Geoderma 285 (2017) 117–131

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Acidity generation accompanying iron and sulfur transformations during drought simulation of freshwater re-flooded acid sulfate soils

Niloofar Karimian *, Scott G. Johnston, Edward D. Burton

Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia

ARTICLE INFO

Article history:
Received 1 May 2016
Received in revised form 30 August 2016
Accepted 24 September 2016
Available online 30 September 2016

Keywords:
Acid sulfate soil
Wetland
Iron
Reduced inorganic sulfur
Titratable actual acidity

ABSTRACT

Remediation of acid sulfate soil (ASS) wetlands by re-flooding with freshwater generates alkalinity and leads to the reformation of reduced inorganic sulfur (RIS) and Fe(II) species in surface soil layers. These contemporary RIS/Fe(II) species are vulnerable to drought-induced oxidation. However, the rates and magnitude of acid-generating reactions and competing acid-neutralisation reactions during such oxidation events are unknown. In this study, ten surface soil samples (0–0.2 m depth) were collected from two freshwater re-flooded ASS wetlands and subjected to oxidative incubation for up to 130 days. The objective was to examine the rate and magnitude of acidity generation and compare this to changes in RIS/Fe speciation. During the incubation, soil pH decreased rapidly by ~2–3 units, while titratable actual acidity increased, largely as a result of H^+ generation from oxidation of RIS species. RIS species (primarily small pyrite framboids and dispersed sub-micron sized, euhedral pyrite crystals), decreased over time in all soil samples while the reactive pool of Fe(III) minerals (e.g. schwertmannite) increased. Importantly, the highest rates of acidity generation occurred within the first 20 days, suggesting that surface soil layers in these remediated wetlands are prone to rapid acidification during future droughts. Variations in the magnitude of soil acidification largely reflect differences in both initial RIS content and acid neutralisation capacity (ANC). Spatial variations were evident, with sites located at lower elevations generally containing higher initial RIS and generating more acidity in a shorter time period. However, the magnitude of acidity generation was consistently less than that predicted by theoretical calculations. These results provide new information that is directly relevant to the future management and mitigation of risks to water quality associated with freshwater re-flooding of ASS wetlands.

1. Introduction

In Eastern Australia, large areas of ecologically important freshwater coastal wetlands have been degraded by over-drainage (Burton et al., 2006a; Johnston et al., 2004; Sammut et al., 1996; White et al., 1997). In many circumstances, over-drainage has led to oxidation of iron sulfides (Bush and Sullivan, 1997) and the release of large quantities of iron and sulfate and led to the generation of acid sulfate soils (ASS) (Burton et al., 2006b; Walker, 1972). Given that wetlands play important roles in regulating water quality and maintaining biodiversity (Barbier et al., 2011; Herbert et al., 2015; Zedler and Kercher, 2005), the adverse environmental outcomes caused by over-drainage have led to various attempts to remediate coastal freshwater ASS wetlands (Åström et al., 2007; Blunden and Indraratna, 2000; Indraratna et al., 2002; Johnston et al., 2014).

Re-flooding of acid sulfate soil (ASS) wetlands is a relatively inexpensive and effective remediation technique which is based on the establishment of predominantly reducing soil conditions. Although a number of studies have examined the consequences of sea water inundation for remediating ASS (e.g. Burton et al., 2011; Johnston et al., 2009a, 2010, 2012; Keene et al., 2011), remediation of ASS via re-flooding with freshwater has received comparatively limited attention (Burton et al., 2008a; Johnston et al., 2014; Creeper et al., 2015).

Although freshwater re-flooding of ASS has demonstrably favourable environmental outcomes, such as increasing soil pH, decreasing exchangeable acidity and preventing further pyrite oxidation (Blunden and Indraratna, 2000; Johnston et al., 2014), it can also trigger wide ranging consequences for the cycling of iron, sulfur, carbon and associated trace elements (Burton et al., 2008b; Johnston et al., 2005). For example, Johnston et al. (2014) reported that long-term (~8–10 yr) freshwater re-flooding of ASS, led to the accumulation of substantial porewater Fe^{2+}, non-sulfidic solid-phase Fe(II) and a mixture of newly formed RIS species (including pyrite, greigite, mackinawite and elemental sulfur), in near-surface sediments. While pyrite was the dominant RIS species, there was considerable accumulation of elemental sulfur [S(0)] and acid volatile sulfide (S_{AVS}) in some surface soils. Both S(0) and S_{AVS} can oxidise relatively quickly (Burton et al., 2006a, 2009), potentially rendering these sediments vulnerable to rapid re-acidification during a future drought episode.

* Corresponding author.
E-mail address: n.karimian.11@student.scu.edu.au (N. Karimian).

http://dx.doi.org/10.1016/j.geoderma.2016.09.030

In contrast with tidal environments, hydrology and redox conditions in re-flooded freshwater ASS wetland soils are mainly controlled by rainfall. Rainfall in eastern Australia is highly episodic with frequent wet-dry cycles that drive large fluctuations in wetland water levels (Johnston et al., 2014). Climatic variability is thus an important feature of remediation of ASS by freshwater re-flooding, as a major drought episode which causes a significant drop in water levels in re-flooded ASS wetlands risks exposing re-formed RIS and Fe(II) species to oxygen, driving oxidative generation of H^+. If the magnitude of H^+ generation exceeds the soil's acid neutralising capacity (ANC), these wetlands may produce highly acidic, poor-quality surface water upon eventual re-wetting.

