Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation

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\textbf{A R T I C L E   I N F O}

\textbf{A B S T R A C T}

Marine tidal inundation was partially restored to a severely degraded tropical acid sulfate soil landscape after having been excluded for over 30 years. The effects on soil acidity and iron-sulfide mineral formation were investigated by comparing the geochemistry of soils before and after five years of regular tidal inundation. The soil pH increased by 2-3 units and titratable acidity (TAA) decreased by ~40-50 \textmu mol H\textsuperscript{+} g\textsuperscript{-1} within former sulfatic horizons. Relict acidity remained at depth (~1 m) in the underlying sulfatic horizons. \textsuperscript{14}C\textsuperscript{S} data indicate that tidal inundation caused exchange of marine solutes within former sulfatic horizons, but not within underlying sulfatic material. There was considerable reformation of pyrite within former sulfatic horizons after tidal inundation with reduced morgonite surfacing increasing by ~60 \textmu mol g\textsuperscript{-1}. Acid-sulfate surface also accumulated, but mainly near the soil surface (up to 4 \textmu mol g\textsuperscript{-1}). Reduction of Fe(II) minerals strongly influences the geochemistry of the study area. Tidal inundation the soil pH and TAA slowly followed the area reduces. Thus, there was no evidence that tidal inundation has increased paddy rice yields. There was a slow uplift of poorly crystalline Fe-oxides near the soil surface following tidal inundation, with reactive Fe(II) spurring up to 400 \textmu mol g\textsuperscript{-1}. While the decreases in soil acidity documented here are likely due to a combination of marine alteration and redox of Fe(II) and SO\textsubscript{4}, the relative importance of each process remains to be determined. This study demonstrates that marine tidal inundation can be an effective landscape-scale strategy for ameliorating severe acidity associated with drained acid sulfate soils.

\textbf{1. Introduction}

Tropical coastal floodplains throughout the world are subject to increasing development pressures. These floodplains are often underlain by Holocene sulfidic sediments containing biogeochemically active sulfide minerals (e.g. pyrite, FeS\textsubscript{2}). Drainage and reclamation of these environments can cause oxidation of sulfides and lead to the formation of acid sulfate soils (e.g. van Breemen, 1982; Peeters, 1986). The global extent of mangrove land and acid sulfate soils (CLASS) is estimated at ~12–13 million ha, most of which are located in tropical regions (Andriesse and van Mansvoot, 2006). The soil and ground water in CLASS can become severely acidic and develop similar geochemical characteristics to acid mine drainage environments (Evangelou, 1995; Dugham et al., 1990; Burton et al., 2002). Seasonal mobilisation and transport of acidic solutes and trace metals from drained CLASS can contaminate adjacent waterways and is a cause of considerable environmental degradation (e.g. Saini et al., 1990; Mitti et al., 1997; Sundstrom et al., 2002; Jukkainen and Yli-Halla, 2003; Johnston et al., 2004a; Macdonald et al., 2004). The development of effective and low-cost, landscape-scale techniques for remediating the environmental impacts of drained CLASS has been the subject of substantial research efforts. Many techniques focus on decreasing the severity of off-site water quality impacts via hydrological containment, neutralisation or dilution of aqueous acid products (e.g. Mcelneea et al., 1990; Andriesse et al., 2000; Johnston et al., 2005; Green et al., 2006; Åström et al., 2007). However most of these techniques have been applied within a context of maintaining existing agricultural landuse. This constrains the extent to which hydrology and drainage outcomes can be modified and as a consequence they fail to provide only partial solutions to environmental problems.

