



## Research article

## Changes in soil organic carbon fractions after remediation of a coastal floodplain soil

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## ABSTRACT

Coastal floodplain soils and wetland sediments can store large amounts of soil organic carbon (SOC). These environments are also commonly underlain by sulfidic sediments which can oxidise to form coastal acid sulfate soils (CASS) and contain high concentrations of acidity and trace metals. CASS are found on every continent globally except Antarctica. When sulfidic sediments are oxidised, scalds can form, which are large bare patches without vegetation. However, SOC stocks and fractions have not been quantified in these coastal floodplain environments. We studied the changes in soil geochemistry and SOC stocks and fractions three years after remediation of a CASS scald. Remediation treatments included raising water levels, and addition of either lime (LO) or lime and mulch (LM) relative to a control (C) site. We found SOC concentrations in the remediated sites (LO and LM) were more than double than that found at site C, reflected in the higher SOC stocks to a depth of 1.6 m (426 Mg C/ha, 478 Mg C/ha and 473 Mg C/ha at sites C, LO and LM, respectively). The particulate organic C (POC) fraction was higher at sites LO and LM due to increased vegetation and biomass inputs, compared to site C. Reformation of acid volatile sulfide (AVS) occurred throughout the profile at site LM, whereas only limited AVS reformation occurred at sites LO and C. Higher AVS at site LM may be linked to the additional source of organic matter provided by the mulch. POC can also potentially contribute to decreasing acidity as a labile SOC source for  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  reduction. Therefore, coastal floodplains and wetlands are a large store of SOC and can potentially increase SOC following remediation due to i) reduced decomposition rates with higher water levels and waterlogging, and ii) high C inputs due to rapid revegetation of scalded areas and high rates of biomass production. These results highlight the importance of maintaining vegetation cover in coastal floodplains and wetlands for sequestering SOC.

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## 1. Introduction

Coastal floodplains and wetlands are important sinks for carbon and can potentially store large amounts of soil organic carbon (SOC). This SOC is sourced from either autochthonous sources as a result of high rates of biomass production and subsequent inputs, or allochthonous sources, from deposition of organic matter and sediment during flood events (Noe and Hupp, 2009). In these environments, SOC accumulation can be further enhanced, particularly where waterlogging of the soil occurs which can create anoxic conditions and slow decomposition processes. However, globally, coastal floodplains and wetlands have been extensively drained to allow for urban and agricultural expansion, leading to substantial

losses of SOC (Armentano, 1980; Page and Dalal, 2011). Decreasing the moisture content of previously waterlogged soils exposes soil organic matter to oxygen and increases decomposition rates, leading to a reduction of SOC stocks (Raich and Schlesinger, 1992).

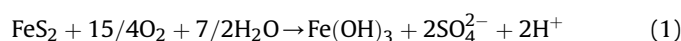
There is potential to sequester large amounts of atmospheric  $\text{CO}_2$  in soils of coastal floodplains and wetlands following rehabilitation of degraded areas by raising water levels to increase moisture content and revegetation to increase biomass production. Following restoration of degraded wetlands, SOC concentrations can more than double after 15 years (Mitsch et al., 2013) and can continue to sequester C for up to 33 years (Badiou et al., 2011). Similarly, in constructed salt marsh environments, rates of SOC accumulation can be comparable to natural wetlands (Craft et al., 1999).

Coastal floodplains and wetlands are also frequently underlain by sulfidic sediments and cover an estimated area of 17 million ha (Andriessse and van Mensvoort, 2006). These sediments are

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dominated by pyrite (FeS<sub>2</sub>) and iron monosulfides such as mackinawite (FeS). Under reducing conditions when watertables are high, these sediments do not pose a threat to soil or water quality. However, oxidation of sulfidic sediments, such as via drainage, drought conditions or isostatic uplift results in acidity generation (Boman et al., 2008, 2010; Grealish et al., 2014; Johnston et al., 2004; Mosley et al., 2014) to form coastal acid sulfate soils (CASS), according to Eq. (1) (Dent, 1986). CASS-affected coastal floodplains and wetlands are found globally, including in extensive areas in eastern and northern Australia, boreal and western Europe, south and south-east Asia, west Africa, north-eastern coast of South America, and North America (Andriessse and van Mensvoort, 2006). The geochemical processes which occur in these environments are analogous to acid mine drainage environments.



Decreases in pH due to oxidation of pyrite results in the mobilisation of trace metals such as Fe, Al, Mn, Ni and Zn in porewaters and waterways which adversely affects vegetation health, soil and water quality and aquatic ecosystems (Boman et al., 2010; Johnston et al., 2004; Nystrand and Österholm, 2013; Sohlenius and Öborn, 2004). In extreme cases, scalded areas can form, which are persistently bare areas of land. Scalds are characterised by high concentrations of trace metals, acidity and significant accumulations of Fe (oxy)hydroxide minerals which prevent plant germination and growth (Rosicky et al., 2004).

The changes in sediment and surface water geochemistry during and following remediation are relatively well understood. Previous rehabilitation efforts in CASS environments have focused on re-introduction of brackish water, tidal inundation, and incorporation of lime and other alkaline amendments (Johnston et al., 2009a, 2009b, 2005). Rehabilitation of CASS environments is largely dependent on increasing water levels to maintain reduced conditions (Johnston et al., 2012), resulting in the generation of alkalinity when acidic products such as jarosite and schwertmannite are reduced over periods of less than 12 months (Vithana et al., 2015). This process requires a source of labile SOC for reduction of Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> to occur (Chu et al., 2006).

