. Following the reintroduction of tidal inundation there were significant increases in the mean daily pH of surface waters in Firewood Creek (Figure 3). The mean daily pH values displayed a clear increase with time, whilst the variability of mean daily pH values also decreased (Figure 3).
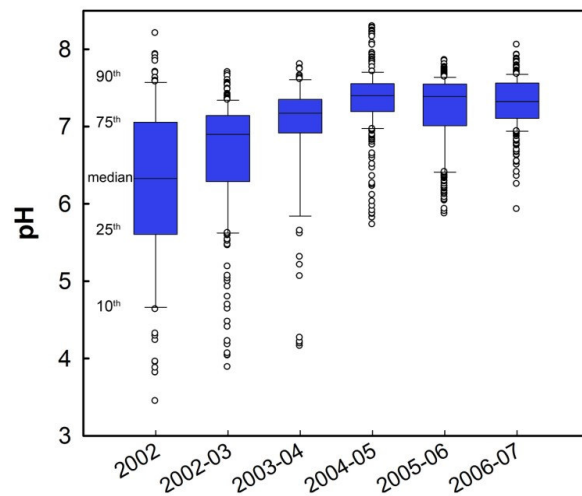
Figure 3: Improvements in surface water pH over time at Firewood Creek following the reintroduction of tidal exchange / inundation.

Further examination of water quality / climate interactions demonstrates that fresh / brackish discharge events became less acidic (Figure 4), and there was a substantial decrease over time in the magnitude of creek acidification per given quantity of antecedent rainfall (Johnston et al., 2009a).
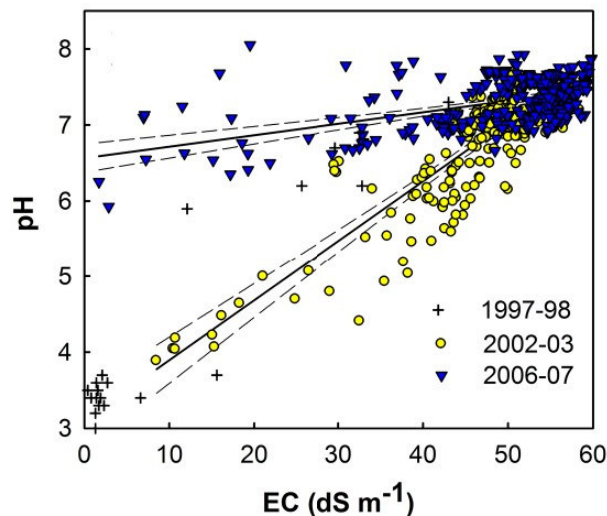

Figure 4: Changes in the relationship between mean daily surface water pH and EC over time at Firewood Creek.

Geochemical regime shift – reductive pedogenesis

Tidal inundation of ASS has caused a major transition in the soil redox regime, triggering a shift from oxic-acidic to reducing-circumneutral conditions. A stability field diagram comparing the redox potential and pH of porewaters collected before (2001-02) and after (2008) tidal inundation (Figure 5) indicates the direction of change.

The pH and Eh of soils after tidal inundation lie close to the Fe(II)/Fe(III) boundary, which suggests that reduction of Fe(III) minerals is exerting a controlling influence on the soil geochemical conditions following tidal inundation (Figure 5). Reduction of Fe(III) minerals is a well recognised and fundamental component of the geochemistry of acid sulfate soils after reflooding (Dent, 1986; Burton et al., 2006). Examination of Fe speciation in soil samples collected after regular tidal inundation revealed that non-sulfidic, solid phase Fe(II) content was high (~0.1–0.6 mmol g^{-1}), thus confirming that the reduction of Fe(III) minerals was an important consequence of tidal inundation.
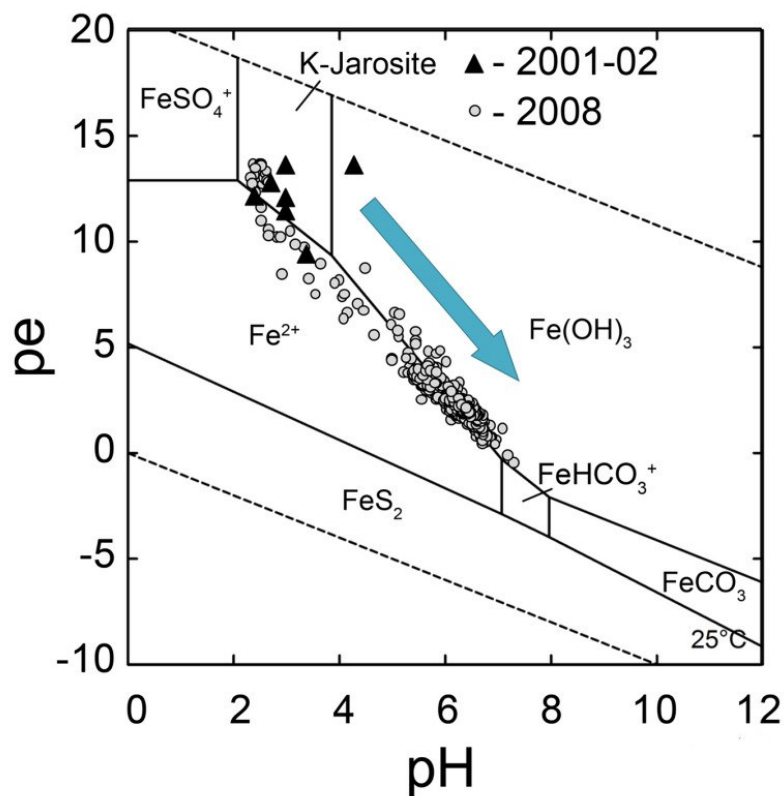

Figure 5: pE-pH diagram for pore-waters before (2001-02) and after (2008) tidal inundation. Stability fields of relevant Fe species are shown with an arrow indicating the direction of change.