Tidal inundation of CLASS is a potentially low-cost, landscape-scale remediation technique. In addition to dilution and neutralisation, it has potential to suppress the hydrological transport of aqueous acid products and encourage the in situ reformation of solid phase iron-sulfide minerals (Mitchel et al., 2003; Parvee and Martin, 2003). It is most applicable in situations where the elevation of CLASS is close to mean sea level and conventional agricultural landuse has been abandoned. However this technique has rarely been applied on a large scale.
Tidal exchange with marine waters will supply bicarbonate alkalinity that may neutralise some soil acidity. Tidal inundation may also ameliorate acidity by stimulating upward migration of the redox boundary, causing the reduction dissolution of Fe(III) minerals and SO_{4}^{2-}, as well as curtailing further sulfide oxidation. When Fe(III) minerals and SO_{4}^{2-} are reduced at terminal electron acceptors during bacterially mediated oxidation of organic matter, protons are concomitantly released which results in increased bicarbonate alkalinity. These reactions can be simplified as per Eqs. (1) and (2).

$$\text{Fe}_2\text{O}_3 + 3\text{SO}_{4}^{2-} + 14\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 7\text{H}_2\text{O}$$  
$$\text{Fe}_2\text{O}_3 + 3\text{SO}_{4}^{2-} + 6\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 7\text{H}_2\text{O}$$

Although reduction of Fe(III) and SO_{4}^{2-} generates alkalinity, both reactions also generate potentially mobile aqueous ions that may re-oxidise and release acidity (i.e. Fe_{2}^{3+} and H_{2}SO_{4}). 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. Iron-sulfur minerals can form through a variety of complex pathways in intertidal environments (Richard and Luther, 2007). Their incorporation is strongly influenced by soil solution pH, redox status, organic carbon substrates, as well as the abundance and reactivity of iron oxide minerals present (Postma and Jilbertsen, 1996). The formation of pyrite can be represented by Eq. (3).

$$\text{Fe}_2\text{O}_3 + 4\text{SO}_{4}^{2-} + 8\text{CH}_4 + 1/2\text{O}_2 \rightarrow 2\text{FeS}_2 + 8\text{CO}_3^{2-} + 4\text{H}_2\text{O}$$

The shift to reducing conditions initiated by tidal inundation of class may therefore favor incorporation of iron-sulfur minerals and the in-situ transformation of soil acidity (Burton et al., 2006). Pyrite formation can be rapid in natural intertidal environments (Howarth, 1979). Both pyrite and monosulfides are known to be retained in class landscapes due to seasonal shifts in hydrology or the formation of low tide, highly reducing, sub-environments (Bush and Sullivan, 1997; Rosselet et al., 2004; Burton et al., 2006, 2007). Pyrite and Gahani (1999a) demonstrated that sequestering a drained and acidified former saltmarsh with seawater stimulated both Fe(III) and SO_{4}^{2-} reduction. However, there are few examples of field-based investigations in acid soils to evaluate the effectiveness of re-establishing tidal inundation at either ameliorating acidity or sequintising Fe(II)-sulfur minerals such as pyrite. This study investigates the geochronology of a transect and reclaimed tropical floodplain containing and saline soils that have undergone controlled, partial re-introduction of tidal inundation. It aims to assess the effects of re-introducing tidal inundation on soil acidity and the distribution of Fe(II)-sulfur minerals within that landscape.

2. Methods

2.1. Study site

The study site, East Trinity, is an ~800 ha Holocene sedimentary coastal plain located near Cairns in northern Australia (145°4′E, 16°56′S; Fig. 1). It experiences a tropical monsoonal climate with summer-dominant rainfall. The site originally contained large areas of estuarine wetlands, including mangrove and saltmarsh communities. A tide-excluding bund wall was constructed around the site in the 1970s (Powell and Martens, 2005). This was followed by extensive drainage and widespread clearing for sugar cane production. There are several earthen creeks located at the site; Hill Creek, Magazine Creek, Firewood Creek and Georges Creek. The bund wall effectively prevented tidal exchange from these creeks. One-way floodgates allowed drainage waters to exit the site during the ebb tide. Exclusion of tidal exchange combined with intensive drainage led to lowering of water tables and subsequent oxidation of sulfidic sediments (Hicks et al., 1999). This led to the formation of evapourative saline soils and seasonal export of large quantities of acidity from the site (Creek et al., 2003; Hicks et al., 2007; Russell and Holmberg, 2007; Smith et al., 2007; Powall and Martens, 2005). This study focuses on soils located in the Firewood Creek sub-catchment (Fig. 1) and examines changes occurring due to the re-introduction of regular tidal inundation.

