



# Sulfur, iron and carbon cycling following hydrological restoration of acidic freshwater wetlands



Scott G. Johnston<sup>a,\*</sup>, Edward D. Burton<sup>a</sup>, Thor Aaso<sup>b</sup>, Gerard Tuckerman<sup>c</sup>

<sup>a</sup> Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia

<sup>b</sup> Port Macquarie-Hastings Council, Port Macquarie, NSW 2444, Australia

<sup>c</sup> Great Lakes Council, Forster, NSW 2428, Australia

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## ABSTRACT

Freshwater re-flooding is a relatively novel approach to remediate drained acid sulfate soil (ASS) wetlands. This study documents the geochemical consequences of restoring freshwater re-flooding for contemporary reduced inorganic sulfur (RIS) and iron species in two coastal floodplain ASS wetlands. Re-flooding has established predominantly reducing/suboxic conditions and encouraged organic carbon accumulation in surface sediments (~20–30%). The pH of former sulfuric horizons has increased by ~2–3 units, partly in response to alkalinity generation from anaerobic metabolism of organic carbon coupled with Fe(III) and  $\text{SO}_4^{2-}$  reduction. Despite considerable sulfidisation, reactive Fe ( $\text{Fe}_R$ ; sum of 1 M HCl and citrate–dithionite extracts) and non-sulfidic Fe(II) remain abundant in both wetlands. High concentrations of  $\text{Fe}^{2+}$  (up to ~5 mM) in wetland porewaters represent a considerable pool of labile net acidity and is partly a result of insufficient S(–II) to sequester excess  $\text{Fe}^{2+}$ . Accumulation of iron sulfides appears to be constrained more by  $\text{SO}_4^{2-}$  and carbon availability rather than  $\text{Fe}_R$ . Reformation and accumulation of RIS species is greatest in organic-rich surface horizons (~40–500  $\mu\text{mol g}^{-1}$ ), where time integrated RIS accumulation rates approximate 10–100  $\text{nmol g}^{-1} \text{d}^{-1}$ . While pyrite is the dominant RIS species to have formed since re-flooding, there is anomalous accumulation of S(0) (up to 80  $\mu\text{mol g}^{-1}$ ), accounting for ~50% of the RIS pool in some samples. Greigite ( $\text{Fe}_3\text{S}_4$ ) has formed in near-surface sediments and while AVS-S is a minor component of the RIS pool overall, at some locations maximum concentrations exceed 300  $\mu\text{mol g}^{-1}$ . Contemporary near-surface pyrite is characterised by abundant small (200–300 nm) crystals, in contrast to relic sedimentary pyrite of estuarine origin that is dominated by larger crystals with diverse habit. Although Fe and  $\text{SO}_4^{2-}$  reduction are partly responsible for wetland-scale recovery from acute acidification, the resultant accumulation of diverse RIS species in surficial sediments indicates an oxidative component to the S-cycle and represents a hysteresis in S-cycling that contrasts markedly with the drained conditions existing before remediation. Analysis of seasonal climate fluctuations suggests that near-surface sediments containing contemporary RIS are vulnerable to oxidation and possible temporary re-acidification during future drought episodes. This study underscores the long-term legacy of ASS wetland drainage and highlights the need for both considered hydrological management of re-flooded wetlands and further study to quantify possible re-acidification risks associated with seasonal drought.

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## 1. Introduction

Freshwater wetlands have high primary productivity and their complex biogeochemistry has a globally significant influence on water quality, trace element cycling and the atmospheric composition of trace gases (Mitsch and Gosselink, 2007). Human impacts have considerably diminished freshwater ecosystem services globally (Dodds et al., 2013). In Eastern Australia, drainage of many ecologically significant freshwater wetlands on coastal floodplains has disturbed their biogeochemical functions and severely degraded water quality. In particular, over-drainage for agriculture has encouraged acute acidification from

oxidation of bioauthigenic pyrite, thereby leading to the development of acid sulfate soils (e.g. Walker, 1972; White et al., 1997). Over-drained coastal acid sulfate soil (CASS) wetlands typically have abundant reactive-Fe(III) minerals, including schwertmannite and jarosite, and display complex Fe and S-cycling (Burton et al., 2006c,d, 2007, 2011; Boman et al., 2008, 2010; Johnston et al., 2011b). CASS wetlands also episodically discharge extremely poor water quality into adjacent aquatic environments (Sammut et al., 1996; Wilson et al., 1999; Sundström et al., 2002; Johnston et al., 2003b, 2004a, 2009a; Wong et al., 2010).