The driver behind this major shift in the soil redox regime is the tidally influenced hydrology. This is clearly demonstrated in Figure 6, which shows a sharp geochemical boundary associated with the water levels at the tidal inundation front. Former sulfuric horizons that lie within the intertidal zone are reducing and have largely circumneutral pH (Figure 6). In contrast, near surface soils within the supratidal zone, which has lower and variable water levels due attenuated tidal influence, remain both oxic and contain residual acidity.
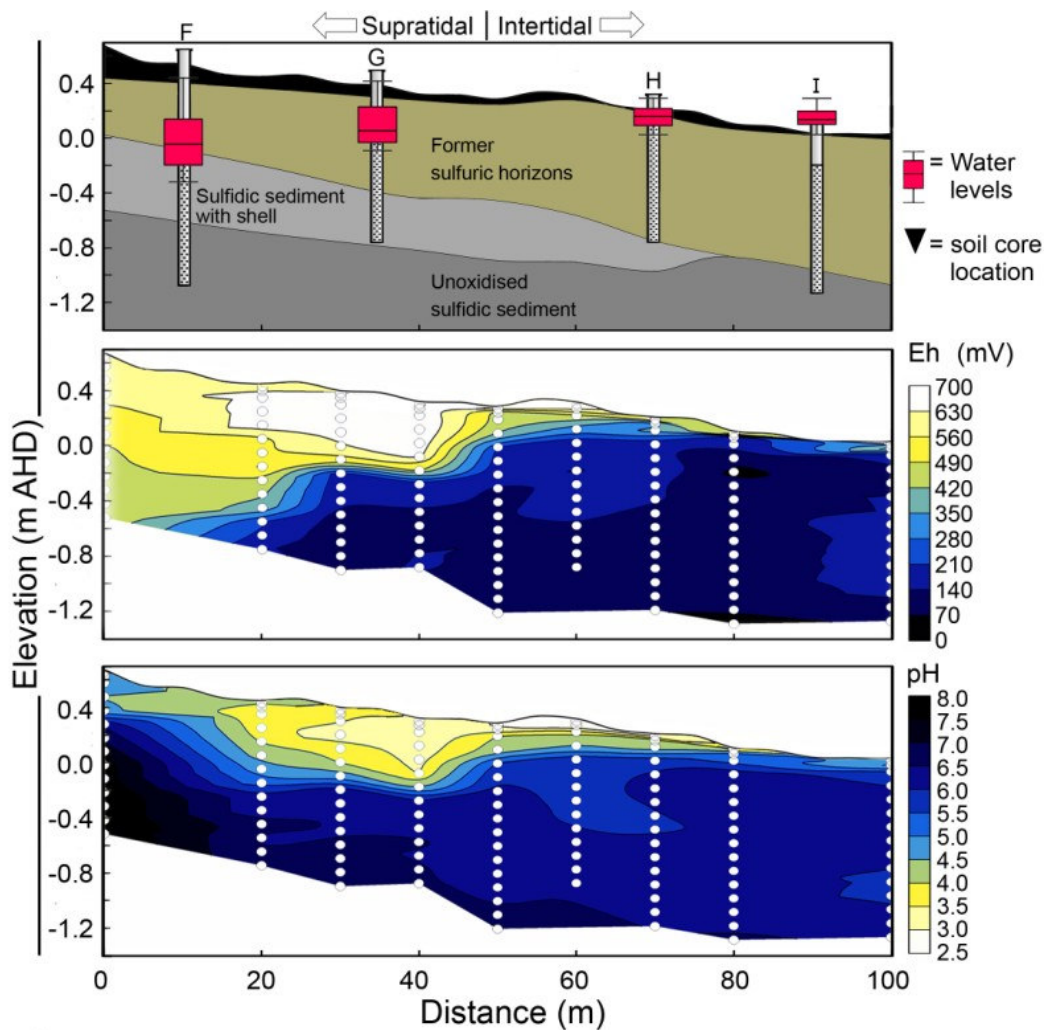
Figure 6: Transect 2 stratigraphy, piezometers (F to I), hydrology (mean water levels during 2007-08) and soil redox potential (SHE) and pH. White circles represent duplicate measurement points.

Consumption of soil acidity and reformation of pyrite

The effects of tidal inundation on soil acidity and iron-sulfide mineral reformation were investigated by comparing the geochemistry of soils from multiple locations before and after five years of regular tidal inundation. An example of this before / after comparative data from one location is provided in Figure 7.

