Effect of organic matter and sulfidic clay addition on pH and redox potential of inland acid sulfate soils

Nilmini Jayalath

A thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

2016

School of Agriculture, Food and Wine

The University of Adelaide

I. TABLE OF CONTENTS

II. ABSTRACT

Acid sulfate soils (ASS) are soils or sediments that contain sulfuric, hypersulfidic or hyposulfidic materials or are affected by transformation of sulfidic minerals (e.g., pyritic, FeS_2). ASS are widely distributed globally and typical in environments such as coastal and inland wetlands. The main biogeochemical processes influencing the pH in ASS are sulfate reduction and pyrite oxidation. Under flooded conditions (low redox potential), sulfate reducing bacteria (SRB) using easily decomposable organic matter (OM) as their energy source, produce sulfide, which reacts with iron in sediments to form pyrite or mono-sulfides, which are stable under flooded conditions. Sulfate reduction consumes protons and therefore, results in a pH increase. When sulfidic sediments dry, pyrite can oxidise and generates acidity. In soils with low pH buffer capacity (pHBC), this can result in severe acidification and metal solubilisation. Often sulfate reduction does not occur even after pro-longed flooding which may be due to lack of organic carbon (C) availability.

Management strategies aiming to ameliorate ASS include liming or inundation. However, they may be uneconomical, unsustainable or can be ineffective. Therefore, alternative strategies are required to manage ASS.

OM addition could be an effective strategy to ameliorate ASS due to its role during sulfate reduction. It may also maintain higher level of pH even during dry periods by buffering the acid generated and stimulating microbial activity and thus oxygen consumption through. Readily degradable C of OM and duration, in which OM remain available to sulfate reducing bacteria, may be important in maintaining wetland ASS. Management of wetlands often involves introduction of wet and dry periods to restore ecosystem health. OM addition could be included to improve the effectiveness of this strategy.

In this thesis, soils from Banrock station wetland were used in a series of incubation experiments. The wetland has extensive ASS and acidification was observed in many areas in a survey conducted in 2009. Since then, wetland managers have introduced wet-dry cycles to improve wetland health.

The aim of this thesis was to determine the effect of type of organic C or sulfidic clay soils added on pH and redox potential (Eh) in ASS during wet and dry periods.

The hypotheses to be tested were:

(¡) Addition of easily decomposable OM will have a greater effect on pH and redox potential than poorly decomposable OM

(¡¡) Acidification during the dry period will be smaller at high compared to low water content because high water content limits diffusion of oxygen

(¡¡¡) Mixing sulfidic clay soils into ASS will minimise pH changes during wet and dry periods, particularly clay soils with high pH buffer capacity.

In the first experiment, the effect of type of organic amendment was investigated. Three wetland ASS (sulfuric, hypersulfidic and hyposulfidic) collected from different depths were used. The soils, unamended or amended with 10 g C kg^{-1} as glucose, wheat straw, pea straw or Phragmites litter, were incubated for 18 weeks under flooded conditions ("wet period") followed by 10 weeks during which the soils were maintained at 100% of maximum water-holding capacity (WHC) ("dry period"). During the wet period, the pH decreased in the control and with glucose to pH 3-4, but increased or was maintained in residue-amended soils (pH at the end of the wet period about 7). In the dry period, the pH of the control and glucose amended soils remained low, whereas the pH in residue amended soils decreased. However, at end of the dry period, the pH was higher in residue amended soils than in the control or glucose amended soils, particularly with pea straw (carbon: nitrogen 50, C/N 50). It can be concluded that amendment of ASS with plant residues (particularly those with low to moderate C/N ratio) can stimulate pH increase during flooding and reduce acidification under oxidizing conditions.

