Geoderma 308 (2017) 312–320

Contents lists available at ScienceDirect

Geoderma

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

Prolonged recovery of acid sulfate soils with sulfuric materials following severe drought: causes and implications

L.M. Mosley [a,b,*], T.K. Biswas [c,d], F.J. Cook [e], P. Marschner [f], D. Palmer [g], P. Shand [a,b,h], C. Yuan [a,f], R.W. Fitzpatrick [a,b]

[a] *Acid Sulfate Soils Centre, The University of Adelaide, South Australia, Australia*
[b] *CSIRO Land and Water Flagship, Glen Osmond, South Australia, Australia*
[c] *Murray-Darling Basin Authority, Canberra, Australia*
[d] *College of Medicine, Biology and Environment, Australian National University, Canberra, Australia*
[e] *Freeman Cook Pty Ltd, Glass House Mountains, Queensland, Australia*
[f] *The School of Agriculture, Food and Wine, The University of Adelaide, South Australia, Australia*
[g] *Environment Protection Authority South Australia, Adelaide, South Australia, Australia*
[h] *School of the Environment, Flinders University, Adelaide, South Australia, Australia*

ARTICLE INFO

Article history:
Received 16 October 2016
Received in revised form 24 February 2017
Accepted 19 March 2017
Available online 31 March 2017

Keywords:
Acid sulfate soils
Pyrite
Acid drainage
Drought
Climate change
River Murray

ABSTRACT

Pyrite in acid sulfate soils can get oxidised during drought resulting in severe soil and water acidification ($pH < 4$). The frequency and severity of drought and flooding is increasing in many regions of the world due to climate change but there has been limited research on the ability of acid sulfate soils to recover from these events. We studied the recovery of heavy clay soils in the Lower Murray River (South Australia) irrigated agricultural areas over a 5 year period (2011–2015). The heavy clay acid sulfate soils in this region dried, cracked and acidified due to river and groundwater levels falling by nearly 200 cm during the 2007–2010 severe "Millennium" drought followed by reflooding events between 2011 and 2015. Approximately 300 cm deep soil cores were collected from three locations along a transect in 2011, 2012, 2013, and 2015. The soil properties measured were pH, reduced inorganic sulfur (RIS, pyrite), titratable actual acidity (TAA), retained acidity, and acid neutralising capacity. Soil pH showed very little change over the post-drought period with a very acidic (pH 3.5–4.5) layer at approximately 100–225 cm depth in all three soil profiles. In this acidic layer there also were substantial amounts of TAA (up to 200 mol H^+ $tonne^{-1}$ dry weight) and retained acidity (up to 70 mol H^+ $tonne^{-1}$ dry weight) in the form of the Fe oxyhydroxy sulfate mineral jarosite. There was limited reformation of RIS. To assess why the sulfuric material in the acid sulfate soils has not recovered post-drought we conducted (i) laboratory incubation experiments with and without organic matter amendment, and (ii) modelling of the flushing of acidity from the soil due to irrigation, rainfall and drainage. Based on the field and laboratory results the causes of slow recovery appear to be: (i) lack of available organic carbon and too low a pH to enable microbial reduction reactions that generate alkalinity, ii) slow flushing of acidity due to the low hydraulic conductivity in the heavy clay layers with the main zone of below the drain depth, and (iii) slow dissolution of the sparingly soluble jarosite mineral, which is likely buffering the sub-surface soil layers at approximately pH 4. The implications are that acid sulfate soils with sulfuric materials have long recovery times following droughts and impacts are likely to increase in the future.

1. Introduction

Drainage and runoff from acid sulfate soils can have significant negative impacts on surface water quality and aquatic ecosystems (Cook et al., 2000; Dove and Sammut, 2007; Mosley et al., 2014a). The drivers of acid sulfate soil exposure to air are multiple and include artificial drainage (Kinsela and Melville, 2004), post-glacial rebound (Boman et al., 2010), drought and increased water extraction (Appleyard and Cook, 2009; Shand et al., 2010; Mosley et al., 2014a, 2014b). Increasingly severe and widespread droughts are occurring and will further increase in the next 30–90 years over many regions of the world due to either decreased precipitation and/or increased evaporation due to climate change (Dai, 2013). Acid sulfate soils will be greatly impacted by increased drought due to the rapid oxidation of sulfidic materials upon exposure to air, and transformation to sulfuric ($pH < 4$) materials.