The re-mediation strategy for the study site is summarised in Powall and Martens (2005) and mainly consists of incrementally increasing tidal exchange via controlled opening of the floodgates. This is intended to provide regular tidal inundation of acidified areas of Firewood Creek sub-catchment on the landward side of the bund wall. The remediation strategy also involved extending seawater quality monitoring and statistical treatment of acid drainage water with lithogenic alkali (CaO/HO). Treatments of acidic drainage water with an alkali reagent was considered an important adjunct to the main strategy, particularly during the early stages of reintroducing tidal exchange when the potential for mobilisation of stored acidity from the system was greatest (see Smith et al., 2003, Powall and Martens, 2005 for further details).

2.2. Tidal water levels and electrical conductivity

Water levels were monitored at Firewood Creek immediately inside the bund wall from 2001 to 2007. Water levels were measured by pressure transducers (Geospace PS700, PSI100) at either hourly or 10 minute intervals, recorded by a data-logger (Campbell CR10X) and downloaded daily using telemetry. Pressure transducers recorded only relative water levels. These relative water levels were offset and corrected to Australian Height Datum (AHD where 0 AHD = mean sea level) using manual readings taken at an adjacent tidal gauge board which had been arranged to AHD. Data used in this study was averaged from dry season periods only (May–Nov) to minimise the influence of rainfall on the tidal signal in Firewood Creek. The Firewood Creek floodgate was subject to a short period of uncontrolled opening in early 2001 due to failure, prior to being closed again. This was followed by more extensive, controlled tidal exchange commencing in 2002. The electrical conductivity (EC) of tidal waters was monitored immediately inside the bund wall using either TPS301 or Hydrotest (Quanta) multi-parameter sondes in combination with Campbell Scientific CR10X loggers. Salinity probes were situated in the upper 3 m of the water column and were maintained and serviced regularly with calibration intervals ranging from 1 to 2 weeks.

2.2.1. Collection of soil samples

2.2.1. Prior to re-introduction of tidal inundation

Five sites in the Firewood Creek sub-catchment were chosen for comparative assessment of key soil properties before and after reintroduction of tidal inundation. Initial sampling was conducted in August 2001 (sites 41, 42, 43 and 46) and June 2003 (site 95) (Fig. 1a). While there had been some limited tidal inundation of sites 41, 42, 43 and 46 prior to this initial sampling (due to the above-mentioned period of dike failure), this essentially represents the soils in their acidified, oxidised and large pre-tidal inundation state. Soils were collected using hand augers. Site locations were recorded by hand held GPS receiver and marked by an orange stake. Analysis of field pH (mH) was conducted by inserting a freshly calibrated pH probe into a 1:1 fresh soil:water paste. Profiles were described according to McDonald et al. (1999) and soil samples collected from selected horizons. Samples were placed in a portable refrigerator and transferred to a freezer at the end of each field day to avoid oxidation of sulfides. Soil samples were oven dried at ~85 °C and crushed to ~0.5 mm before analysis.

2.2.2. After tidal inundation

Sampling after regular tidal inundation was conducted in October 2007. Sites were identified by locating the original wooden stakes
stages with the aid of a hand held GPS. The ground surface was surveyed in AHD at each location. At each soil sampling location two soil cores were collected 1 m apart using a gouge auger or push corer to a depth of ~1.3–1.4 m. Soils were classified according to Soil Survey Staff (1998). Analysis of pH and field redox potential (Eh) was conducted immediately after core retrieval by inserting freshly calibrated probes (intermediate junction Ag/AgCl) directly into freshly excavated soil, with electrode calibration and KCl electrolyte.
replacement between sampling sites. All redox data presented here has been corrected to the standard hydrogen electrode. Sub-samples from each pair of cores were collected at 0–0.05 m, 0.05–0.15 m and in 0.1 m increments thereafter to a depth of 1.25 m below ground surface. Samples from the corresponding depth increments of the duplicate cores were combined in equal quantities in order to reduce errors arising from spatial heterogeneity. Figures in this study display soil data using the midpoint of sampling depth increments. Samples were frozen within 12 h of collection to avoid oxidation of sulfides. A portion of each sample was retained for wet extraction procedure and the remainder air-dried at 55 °C and crushed to <0.5 mm.

