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Effect of schwertmannite and jarosite on the formation of hypoxic blackwater during inundation of grass material

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ABSTRACT

This study focused on understanding the effect of schwertmannite and jarosite, commonly found in floodplains containing acid sulfate soil materials, on the characteristics of the hypoxic blackwaters that can form when floodplain vegetation experiences prolonged inundation. The formation of these 'blackwaters' was simulated in the laboratory by inundating flood-intolerant pasture grass leaf material in both the presence of schwertmannite/jarosite (schwertmannite and jarosite treatments) minerals and their absence (control treatment) at 27.5 °C for 32 days. The presence of either schwertmannite or jarosite was able to decrease the concentrations of DOC, nutrients (e.g. NH_3 and $PO_4^{3-)}$ and the biological oxygen demand (BOD) in the incubating water compared to the control treatment. Being fresh and labile, the pasture grass material liberated DOC immediately following inundation with a concomitant decrease in dissolved O_2 thereby resulting in anoxic and reducing conditions in the incubating water. With the onset of anoxic and reducing conditions, the biogeochemical cycling of DOC in schwertmannite and jarosite treatments might have proceeded via microbially mediated iron(III) and sulfate reduction and electron shuttling processes. Under anoxic, slightly acidic conditions, microbially mediated iron(III) reduction and subsequent dissolution of schwertmannite and jarosite were triggered by liberating Fe^{2+}, SO_4^{2-} and alkalinity to the incubating water. The resultant increase in pH led to SO_4^{2-} reduction in schwertmannite, and the Fe^{2+} catalysed transformation of both schwertmannite and jarosite to goethite. Schwertmannite almost completely transformed to goethite within two weeks of incubation. Iron(III) in goethite (formed from schwertmannie transformation) was also reduced and likely proceeded via direct microbial reduction or via electron shuttling using the humic acids in the incubating water derived from pasture grass. These findings are highly useful in managing the coastal low lying acid sulfate soils landscapes which are subject to frequent flooding during wet seasons.

1. Introduction

"Blackwater" is one of the major contributing factors for riverine deoxygenation and forms in floodplains during flooding and discharges to rivers and other waterbodies during the flood recession period (Johnston et al., 2005; Wong et al., 2010; Hladyz et al., 2011; Whitworth et al., 2012). "Blackwater" forms after 6–10 days of the floodpeak and has a characteristic black-tea colour due to being rich in organic matter derived from the microbial mineralization of inundated vegetation in the floodplain (Howitt et al., 2007; Wong et al., 2010; Whitworth et al., 2012). According to Junk et al. (1989), blackwater formation and its discharge to rivers and other water bodies are key components in the carbon cycling in these environments. While these flood pulses remove the reactive carbon from the floodplains, they help to sustain the health and the productivity of the riverine ecosystems by providing organic matter and nutrients (Junk et al., 1989).

Hypoxic (dissolved oxygen < 2 mg L^{-1}) blackwater develops due to rapid consumption of oxygen by microorganisms during mineralization of labile organic matter in the "blackwater" (Johnston et al., 2005; Howitt et al., 2007; Wong et al., 2010). Apart from having higher concentrations of organic matter (>30 mg L^{-1}) (Whitworth et al., 2012), blackwater also has high chemical oxygen demand (COD) and is enriched with other oxidisable cations such as $Fe^{2+}$and Mn^{2+} (Johnston et al., 2005; Wong et al., 2010). Owing to higher concentrations of labile organic carbon and reduced

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species (e.g. Fe^{2+}, Mn^{2+}), blackwater has a potential to deoxygenate and to exert adverse pressure on the ecosystem of the receiving water bodies (Johnston et al., 2005; Wong et al., 2010). Severe deoxygenation caused by hypoxic blackwater events in riverine ecosystems can cause massive fish kills and death of other aquatic fauna (King et al., 2012; Whitworth et al., 2012; Kerr et al., 2013) and have been reported in forested and agricultural low-lying floodplains in northern (Townsend et al., 1992), eastern (Johnston et al., 2003b; Wong et al., 2010) and southern (Baldwin et al., 2011; Hladyz et al., 2011) Australia.

A majority of the coastal low-lying floodplains in eastern Australia contain acid sulfate soil (ASS) materials (Walker, 1972; Willett and Walker, 1982). Large areas of sulfidic materials which were deposited during the sea-level rise in the Holocene period underlay these floodplains (Walker, 1972; Willett and Walker, 1982; Naylor et al., 1998). These low-lying coastal ASS floodplain environments are highly dynamic and subject to wet and dry cycles due to seasonal weather patterns which can lead to prolonged flooding and drought seasons (White et al., 1997; Johnston et al., 2003a; Wong et al., 2010). The hydrology and the geochemistry of the backswamps in these coastal low-lying floodplains were greatly affected and modified by the artificial drainage system constructed to mitigate flooding related issues (Sammut et al., 1996; White et al., 1997). As a result of the altered hydrology and geochemistry, the vegetation structure in these floodplains gradually shifted from flood-tolerant (e.g. reed and rushes) to flood-intolerant (e.g. improved pasture grass) vegetation (Tulau, 1999; Eyre et al., 2006). Being rich in labile organic carbon, these flood-intolerant vegetation species are subject to rapid microbial mineralization when inundated and thereby accelerate the formation of "blackwater" during flooding (Johnston et al., 2005; Eyre et al., 2006). During prolonged drought seasons, organic matter accumulates due to the decrease in microbial mineralization (Collins et al., 2010).