While there have been multiple descriptions of acid sulfate soil disturbance resulting in acidification (see Dent and Pons, 1995), the recovery of soils following resubmergence (e.g. post-drought) has received

---

* Corresponding author at: The University of Adelaide, Waite Campus, PMB1, Glen Osmond SA 5064, Australia.
E-mail address: luke.mosley@adelaide.edu.au (L.M. Mosley).

http://dx.doi.org/10.1016/j.geoderma.2017.03.019
0016-7061/

much less attention. If oxidised soils are resubmerged (e.g. due to reflooding), oxygen replenishment from the atmosphere is markedly reduced and they are converted through microbial respiration to a biochemically reduced state (Ponnamperuma, 1972). The source of electrons for microbially-mediated reduction is organic matter, and these electrons are "accepted' by oxidised (redox-active) species which are reduced. The sequence of reduction reactions and microbial succession typically proceeds in the order predicted by thermodynamics: NO_3^- to N_2, Mn(IV) to Mn(II), Fe(III) to Fe(II), SO_4^{-2} to H_2S, and CO_2 to CH_4. Fe(III) and Mn(IV) form relatively stable oxide minerals (e.g. FeOOH, MnO_2) in mildly acidic to alkaline soils and these are electroactive and participate in the redox reactions (Essington, 2004). Under the very acidic (pH < 4.5) conditions commonly found in acid sulfate soils, additional Fe(III) -oxyhydroxy sulfate minerals such as jarosite and schwertmannite may form (Bigham et al., 1996; Mosley et al., 2014c).

The sequence of reduction reactions following soil resubmergence are also accompanied by consumption of protons, thus increasing the pH (e.g. for sulfate, $1/8\ SO_4^{2-} + 5/4H^+ + e^- \rightarrow 1/8\ H_2S + 1/2\ H_2O$, half reaction from Essington, 2004). How far and fast the redox sequence proceeds will depend on whether there is sufficient available organic matter for microbes to consume and reduce the concentration of electron acceptors present (Yuan et al., 2015a, 2015b). The availability of organic matter to a certain group of microorganisms likely relates to: (i) soil organic matter content and its availability to decomposers which is influenced by the chemical properties of organic matter; and (ii) stabilisation by physical protection or chemical interactions with mineral surfaces and metal ions (Lützow et al., 2006).

The limited knowledge on how acid sulfate soils recover from drought creates uncertainties and risks as to how they will respond to the increasing severity and frequency of drought in many regions of the world under global climate change. Previously we have reported the exposure of acid sulfate soils and associated water quality risks following the severe "Millennium" drought in the Murray-Darling Basin, Australia's largest river system (Mosley et al., 2014a,b,c). The 2007–2010 period of the Millennium drought was particularly extreme and the lower reaches of the River Murray in South Australia experienced the worst drought and lowest water levels in over 90 years of records (Mosley et al., 2012, see Supplementary material Fig. S1). The heavy clay vertisols in this region developed deep (1–2 m) cracks during the drought that allowed oxygen to penetrate and oxidise pyrite at depth in the sulfidic material (see Mosley et al., 2014b; Fitzpatrick et al., 2017). The hydrological drought ended in late 2010 when River Murray and groundwater levels returned to normal and exposed acid sulfate soils were submerged as discussed further below.

The aims of this study were to: (i) assess whether the sulfuric material in the acid sulfate soils in the Lower Murray floodplains has recovered following post-drought reflooding; and (ii) what conditions may be inhibiting their recovery. We assessed these aims by: (a) analysing soil chemical properties in three deep (300 cm) profiles along a transect across the floodplain over a 5 year period following the post-drought conditions of reflooding; (b) conducting laboratory incubation experiments with and without organic matter amendment; and (c) modelling of the flushing of acidity from the soil due to irrigation, rainfall and drainage. The findings help improve the understanding of acid sulfate soil hydro-geochemistry following resubmergence post-drought, and have wider implications in terms of highlighting future global environmental risks from these soils.