2.4 Sediment moisture content was determined by weight loss after oven drying at 105 °C. The IC and pH of a 1:5 water extract was determined for each sample (Raymond and Higginson, 1992). Total iron (III) oxide (TFA) was determined via titration of a HCl suspension using the method outlined by McElnea et al. (2002) and duplicate analysis (n=6) showed that precision was within 12%. The reduced inorganic sulfur (RIS) concentration of all dried and crushed samples was determined using the chromic acid reduction technique (Swain – Sullivan et al., 2003) and used as a proxy for pyritic concentration. Duplicate Sx extractions (n=9) had a precision within 6%. Total sulfur (Sx) and total organic carbon (TOC) were determined using an Elemental combustion analyser. Water soluble SO4 (Sxw) was determined on an aliquot of a 1:5 water extract using ICP-OES (Raymond and Higginson, 1992).

A sequential extraction procedure was used to assess Fe fractions. This comprised of an exchangeable Fe extract (1 M NaCl, 1:40 soil:solution, 1 h extraction), followed by a reactive Fe extract (1 M HCl, 1:40 soil:solution, 4 h extraction) and then a near total digestion employing hot aqua regia (1:3 HNO3:HCl, 110 °C, 4 h soil:solution, 1 h extraction). Aluminosilicate extracts were analysed for Fe by ICP-MS (APHA, 1998) and near total Fe (Sx) was calculated by the sum of the sequential extracts. While a range of extraction techniques are available for determining reactive Fe, 1 M HCl was chosen due to its high selectivity for amorphous, poorly crystalline and readily redissolvable iron (III) oxides (Wallmann et al., 1993; Raiswell et al., 1994; Boden and Wetzel, 2002).

Further discrimination of RIS and reactive Fe species was made on soil samples collected after regular tidal inundation. Acid-volatile sulfide (AVS) was extracted in triplicate from wet samples deflocculated under an N2 atmosphere using the diffusion method of Hincha et al. (2002) and modified approach as described by Liu et al. (2007). This method includes the addition of ascorbic acid to prevent Fe(II) interference and does not extract pyrite-S. Briefly, 2 g of sediment was extracted with 10 M HCl in a glass test tube for 18 h. The evolved H2S was trapped in 4 ml 3% Zn acetate and quantified via iodometric titration. Residual S (Sx–Sxw) was calculated using Sx = (Sx – Sxw – AVS). Reactive solid phase Fe(II) and total Fe was determined in replicate on wet sediment deflocculated under an N2 atmosphere by 1 M HCl extraction of (1:50 soil:solution, 24 h extraction) — a technique which conserves the Fe redox state (Wallmann et al., 1993). Aliquots of extract were analysed for Fe(II) and total Fe by spectrophotometry using the 1,10-phenanthroline method, with the addition of hydroxyammonium chloride for total Fe (APHA, 1998). Fe(III) was determined by the difference between Fe(II) and total Fe.

Scanning electron microscopy (SEM; Leica 440; Coated samples) was used to examine selected soil samples collected after tidal inundation for the occurrence of pyrite. The elemental composition of pyrite frambois and individual crystals was determined with an ISIS energy dispersive X-ray (EDX) microanalysis system, utilising a quantitative peak-to-background EDX method optimised for rough-surfaced sediments (Sullivan and Bush, 1997).

Selected samples of Sx-extracted S and water soluble S were analysed for Sx by Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) using a Thermo Flash FA 1110 coupled to a Thermo Delta V Plus IRMS. Reference material NIST987 (NIST) was used for calibration. A calibrated standard (10A Analysierentwikel der K. Hochreutner) was used to check for any changes due to sample preparation and isotopic drift. Replicates of reference material indicated a standard deviation of 0.06 per mil (n=10).

