Geoderma 269 (2016) 153–159

Contents lists available at ScienceDirect

Geoderma

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

Addition of clayey soils with high net negative acidity to sulfuric sandy soil can minimise pH changes during wet and dry periods

N. Jayalath [a,b,c], L.M. Mosley [c], R.W. Fitzpatrick [c], P. Marschner [b,c,*]

[a] CSIRO Land and Water Flagship, Private Bag No. 2, Glen Osmond, SA, 5064, Australia
[b] School of Agriculture, Food & Wine, The University of Adelaide, Adelaide, SA 5005, Australia
[c] Acid Sulfate Soils Centre, School of Biological Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

ARTICLE INFO

Article history:
Received 12 August 2015
Received in revised form 22 January 2016
Accepted 26 January 2016
Available online 12 February 2016

Keywords:
Acid sulfate soils
Clay addition
Management
Net acidity
Organic matter
Wetlands
Wet and dry periods

ABSTRACT

Wetland environments may have hypersulfidic soils, that contain pyrite, which can generate extreme acidity and form sulfuric soils (pH < 4), when exposed to oxygen which poses a threat to the environment. Management of sulfuric soils by addition of neutralising agents such as lime or inundation with seawater may be uneconomical or ineffective in inland environments. In this study, we tested the effects of the addition of three clayey soils with different net negative acidities to a sulfuric sandy soil as an amelioration option. The aim of this experiment was to investigate the effect of addition of hyposulfidic clay soils to a sulfuric sandy soil on pH changes in reduced and oxidised conditions. A sulfuric sandy soil (pH 4.1) was mixed with three hyposulfidic clay soils (with clay contents ranging between 38 and 72%) to give clay soil proportions of 0, 25, 50, 75 and 100 (%dry soil). According to their net negative acidity, the three clay soils are referred to as: NA-334, NA-54 and NA-8 (values in mol H^+ tonne^{-1}). All soils were collected in a Ramsar wetland in South Australia. The soils were amended with wheat straw at 10 g of C kg^{-1} and then incubated for 14 weeks under reducing conditions (wet period) followed by 11 weeks incubation under oxidising conditions (dry period) during which they were maintained at 100% of maximum water holding capacity. The pH of the sulfuric soil alone increased during the wet period by about two pH units (to pH 6) and decreased by more than two pH units (to pH < 4) during the dry period. In the clay soils alone and treatments with sulfuric soil, the pH during the wet period decreased by 0.5 to 1 unit with NA-334 and NA-54 and increased by one unit with NA-8. The pH was > 6 in all clay treatments at the end of the wet period. During the dry period, the pH remained above pH 7 with NA-334 and decreased by about one unit (to pH 5.5) with NA-8. In treatments with NA-54, the pH decrease during the dry period depended on the proportion of clay soil, ranging from 0.5 pH unit with 75% clay soil to two pH units with 25% clay soil. The capacity of the clay soil treatments to maintain stable pH during wet and dry periods depended mainly on the negative net acidity of the added clay soils, but was not related to their concentration of reduced inorganic sulfur or clay content. It can be concluded that addition of clay soils with high negative net acidity could be used to ameliorate acidity in acid sulfate soils with sulfuric materials.

1. Introduction

Wetlands contribute a wide range of benefits and services to the environment such as providing habitats to flora and fauna, nutrient cycling and retention, water recharge and discharge, as well as flood and erosion control (Burton and Tiner, 2009; Jha, 2004; Reddy and Gale, 1994). Wetland soils often contain reduced inorganic sulfur [mainly Fe disulfide (FeS_2) – pyrite and metastable FeS], referred to as acid sulfate soils (Dent and Pons, 1995; Fitzpatrick et al., 2008; Hall et al., 2006). Acid sulfate soils (ASS) are soils or sediments that contain sulfidic or hypersulfidic/hyposulfidic materials (IUSS Working Group WRB, 2014; Sullivan et al., 2010) or are affected by transformations of sulfide minerals (e.g. pyritic, FeS_2) (Soil Survey Staff, 2014; Isbell and National Committee on Soils and Terrain, 2016). Sulfate reduction to form sulfide is catalysed by sulfate reducing bacteria, which require decomposable organic matter as energy source. Sulfide then reacts with dissolved Fe to form pyrite (Berner et al., 1985). These pyrite-rich sediments or soils are stable in reduced conditions, but can become extremely acidic/sulfuric (<pH 4) when exposed to oxygen due to pyrite oxidation (van Breemen, 1973) when the soils have limited acid neutralising capacity (Fitzpatrick et al., 2009; Fitzpatrick, 2013). The extent of acidification can be estimated according to Eq. (1):

