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The role of organic matter in ameliorating acid sulfate soils with sulfuric horizons

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ABSTRACT

Acid sulfate soils with sulfuric horizons (pH < 4) can exert a range of negative impacts on the ecology and productivity of soils. The primary treatment for these soils is to raise the pH of the sulfuric horizons using lime. Although often effective, this treatment can be expensive and not well suited to large areas. In this laboratory study, we have investigated the possible use of plant organic matter (OM) to ameliorate: (i) "sulfuric soils" [produced by the oxidization of clayey sulfidic material (pH > 4) samples to form "sulfuric horizon material" (pH < 4)] and (ii) "neutralized sulfuric soils" [produced by the neutralization of peaty sulfuric horizon material (pH < 4) with alkaline sandy loam]. The advantage of this approach is that organic matter is readily available and inexpensive. The experimental treatments used leaf material from *Phragmites australis* as the source of organic matter, which was either incorporated into the two manufactured soils or applied to the surface. After 6 months of incubation under either aerobic or anaerobic soil conditions, pH, Eh and sulfate content were measured. The results showed that incorporation of OM into the sulfuric soil significantly increased soil pH, the extent depending on the moisture level. Changes in pH and sulfate content were correlated with Eh. Application of OM to the "neutralized sulfuric soil" was only partially effective in preventing acidification. It was concluded that the decomposition of OM by aerobic bacteria results in oxygen depletion, which then favors metabolic conversion of sulfates to sulfides by anaerobic bacteria. The results of this study have important implications for the broad scale management of acid sulfate soils.

1. Introduction

Acid sulfate soils (ASS) are naturally occurring soil materials formed under anaerobic conditions, which either contain sulfuric acid or have the potential to form it, in an amount that can have significant impacts on other soil characteristics (Dent and Pons, 1995). Many ASS originated when the sea level rose and inundated the land with sulfate from seawater mixed with iron oxides in the sediments, allowing microorganisms to form iron sulfides (pyrite, FeS_2) under anaerobic conditions according to Eq. (1) (Bloomfield and Coulter, 1973; Fitzpatrick et al., 2009c).

$$Fe_2O_3 + 4SO^{2-} + 8CH_2O + ½\ O_2 \rightarrow 2FeS_2 + 8CHO_3^{-} + 4H_2O \quad (1)$$

In an undisturbed state below the water table, sulfide minerals pose a limited threat unless the water table is lowered and the sulfides are exposed, whereupon the sulfide minerals react with oxygen to produce large amounts of sulfuric acid (Eq. (2)), which in turn acidifies the surrounding soils (Nordmyr et al., 2008).

$$FeS_2 + 3½\ O_2 + 3\ ½H_2O \rightarrow Fe(OH)_3 + 4H^{+} + SO_4^{2-}. \quad (2)$$

The acidification process then solubilizes soil matrices in which potentially toxic metals are held (Nordmyr et al., 2006). The lower pH also releases adsorbed toxic metals and deoxygenation can exert a range of negative impacts on local environments (Michael, 2013). These impacts can be severe in soils where the pH has dropped below a critical value of less than 4 (Reid and Butcher, 2011), or where the acidity produced has exceeded the soil's capacity to neutralize it (Fitzpatrick et al., 2010), and where solubilized toxic metals are present in elevated concentrations (Baldwin and Fraser, 2009).

In association with pH, redox status of soil influences the solubility of toxic metals, their stability and availability for various biochemical reactions under both aerobic and anaerobic conditions. Adverse redox potential (Eh) and pH can result in impoverished agricultural soils (Delaune and Reddy, 2005), poor crop productivities and unbalanced microbial ecological environments (Moore et al., 1990). The principle management strategies established for sulfuric soils are to neutralize

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the actual acidity and minimize its byproduct discharge by application of an alkaline material such as mineral lime (Ward et al., 2004) while for that of a sulfidic soil material is to minimize exposure and curtail oxidation (Thomas, 2010). In some localities such as in the tropics, however, availability of mineral lime is an issue (Hue, 1992) and in most situations considered impractical because of excessive costs and the need for large quantities (Powell and Martens, 2005). Shamshuddin et al. (2004) compared the effect of lime with addition of various organic amendments on the productivity of cocoa in acidic soils and found that OM was as effective as lime applications, either by increasing soil pH or by reducing the availability of free aluminum ions, which are highly toxic to plant roots. In contrast, Reid and Butcher (2011) found that plant growth into ASS with sulfidic material was more likely to increase acidity.

Organic matter is often readily available in poorer economies and may be a viable alternative to liming, especially if agricultural lime is not easily available. Moreover, in Ramsar wetlands even if lime is readily available, lime application is often not recommended because of the potential harm it may cause to such protected environments (e.g. benthic invertebrates). In this study we have investigated the impact on soil chemical properties (pH, Eh and sulfate content) after adding OM to ASS from two perspectives:

1. Could OM reduce the acidity of "sulfuric soils" [manufactured by the oxidation of sulfidic material (pH > 4) samples to form sulfuric horizon (Soil Survey Staff, 2014) material]?
2. Could OM prevent the acidification of "neutralized sulfuric soils" [formed by adding alkaline sandy loam to peaty sulfuric horizon (pH < 4) material samples to neutralize the sample]?