Table 2: Soil monitoring site surface elevations and a total inundation frequency analysis showing the proportion of time per month that each site was subjected to tidal inundation during 2003 and 2004.

<table>
<thead>
<tr>
<th>Site</th>
<th>Elevation</th>
<th>Time per month subject to tidal inundation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(m NHU)</td>
<td></td>
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<tr>
<td></td>
<td>x</td>
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</tr>
<tr>
<td>A</td>
<td>0-0.05</td>
<td>0.05-0.15</td>
</tr>
<tr>
<td>B</td>
<td>0-0.05</td>
<td>0.05-0.15</td>
</tr>
<tr>
<td>C</td>
<td>0-0.05</td>
<td>0.05-0.15</td>
</tr>
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</table>

* NHU is Australian Height Datum, where 0 NHU = mean sea level.
* Time per month subject to tidal inundation was calculated using a cumulative distribution method.

Fig. 2. Tidal water level dynamic within Firewood Creek during a period of footbridge closure (2003–2004). Inflow tide level was determined from a humidity sensor installed in the creek wall (Fig. 1) and calculated for normal dry season periods only (May–Nov). Tide data available for 2003 and 2004 due to presence of floodwater. Flow periods are associated with high flow (Trinity inlet).
3. Results and discussion

3.1 Tidal inundation

Tidal dynamics in Firewood Creek changed substantially following floodgate opening. During floodgate closure in 2000 (mean water level = -0.8 m AHD) approached equilibrium with that of the minimum low water levels outside the bund wall and there was little diel variation (Fig. 2). This hydrological behaviour is consistent with the known effects of floodgates on estuarine waterways (Johnston et al., 2005). Mean water levels in Firewood Creek increased by about 0.6 m following the initial floodgate opening (Fig. 2). This caused relatively frequent tidal inundation to about 0 to 0.1 m AHD until 2006, although mean tidal water levels during this period were about 0.2 m AHD. Additional raising of the floodgates in 2007 increased the tidal inundation magnitude to about -0.3 m AHD (Fig. 2). Whilst the tidal amplitude and mean water levels in Firewood Creek have increased markedly following floodgate opening, the amplitude is still greatly attenuated compared to outside the bund wall (Fig. 2).

An analysis of tidal inundation frequency for all 5 sites was conducted for 2003 and 2007. For the purpose of this analysis, tidal inundation was defined as occurring when the tidally modulated water levels recorded at the Firewood Creek monitoring station was higher than the surface elevation at a given site. This analysis revealed that sites 41, 42, 43 and 46 were tidally inundated from 50% to 80% of the time per month during 2003 (Table 1), depending on the elevation of individual sites. This increased to 90% for these sites following the additional raising of the floodgates in 2007. Site 65 has a higher surface elevation and is estimated to have been subject to only ~ 1 year of regular tidal inundation (Table 1).

Firewood Creek is located several km from the estuary entrance (Fig. 1). Tidal inundation waters are expected to have a high salinity, reflecting this proximity to the ocean. This is confirmed by a cumulative frequency analysis of mean daily EC which demonstrates that waters in Firewood Creek (near the bund wall) were ~ 40 dS m⁻¹ for ~ 50% of the time between 2002 and 2007.

3.2 Soils prior to reintroduction of tidal inundation

Soils before the re-introduction of tidal inundation were hydromorphic silt loams (Soil Survey Staff, 1998) with high organic matter content in the top ~ 0.1 m. Beneath the organic rich surface layer were

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Fig. 1. Changes in field pH ($pH_F$) and citrate-extractable acidity (TA) with depth prior to tidal inundation (2001, 2003) and after regular tidal inundation (2007). Redox potentials ($Eh_F$) for the 2007 sampling period are also shown.
sulfuric horizons (pH ≈ 4) with jarosite mottles extending to a depth of ∼0.1–1.3 m below ground surface, immediately below this was reduced sulfide material containing ∼600 μmol g⁻¹ S₂O₃. Soil texture was predominantly silty clay. Individual sites showed varying degrees of oxidation related pedogenic features typical of drained and sulfate soils (e.g., Fe (III) oxide and jarosite mottles). Table 2 provides an example of a typical soil profile description prior to the reintroduction of tidal inundation.