The second experiment was carried out to assess the effect of OM addition on pH in a wet-dry cycle followed by a second wet period. A further aim was to investigate the influence of water content during the dry period on acidification. Three ASS (sulfuric, hypersulfidic and hyposulfidic) were collected from one profile and unamended or amended with 10 g C kg^{-1} as finely ground wheat straw. The soils were

exposed to a submerged (wet) period, a dry period, followed by another wet period. In the first wet period (10 weeks), the pH increased only in the amended soils, which was accompanied by a strong decrease in Eh. To investigate the effect of water content during the dry period on pH, the soils were rapidly dried to 40, 60, 80 or 100% of WHC at the start of the dry period. This water content was maintained during the dry period. The pH decrease during the 10-week dry period was greater in amended than in unamended soils and greater at 60, 80 or 100% than at 40% of WHC. At the end of the dry period, the pH was higher in amended than in unamended soils and higher at 40% of WHC than at the higher water contents. In the second wet period (16 weeks), the pH increased only in the amended soils. The pH increase was accompanied by a decrease in Eh in the amended soils. The water content in the previous dry period did not influence pH in the second wet period in the unamended soils, but in the amended soils, the pH was higher in soils previously maintained at 40% of WHC than that maintained at higher water contents. At the end of the second wet period, the pH was higher in amended than in unamended soils. This study shows the ameliorative effect of OM addition in ASS. OM addition can improve energy supply for sulfate reducers which results in an increase in pH during the wet period and lead to a higher pH in the oxidation period. The smaller pH increase and Eh decrease in amended soils in the second compared to the first wet period suggests that OM decomposition was lower in the second wet period likely because rapidly decomposable compounds had been utilised in the previous wet and dry periods and only recalcitrant OM remained. Therefore OM may have to be added repeatedly for sustained amelioration of ASS.

The aim of the third experiment was to investigate the effect of addition of hyposulfidic clay soils to a sufuric 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 moles H^+ tonne$^-$). 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 WHC. 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 ASS.

The fourth experiment was conducted to determine the effect of OM addition over two successive wet-dry cycles in four ASS. Four soils differing in clay content (10, 15, 23, 38% referred to as C10, C15, C23 and C38) were unamended or amended with 10 g C kg^{-1} finely ground wheat straw and incubated over 24 weeks with each wet and each dry period lasting 6 weeks. Soil pH increased in both wet periods, particularly in amended soils with low clay content (C10 and C15). The Eh decreased more strongly in amended soils than in unamended soils and became negative from week 2 onwards whereas the Eh stayed positive in unamended soils except C38. In the dry periods, the pH decreased more strongly in amended soils than in unamended soils, particularly in C10 and C15. Changes in pH during wet and dry periods were greater in soils with low clay content (C10, C15) than those with high clay content (C23, C38). The effect of wheat straw addition on pH at the end of wet and dry periods did not differ between the two wet-dry periods, with a higher pH in amended than unamended soils. This study showed that wheat straw addition maintains its ameliorative effect on soil pH for at least two wet-dry cycles, but the pH effect depends on clay content, being greater in soils with low clay content. The effectiveness of this method would have to be tested under field conditions, particularly where wet and dry periods continue for longer periods.

III. DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint award of this degree.

I give consent to this copy of my thesis when deposited in University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained this thesis resides with the copyright holders(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Nilmini Jayalath

25 May 2016

IV. ACKNOWLEDGEMENTS

I would like to thank my principle supervisor, Professor Petra Marschner in the School of Agriculture, Food and Wine at the University of Adelaide, for her sincere support provided me during my PhD study. Her prompt feedback, in terms of reviewing my manuscripts even on weekends and holidays and providing answers to my questions, is valuable and admirable. My enthusiasm to transfer from the Master's degree into a PhD was enhanced by her motivation, direction and guidance. I was further motivated to continue my PhD by her great flexibility, reliability, patience as a supervisor. Beyond her excellent supervisory qualities, I thank Professor Petra Marschner for being as an effective mentor to me who provided me intelligent advice, which were very useful to my professional life. Further, the immense moral support provided me by Petra Marschner during my candidature, is unforgettable and highly acknowledged.