However, quantifying changes in SOC concentrations and fractions have not previously been determined following restoration of CASS floodplains and wetlands. Understanding the SOC cycling processes is critical due to the interaction with redox sensitive species in these environments. There is the potential to both improve soil and water quality and increase SOC stocks during remediation. This study quantifies the changes in soil geochemistry and soil organic carbon stocks and fractions following remediation of a CLASS coastal floodplain wetland in eastern Australia.

## 2. Methods

### 2.1. Study site

The study site was located in the Tuckean Nature Reserve (TNR) in the sub-tropical region of eastern Australia (Fig. 1 and Supplementary Geospatial Data). The soil type was a Sulfuric/Sulfidic Oxyaquic Hydrosol (Isbell, 1996) or a Hydraquentic Sulfaquept (Soil Survey Staff US, 1998). The TNR covers approximately 916 ha of the Tuckean Swamp, a 5000 ha coastal floodplain on the lower Richmond River. The TNR is drained via the Tuckean-Broadwater, which eventually discharges into the Richmond River. The Tuckean Barrage (Fig. 1) was originally constructed for flood mitigation and as a result, water levels decreased which exposed sulfidic sediment layers resulting in oxidation. Acute and chronic discharges of acidity in to the drainage channels and persistent acidic conditions

with high salinity and high concentrations of trace metals (Sammut et al., 1996) resulted in bare patches forming and expanding. These bare areas reached a maximum area of 1.2 ha prior to remediation taking place.

Remediation of the scalded area began in 2010 via drain infilling. Fences were installed to exclude stock and the water table was raised through the placement of a bund in the main drain and the shallowing of side drains. The scalded area was rotary hoed and mounded. The area was subjected to two treatments – limed only (LO), and limed and mulched (LM) (Fig. 1). Lime was added at a rate of 3.7 t/ha, and mulch was added in the form of cut and dried sedge (*Eleocharis* spp.) to encourage recolonising by grey rush (*Lepironia articulata*) from adjacent areas and to provide a source of organic matter for Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> reduction. The sedge was sourced from an adjacent unscalded area, cut, transported to the scald, and added to a depth of approximately 0.3 m. There was also one control site (C) which had been rotary hoed without any amendments and remained scalded (Supplementary Material; Fig. S1). At the time of sampling, vegetation at sites LO and LM was dominated by grey rush (Supplementary Material; Fig. S1).

### 2.2. Field sampling

Three cores of 160 cm were sampled from each of the sites in March 2013. Samples were taken from the 0–0.1, 0.1–0.2, 0.2–0.3, 0.3–0.5, 0.5–0.7, 0.7–1.0, 1.0–1.3 and 1.3–1.6 m depths. The same depth increments from each of the three cores sampled were bulked in to one sample, placed in to polyethylene bags with the air expelled and frozen.

Extensive flooding had occurred prior to sampling in March 2013 and there was approximately 0.5 m of overlying water at the time of sampling. Therefore, bulk density could not be determined. However, previous studies at this site had determined a bulk density of 1.0 g/cm<sup>3</sup> (Sammut et al., 1996).

### 2.3. Laboratory analysis

Samples used for geochemical analysis were thawed under a N<sub>2</sub> atmosphere prior to analysis. Moisture content was determined after drying at 105 °C for at least 24 h. Samples for pH, EC, soluble and exchangeable metals and cations, organic C and total N were dried at 85 °C, lightly crushed with a mortar and pestle to pass through a 2 mm sieve (Ahern et al., 2004).

Soil pH, EC and soluble cations and metals were determined on 1:5 soil:water extracts (Rayment and Lyons, 2011). Exchangeable cations and metals were extracted with BaCl<sub>2</sub>/NH<sub>4</sub>Cl extracts (Rayment and Lyons, 2011). Where the EC<sub>1:5</sub> ≥ 0.3 dS/m, soluble salts were removed by washing three times with an ethanol/glycerol solution. The extracts were filtered through 0.45 μm filters, preserved with concentrated HNO<sub>3</sub> and analysed on a Perkin Elmer Elan DRC-e Inductively Coupled Mass Spectrometer. Particle size analysis was determined by laser granulometry on a Beckman Coulter LS100 after pre-treatment with H<sub>2</sub>O<sub>2</sub> to remove organic matter and 5% Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> for dispersion. Titratable actual acidity (TAA) was determined by titration with 0.05 M NaOH to pH 7.0 on 1:5 soil:1 M KCl extracts (Ahern et al., 2004).

Reduced inorganic S (RIS) speciation was determined via a three step sequential extraction procedure to extract 1) monosulfides, operationally defined as acid volatile sulfide (AVS); 2) elemental S<sup>0</sup>, and 3) disulfides (primarily pyrite), operationally defined as Cr-reducible S (CRS) (Burton et al., 2008). AVS was extracted using the cold diffusion method by Hsieh et al., (2002) and Burton et al. (2006) by shaking sediment with 6 M HCl/0.1 M ascorbic acid. The evolved H<sub>2</sub>S was trapped in 3% Zn acetate in 1 M NaOH and analysed by iodometric titration. Elemental S<sup>0</sup> was then extracted

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