In former sulfuric horizons that had been subject to tidal inundation for ~five years, the pH increased by 2–3 units and titratable actual acidity (TAA) decreased by ~40–50 µmol H^+ g^{-1} (Figure 7). At this location some relict acidity remained at depth (>1 m) in the upper part of the underlying sulfidic horizons. There was considerable reformation of pyrite within former sulfuric horizons after tidal inundation, with reduced inorganic sulfur increasing by ~60 µmol g^{-1} (Figure 7).
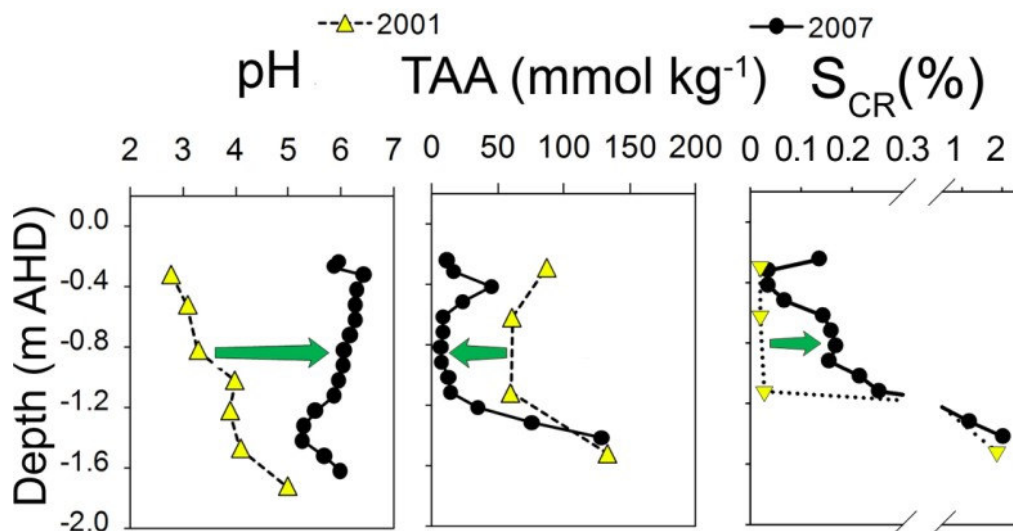
Figure 7: Example of changes in key soil properties before (2001) vs after (2007) reintroduction of tidal inundation. Arrows represent direction of change.

The presence of newly-formed pyrite in former sulfuric horizons subjected to tidal inundation was confirmed using SEM and EDX analysis. Analysis of soils collected after tidal inundation revealed multiple spheroidal crystalline structures matching the morphology of pyrite framboids as well as individual euhedral crystals and euhedral clusters (Figure 8). EDX spectra on framboids and individual crystals were consistent with the elemental composition and stoichiometry of pyrite. This is clear evidence of tidal inundation causing contemporary pyrite formation in formerly oxidised sulfuric horizons.
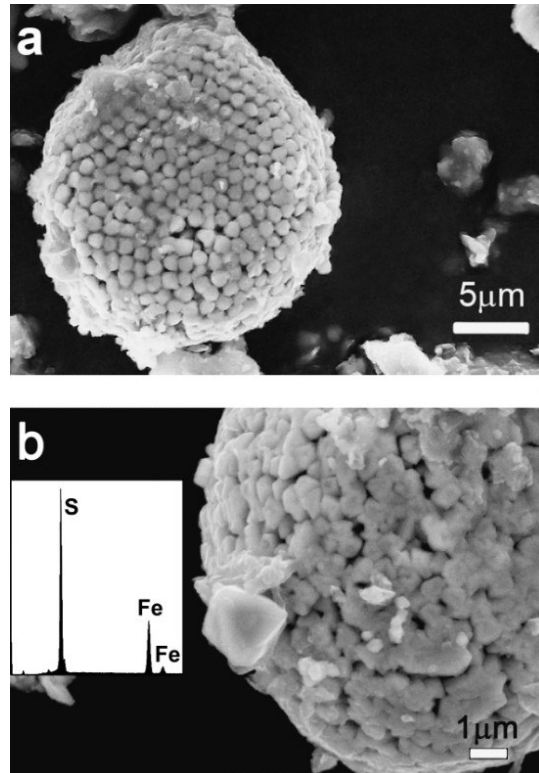

Figure 8: Scanning electron microscope images and EDX spectra of (a) and (b) pyrite accumulations in former sulfuric horizons subject to tidal inundation. From soil materials collected in 2007.

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Sources of alkalinity

Whilst there is evidence to suggest that both marine-derived alkalinity and reductive processes were jointly responsible for the decreases in acidity, reductive processes appear to have been particularly significant. A positive relationship between redox potential and TAA in the tidally inundated soils (data not shown) suggests that internal alkalinity generation due to reductive processes was an important means of proton consumption. Porewater alkalinity exceeded 20 mmol L^{-1} in some intertidal sediments (seawater is ~2.2 mmol L^{-1}), which clearly points toward an additional, internally-derived source.

It is possible to calculate the theoretical consumption of H^+ that could be accounted for by reformation of pyrite in the former sulfuric horizons. Assuming that the S_{CR} fraction comprises solely of pyrite and 4 mol H^+ is consumed for every mol of FeS_2 produced, then a 30–60 µmol g^{-1} increase in S_{CR} is equivalent to a consumption of 60–120 µmol H^+ g^{-1}. This corresponds reasonably well with the observed decreases in TAA in former sulfuric horizons of ~40–50 µmol H^+ g^{-1}.

