

REMEDICATION OF COASTAL ACID SULFATE SOILS BY FRESHWATER RE-FLOODING

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Abstract

Coastal acid sulfate soils (CASS) pose serious risks for estuarine water quality and present considerable management challenges for state and local government agencies. Despite a plethora of attempts to reduce acid discharge by small-scale changes to floodplain management (e.g. floodgate modification; enhanced tidal exchange; drain water retention), there are few documented examples of floodplain management that aim to reverse acid-generating geochemical processes at a landscape or sub-catchment scale.

This study explores the remediation and partial restoration of natural hydrology of two large CASS wetlands by freshwater re-flooding. We examine the generation of alkalinity and amelioration of *in situ* acidity by reductive geochemical processes. We quantify the re-formation of reduced inorganic sulfur species (including pyrite) within re-flooded soils and explore key relationships between the abundance / distribution of these species and iron and organic carbon. Although surface waters are now mostly near neutral pH, some mobilisation of redox sensitive elements (Fe, Mn) occurs.

While the reformation of reduced inorganic sulfur species (RIS) is partly responsible for the generation of alkalinity and wetland-scale recovery from acute acidification, the fact that these species tend to be most abundant near the surface 0.2 m of the re-flooded soils, presents a longer term management challenge. In particular, these near-surface stores of RIS are potentially vulnerable to exposure to atmospheric oxygen during the next ENSO induced drought episode. Such exposure may lead to pyrite oxidation and temporary re-acidification of surface sediments and waters with attendant risks for surface water quality degradation. The environmental consequences, challenges and long term implications of this management approach are discussed in the context of Australia's dynamic climate controls on coastal wetland hydrology.

Introduction

Large areas of ecologically significant freshwater wetlands on coastal floodplains in Eastern Australia have been severely degraded by over-drainage. Many coastal floodplain wetlands are underlain by acid sulfate soils and display acute soil / water acidification from oxidation of pyrite (e.g. Walker, 1972, White et al., 1997). Over-drained coastal acid sulfate soil (CASS) wetlands episodically discharge extremely poor water quality into adjacent estuaries (Johnston et al., 2004a, Wong et al., 2010, Johnston et al., 2009a, Sammut et al., 1996).

Various remediation techniques have been developed to reduce the impacts of CASS wetland drainage on downstream water quality. However, most remediation techniques involve relatively small-scale changes to floodplain management, such as manipulating floodgates

to enhance tidal exchange and dilution, or partially blocking drains to help retain acidic waters and decrease acid export. However, reflooding the landscape with freshwater to mimic more natural, pre-drainage hydrology is an alternative, and far more substantive, remediation strategy. Such reflooding may achieve a variety of environmentally beneficial aims simultaneously, including:

- a) preventing further pyrite oxidation
- b) containing acidity in the landscape / decreasing acid export
- c) ecological restoration and
- d) neutralising in situ acidity within the wetland by reversing key geochemical processes.

Achieving the latter aim is unique to reflooding and is a result of encouraging natural anaerobic microbial processes in soils. If there is sufficient organic matter, reflooding can effectively stimulate lower redox potential and alkalinity-producing geochemical processes such as Fe(III) and SO_4^{2-} reduction (Johnston et al., 2012, Johnston et al., 2009b, Johnston et al., 2009a). Recent studies have explored tidal seawater re-flooding of CASS and demonstrated this can effectively decrease soil acidity and immobilise trace metals (Johnston et al., 2012, Johnston et al., 2009b, Johnston et al., 2009a, Johnston et al., 2010, Burton et al., 2011, Keene et al., 2011).

However, there have been no comparable field-scale studies examining the geochemical consequences of freshwater re-flooding of CASS wetlands. This is an important omission, as there are some fundamental geochemical and hydrological differences between tidal seawater re-flooding and freshwater re-flooding approaches. These differences may drive contrasting geochemical trajectories and thereby result in contrasting environmental outcomes and risks.

Here, we present the findings of a study which explores the geochemical consequences of freshwater re-flooding of two CASS wetlands. We aim to quantify abundance and vertical distribution of RIS species and reactive iron species after freshwater re-flooding for 8-9 years. We examine the beneficial environmental outcomes for water quality, explore the factors that appear to be influencing RIS abundance, speciation and spatial distribution and examine possible longer-term management implications, as well as identify future research needs.

Study sites and methods

Both study sites are located on Holocene coastal floodplains in Eastern Australia (Fig. 1). Darawakh is a ~1000 ha freshwater wetland on the Wallamba River floodplain (Fig. 1a). It is characterised by a sinuous, North-South orientated depression, which is an infilled estuarine channel feature several hundred metres wide with an elevation range from about 0.2 to 0.8 m AHD (AHD = Australian height datum; 0 AHD \approx mean sea level). The channel-infill is underlain by Holocene sulfidic estuarine muds and bounded to the east and west by Aeolian Pleistocene sand plains. Acid sulfate soils are largely confined to the channel-infill geomorphic unit. Remediation commenced in 2005 and consisted of raising water levels via infilling and removing artificial ditch drains to restore the natural hydrological functioning of the wetland.

Partridge Creek is a 542 ha freshwater wetland backswamp distributary system on the Hastings River floodplain that is underlain by sulfidic estuarine sediments (Fig. 1b). Elevation across the backswamp ranges from about 0.6 to 1.2 m AHD. Prior to remediation, acidic discharge from the sites drainage system was estimated to be in the order of >800 tonnes of H_2SO_4 equivalent for an average rainfall year (Aaso, 2004). The site was identified by the NSW state government as an acid sulfate soil priority

management area (Tulau, 1999) and a freshwater re-flooding strategy commenced in 2004. This consisted of retaining freshwater on-site by blocking the main drain outlet with a hinge-weir and raising the wetland water level to a target of 0.9 m AHD.

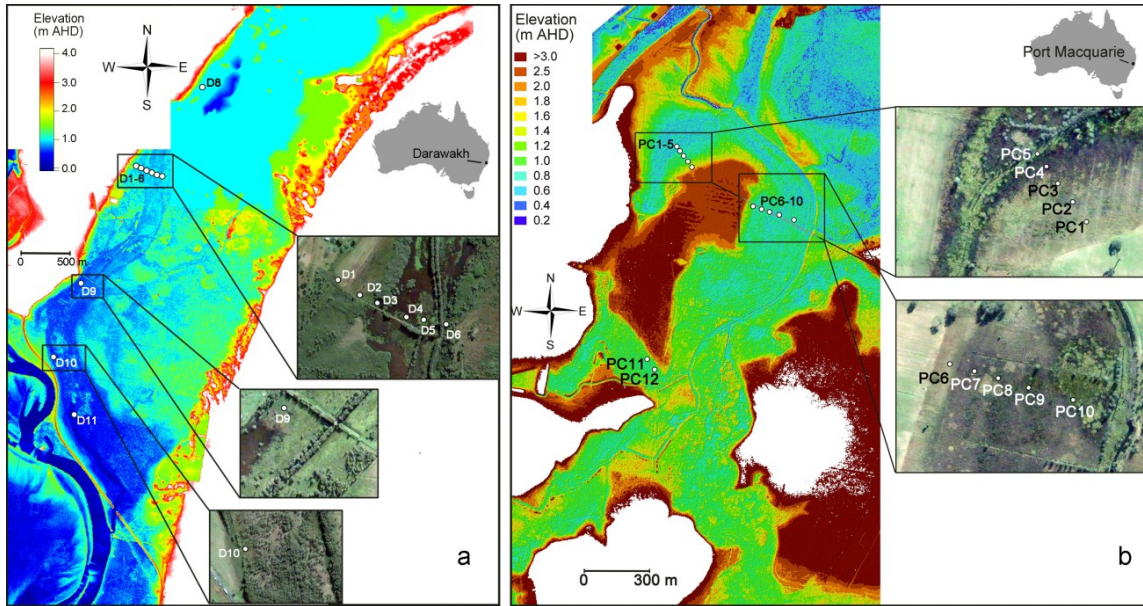


Figure 1: a) Darawakh wetland and b) Partridge Creek wetland study areas.