Next, I would like to acknowledge Professor Rob Fitzpatrick, one of my co supervisor, a Professorial Research Fellow at CSIRO, Land and Water, Waite campus; Director, Acid Sulfate Soil Centre (ASSC) and Environmental Sciences at the University of Adelaide, who used to be once my line manager at CSIRO. Professor Rob Fitzpatrick's immense knowledge on acid sulfate soils was the basis of my project and a great help in interpretation of the results. I would also like to thank Rob for providing funds from the ASSC to conduct my experiments.

Dr. Luke Mosley, my other co-supervisor, a Senior Research Fellow in the School of Biological Sciences at the University of Adelaide, is also highly acknowledged for his insightful comments based on his knowledge of soil chemistry throughout my candidature which were also important for interpretation of the results.

Dr. Christophe Tourenq, Wetland Manager of Banrock Station Wetland is thanked for permitting the sampling of the soils and for being my external advisor during my candidature.

I thank Dr. Paul Shand, Contaminant Chemistry and Eco-toxicology group at CSIRO, Land and Water, who had once been my work place line manager and permitted me to engage in my PhD after finishing

my work commitments. It would not be possible to finish the study within a short time period without the time that I granted during my work time.

Further, Dr. Jonathan Sanderman, a Research Scientist who worked for the Soil Carbon and Nutrients group at CSIRO, Land and Water, is also thanked for permitting me an hour a day to work towards my PhD in 2013, when I was working for him for ten months.

I thank my contemporary PhD friends, Ms. Shermeen Tahir, Mr. Chaolei Yuan and Mr. Tan Thanh Dang in Petra Marschner’s laboratory for sharing their experimental knowledge and skills with me during my PhD study.

My CSIRO friend, Ms. Sonia Grocke, is also thanked for providing me operational instructions of CSIRO anaerobic chamber and Mr. Colin Rivers and Ms. Bogumila Tomczak at the University of Adelaide are thanked for their support through analyzing my soil extracts by ICP.

I convey my gratitude to my husband, Lionel Rathnayake, and my son, Leron Rathnayake, for their great patience during my absence from home when I worked afterhours during the week, entire weekends as well as holidays during the candidature. Leron is especially thanked for motivating me to peruse this PhD.

Nilmini Jayalath

V. LIST OF ABBREVIATIONS

Aluminium (Al)

Acid Neutralising Capacity (ANC)

Analysis of Variance (ANOVA)

Arsenic (As)

Acid Sulfate Soils (ASS)

Acid Volatile Sulfur (AVS)

Carbon (C)

Calcium (Ca)

Chromium (Cr)

Carbon: Nitrogen ratio (C/N ratio)

Cobalt (Co)

Copper (Cu)

Redox Potential (Eh)

Inductively Coupled Plasma (ICP)

Iron (Fe)

Monosulfidic black ooze (MBO)

Manganese (Mn)

Murray Darling Basin (MDB)

Murray Darling Basin Authority (MDBA)

Nickel (Ni)

Nitrogen (N)

N concentration (Nitrogen concentration)

N demand (Nitrogen demand)

N Transformations (Nitrogen transformations)

Millivolts (mV)

Organic Carbon (Organic C)

Organic Matter (OM)

pH measured in a 1:1 soil to water ratio (pH 1:1)

Phosphorous (P)

Revolutions per minute (rpm)

Reduced Inorganic Sulfur (RIS)

Chromium Reducible Sulfur (Scr)

4M HCl extractable sulfur (S_{HCl})

1M KCl extractable sulfur (S_{KCl})

Soil Organic Matter (SOM)

Sulfate Reducing Bacteria (SRB)

Total C (Total carbon)

Total N (Total nitrogen)

Zn (Zinc)