There was a strong negative relationship between the mean pH of former sulfuric horizons and the surface elevation of the sampling location – which serves as a proxy for duration of tidal inundation (Figure 9). Lower elevation areas (subjected to tidal inundation for longer) clearly had higher pH values, which is consistent with increasing generation of internal alkalinity over time. As demonstrated in equation 2, reduction of Fe(III) minerals generates alkalinity. There was a strong positive relationship between the solid-phase Fe(II) content of former sulfuric horizons subjected to tidal inundation and their mean pH (Figure 9). This is consistent with Fe reduction being an important mechanism for the generation of alkalinity within the tidally inundated ASS.
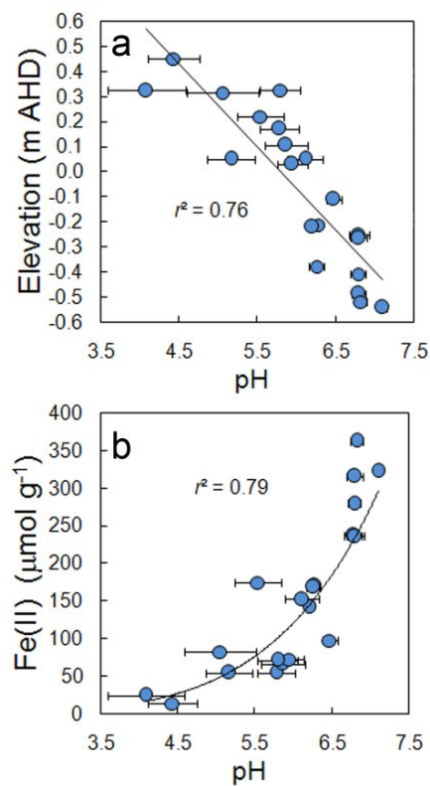

Figure 9: Relationships between the mean soil pH of former sulfuric horizons (0–0.7 m bgl) and (a) surface elevation, (b) solid-phase Fe(II) contents. Error bars are ±standard deviation.

Decreases in labile aluminium

There were large decreases in water-soluble and exchangeable Al fractions within former sulfuric horizons following reintroduction of tidal inundation. This was strongly associated with decreased soil acidity and increases in pH (Figure 10a), suggesting pH-dependent immobilisation of Al via precipitation as poorly soluble phases.

Aluminium is one of the most environmentally significant elements associated with ASS. It is readily leached from acidified soils into adjacent waterways (Sammut et al., 1996) and can have severe deleterious effects on fish (Lydersen et al., 2002), fish larvae (Hyne and Wilson, 1997), oysters (Dove and Sammut, 2007) and a host of other gilled organisms. Thus, the large decrease in labile Al fractions of soils after tidal inundation is an important finding of this study from an eco-toxicological and site-remediation perspective.
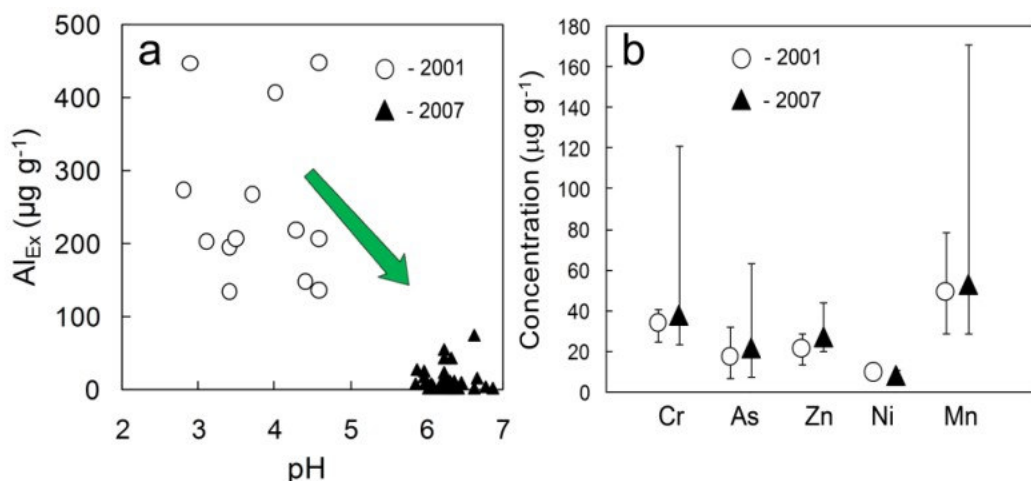

Figure 10: (a) Changes in the exchangeable aluminium of former sulfuric horizons in relation to pH at four sites in Firewood Creek between 2001 to 2007, (b) comparison of the mean and range (error bars) of selected total trace metals at four sites in Firewood Creek between 2001 to 2007.

The water-soluble fractions of Zn, Ni and Mn also decreased in accord with the rise in pH. While mean total concentrations of Cr, Zn, As, Ni and Mn were very similar before and after the reintroduction of tidal inundation, the maximum total concentrations of Cr, Zn, As and Mn appear to be elevated (Figure 10b). These elevated trace metal contents were closely associated with an enrichment of reactive Fe near the sediment surface, which is discussed in more detail below.

Enrichment in reactive-Fe near the sediment surface

One of the most important geochemical consequences of tidal inundation is the enrichment in poorly crystalline, reactive Fe(III) minerals near the surface of the sediment (up to 5–40% Fe by weight in upper several cm; Figure 11). The reason for this enrichment is the hydro-geochemical coupling that occurs between reductive processes and tidal pumping.