Surface and groundwater levels were monitored in each wetland hourly using submersible pressure transducers from July 2012, with all readings corrected for atmospheric pressure and referenced to AHD. Soils were collected from each wetland in July 2012 (Darawakh, n = 10; Partridge Creek = 12), with sample sites arranged as toposquence transects where possible to ensure representation of a wide range of elevations and thus wetland inundation depths. Soil pH and redox were determined in the field and sub-samples subject to a range of chemical extractions to quantify reduced inorganic sulfur species (RIS) (Burton et al., 2009), reactive iron fractions (Claff et al., 2010) and organic carbon fractions. Selected samples were analysed via scanning electron microscopy (SEM) to characterise pyrite morphology. Surface waters and groundwaters were collected in 2012 and subject to a wide range of chemical analysis, including; pH, Eh, electrical conductivity, dissolved oxygen, Fe^{2+} , HCO_3^- , S(-II), dissolved organic carbon, Uv-Vis spectroscopy, major ions and trace elements (via ICP-MS).

Groundwaters in CASS can have high concentrations of acidic metal cations such as Fe^{2+} (analogous to acid mine drainage settings), which can produce H^+ through oxidation and subsequent hydrolysis. As a consequence, solution pH can substantially underestimate net acidity. Hence, the net acidity of porewaters was determined according to Kirby and Cravotta (2005) (Eq. (1) and (2)):

$$\text{Acidity}_{\text{calc}} = 50 [1000(10-\text{pH}) + [2(\text{Fe}^{2+}) + 3(\text{Fe}^{3+})]/56 + 2(\text{Mn})/55 + 3(\text{Al})/27] \quad (1)$$

$$\text{Net acidity} = \text{acidity}_{\text{calc}} - \text{alkalinity} \quad (2)$$

where $\text{Acidity}_{\text{calc}}$ is expressed as mg L^{-1} CaCO_3 equivalent, Fe^{2+} , Fe^{3+} , Mn and Al are in mg L^{-1} and alkalinity is derived from HCO_3^- . All Net acidity values are reported in mM H^+ .

Environmental outcomes

Substantial fluctuations occur in water levels (>1 m) at both wetlands due to seasonal rainfall. Although water level measurements span a limited time period, they nonetheless provide a recent snapshot of water level variation at each site. They clearly indicate that reflooding has been effective at maintaining water levels above the ground surface in acid sulfate soil areas of both wetlands for much of the year, under current seasonal conditions.

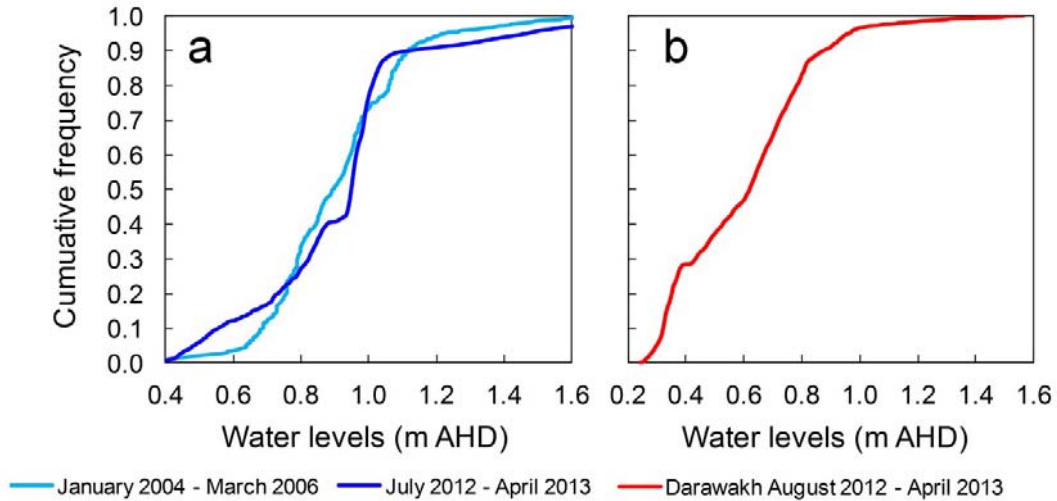


Figure 2: Cumulative frequency of water levels measured at a) Partridge Creek wetland during 2004-2006, 2012-2013 and b) Darawakh wetland during 2012-2013.

Since reflooding, there have been substantial increases in both the pH of acid sulfate soils and the pH of drain discharge waters at Partridge Creek wetland (Fig. 3). The increase in soil pH of approximately 2-3 pH units represents a major improvement upon the highly acidic conditions that existed prior to remediation (Fig. 3a).

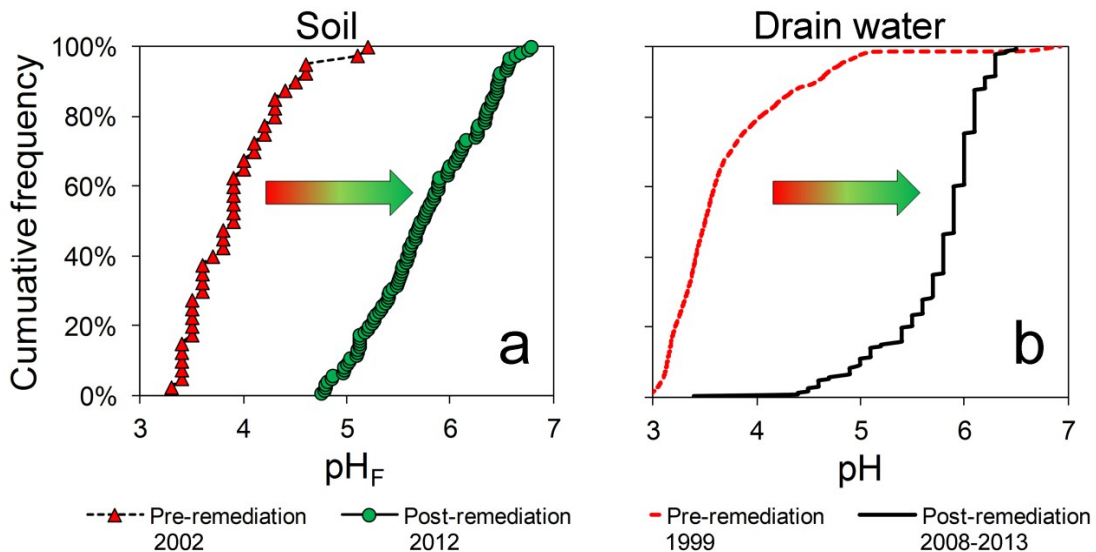
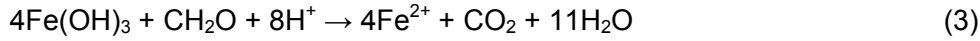


Figure 3: Increases in a) soil pH (sulfuric horizons) and b) drain water pH at Partridge Creek wetland following remediation by reflooding.

Reflooding the wetlands has altered the dominant soil redox regime, triggering a shift from oxic-acidic to reducing-circumneutral conditions. The increase in soil pH is a direct result of reflooding encouraging geochemical reactions that produce alkalinity / consume protons, including iron and sulfate reduction. According to equations (3) and (4), for each mol of sulfate or iron reduced, approximately 2 mol of alkalinity are generated (or 2 mol of protons consumed).



Both of these reactions can occur only if there is sufficiently reducing conditions, such as caused by soil reflooding (Fig. 4) and sufficient organic matter. One of the important consequences of reflooding has been re-colonisation and re-invigoration of wetland plant species at both wetlands. This has led to substantial accumulation of organic carbon (~20% to 30%) in near-surface sediments (Fig. 4).