$$NA = (SA - TAA) - ANC \quad (1)$$

where NA is net acidity, SA is sulfidic acidity, TAA is total actual acidity and ANC is acid neutralising capacity (Ahern et al., 2004). The low pH releases

* Corresponding author at: School of Agriculture, Food & Wine, The University of Adelaide, Adelaide, SA 5005, Australia.
E-mail address: petra.marschner@adelaide.edu.au (P. Marschner).

http://dx.doi.org/10.1016/j.geoderma.2016.01.040

metals (Mosley et al., 2014a,b), which together with protons, reduce water and soil quality, crop production and damage infrastructure (Berner et al., 1985; Dent, 1986; Dent and Pons, 1995; van Breemen, 1973).

It has been shown that neutralisation of acidic water such as mine drainage is possible by passage through limestone channels or permeable reactive barriers (Batty and Younger, 2004; Skousen et al., 2000; Younger et al., 2003). However, such treatments are not possible for acidic soil where in-situ remediation methods are required.

Typical amelioration strategies for sulfuric soils (pH < 4) include addition of chemical ameliorants such as calcium carbonate ($CaCO_3$) or slaked/hydrated lime [$Ca(OH)_2$] or, for coastal areas, tidal inundation (Dear et al., 2002). However, chemical treatments are costly and may not be allowed in wetlands managed under strict environmental regulations. Tidal inundation is not possible for most inland wetlands (Johnston et al., 2009). Therefore, alternative strategies to ameliorate sulfuric soils have to be developed. In previous studies we showed that addition of plant residues to acid sulfate soils can stimulate sulfate reduction and proton consumption under reduced conditions (Jayalath et al., 2015a,b; Yuan et al., 2015a,b) and minimise pH decrease during oxidation of acid sulfate soils (Jayalath et al., 2015a,b). However, organic matter may need to be added repeatedly for long-term amelioration. Another amelioration strategy may be addition of clayey soils to sulfuric soils because aluminosilicate or phyllosilicate minerals have the potential to buffer pH (Ahern et al., 2004). However, Fraser et al. (2012) found in a field study that addition of clayey soil to a lighter textured top soil did not prevent acidification, possibly because the disturbance resulted in oxidation of clayey materials which may have had low pH buffer capacity and positive net acidity. On the other hand, wetland soils may also include sulfide-rich clayey layers with high pH buffer capacity and negative net acidity. More studies are required to test the effectiveness of adding clayey soils to sulfuric soils in relation to their properties such as clay content and net acidity.

The aims of this study were to (i) determine the effect of mixing clay-rich soils varying in pH buffer capacity and negative net acidity with sulfuric sandy soil on pH changes during a wet and a following dry period, and (ii) investigate how the pH effect is related to clay soil properties such as clay content, reduced inorganic sulfur concentration, pH buffer capacity and net acidity. The following hypotheses were tested (i) clay soils with high pH buffer capacity and negative net acidity will minimise pH changes during the wet and dry period, and (ii) acidification during the dry period will be greater with higher initial RIS concentrations in the soil mixtures.

2. Materials and methods

2.1. Soils

The soils were collected in the Banrock Station Wetland, South Australia (34°11′50′S, 140°20′20′E), which is a wetland of international importance listed in the Ramsar Convention (Ramsar Convention, 1998). It was inundated in 1925 after construction of Lock 3 on the River Murray and remained flooded until severe drought in Southern Australia from 2001 to 2009 during which large parts of the wetland dried and water tables lowered. As a consequence, hyposulfidic soils (pH > 4) in the wetland were exposed to atmospheric oxygen and transformed to sulfuric soils (pH < 4) (Fitzpatrick et al., 2015). To manage the wetland sustainably, the site managers implemented annual wet and dry cycles with each dry and wet period lasting approximately six months.