The reductive dissolution of Fe(III) minerals, including jarosite, leads to very high concentrations of porewater aqueous Fe^{2+} (>2000 mg L^{-1}) in former sulfuric horizons in the upper-intertidal zone. This mobile Fe^{2+} is able to be re-distributed according to the
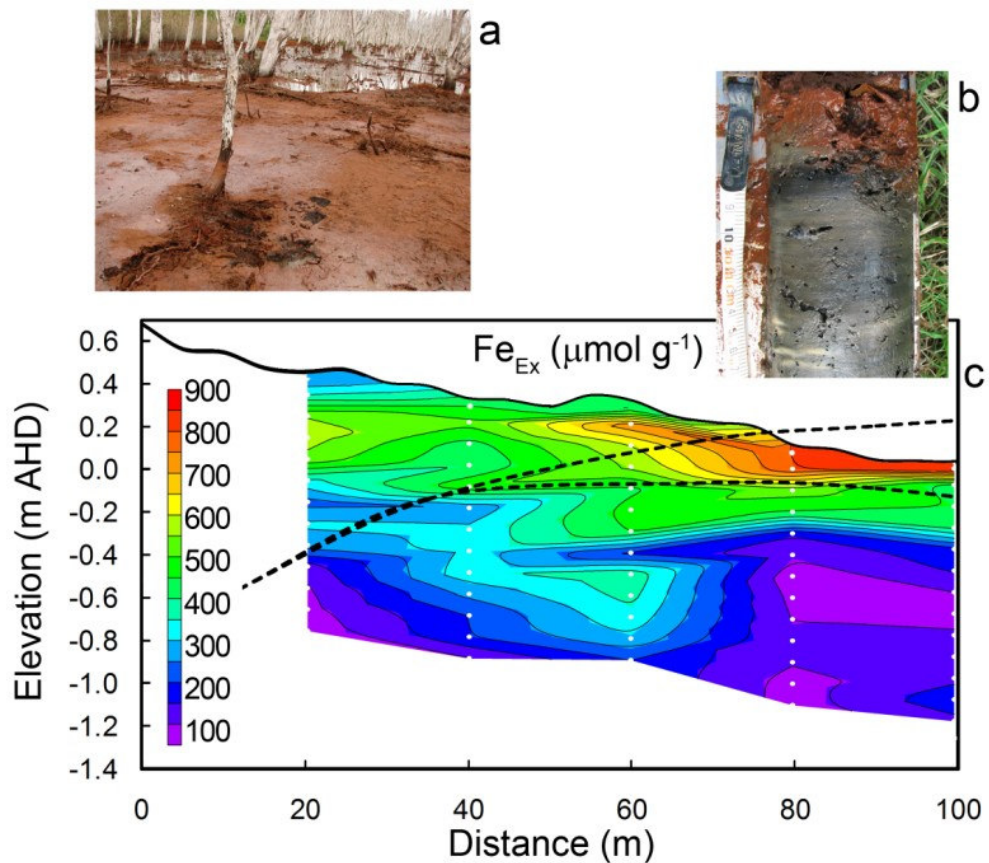
Figure 11: (a) Surface accumulations of poorly crystalline Fe(III) minerals, (b) surficial enrichment of Fe(III) minerals in a soil core, (c) surface enrichment of poorly crystalline reactive Fe fractions (Fe$_{Ex}$) within the intertidal zone at Transect 2. Dashed lines represent tidal water table minima and maxima at time of sampling.
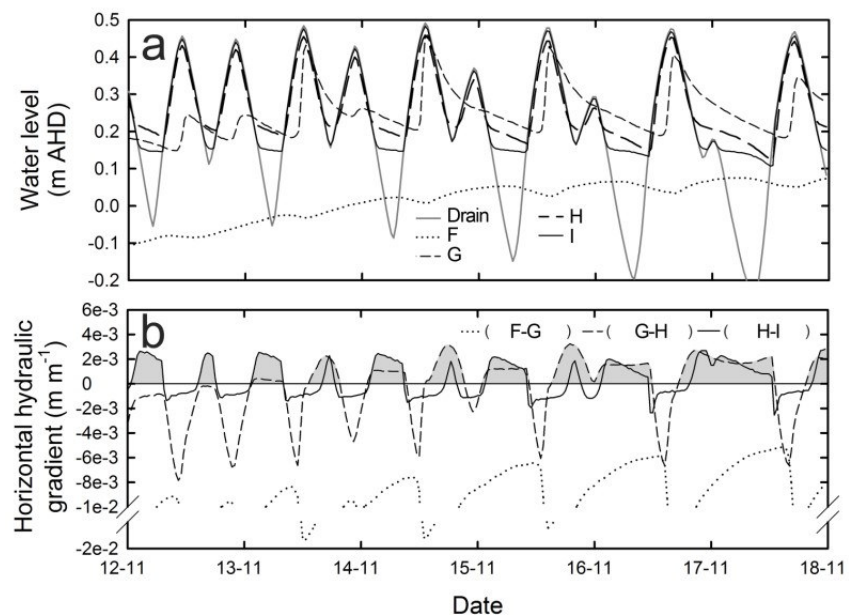

Figure 12: Transect 2 (a) tidal pumping of groundwater levels (piezometers F to I – see Figure 6) and (b) corresponding horizontal hydraulic gradients. Periods of effluent (seaward) gradients shaded gray.

prevailing tidally-influenced hydrology. Tidal pumping in the fringing aquifer generates oscillating hydraulic gradients, which can drive upward advection of Fe^{2+}-enriched porewater during the ebb-tide phase (Figure 12). This is followed oxidation of Fe^{2+}, precipitation and subsequent accumulation of Fe(III) minerals in surficial tidal sediments (Figure 11). Fe(III)-precipitates at the sediment surface-water interface are poorly crystalline and displayed a mineralisation sequence that is related to tidal zonation.

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. Evidence from the site to date suggests that there is a corresponding surficial enrichment of a number of trace metals.