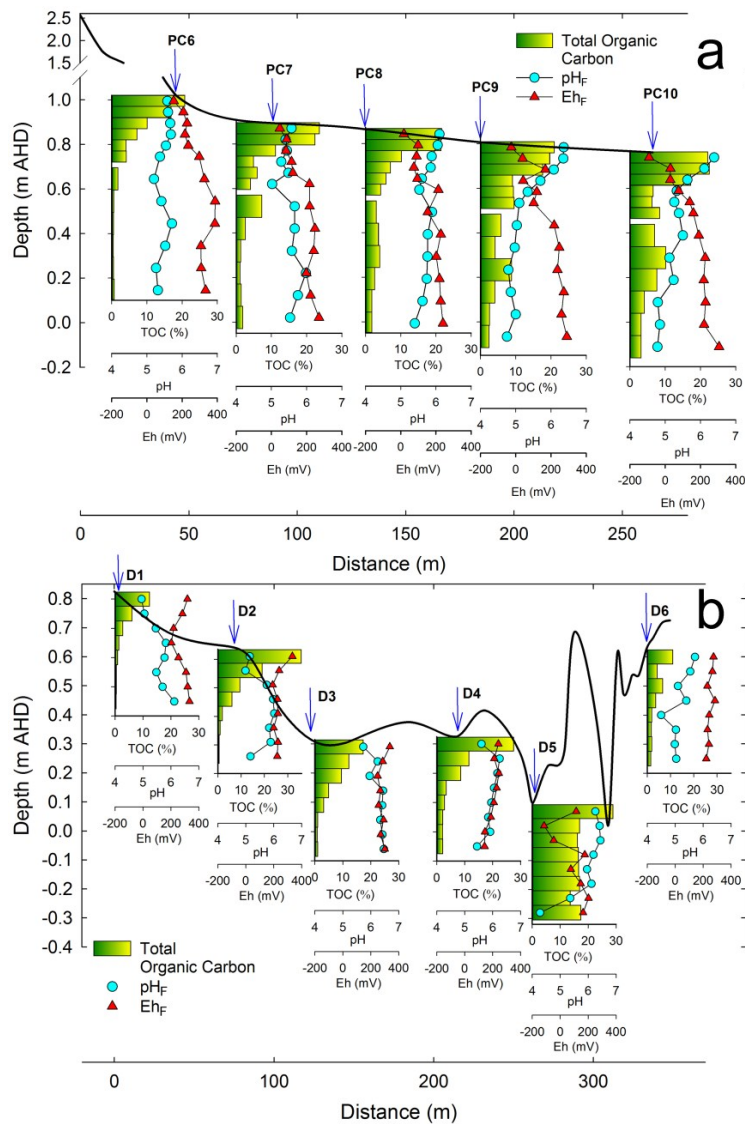


Figure 4: Total organic carbon, soil pH and redox potential (Eh) at a) Partridge Creek sites PC6-10 and b) Darawakh sites D1-6.

The pH of discharging drain waters at Partridge Creek has increased by around 2.5 to 3 pH units (Fig. 3b). This is a very important environmental outcome of the reflooding remediation as Al^{3+} , which is highly toxic for aquatic organisms, is only soluble under low pH conditions. Therefore, the higher pH of drainage waters effectively curtails the export of Al^{3+} species from the site.

There are a variety of reasons for the large increase in drain water pH. One reason is there has been an increase in porewater / groundwater pH accompanying the onset of reducing conditions (see section below on *Surface and groundwaters*) – a feature reflected by the increase in soil pH. Another very important reason is that the remediation process at both sites has effectively shut-down groundwater seepage as a hydrological pathway of acid export (see Fig. 5) – by using a weir at Partridge Creek and by infilling drains at Darawakh.

Acid sulfate soils at Partridge Creek are known to have a very high hydraulic conductivity, which makes this site particularly vulnerable to rapid groundwater seepage. The use of a weir at Partridge Creek effectively keeps drain water levels high and stable and limits the development of positive hydraulic gradients between the groundwater and drain, thereby greatly inhibiting groundwater seepage (e.g. Johnston et al., 2004b). The infilling of drains at Darawakh, is also a highly effective and efficient means of preventing acid groundwater seepage.

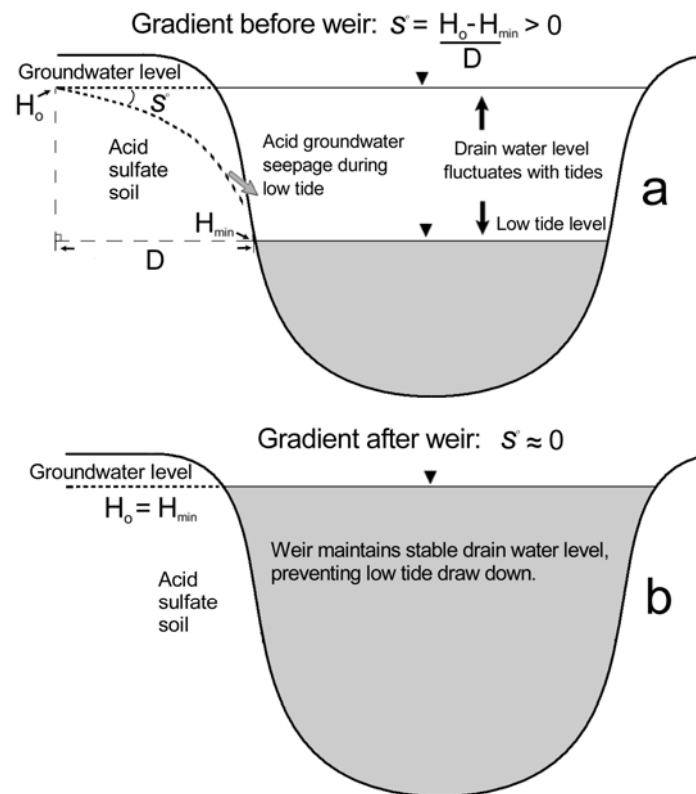


Figure 5: Schematic representation of the effects of a weir at reducing groundwater seepage by limiting the development of effluent groundwater gradients (S°). H_o is the equilibrium water table level in adjacent acid sulfate soils at distance (D) from the drain and H_{min} is the minimum low tide water level in the drain.

Source; Johnston et al. 2004b.

Sediment geochemistry reversal

The reformation of reduced inorganic sulfur (RIS) species in wetland sediments is a vital, yet nuanced part of the reflooding remediation strategy. On the one hand it is a direct outcome of alkalinity generating geochemical processes, yet on the other hand RIS is only stable whilst inundated and represents a form of potential acidity, stored within the sediments. If hydrological conditions shift in the future and expose currently reflooded sediments to the atmosphere (ie. during a drought), the reformed RIS will be at risk of oxidation and subsequent production of acidity. RIS that accumulates near the sediment surface will obviously be at greater risk than RIS deeper in the soil profile. Elemental sulfur [S(0)] and AVS-S species are also more oxidation prone than pyrite. Hence, understanding the controls on RIS vertical distribution, abundance and speciation is important.

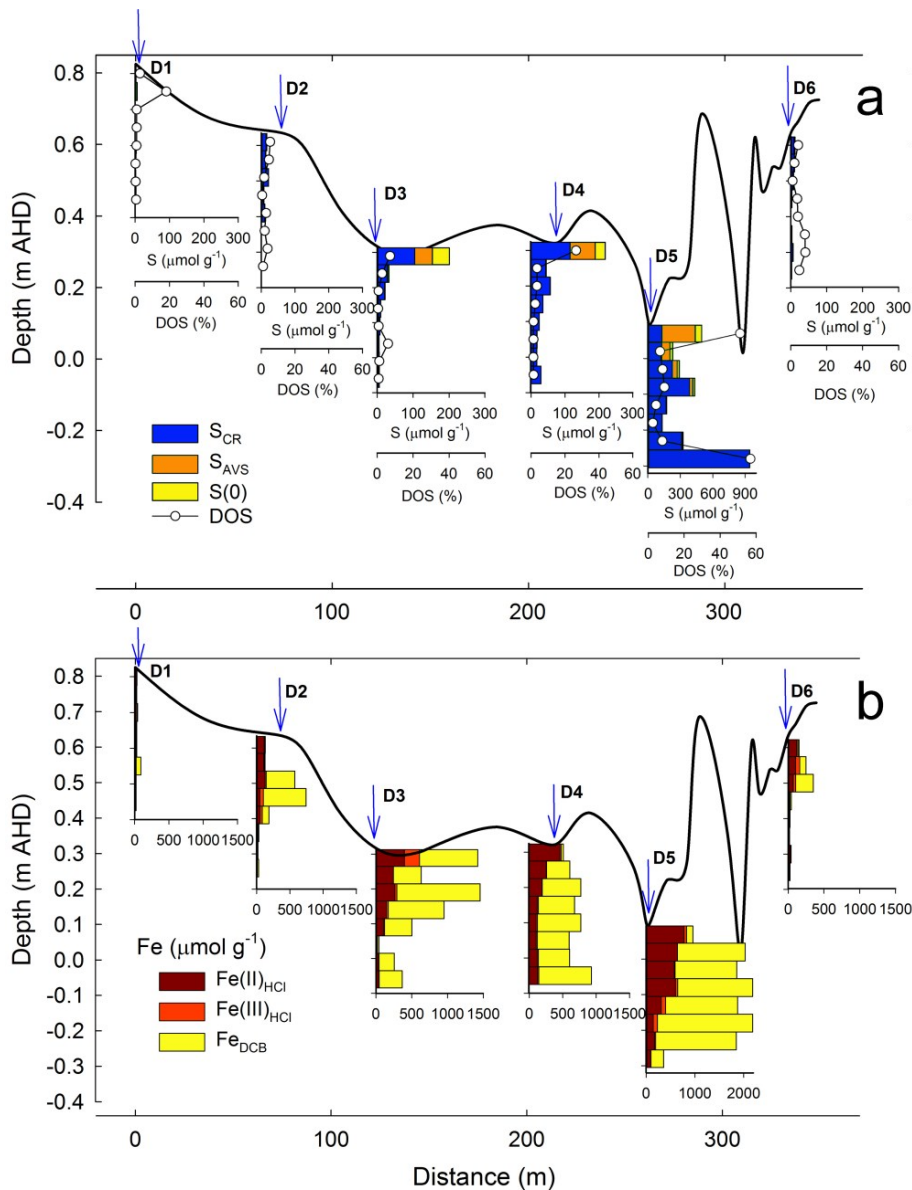


Figure 6: Darawakh, Transect D1-5 topography, a) reduced inorganic sulfur speciation, DOS and b) reactive Fe speciation.