Freshwater CASS wetlands pose unique land and water management challenges. Various remediation approaches have been developed to decrease the environmental impacts of CASS wetland drainage upon downstream water quality (Blunden and Indraratna, 2000; Indraratna

\* Corresponding author.

E-mail address: [scott.johnston@scu.edu.au](mailto:scott.johnston@scu.edu.au) (S.G. Johnston).

et al., 2002; Johnston et al., 2004b, 2005; Åström et al., 2007). One remediation approach involves re-flooding and restoration of natural wetland hydrology. This can stimulate lower redox conditions and encourage alkalinity-producing geochemical processes such as Fe(III) and  $\text{SO}_4^{2-}$  reduction, thereby neutralising acidity in situ at a wetland-scale (Johnston et al., 2009a,c, 2012b).

Remediation of CASS by tidal re-flooding with seawater has received some attention in a series of recent studies (Johnston et al., 2009a,c, 2010, 2012b; Burton et al., 2011; Keene et al., 2011). These studies demonstrated that tidal re-flooding of CASS wetlands with seawater can be an effective means of decreasing acidity, reforming reduced inorganic sulfur (RIS) species and immobilising trace metal cations. However, in contrast to seawater re-flooding, there have been no comparable field-scale hydro-geochemical studies examining freshwater re-flooding of CASS wetlands.

This is an important omission, as there are fundamental geochemical and hydrological differences between tidal seawater re-flooding and freshwater re-flooding. These differences may drive contrasting geochemical trajectories and divergent Fe and S bio-mineralisation pathways that may result in contrasting environmental risks. For example, during CASS wetland drainage, some S from pyrite oxidation is exported as highly soluble  $\text{SO}_4^{2-}$ , while much of the iron is typically retained within the landscape as poorly soluble, reactive-Fe(III) minerals (Van Breemen, 1975, 1993; Burton et al., 2006d). While seawater re-flooding leads to import and replenishment of various anions, including  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ , freshwater re-flooding lacks this regenerative external source of  $\text{SO}_4^{2-}$ .

This depletion of  $\text{SO}_4^{2-}$  relative to reactive-Fe(III) minerals could have multiple implications for S and Fe cycling in re-flooded freshwater CASS wetlands. Firstly, this creates a fundamental stoichiometric imbalance whereby the lack of  $\text{SO}_4^{2-}$  may cause freshwater wetlands, upon re-flooding, to produce insufficient S(–II) to react with all of the  $\text{Fe}^{2+}$  produced by dissimilatory iron reduction, thereby preventing complete sequestration of  $\text{Fe}^{2+}$  as iron-sulfide minerals. Such a relative lack of  $\text{SO}_4^{2-}$  may pose a fundamental constraint of RIS reformation and lead to porewaters highly enriched in  $\text{Fe}^{2+}$  (White et al., 1997), thereby creating a relatively labile store of net acidity (Johnston et al., 2011a). Secondly, abundant reactive-Fe(III) minerals can alter sulfur biomineralisation pathways, favouring the formation of highly reactive sulfur species such as elemental sulfur (S(0)) and nano-particulate mackinawite (Carignan and Tessier, 1988; Burton et al., 2006b, 2011; Keene et al., 2011). In addition, abundant bio-available Fe(III) can retard both sulfate reduction and methanogenesis via competitive exclusion and thereby influence carbon mineralisation pathways (Postma and Jakobsen, 1996; Heimann et al., 2010).

There remains considerable uncertainty regarding the abundance, vertical distribution and speciation of reduced inorganic sulfur (RIS) that may reform in freshwater re-flooded CASS wetland sediments. Will pyrite formation be favoured over more reactive RIS species or vice-versa? If conditions do favour the accumulation of reactive-RIS species (i.e. S(0) and AVS extractable species including mackinawite and greigite), especially near the sediment surface, such species may be at risk of rapid oxidation and acid generation during future drought episodes (Burton et al., 2006a,c, 2009). Given that Australia's climate is characterised by cyclic drought episodes, freshwater re-flooded CASS are at long term risk of drought-induced water level lowering causing oxidation of RIS species that have reformed near the sediment surface. This is a major contrast with seawater re-flooded CASS – for although water levels in seawater re-flooded CASS do fluctuate, they are controlled by tides and fluctuate within a narrow range and are thereby relatively immune to drought influence (Johnston et al., 2011b). Therefore, identifying the vertical distribution and speciation of RIS fractions that reform following freshwater re-flooding of CASS will assist in understanding the management risks associated with the strategy.