Fig. 5. Electron backscatter and EDS spectra of pyrite accumulations in former sulfuric horizons subject to tidal inundation, from soil materials collected in 2007. (a) Bambordal pyrite and (b) euhedral pyrite crystal clusters from site 42 (sample depth = 0.72 m AHD). (c) and (d) Bambordal pyrite from site 48 (sample depth = 0.34 m AHD).

3.3 Decrease in soil acidity

The pH of the soil increased markedly following regular tidal inundation, typically in the order of 2–3 pH units. Increases were generally most pronounced in the upper part of the profile, which corresponds to the former sulfuric horizons (Fig. 2). However, there was a distinct trough evident in the pH of soils after tidal inundation, at a depth approximately corresponding to the upper part of the sulfidic horizon (i.e., between 1 to 3.4 m AHD). This likely represents

\[ \text{site acidity from the immediately overlying former sulfuric horizon} \]

which has diffused downward and been displaced downward by tidal overtopping as suggested by Hircles et al. (2003). The occurrence of low Cl:SO_4^2- molar ratios [2–4; marine water = 10.4] within this zone lends qualitative support to this suggestion, as low Cl:SO_4^2- ratios are a well-documented feature of acidity derived from sulfide oxidation (Mulvey, 1993).

In general, there was a high degree of consistency in the pH, profiles after tidal inundation, particularly at sites 41, 42, 43 and 46. In contrast,

Fig. 6. Changes in the relative abundance of sulfur fractions with depth, before (2001, 2003) and after (2007) regular tidal inundation. \( S_{\text{tot}} \) = total sulfur, \( S_{\text{org}} \) = organic sulfur, \( S_{\text{av}} \) = remaining sulfur, \( S_{\text{av}} = S_{\text{org}} - (S_{\text{tot}} - S_{\text{av}}) \). AVS = acid volatile sulfur.

the surface soil at site 95 remains moderately acidic (pH 5.4). This may be due to the higher relax status of surface soils at this location (Fig. 2). For example, the near surface soil (0-0.5 m below ground surface) at sites 41, 42, 43 and 46 had pH values of 3.0-3.5. Comparatively, the near surface soil at site 95 was strongly acidotic (200-400 mV, Fig. 3). This is a result of less frequent tidal inundation and exposure to the atmosphere during low tides due to its higher elevation (1400 ft).

TAA decreased by up to 40-80% in former sulfureous horizons following tidal inundation (Fig. 4). Decreases were in the order of 40-50 μmol g⁻¹ h⁻¹. Marine derived bicarbonate alkalinity from tidal exchange waters is likely to have contributed to these decreases in acidity. In addition, proton consumption and the generation of bicarbonate alkalinity accompanying reduction of sulfate and Fe(III) oxides (e.g. Eq. (1) and (2)) are also likely causes for the observed decreases in TAA. These different sources of alkalinity are discussed further in Section 3.6.

3.4. Formation of iron-sulfur minerals

There were substantial increases in the Sₑₒ concentration at 700°C following regular tidal inundation. This was particularly evident in the former sulfureous horizons and at the surface at sites 41, 42, 43 and 46 (Fig. 4), where Sₑₒ increased by an order of magnitude from 3-6 μmol g⁻¹ to 30-60 μmol g⁻¹. This equilibration of sulfide minerals due to regular tidal inundation has rapidly (5 years) transformed soils at these four sites from Hydrogenatic Sulfateaceous to Typic Sulfateaceous. However, at site 05 there was minimal change in the Sₑₒ content of former sulfureous horizons. This is likely due to less time being available for sulfide mineral formation as a result of the shorter period of regular tidal inundation at this site (~1 year), plus the occurrence of less favorable soil redox and pH conditions. Tidal inundation has resulted in the soil at site 95 transforming from a Hydrogenatic Sulfateaceous into a Sulfacic Hydrosulfatic.