Reflooding has clearly stimulated reformation of reduced inorganic sulfur species in the near surface sediments at both wetlands (Fig. 6 and 7). Topographic trends are evident, whereby lower elevation sites tend to display more RIS. Although pyrite, as measured by S_{CR} , is the most abundant RIS species at both sites, there is also substantial $S(0)$ at Partridge Creek and some AVS-S at Darawakh (Fig. 8). This is significant as $S(0)$ and AVS-S react to oxygen much faster than pyrite and hence may generate acidity relatively quickly (Burton et al., 2009).

Reactive iron fractions are shown in Fig. 6b and 7b. A considerable proportion of reactive iron is comprised of Fe(II) – which is partly a by-product of reflooding causing the reduction of poorly crystalline Fe(III) minerals. Topographic trends in iron fractions are also evident, whereby lower elevation sites have greater concentrations of reactive Fe. Concentrations of reactive Fe are also generally higher near the sediment surface, which likely reflects accumulation via upward evaporative advection (ie. Rosicky et al., 2004).

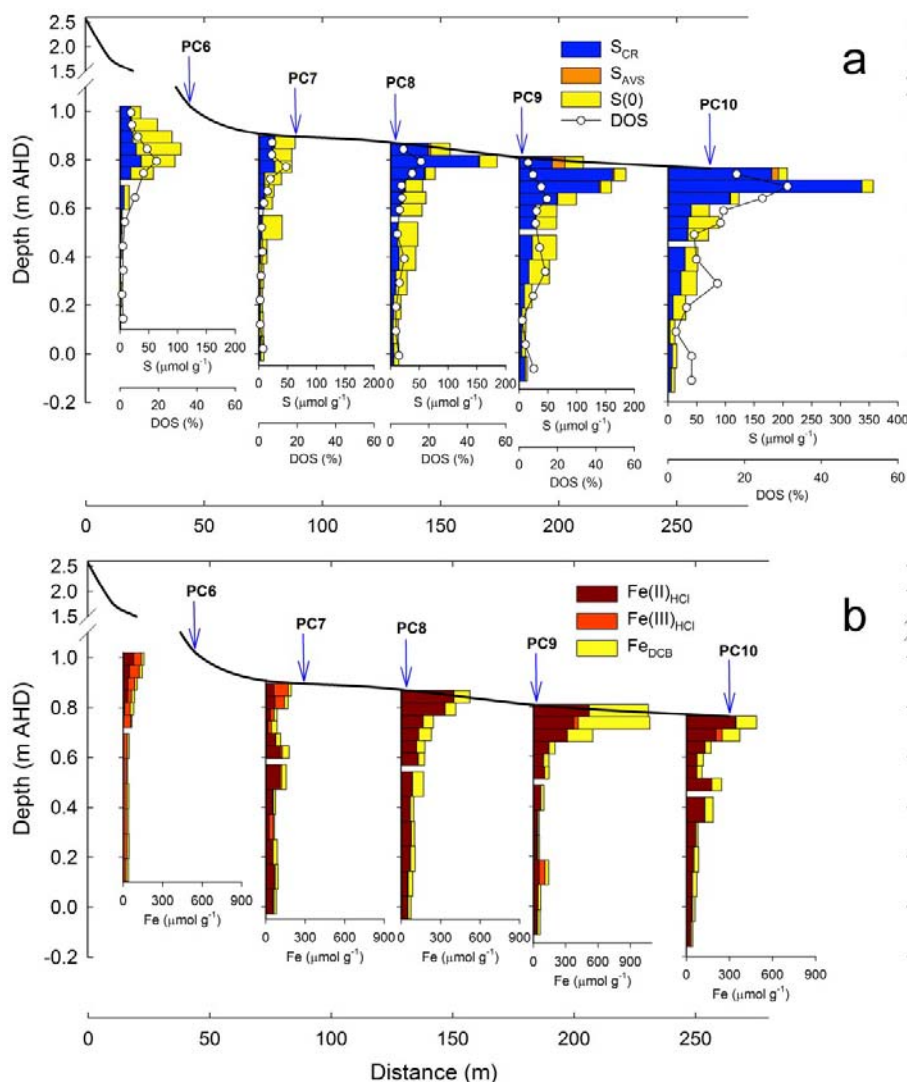


Figure 7: Partridge Creek, Transect PC6-10 topography a) reduced inorganic sulfur speciation, DOS and b) reactive Fe speciation.

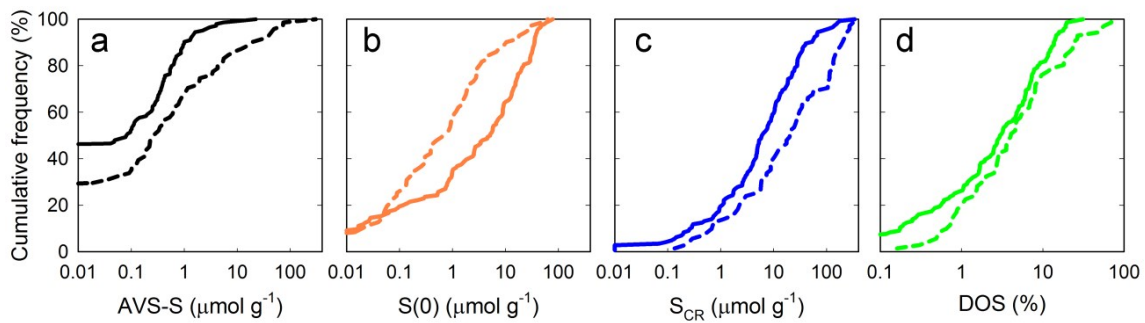


Figure 8: Cumulative frequency distribution of contemporary RIS species and DOS at Partridge Creek (solid-lines) and Darawakh wetland (dashed-lines) soil sampling sites. Plot excludes RIS species data from relic sulfidic horizons at Darawakh wetland.

Several essential conditions are required to reform RIS species. Apart from generally anaerobic soils, these conditions include a) a source of labile organic matter, b) a source of sulfate and c) a source of bio-available iron. All three of these are clearly present in the wetland sediments. An important question that arises is “are all of these reactants equally available or do some of them have limited supply and therefore acting as key controls on RIS abundance / speciation”?

A very simple, indirect approach to examine this question is presented in Fig. 9 which shows RIS abundance in relation to total organic carbon (TOC), total S and reactive iron fractions (Fe_R). Strong positive correlations between RIS and both TOC and total S, spanning several orders of magnitude, are consistent with carbon and sulfur acting as important limiting reactants. The poor correlation between RIS and reactive iron suggests that iron is sufficiently abundant at both sites that it is not yet behaving as a limiting control on overall RIS abundance.