This study aims to quantify abundance and vertical distribution of RIS species, reactive iron fractions and organic carbon in two CASS

wetlands subject to hydrological restoration by freshwater re-flooding for 8–9 years. We identify key geochemical processes that appear to be influencing RIS abundance, speciation and spatial distribution and explore the likely geochemical trajectory of the wetlands in the context of an El-Niño Southern Oscillation (ENSO) dominated climate regime. Possible implications for future management are identified along with future research needs.

## 2. Methods

### 2.1. Study sites

Both study sites are located on Holocene coastal floodplains in Eastern Australia (Figs. 1 and 2). Partridge Creek (Fig. 1) is a 542 ha freshwater wetland backswamp distributary system on the Hastings River floodplain (lat. 31.426° S, long. 152.848° E) that is underlain by estuarine sulfidic sediments at a depth of about 1.3 m below ground level (bgl) (Burton et al., 2008). Backswamp elevation ranges from about 0.6 to 1.2 m AHD (AHD = Australian height datum; 0 AHD  $\approx$  mean sea level). The hydrology of the wetland was substantially modified by open ditch drains, thereby enhancing oxidation of underlying sulfidic sediments and the transport of sulfide oxidation products off-site (Aaso, 2004). Prior to remediation, there was regular acidic discharge from the wetland drainage system and the flux of  $\text{H}^+$  was estimated to be in the order of  $\sim 800$  tonnes of  $\text{H}_2\text{SO}_4$  equivalent for an average rainfall year (Aaso, 2004). Before re-flooding, the wetland acid sulfate soils were Hydraquentic Sulfaquepts (Soil Survey Staff, 1998) with acutely acidic (pH 3.2 to 4) and predominantly oxalic horizons exhibiting Fe(III) oxide and jarosite pedofeatures, extending to a depth of  $\sim 1.3$  m bgl (Aaso, 2002). The wetland was identified by the NSW government as an acid sulfate soil priority management area (Tulau, 1999) and a freshwater re-flooding strategy commenced in 2004. This consisted of retaining rainfall on-site by blocking the main drain outlet with a weir and raising the wetland water level to a target of  $\sim 0.9$ – $1.0$  m AHD.

Darawakh (Fig. 2) is an  $\sim 1000$  ha freshwater wetland on the Wallamba River floodplain (lat. 32.088° S, long. 152.488° E). It is characterised by a sinuous, North–south orientated depression, which is an infilled estuarine channel feature several hundred metres wide with an elevation ranging from about 0.2 to 0.8 m AHD. The channel-infill is underlain by Holocene sulfidic estuarine muds and bounded to the east and west by Pleistocene aeolian sand plains. Acid sulfate soils are largely confined to the channel-infill geomorphic unit (Roberts et al., 2002). Soils from the upper  $\sim 0.5$  m collected prior to the commencement of re-flooding reflect a predominantly oxalic status and contained negligible RIS ( $< 5 \mu\text{mol g}^{-1}$  chromium reducible sulfur,  $S_{\text{CR}}$ ) (Roberts et al., 2002). The natural hydrology of this wetland was also highly modified by open ditch drains and the site was responsible for seasonal discharge of highly acidic water into the adjacent Wallamba River estuary (Smith, 2003). Remediation commenced in 2005 and consisted of retaining rainfall and raising water levels by infilling and removing artificial ditch drains, thereby helping restore the natural hydrological functioning of the wetland.

### 2.2. Soil sample collection

Soils were collected from a series of sites in each wetland (Darawakh,  $n = 10$ ; Partridge Creek,  $n = 12$ ), with sample sites arranged as toposequence transects where possible to ensure representation of a wide range of elevations and thus soil inundation depths. The ground surface at each transect was surveyed to AHD from a known AHD with a Leica NA730 automatic level. Soils were collected from each wetland in July 2012. At each sampling location at least three replicate soil cores were collected 0.5 m apart, using either a 1.5 m gouge auger or a push-tube coring device to a maximum depth of 0.8 m bgl. Cores were immediately sectioned at either 0.05 m or 0.1 m increments,

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