The underlying sulfidic sediments can be exposed during drainage and prolonged drought seasons and partially oxidised to form secondary iron(III) minerals which are common on the surface of these floodplains (Sullivan and Bush, 2004). Schwertmannite and jarosite are the main secondary iron(III) minerals found in these oxidised and drained floodplains (Sullivan and Bush, 2004). The behaviour of both minerals is highly variable depending on the conditions in the surrounding environment (i.e. pH and redox status). They are stable in acidic-oxic environments and transform to more stable mineral phases such as goethite with concurrent release of acidity (Bigham and Nordstrom, 2000; Stoffregen et al., 2000).

During prolonged flooding, mineralization of flood-intolerant vegetation can generate anoxic and reducing conditions which can promote microbially mediated iron(IIII) reduction and subsequent dissolution of schwertmannite and jarosite (reductive dissolution). The reductive dissolution of both minerals liberates Fe^{2+}, SO_4^{2-} and alkalinity (Burton et al., 2007; Johnston et al., 2011; Vithana et al., 2015). Therefore, under anoxic and reducing conditions, schwertmannite and jarosite may assist in driving the microbial mineralization of organic matter in these environments. Furthermore, under acidic conditions, both minerals can provide sorption sites for the organic matter derived from the microbial mineralization of the inundated vegetation during flooding (Jones et al., 2009; Burton and Johnston, 2012). These closely related biogeochemical processes indicate a strong relationship between the two minerals (i.e. schwertmannite and jarosite) and carbon cycling (i.e. microbial mineralization of flood-intolerant vegetation) in these floodplains.

Previous research has been mainly concerned either on the deoxygenation issues caused by "blackwater" (Johnston et al., 2005; Wong et al., 2010) or on the behaviour of the secondary iron(III) minerals (Sullivan and Bush, 2004; Burton et al., 2007; Vithana et al., 2015) in coastal low-lying ASS floodplains. However, the relationship between schwertmannite and jarosite and the formation of hypoxic "Blackwater" during post-flood periods has yet to be systematically investigated. Our main objective of this study was to understand the effect of both schwertmannite and jarosite on the formation of hypoxic "blackwater" during prolonged inundation of flood intolerant vegetation. We hypothesised that the presence of both minerals would a) enhance the mineralization of DOC liberated from inundated pasture grass, thus leading to b) a lower level of deoxygenation potential in the blackwaters due to the presence of lower amounts of dissolved labile organic carbon (DOC). To investigate these hypotheses we conducted a laboratory incubation experiment to simulate a prolonged inundation of flood-intolerant vegetation (i.e. pasture grass) in the presence of schwertmannite/jarosite.

2. Materials and methods

2.1. Incubation experiment

A batch experiment using glass jars was conducted to simulate the long term inundation of pasture grass during flooding. In this batch experiment, three sets of treatments were prepared: Control treatment-without schwertmannite/jarosite, schwertmannite treatment-with schwertmannite, and jarosite treatment-with jarosite. All three treatments contained leaf material of *Paspallum urvilli,* a common flood intolerant grass species found in floodplains in northern NSW, Australia. Each jar contained 2.6 g of fresh pasture grass leaves cut into 3–4 cm pieces, and 5 cm^3 of wet-soil collected from the Tuckean Swamp, northern NSW, Australia, as the source of microorganisms. The jar was filled with freshly sampled 250 mL of Wilsons River water (pH 6.5–7.5) (Table S1) upto the top and closed with a paraffin and a plastic lid. A small plastic mesh was placed on the grass leaves to prevent them floating in the water. The glass jars were then wrapped up with aluminium foil and incubated at 27.5 °C in a water bath for 8 different sampling days (Day 0, 4, 6, 8, 12, 18, 22, and 32). Each treatment contained 24 glass jars (250 mL volume) in which three replicates were surrendered for various analyses on each sampling day. The amount of fresh pasture grass required for the incubation was calculated to simulate field conditions based on the biomass of the pasture grass, the moisture content and the height of the water during flooding. With 75% of moisture content, the calculated bio-mass of pasture grass was 767.45 g m^{-2} and the height of the floodwater was assumed as 0.3 m. In order to obtain an equal amount of solid Fe^{3+} concentration (i.e. 25 mM Fe L^{-1}), 0.64 g of schwertmannite and 1.5 g of jarosite were added in each schwertmannite and jarosite treatment respectively. The amount of schwertmannite and jarosite added was calculated based on the corresponding molecular formula and on the desired volume of incubating water (i.e. 250 mL) and is described in the supplementary section (Materials and Methods S1). Schwertmannite was synthesised via fast oxidation of $FeSO_4$ by H_2O_2 as described in Regenspurg et al. (2004). Jarosite was synthesised by dissolving KOH and $Fe_2(SO_4)_3$ in ultrapure water at 95 °C as described in Baron and Palmer (1996). The mineralogy of both minerals were verified using X-ray Diffractometry (XRD) and the sample preparation procedure is described in the supplementary section (Materials and Methods S1).

2.2. Analysis of water quality parameters and change in mineralogy

On each sampling day, three jars from each treatment were