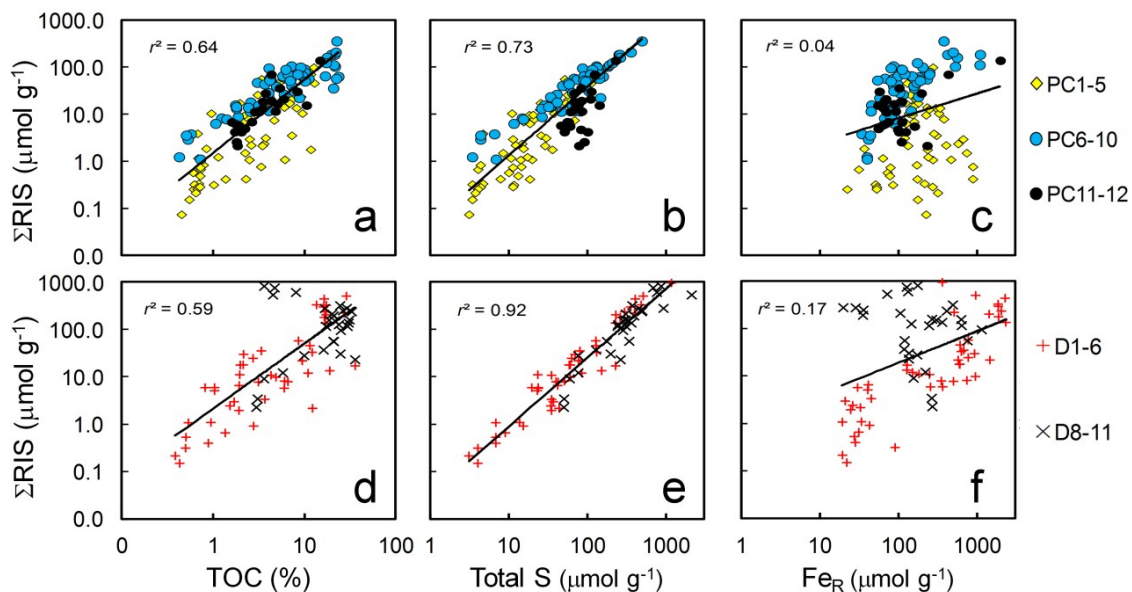


Figure 9: Correlation plots of Σ RIS in relation to TOC, Total S, Fe_R at a) b) c) Partridge Creek and d) e) f) Darawakh wetland.

Another approach to exploring this question of limiting controls on RIS reformation is to quantify a) the proportion of reactive iron that has been converted to either pyrite (FeS_2) or AVS-S (FeS) (represented by the term DOS) and b) the proportion of total sulfur that has likewise formed either pyrite or AVS-S (represented by $\Sigma\text{RIS}/\text{Total S}$). According to this analysis, only a small proportion of the available reactive Fe pool has actually been converted to either FeS_2 or FeS (mostly <20%; Fig. 10). Comparatively, a far higher proportion of the total sulfur pool has been transformed to FeS_2 or FeS – which is consistent with sulfur behaving as a limiting reactant. An exception to this are deeper sediments from Darawakh that are derived from relic sulfidic horizons, which have a clearly contrasting DOS: $\Sigma\text{RIS}/\text{Total S}$ signature (Fig. 10b).

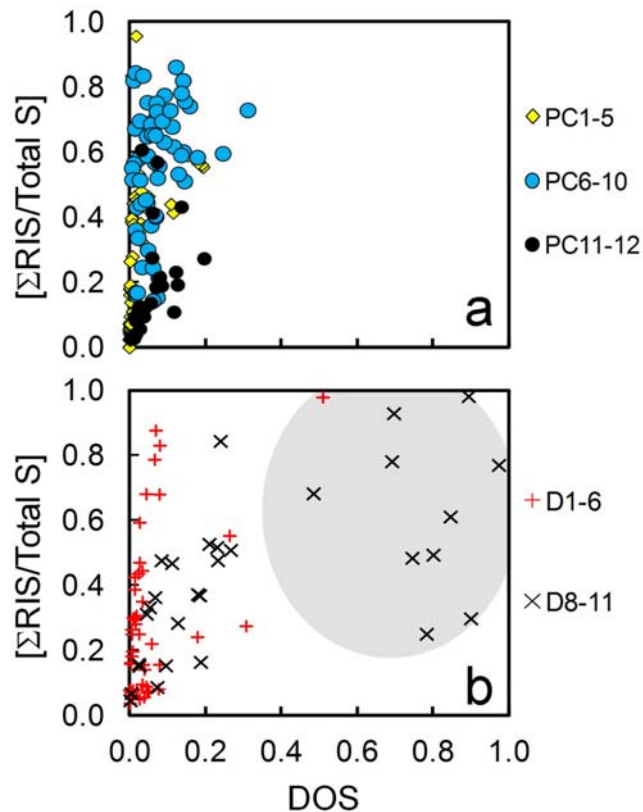


Figure 10: Proportion of Fe_R sulfidised (DOS) in relation to the proportion of total sulfur sulfidised ($\Sigma\text{RIS}/\text{Total S}$) in sediments at a) Partridge Creek and b) Darawakh wetland. Shaded area indicates samples associated with relic sulfidic horizons at Darawakh.

The possibility of S limiting RIS reformation is not entirely unexpected. During past CASS wetland drainage, some of the S from pyrite oxidation was exported as highly soluble SO_4^{2-} , while much of the iron was retained within the landscape as poorly soluble, reactive-Fe(III) minerals (Burton et al., 2006b, Van Breemen, 1975). This relative depletion of SO_4^{2-} compared to reactive-Fe(III) minerals has two important consequences. Firstly, it creates a fundamental stoichiometric imbalance, whereby the relative lack of SO_4^{2-} means that upon re-flooding, there may be insufficient S(-II) formed to react with all of the Fe^{2+} produced by iron reduction. Secondly, abundant reactive-Fe(III) minerals can favour the formation of highly reactive sulfur species such as S(0) and nano-particulate mackinawite (FeS) (Burton et al., 2006a, Keene et al., 2011, Carignan and Tessier, 1988, Burton et al., 2011).

Backscatter SEM analysis of near-surface sediments from Darawakh wetland reveals that contemporary pyrite consists of many small (~200-300 nm diameter) crystals dispersed in a diatom-rich matrix, with occasional spheroidal framboids (<8-10 μm diameter) (Fig. 11). In contrast, the pyrite in deeper, relic sulfidic sediments consisted mainly of much larger crystals with diverse crystal habit, including poorly ordered sub-spheroidal framboids, large (~50 μm diameter) framboid clusters, large inter-grown euhedral clusters and massive infillings in organic matter.

The higher surface area to mass ratio associated with the smaller contemporary pyrite crystals in the near-surface sediments, is more likely to favour rapid oxidation when compared to the deeper, relic sulfidic sediments that contain much larger crystals.