Since moisture content has a major impact on soil redox conditions, the effects of OM were examined under both inundated (low soil oxygen) and aerobic conditions.

2. Materials and methods

2.1. Soils

The ASS profiles used in this research were collected from the following two sites (Fig. 1):

- Gillman in Barker Inlet (34°82′92.3″S, 138°54′05.0″E) and
- Finniss River at Wally's Landing (35°24′28.28″S; 138°49′54.37″E).

The first study used sulfidic material, which was collected from a "sulfuric subaqueous clayey soil" (Fitzpatrick, 2013) in the Finniss River at a depth of approximately 1 m below the water surface. Detailed information on the soil classification of this soil profile is given in Table 1, together with a list of comprehensive references, which contain further information on the soil morphology and geochemistry prior to rewetting (i.e. sites AA26.3 and FIN26) in Fitzpatrick et al. (2009a) and after reflooding can be found in Fitzpatrick et al. (2011). When the sample of sulfidic material was freshly collected in 2012, the pH measured in water$_{1:5}$ (henceforth referred to as pH_w) was 6.7. After peroxide treatment (henceforth referred to as pH_{ox}) the pH decreased to 1.4 with a field capacity of 49%.

The sampled sulfidic material was spread thinly on plastic sheets and kept moist in order to oxidize sulfides to produce sulfuric acid (Eq. (2)) so as to manufacture "sulfuric horizon material" or a "sulfuric soil" ($pH_W = 3.8$, $pH_{Ox} = 2.7$). The manufactured "sulfuric soil" was added to: (i) Falcon tubes to conduct the soil organic matter experiments (data presented in Figs. 2–5) and (ii) small pots (140 mm high and capacity 1.1 L) for the soil neutralization experiment (data presented in Figs. 6–8).

The soil profile in the Finniss River when dry during the Millennium Drought across SE Australia between 2006 and early 2010 (Heberger, 2012), was classified as a sulfuric clayey soil (Fitzpatrick et al., 2009c) or Hydraquentic Sulfaquept (Soil Survey Staff, 2014) prior to the rewetting event in 2010 (Table 1). However, following rewetting in 2010 (post 2010) this subaqueous soil continued to maintain a sulfuric horizon with an underlying sulfidic material for several years (Table 1). Currently no subgroup exists in Soil Taxonomy (Soil Survey Staff, 2014) that adequately describes these Finniss River soils following their rewetting. They are best described as subaqueous soils with sulfuric horizons or "Sulfuric subaqueous clayey soils" in accordance with the Australian ASS classification key (Fitzpatrick et al., 2008; Fitzpatrick, 2013). This presents little issue if these soils exist in this transient state for a short period of time (e.g. during transformation from Hydraquentic Sulfaquept to Sulfic Hydraquent). However, in several instances these soils have persisted for a number of years. In these

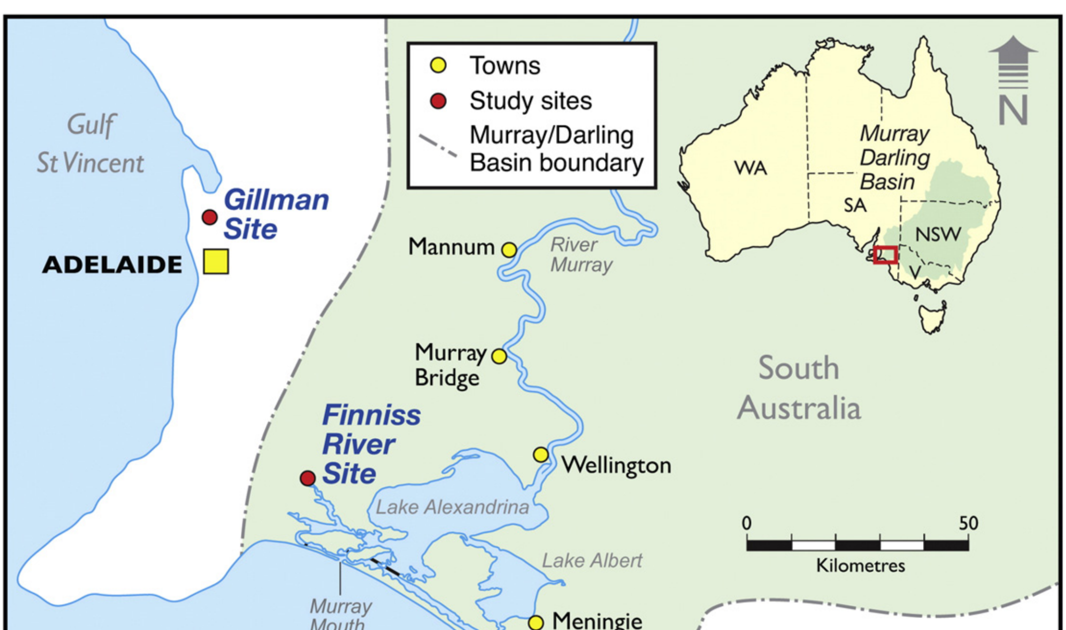

Fig. 1. Locality of samples from the Gillman site in Barker Inlet and Finniss River site at Wally's Landing.