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 (Poulton et al., 2004; Burton et al., 2007). Examination of reduced inorganic sulfur speciation in tidally inundated former acid sulfate soils did indeed show higher concentrations of these more reactive S fractions near the surface (Figure 13). This was positively correlated with poorly crystalline Fe contents (data not shown).
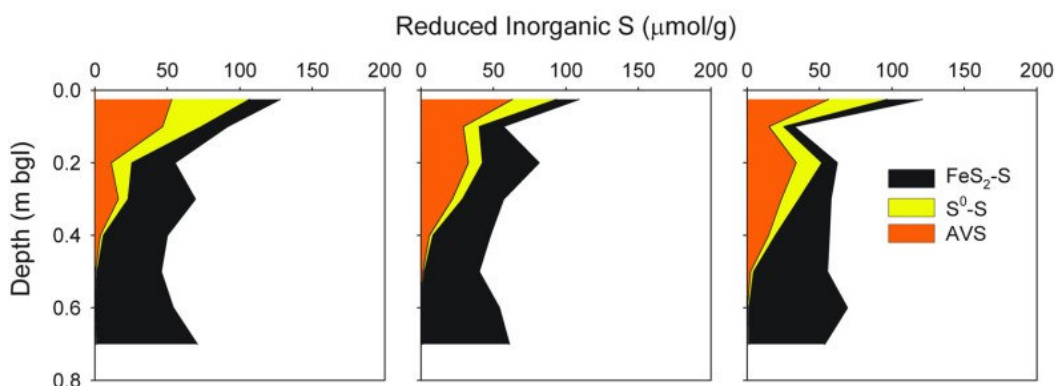

Figure 13: Reduced inorganic sulfur speciation in tidally inundated former acid sulfate soils.

Poorly crystalline reactive Fe is also is one of the main factors limiting the long-term accumulation of FeS_2 in tidal marsh environments (Rickard and Luther, 2007). Thus, its accumulation within intertidal surficial sediments may favour the eventual formation of very high concentrations of FeS_2. Preliminary calculations suggest that if approximately 80% of this surficial reactive Fe is eventually converted to pyrite, this may result in pyrite concentrations of 15–20% - which is about an order of magnitude higher than the original mangrove sediments at the site. This is an important potential longer term consequence which has obvious implications if tidal inundation were ceased.

Mobilisation of arsenic during the redox transition

It is well recognized that As is prone to aqueous mobilization during redox transitions associated with re-flooding of oxic sediments (Smedley and Kinniburgh, 2002). The mechanisms of As mobilization and attenuation in coastal aquifers are complex, yet are often intimately coupled with fate and geochemical cycling of Fe (hydr)oxides and sulfide minerals. Fe(III) minerals such as jarosite ($KFe_3(SO_4)_2(OH)_6$) are widely regarded as important sorbents for As (Smedley and Kinniburgh, 2002) and can become highly enriched in adsorbed As(V) under oxic conditions in acid sulfate soils. Such preferential partitioning of As was observed at the study site where jarosite was

enriched by a factor of ~4–5 x (75µg/g) compared to immediately surrounding soil matrix (Table 1).

Table 1: As in Transect soils and key Fe fractions, mean (±standard deviation)

Location/soil fraction (*n*)	Near-Total extract (µg/g)
Transect 1 & 2 (*110*)	18.3 ±6.5
Matrix[A](*4*)	13.1 ±4.6
Jarosite(*4*)	75.7 ±14.7
Surface Fe(III)-rich accumulations[B] (*34*)	36.1 ±26.3
Pyrite(*2*)	279.0 ±24.9

[A]Soil matrix surrounding jarosite pedofeatures.
[B]Collected from 0–0.01 m depth bgl.

Evidence suggests that reductive dissolution of jarosite is occurring as a consequence of tidal inundation, and that this dissolution is a substantial source of porewater Fe^{2+} at the study site. The reductive dissolution of jarosite (and other Fe(III) minerals) not only releases Fe^{2+} into solution, but may also mobilise any associated arsenic.

A series of jarosite pedofeatures collected from either side of the supratidal/intertidal boundary along Transect 2 were subjected to SEM-EDX analysis (Figure 14). Jarosite from the supratidal zone (i.e. 20 m) generally comprised of inter-grown euhedral crystals >1 µm with clearly defined edges and planar surface features (Figure 14 a, b). In contrast, jarosite from within the intertidal zone (i.e. 100 m) exhibited features consistent with dissolution, including smaller, sub-rounded crystals with clearly visible etch pits (Figure 14 c, d).
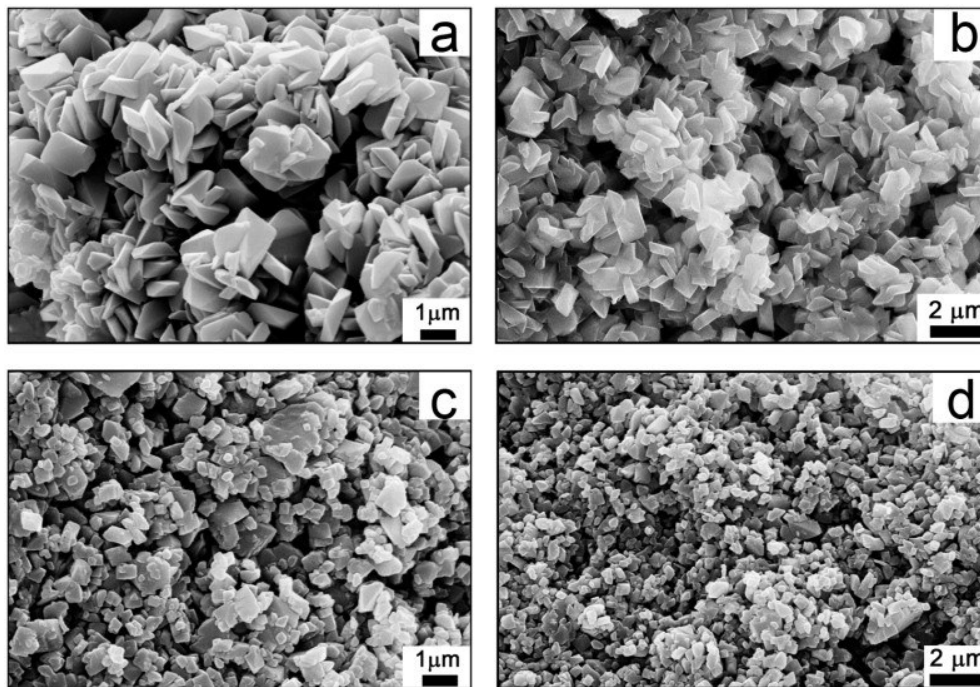