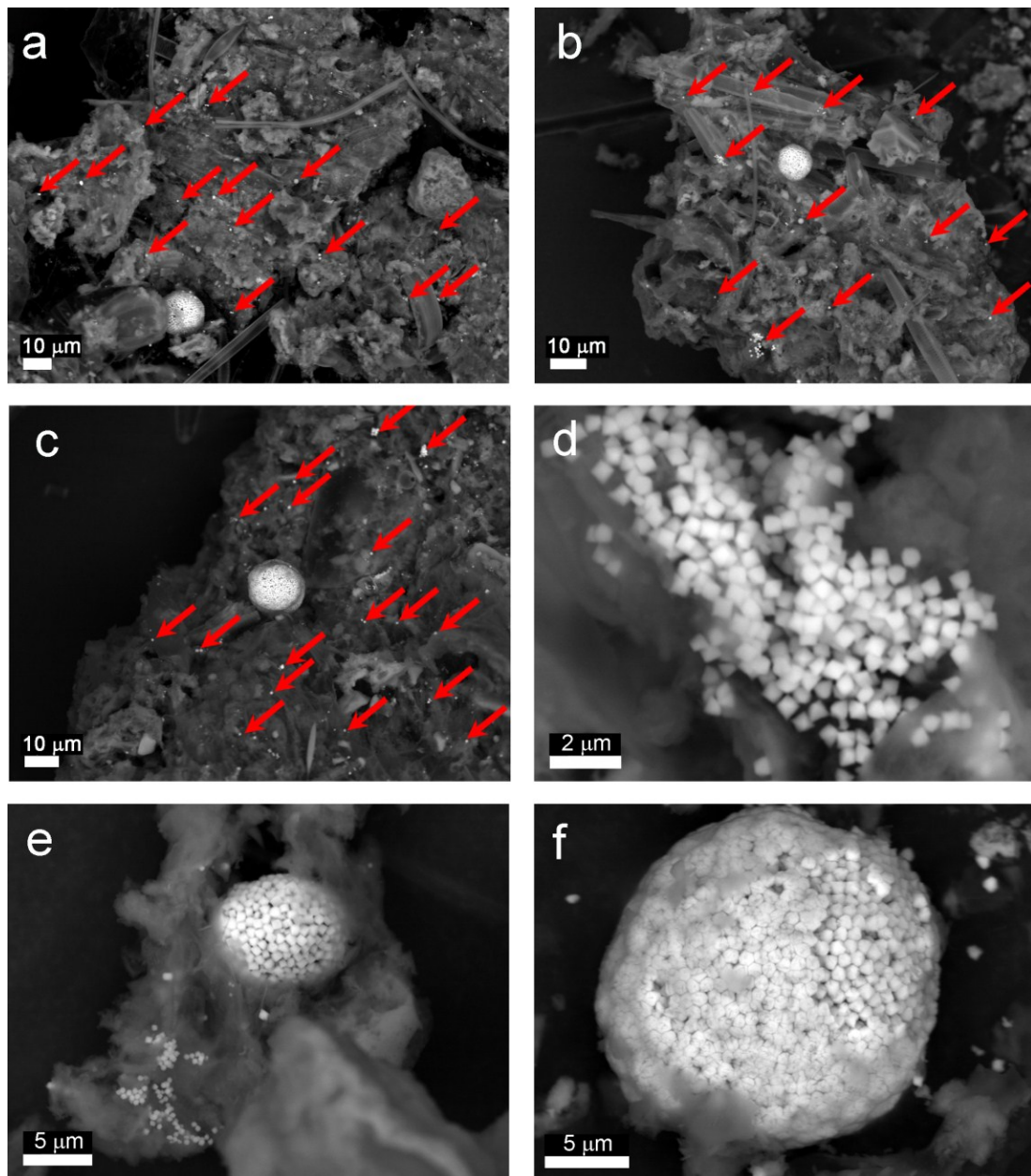


Figure 11: Scanning electron microscope images in backscatter mode of contemporary pyrite from surficial sediments at Darawakh wetland.

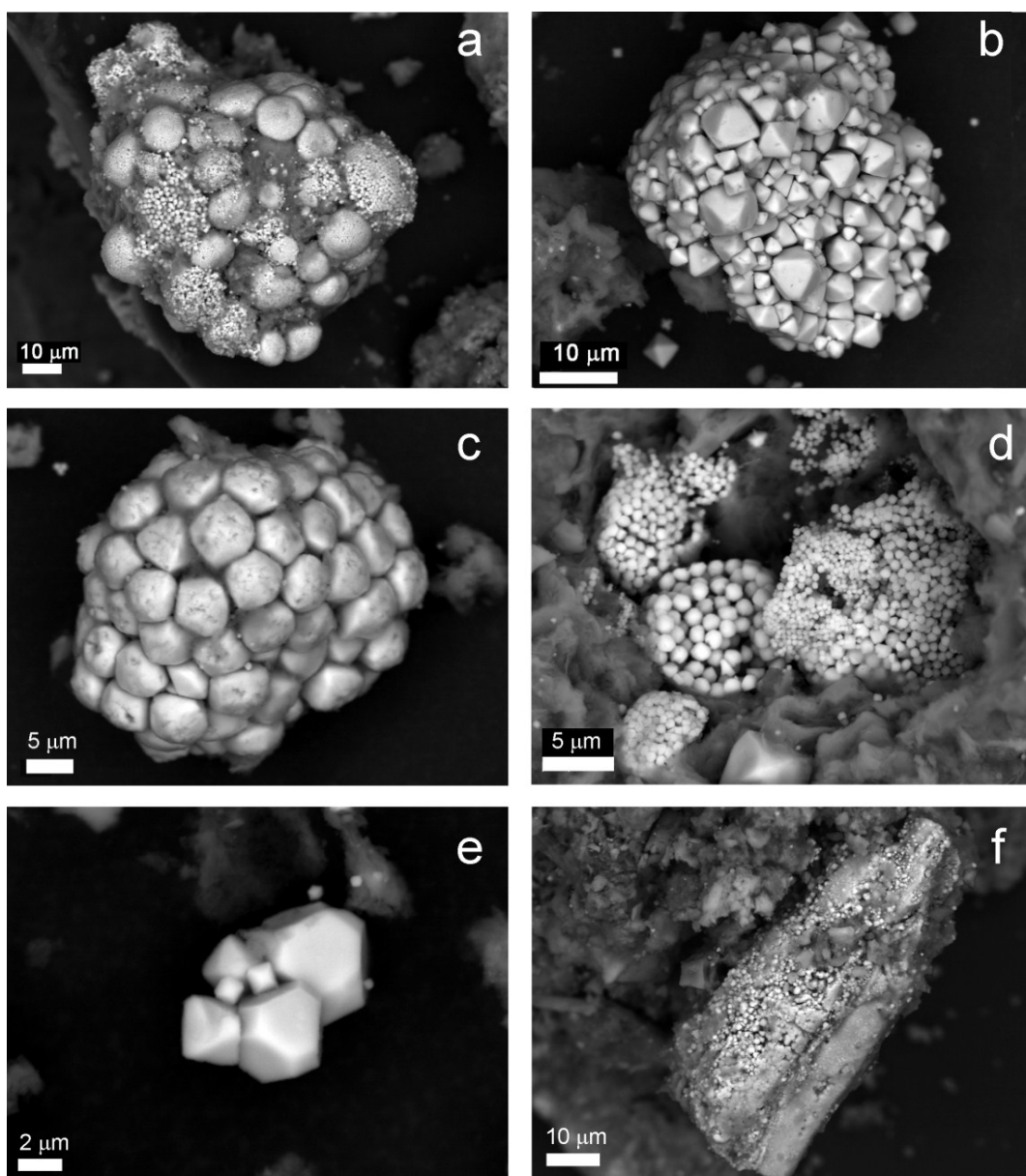


Figure 12: Scanning electron microscope images in backscatter mode of pyrite from relic sulfidic sediments at Darawakh wetland.

Surface and groundwaters

Surface water pH at both wetlands was mostly between 5.5-6.2 at the time of survey (Fig. 13 and 14). This was accompanied by low electrical conductivity ($<0.6 \text{ mS cm}^{-1}$) and relatively low dissolved oxygen saturation - as expected for organic-rich, freshwater wetland surface waters. Strong stratification of the water column was evident at Partridge Creek and some Fe^{2+} and Mn mobilisation occurred in the oxygen-depleted, mildly-reducing bottom waters. Although dissolved organic carbon was higher at Darawakh than Partridge Creek, the Fe^{2+} and Mn concentrations were lower, with Fe^{2+} remaining mostly below $20 \mu\text{M}$ ($\sim 1.1 \text{ mg L}^{-1}$).

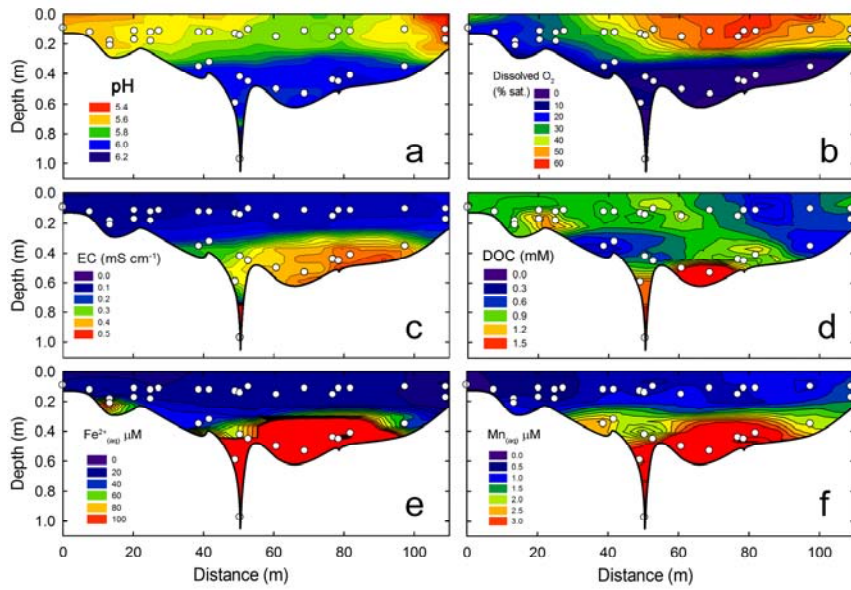


Figure 13: Surface water chemistry near sites PC1-5 at Partridge Creek wetland.

The occurrence of Fe^{2+} in surface waters simply reflects iron reduction due to anaerobic conditions in bottom sediments. Shallow groundwater from Partridge Creek wetland contains abundant Fe^{2+} , with concentrations over an order of magnitude higher than those in surface waters (Fig. 15). This is accompanied by considerable alkalinity (as bicarbonate – HCO_3^-), dissolved organic carbon and pH values between 5.8 to 6.5.

However, when Fe^{2+} oxidises to Fe^{3+} , the subsequent hydrolysis generates acidity. This means that even though the shallow groundwater at Partridge Creek is clearly no longer acidic, the high Fe^{2+} represents a labile pool of potential acidity. When balanced against existing pH and bicarbonate content, some of these groundwaters still have the capacity to generate considerable Net acidity if exposed to oxygen, as indicated in Figure 16.