The presence of pyrite in former sulfureous horizons subjected to tidal inundation was confirmed using SEM and EDX analysis. Analysis of soils collected after tidal inundation revealed multiple subhedral crystalline structures matching the morphology of pyrite and marcasite as well as individual euhedral crystals and euhedral clusters (Fig. 5). EDX spectra on frambois and individual crystals were consistent with the elemental composition and stoichiometry of pyrite (Fig. 5). This is clear evidence of tidal inundation causing contemporary pyrite formation in formerly oxidised sulfureous horizons.

The vertical distribution of total sulfur (Sₜₒₚ) was similar both before and after tidal inundation (Fig. 6). However, there was a large shift in the proportion of Sₜₒₚ that was comprised of Sₑₒ (Fig. 6). Assuming that the Sₑₒ fraction consists primarily of pyrite, this analysis suggests that 20-30% of the Sₑₒ in the former sulfureous horizons has been converted to pyrite at sites 41, 42, 43 and 44. Concentrations of AVS in tidally inundated soils (Fig. 6) were relatively typical of some environments (Burton et al., 2003) and are limited by low compared to some CLASS environments (Burton et al., 2003). AVS was most abundant in the organic-rich near-surface sediments where it comprised a significant proportion of the pore-water AVS species (Fig. 6). The water soluble sulfate concentrations in the former sulfureous horizons before and after tidal inundation was generally between 20 and 40 mmol kg⁻¹ and showed relatively minor changes following tidal inundation (data not shown). The residual Fe fraction is considered a buried analogue to a sparingly soluble 3 natural Fe oxides such as jasperite. There was a substantial decrease in this fraction in the former sulfureous horizons following regular tidal inundation (Fig. 6). This is consistent with visual observations, which indicate a decrease in the abundance, size and prominence of jasperite nodules in the tidally inundated soils. This is also consistent with pH and Eh data which show the geochemical conditions of the highly inundated soils are outside the stability field for jasperite (Fig. 4).

3.5. Iron reduction

A stability field diagram indicates that the pH and Eh of soils after tidal inundation lie close to the Fe(II)/Fe(III) boundary (Fig. 7). This suggests that reduction of Fe(III) minerals is occurring. A diagram indicates that the stability field of Fe(III) oxides, iron oxides, and reduced iron minerals. Fe(II) is more stable under these conditions. The Fe(III) minerals are more stable under these conditions. The Fe(II) minerals are more stable under these conditions. The Fe(III) minerals are more stable under these conditions. The Fe(III) minerals are more stable under these conditions.

3.6. Sources of aluminum

There is evidence to suggest that both marine derived alkalinity and redox processes were jointly responsible for the decreases in acidity after regular tidal inundation. For example, a positive relationship...
between redox potential and TAA in the tidally inundated soils (Fig. 9) suggests that internal alkalinity generation due to reductive processes was an important mean of proton consumption. 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 S₈ fraction comprises solely of pyrite and 4 mol H⁺ is consumed for every mol of Fe₅⁺ produced (Eq. (3)), then a 30–60 μmol g⁻¹ increase in S₈ 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.

Alternatively, δ³⁵S data suggests that marine derived alkalinity may have been an important source of acidity. For example, δ³⁵S data demonstrates there was considerable isotope fractionation during the formation of pyrite-S, both before and after tidal inundation (−25‰).
Table 3. Water soluble sulfate $^{35}$S data from before tidal inundation reflects this environment (particularly at site 05), suggesting that oxidation of pyrite was a primary source of sulfate during this period (Table 3). After tidal inundation the water soluble sulfate $^{35}$S signature shifted markedly (+5.8 to -14.8%), reflecting the input of marine sulfate-S of marine origin. However, this change was greatest in the former sulfuric horizons, whilst the underlying sulfidic material remained substantially enriched in lighter sulfate S ($\approx$16.0 to $\approx$22.8%). This indicates marine derived solutes from inundating tidal waters were mainly confined to the former sulfuric horizons and had minimal exchange with the underlying sulfidic material. This implies that marine derived alkalinity also had limited influence on the underlying sulfidic material, thus offering a potential explanation for the persistence of high TAA and lower pH within the sulfidic horizons.