This study simulates a drought-induced oxidation (130 days) of surficial soils from two freshwater re-flooded ASS wetlands that contain a mixture of neoformed RIS and Fe(II) species. We quantify changes to the speciation of iron and sulfur during this oxidative transition. A primary objective is to determine the rate, magnitude and range of acidity generation during drought simulation and to relate this to observed changes in Fe and RIS speciation. Incubation methods have been used to simulate drought on ASS materials previously to let the soil "speak for itself" (Dent, 1986) and to better account for the potentially divergent kinetics of acid producing and acid neutralising reactions during oxidation (Crockford and Willett, 1995; Sullivan et al., 2009; Ward et al., 2004b). The information derived from this study provides insights into the likely behaviour of these unique soils during future droughts and will assist in refining management strategies for freshwater re-flooded ASS wetlands with wet-dry cycles.

2. Materials and methods

2.1. Description of study sites

The study sites, Partridge Creek and Darawakh wetland, are located on Holocene coastal floodplains in Eastern Australia. Partridge Creek is situated approximately 5 km west of the city of Port Macquarie (Fig. 1) and is a 542 ha freshwater wetland on the Hastings River floodplain within a catchment area of 21.6 km^2 (lat. 31.426° S, long. 152.848° E). It contains relic estuarine sulfidic sediments at a depth of about 1.3 m below ground level (bgl) (Burton et al., 2008c). Wetland surface elevation ranges from about 0.6 to 1.2 m above MSL (Mean Sea Level). Before establishing freshwater re-flooding of this wetland in 2004, the drainage system periodically discharged acutely acidic water into the adjacent estuary (Aaso, 2004). The aim of re-flooding the wetland was to retain rainfall on-site by closing the main drain outlet with a weir, therefore raising the water level in the wetland to ~0.9–1.0 m above MSL (Johnston et al., 2014).

Darawakh wetland is located 10 km north of Tuncurry and is an ~1000 ha freshwater wetland on the Wallamba River floodplain (32.088° S; 152.488° E) with a surface elevation ranging from about 0.2 to 0.8 m AHD (Fig. 2). The wetland is a relic estuarine channel infill situated between Pleistocene/Holocene dune systems. This wetland also had acute acidic discharge impacting downstream water quality prior to remediation by re-flooding. Freshwater re-flooding commenced in 2005, with water levels being increased through retaining rainfall, thus restoring the natural hydrology of the wetland (Johnston et al., 2014).

2.2. Soil sample collection

The ground surface at each sample location was surveyed to (MSL) (Mean Sea Level) from a known datum with a Leica NA730 automatic level. Bulk samples of surface soil (O horizon ~30 cm) were collected at Darawakh (using a Van-Veen grab sampler) and Partridge Creek (using a shovel) from 5 sites in each wetland during October 2013. Sediment sampling locations were determined based on data from earlier field studies of sediment geochemistry (Johnston et al., 2014). Importantly, these sites were selected to bracket a range of organic matter and RIS contents and to span a toposequence elevation range in order to provide an opportunity to explore the oxidation of surface soils derived from different elevations within each wetland. 10 L plastic buckets were filled to the brim with homogenised surface sediment from each site and sealed immediately with air-tight lids and transported to the laboratory. Sub-samples were taken from the homogenised bulk soils within 6 h of collection for initial physico-chemical characterisation of sediments including pH, Eh, electrical conductivity (EC), total organic carbon (TOC), S (total), Fe (total), soil moisture and soil texture, as described in Section 2.3.

To simulate drought conditions, homogenised soil samples were transferred to 10 large (45 × 84 × 17 cm) plastic trays (5 for Partridge Creek and 5 for Darawakh), spread to a uniform thickness (~2 cm) and incubated under oxic conditions in the dark with a constant temperature (20 ± 2 °C) and humidity (34 ± 2%) for 130 days. This approach allowed the soil samples to lose moisture gradually, thereby simulating natural drought conditions. Triplicate homogenised sub-

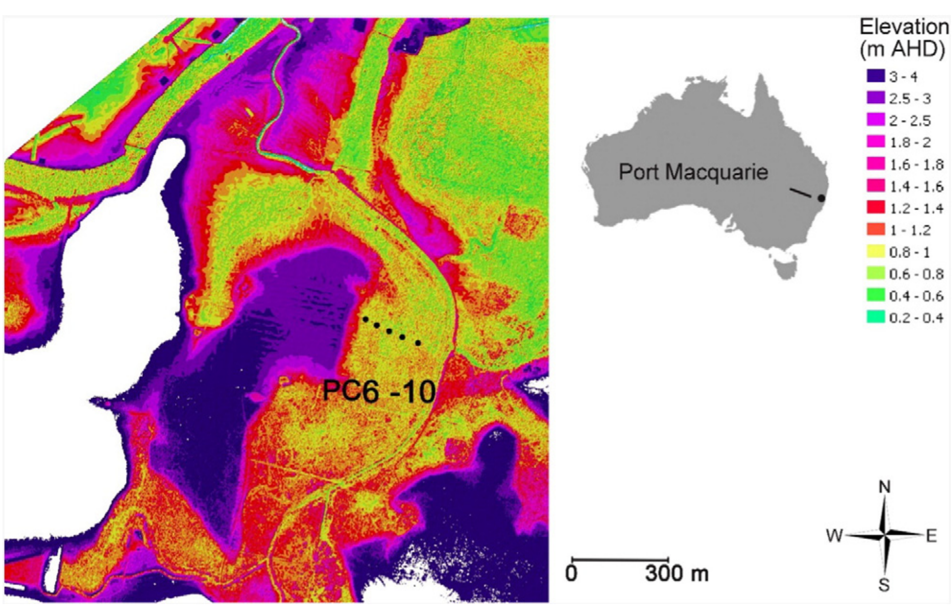

Fig. 1. Partridge Creek wetland sampling sites. Digital elevation model obtained from airborne laser altimetry.