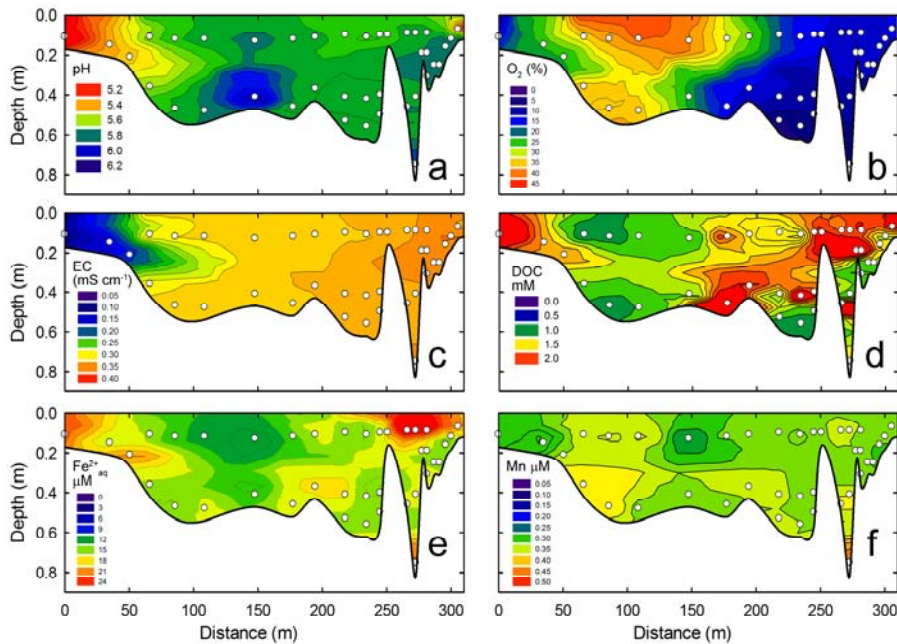


Figure 14: Surface water chemistry near sites D1-6 at Darawakh wetland.

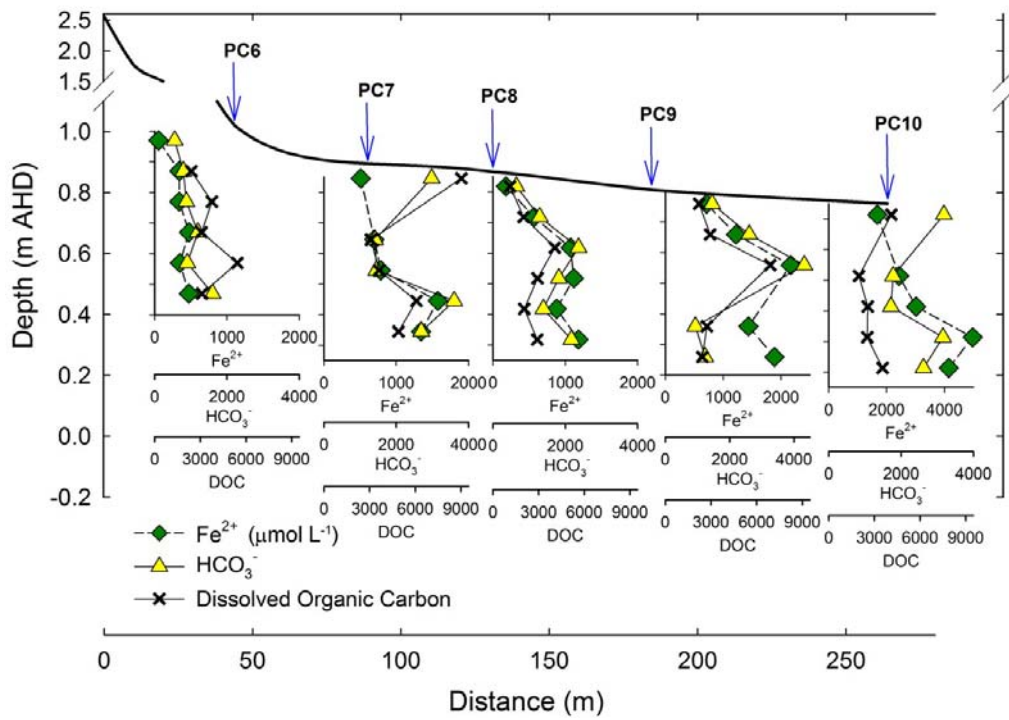


Figure 15: Partridge Creek, Transect PC6-10 topography, porewater Fe^{2+} , HCO_3^- and dissolved organic carbon.

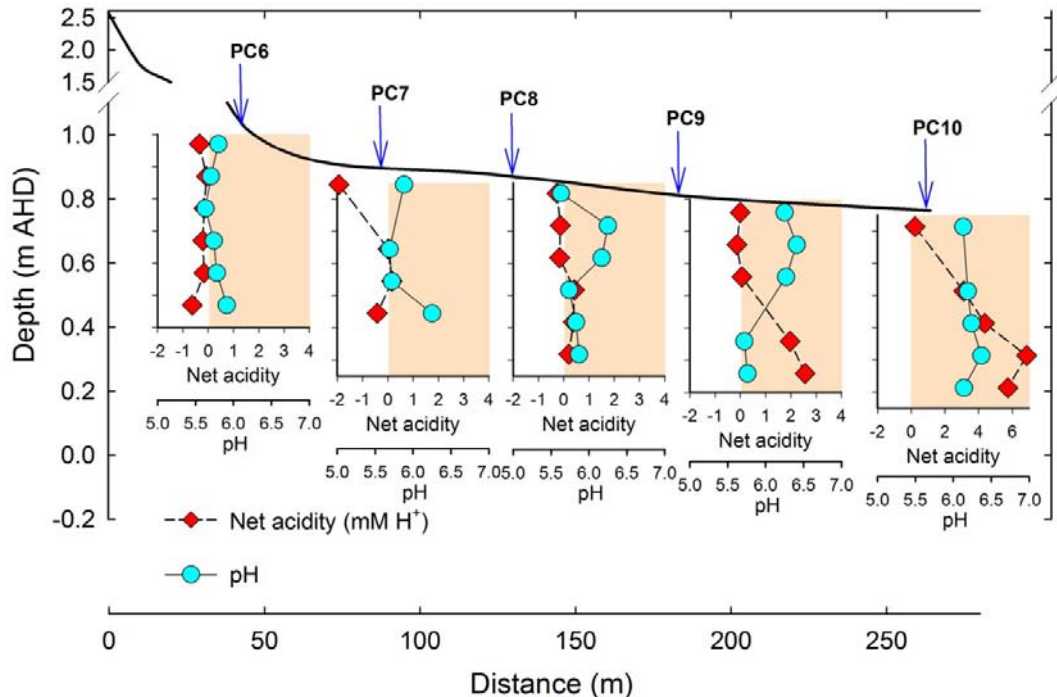


Figure 16: Partridge Creek, Transect PC6-10 topography, porewater pH and calculated Net acidity according to equations (1) and (2).

Conclusions – long-term management challenges and questions

It is clear that from the perspective of soil, groundwater and surface water acidity, both wetlands are in far better condition than before the reflooding remediation began. Regular discharge of acute acidity from drainage waters is largely a thing of the past, leading to improved downstream water quality and less export of toxic metals such as Al. This is evident in the cessation of visual acid plumes entering the estuary and the recovery of local oyster production in the Hastings estuary since remedial works were completed. The ecological recovery of wetland vegetation assemblages is also another important improvement, but the details of this recovery are beyond the scope of this study.

One important long-term management challenge revolves around the stability and likely behaviour of reformed RIS species during future drought episodes. Various questions arise, including “*How fast might reformed RIS species oxidise during a drought?*”, “*How much acidity will they produce and will there be sufficient in-situ alkalinity within the sediments to neutralise or partially neutralise this acidity?*”

While it is a relatively simple procedure to calculate the theoretical amount of acidity that may be released upon oxidation of all reformed RIS species, to answer the above questions quantitatively is non-trivial. Part of the difficulty lies in the current limitations of existing tests used to assess in-situ alkalinity or acid neutralising capacity (ANC). The contrasting kinetics of acid-producing and acidity-consuming chemical reactions, compounds this complexity. One simple, but time-consuming, approach is to subject natural sediments containing reformed RIS to drought simulation experiments. Such experiments are currently in progress.