Four representative acid sulfate soil materials were collected from different horizons in three profiles during a dry period in 2013 (Fitzpatrick et al., 2015) (Tables 1, S1). The sandy soil was collected from the top soil of a profile at the edge of the wetland (RBAc-01) adjacent to *Phragmites* stands. This soil is classified as a Sulfuric Soil in the Australian ASS classification key (Fitzpatrick, 2013), Typic Sulfaquept in Soil Taxonomy (Soil Survey Staff, 2014), and Hypothionic Gleysol (Drainic, Hypersulfidic) in the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). The three clay soils were collected from profiles RBAc-03 and RBAc-06 which are located closer to the lower lying lake bed of the wetland complex. They classify as Hyposulfidic soils in accordance with the Australian ASS classification key (Fitzpatrick, 2013) and Oxygleyic Gleysol (Drainic, Hyposulfidic) in World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). By definition these hyposulfidic soils have a high pH buffer and acid neutralising capacity because when incubated for eight weeks or longer, the pH does not decrease below pH 4. Currently no subgroup exists in Soil Taxonomy (Soil Survey Staff, 2014) that adequately describes these hyposulfidic clayey soils as acid sulfate soils because they do not qualify as having “sulfidic material” as defined in Soil Taxonomy and the term “hyposulfidic material” does not exist in Soil Taxonomy. Consequently, these hyposulfidic clayey soils are classified as Typic Hydraquents in Soil Taxonomy. In this study, the three clay soils are referred to according to their net negative acidity as NA-334, NA-54 and NA-8 (Table 1). After collection, the soils were air-dried, ground and sieved to <2 mm.

2.2. Experimental design

The experiment consisted of a 14-week wet (reduced) and a 10-week dry (oxidised) period. The sulfuric sandy soil and clay soils were used alone or mixed. The mixtures were prepared by mixing the sulfuric sandy soils with each of the clay soils at different proportions: 25, 50 or 75% dry soil. After thorough mixing, 30 g of air-dry soil was placed in 70 ml plastic vials. To provide an organic nutrient source for sulfate reducers and other heterotrophic microorganisms, mature wheat straw (total organic C 423 g kg^{-1}, C/N 108, ANC 0.3% $CaCO_3$ equivalent, finely ground and sieved to <2 mm) was added at 10 g of C kg^{-1}. This C addition rate was selected based on earlier studies in our group in which sulfuric soils were incubated under reducing conditions (Yuan et al., 2015a,b). In those studies, sulfate reduction

Table 1
Collection depth, pH, total organic C, total N, maximum water holding capacity (WHC), particle size distribution, acid neutralising capacity (ANC), net acidity, pH buffer capacity (pHBC), total Fe and reduced inorganic sulfur (RIS) of sulfuric and three hyposulfidic clay soils.

Soil profile[1]	Australian ASS classification[1]	Depth	pH	Max. WHC	Sand	Silt	Clay	ANC	Net acidity[2]	pHBC	Total organic C	Total N	Total Fe	RIS	Soil name[3]
		cm	1:1	g g^{-1}	%			% $CaCO_3$	mol H^+ $tonne^{-1}$	m mole kg^{-1} pH^{-1}	g kg^{-1}				
RBAc 1	Sulfuric	5–20	4.1	0.08	85	5	10	0	37	13	6	0.4	96	0.2	Sulfuric
RBAc 3	Hyposulfidic	0.5–17	7.4	0.23	20	29	51	3.7	−334	172	18	2.0	766	3.0	NA-334
RBAc 3	Hyposulfidic	40–60	7.2	0.28	16	12	72	0.6	−54	147	15	0.7	944	0.2	NA-54
RBAc 6	Hyposulfidic	0–1.5	5.9	0.29	58	4	38	0.2	−8	132	22	2.0	557	0.1	NA-8

[1] See Fitzpatrick (2013) and Fitzpatrick et al. (2015). For further details about classification, see Table S1.
[2] Net acidity (mol H^+ $tonne^{-1}$) = (sulfidic acidity + total actual acidity) − acid neutralising capacity.
[3] Soil name used in this study.