At site 95 there was minimal change in $^{35}$S concentration after tidal inundation, yet there was still a substantial decrease in the TAA within most of the former sulfuric horizon. There was considerable nonsulfuric solid phase Fe(II) at this site after tidal inundation (Fig. 6), thus indicating that alkalinity from either reduction of Fe(II) minerals (according to Eq. (15)) or marine inputs may have been more important processes. This data also suggests that the prevalent type of alkalinity producing processes may undergo a sequential progression in response to regular tidal inundation. In the early stages of regular tidal inundation both marine-derived alkalinity from overtopping tidal waters and alkalinity from Fe(II) reduction are likely to prevail, followed in later stages by alkalinity derived from sulfate reduction. Overall the analysis provided in this section suggests that alkalinity derived from both in situ reduction processes and marine tidal inputs are likely to be contributing to the decreased acidity of the soils. Further research is required to determine their relative importance.

7.7 Other solid-phase properties

Total organic carbon concentrations were greatest near the soil surface and were similar before and after tidal inundation, with concentrations ranging from 1% to 6%. Two important features which act as fundamental constraints on the relative rates of Fe and SO$_4^-$ reduction in acidic sediments are the quantity and leachability of organic carbon (Blodau and Pfeffer, 2002) and the abundance of reactive Fe(III) oxides (Postma and Jolokovsk, 1985). The degree of sulfidation (DOS) is a useful measure that describes the influence of reactive Fe availability on sulfide formation (Hunt et al., 1993). The DOS is calculated as:

\[
DOS = 100 \times \frac{\text{AVS}_{\text{Fe}} + \text{pyrite}_{\text{Fe}}}{\text{reactive Fe}}
\]

where AVS$_{\text{Fe}}$ and pyrite$_{\text{Fe}}$ are Fe associated with solid-phase AVS and S$_4$ and are calculated assuming a stoichiometric relationship with $\text{S}_4$ of 1:2 and 1:3 respectively, and reactive Fe represents 1 M HCl extractable Fe. DOS values increased in the former sulfuric horizons at sites 41, 42, 43, 46 following tidal inundation and also to a lesser extent at site 05 (Fig. 9). However, after tidal inundation the DOS values in soils near the surface were generally very low (3%). This reflects the diagenetic enrichment of reactive Fe near the soil surface and also indicates that only very small fraction of this reactive Fe was being sulfated. Thus, sulfidation in the surface soils was not Fe limited. This is an interesting finding which suggests there may be some other factor limiting sulfidation in these soils. Fe(II) reducing bacteria are able to outcompete sulfate reducing bacteria for limited supply of electron donors in the presence of excess poorly crystalline Fe(II) oxides (Lovley and Philips, 1997; Jensen et al., 2003; Burton et al., 2007). The high abundance of reactive Fe in surface soils (Fig. 8) relative to organic carbon may therefore be inhibiting the formation of pyrite. This is supported qualitatively by a positive correlation between the amount of S$_4$ and the ratio of TOC to reactive Fe in tidally inundated nearsurface soils (0.5 m) at sites 41, 42, 43 and 46 (Fig. 9).

4. Conclusions

Regular tidal inundation has successfully decreased soil acidity in the former sulfuric horizons of a severely acidic tropical CLASS landscape. Field pH increased by 2-3 pH units and TAA decreased by 40-50 pmol H$^+$ g$^{-1}$ dry weight. Evidence suggests that both marine derived alkalinity and tidal inundation were jointly responsible for the decrease in acidity after tidal inundation. Tidal inundation led to the reduction of Fe(III) oxides and the formation of solid phase Fe(II) sulfide minerals, including pyrite. There were also accumulations of