An important consideration in assessing the likely future stability of the reflooding remediation process is the seasonal context since the remediation began. Analysis of long-term climate records and calculated annual water balance data for the North coast of NSW (Yamba Pilot station), reveals that the period from 2007-2012 has been consistently wet (Fig. 17), with over 5 consecutive years of positive water balance (ie. rainfall in excess of evapotranspiration) (Fig. 18).

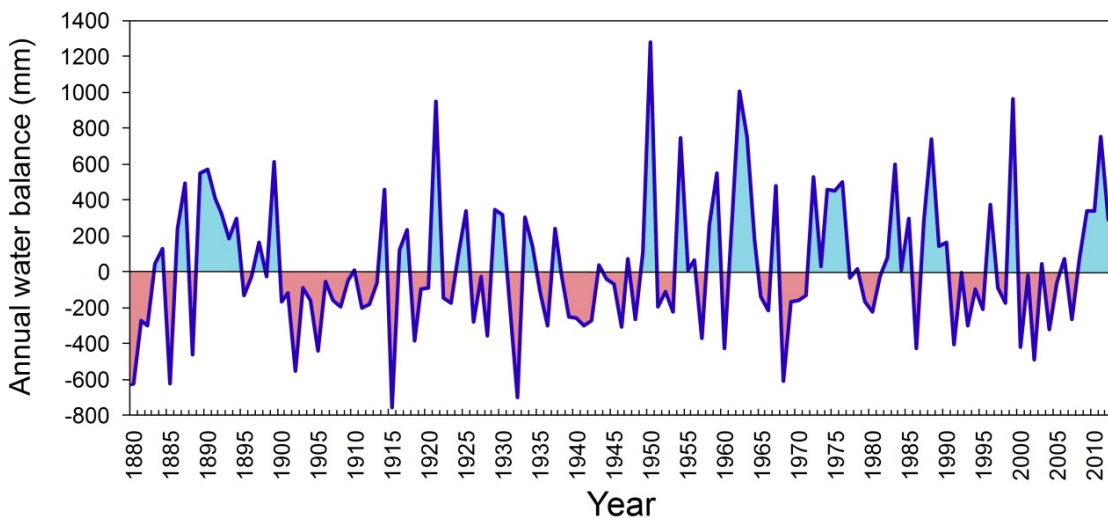


Figure 17: Annual water balance for Yamba Pilot station, 1880-2012. Annual water balance = Σ [monthly rainfall (mm) – average monthly areal evapotranspiration (mm)].

Ranking the past periods of consecutive rainfall excess reveals that the period from 2007-2012 has been the 4th wettest since 1880 (Fig. 18). This provides an important context to the reflooding remediation strategy and its success to date. In particular, it suggests that this period has been somewhat rare and hence there is potential for future drought episodes to trigger drying, sediment oxidation and substantial changes in surface sediment geochemistry.

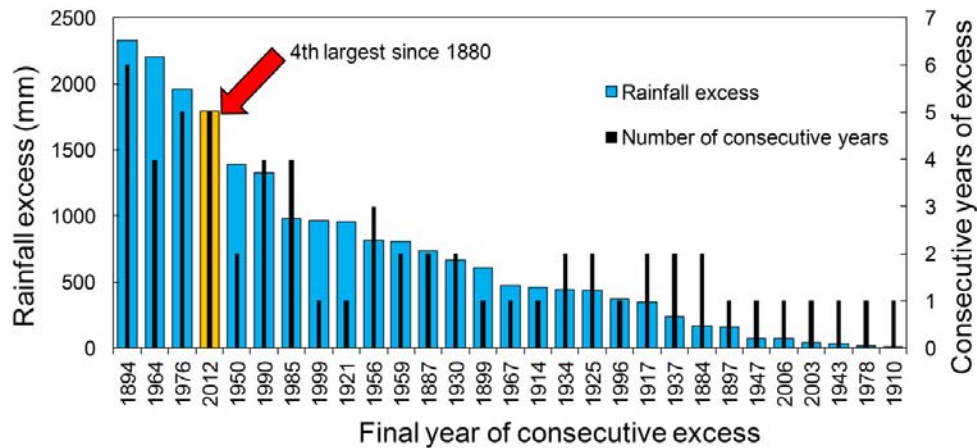


Figure 18: Ranked consecutive rainfall excess for Yamba Pilot station, 1880-2012. Sum of consecutive years when rainfall is in excess, derived from annual water balance in Fig. 17.

If a future drought episode does cause oxidation of reformed RIS species and the production of acidity exceeds sediment ANC, then the wetlands are at risk of producing acidic, poor-quality discharge water following a rewetting rainfall event (Fig. 19). However, it should be noted that because the remediation strategy has effectively inhibited the groundwater hydrological transport pathway, the main acid export pathway remaining is that of surface water runoff. This is important, as surface water runoff is far more episodic by nature and less likely to cause regular, acute acid export (Johnston et al., 2004a).

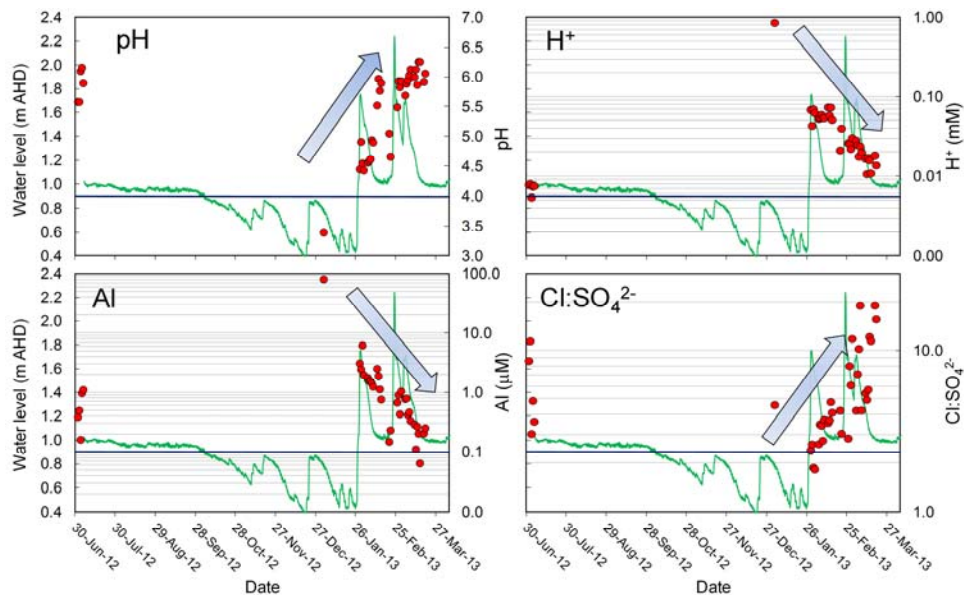


Figure 19: Rapid changes in drain water chemistry (red-circles) and wetland water level (green line) during re-wetting event after a dry period at Partridge Creek.

Also, eventual rewetting / reflooding rainfall event(s) at the conclusion of a drought will also lead to the re-establishment of anaerobic conditions in organic-rich surface sediments. This will reverse the geochemistry again and eventually generate alkalinity due to iron and sulfate reduction, thereby consuming acidity and raising the pH of surface waters. Such seasonal oscillatory behaviour is already evident to some extent at Partridge Creek wetland (Fig. 19).

An important question is “*How fast is such a reversal and generation of alkalinity in surface waters likely to be?*” Figure 19 provides some field data that provides an indication of this and suggests that within 4-6 weeks of reflooding, the geochemical reversal may be sufficient to drive a substantial increase in pH (from 3.5 to 6), major decreases in soluble Al and increases in Cl:SO₄²⁻ ratios - the later strongly suggests the occurrence of sulfate reduction.

This study highlights the long-term management legacy of over-draining acid sulfate soil wetlands. Freshwater reflooding has clearly led to many beneficial environmental outcomes, yet it is not a risk-free, perfect solution and there is no simple “*fix and forget and walk away*” strategy. It is clear that these acid sulfate soil wetlands are likely to present an on-going management legacy, especially in the context of the highly dynamic Australian climate. While the reformation of RIS has been a vital part of neutralising existing acidity, this RIS remains volatile and at some risk of future oxidation. The reformation of RIS near the sediment surface is a form of geochemical hysteresis and represents quite a different situation to the original, undrained conditions when RIS was primarily located at some depth. Some seasonal oscillations in surface water chemistry and acidity are likely to continue. However, the overall export of acidity appears to have decreased substantially as a result of the remediation strategy.

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