Figure 14: Scanning electron microscope images of (a), (b) jarosite from Transect 2, 20 m (supratidal zone) and (c), (d)Transect 2, 100 m (intertidal zone).

A distinct pattern of aqueous arsenic is evident in intertidal fringe porewaters at the transects (Figure 15). Maximum porewater As (>400 µg/L) mobilisation occurred in the shallow aquifer (<1 m) redox transition zone between iron-oxidizing and sulfate reducing conditions. The current WHO drinking water standard for As is <10µg/L. This mobilisation is strongly associated with elevated Fe^{2+}. There is attenuation of porewater As in the areas further downslope which corresponds to the zone of contemporary pyrite re-formation. Pyrite and other Fe-sulfides are well recognized as being highly effective at preferentially sequestering As.
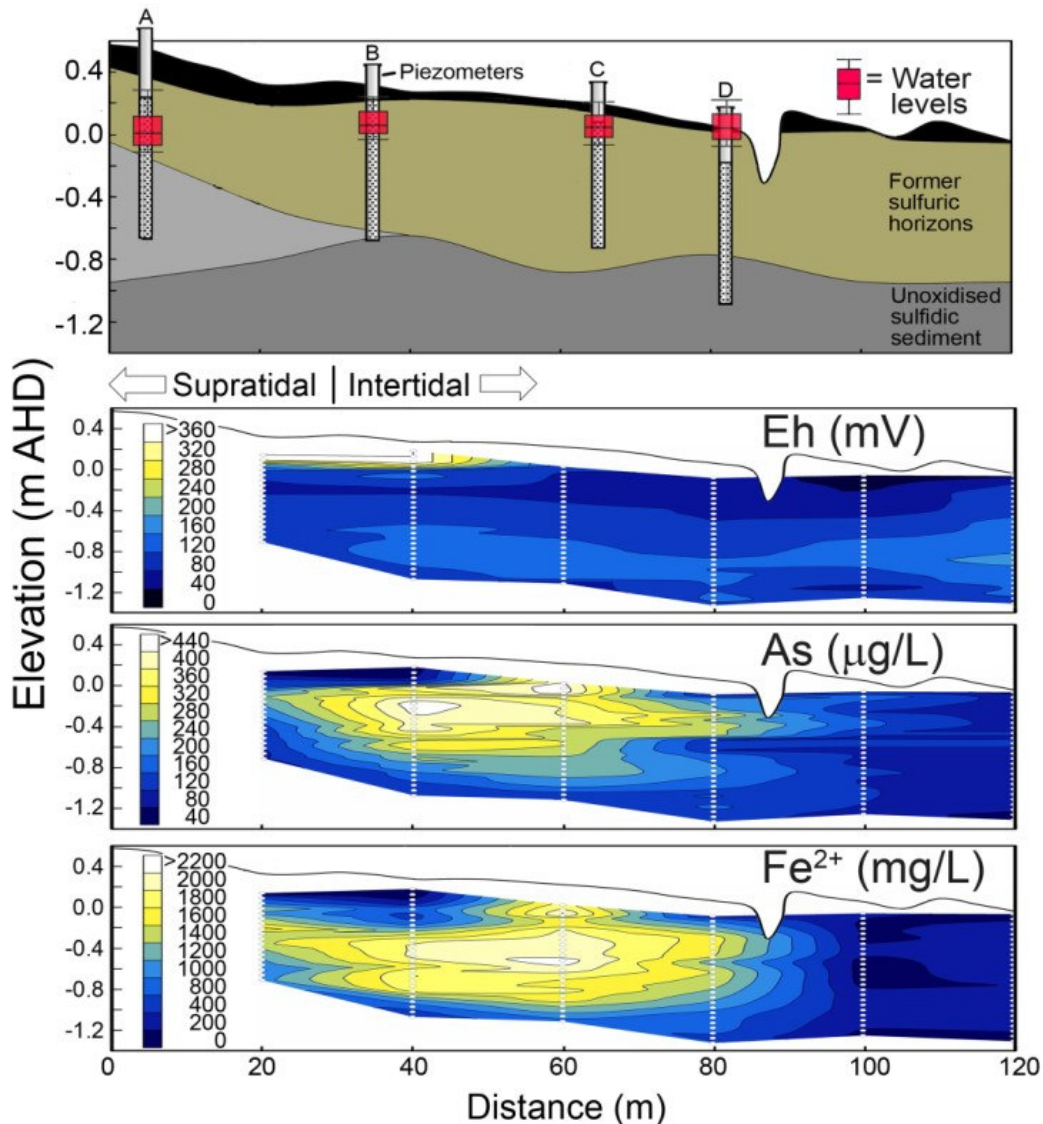

Figure 15: Transect 1 stratigraphy, piezometers (A to D), hydrology (mean water levels during 2007-08) and porewater Eh (SHE), arsenic (As) and Fe^{2+}.