2. Methods

2.1. Study area description

The study site is in the lower Murray-Darling Basin and is part of a region of floodplains known locally as the Lower Murray Reclaimed Irrigation Area (LMRIA, see map in Supplementary material Fig. S2). The LMRIA comprises 27 individual floodplains with a total area of 5200 ha. Historically, the floodplain contained reed beds (*Phragmites* sp.) with regular flooding under a natural river regime (Taylor and Poole, 1931). Drainage channels were constructed to enable farming on the floodplain. Once river levels were raised (via construction of barrages near the river mouth) above the land surface the drains also intercepted rising saline regional groundwater. Drainage water is returned to the River Murray via large drainage pumps. The climate in the region is semi-arid with a mean rainfall of 349 mm and mean maximum temperature of 22.9 °C (Australian Bureau of Meteorology data, Murray Bridge site number 024521).

2.2. Soil sampling and analysis

An hydraulically operated push-tube sampler was used to collect soil cores to a depth of approximately 300 cm at three sites along a toposequence/transect at Long Flat irrigation area (35°7″28.05″ S–139°17″55.17′E) adjacent to the River Murray near Murray Bridge, South Australia. Sampling of all sites/profiles was conducted in 2011, 2012, 2013 and 2015. The general location of the 3 sites is shown in Supplementary material S2. Site A is on the floodplain adjacent to the main drainage channel and furthest away from the river, Site B is in in the middle of the floodplain, and Site C is on the floodplain adjacent to the levee bank and river (see also aerial photograph site locality in Fitzpatrick et al., 2017).

After extracting the cores, soil layers and horizons were defined, classified and soil properties determined for each layer (see Supplementary material Table S3; see also Fitzpatrick et al., 2017 for more detailed soil morphology, chemical and mineralogical information). The Sulfuric clay soils were classified as Sulfuric, Epipedal, Black Vertosols in accordance within the Australian soil classification (Isbell, and National Committee on Soils, and Terrain, 2016) and as Typic or Sulfic Sulfaquerts in Soil Taxonomy (Soil Survey Staff, 2014).

To minimize potential for sulfide oxidation during transportation and storage, wet soil core samples were stored in sealed plastic bags, refrigerated (4 °C) and an inner core section extracted for analyses. pH was measured in 1 M KCl (1:40 soil:water ratio, Ahern et al., 2004) using a calibrated pH electrode in the laboratory. Sub-samples of soil were dried (at 80 °C for 48 h) prior to crushing (<0.5 mm) and analysis for full acid-base characteristics using methods from Ahern et al. (2004) including: (1) Titratable actual acidity (TAA, representing soluble and readily exchangeable acidity) that was determined by titration to pH 6.5 with standardised NaOH; (2) Retained acidity (RA, net acid soluble acidity typically from less soluble iron hydroxysulfate compounds such as jarosite) that was measured by determination of sulfur in a 4 M HCl digest (S_{HCl}) subtracted by sulfur in a 1 M KCl extract (S_{KCl}). The S_{KCl} extraction recovers soluble and readily exchangeable sulfate, while the S_{HCl} extraction also recovers insoluble iron and aluminium oxide and oxyhydroxy sulfate compounds (e.g. jarosite, natrojarosite). The sum of the TAA and RA is termed "existing acidity", that is acidity that is already influencing the acid-base character of the soil; (3) Reduced inorganic sulfur (RIS, typically from pyrite) that was measured following the conversion of sulfides to H_2S in a hot acidic $CrCl_2$ solution with the evolved H_2S trapped in a zinc acetate solution as ZnS. The RIS is termed "potential acidity", that is acidity that could be liberated if pyrite oxidises. It can also give a measure of inorganic sulfides that reform under reducing conditions when a previously oxidised soil is resubmerged; and (4) Acid neutralising capacity (ANC, typically from carbonates) that was measured by addition of standardised HCl followed by back titration with standardised NaOH to pH 7. The ANC, if in sufficient supply, can buffer the soil to prevent acidification. To enable comparison of the different components contributing to the acid-base characteristics, equivalent concentrations were calculated in mol H^+/tonne based on the following calculations (see Ahern et al., 2004 for more details): RIS (mol H^+ $tonne^{-1}$) = RIS (%) × 623.7, assuming that oxidation of one mole of pyrite (FeS_2) provides 4 mol of H^+ acidity following hydrolysis of the soluble Fe^{3+} produced; RA (mol H^+