Hysteresis of tidal remediation

It is clear that tidal inundation of ASS has been effective at decreasing soil and water acidity and reducing the environmental risks associated with labile aluminium fractions. From a broader perspective, tidal inundation has effectively re-established similar diagenetic forces to those which dominated in the original, pre-drainage mangrove environment, thereby encouraging Fe and SO_4 reduction and the reformation of pyrite.

However, the onset of mass reductive dissolution of Fe has effectively mobilised a large store of previously immobile secondary Fe(III) minerals. Hence, one very important feature of the sites geochemistry is now substantially different – i.e. the abundance of reactive Fe in surficial sediments. This has lead to a hysteresis in the geochemical trajectory of remediation which is represented conceptually in Figure 16.
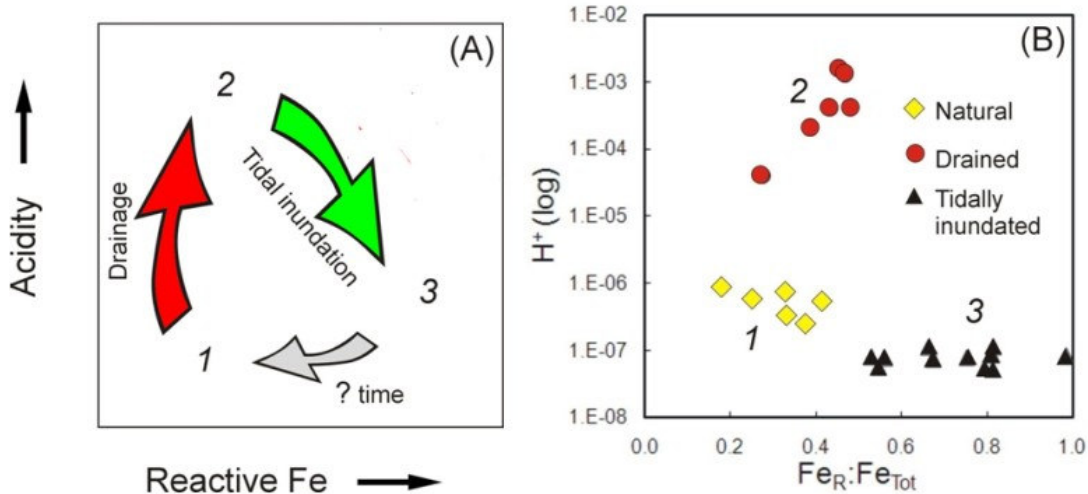

Figure 16: Conceptual representation of hysteresis in tidal remediation of ASS with respect to changes in acidity and the reactive-Fe fraction in surficial sediments

The hysteresis shown in Figure 16a can be described as follows 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 a slight 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 is likely over time, but the kinetics of this process are uncertain. Corresponding field data from the East Trinity site is shown in Figure 16b, for surficial sediments (0–0.1 m) under natural **(1)** and drained **(2)** conditions and after the reintroduction of tidal inundation **(3)**.

Conclusions and applied management implications

This study demonstrates that marine tidal inundation can be an effective landscape-scale strategy for ameliorating severe acidity associated with drained acid sulfate soils. It is effective at raising the pH of soils through internal generation of alkalinity via reductive processes and can greatly decrease the concentration of labile Al fractions. It can be a highly effective means for stimulating Fe / S reduction and the reformation of pyrite.

The transferability of this technique to other areas will be influenced by a range of factors. A major advantage of this technique is its potential for relatively low costs and broad, landscape-scale coverage. However, it is most applicable in situations where the elevation of the ASS is close to mean sea level and conventional agricultural landuse has been abandoned entirely. Proximity to a large, well buffered marine tidal source is also likely to be important. The technique may be less well suited to sites in

mid-estuary locations which tend to have limited bicarbonate buffering and a constrained assimilation capacity in adjacent estuarine waters.

It is important to recognise that the technique is essentially non-reversible without likelihood of severe environmental consequences. The enhanced reformation of reactive reduced inorganic sulfur species (i.e. AVS, S^0) in near-surface sediments, promoted by reactive Fe, means that surface sediments are more likely to produce acidity quickly in the event of oxidation. Whilst it has been identified that there is potential for enhanced long-term accumulation of pyrite near the sediment surface, further monitoring is required to verify this possibility.

Tidal inundation of ASS can cause mass mobilisation of aqueous Fe and co-precipitated / adsorbed trace elements during the redox transition. Tidal pumping provides an important physical forcing mechanism which facilitates the redistribution of aqueous species within shallow intertidal zone sediments, and also drives the surface accumulation of Fe. Minimising the extent of porewater drainage is important to prevent contamination of surface waters, particularly during the redox transition when Fe^{2+} and arsenic are highly mobile. Attenuating the tidal range during the redox transition may be one simple method of reducing such porewater flux.

This study reveals the overarching importance of Fe as key element in tidally inundated acid sulfate soils. The mobilisation, redistribution and subsequent mineralogical transformations of Fe within the landscape underpin the geochemical trajectory of remediation. A clear understanding of the behaviour of Fe is critical in evaluating the transferability of this remediation technique.

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