VI. LIST OF FIGURES

CHAPTER 1. Introduction and literature review

Introduction and literature review

Wetlands are important ecosystems because they provide a wide range of functions and services to the environment (Burton and Tiner, 2009; Jha, 2004; Reddy and Gale, 1994). However, they are also vulnerable to loss and degradation by anthropogenic and natural factors (Cronk and Fennessy, 2001; Crosbie et al., 2009). Wetland soils may be sulfidic, that is, contain pyrite and other sulfides formed in flooded conditions. These soils are termed acid sulfate soils (ASS), which are soils or sediments that contain sulfidic or hypersulfidic/ hyposulfidic materials (IUUS 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). Wetland soils undergo wet-dry cycles, which are important for wetland health and regeneration. But drying can also have negative impacts because when sulfidic soils are exposed to oxygen (O_2), pyrite oxidation results in formation of sulfuric acid (H_2SO_4), which, when insufficient acid neutralising capacity (ANC) is present, can lead to very low pH (<4) and metal release (Berner, 1984; Dent and Pons, 1995). Acidity and metal release can cause wetland degradation and also have a negative impact on the surrounding environment.

Management options to ameliorate ASS such as addition of lime, tidal or fresh water inundation may be expensive or ineffective. Addition of organic matter (OM) could be an alternative management technique because OM influences pH changes in reduced and oxidised ASS soils (Dear, 2002; Dent, 1986; Fitzpatrick et al., 2009; Yuan et al., 2015a; Yuan et al., 2015b). OM increases the pH in submerged soils by stimulating sulfate reduction (Yuan et al., 2015a) and minimises acidification in oxidised soils (Yuan et al., 2015b). However, more information is required to maximise the beneficial effects of OM addition to ASS, e.g., type of organic amendment and duration of the OM effect. Incorporation of hyposulfidic clayey soils in sulfuric soils may be another option to minimise pH changes in sulfuric soils because aluminosilicates and phyllosilicates in clayey soils can help buffer the pH along with carbonates (Ahern et al., 2004). However this option has not been assessed for wetland ASS and further research is required on how pH effects are related to soil properties such as clay content, reduced inorganic sulfur (RIS) concentration, net acidity and pH buffer capacity (pHBC).

Banrock Station Wetland Complex located in Murray Darling Basin (MDB) in South Australia is a Ramsar convention wetland (Butcher et al., 2009; Ramsar, 2014) and includes large areas of ASS (Fitzpatrick et al., 2015; Thomas et al., 2011). Since 2007, the wetland managers have implemented wet and dry cycles to promote wetland health sustainably. However, it is not clear what effect wet-dry cycles have on ASS properties and how potential negative effects can be minimised.

The literature review will cover general aspects and processes in wetlands followed by those specific to inland ASS.

1.1 Wetlands

Wetlands are ecosystems that are inundated with water permanently or seasonally. Wetland water may be flowing or stagnant, and can be tidal, brackish or fresh. Wetlands extend from coastal to interior regions including marshes, rivers, creeks and lakes, swamps, mangroves, bogs, fens etc. (Burton and Tiner, 2009; Finlayson and Rea, 1999; Keddy, 2010).

Wetland biota are adapted to wetland conditions such as flooding and anaerobiosis. Wetland plants are mainly herbaceous species (grasses, sedges, rushes, reeds), which can be floating, have floating leaves with roots anchored in the sediment and be emergent and submerged (Burton and Tiner, 2009; Cronk and Fennessy, 2001; Jha, 2004). Wetland plants are characterised by morphological or anatomical adaptations for survival in specific wetlands (e.g. tidal, subtidal, or freshwater etc.) including different types of roots, pneumatophores, lenticels and intercellular airspaces; presence of aerenchyma, or metabolic strategies (tolerance to toxic compounds) (Reddy and DeLaune, 2008).

Approximately six percent of the earth's surface is made up of wetlands (Hong-Bo et al., 2012; Reddy and DeLaune, 2008), which are an important component in the global ecosystem because of their vital functions and services to the environment (Burton and Tiner, 2009; Jha, 2004; Reddy et al., 2000; Reddy and DeLaune, 2008). These functions include maintaining or improving water quality, ground water discharge and recharge, soil erosion control, nutrient cycling and retention, sediment deposition, flood mitigation, and socio economic benefits such as food/ forage production, recreation, tourism, aesthetic value, sites for research and environmental education (Burton and Tiner, 2009; Jha, 2004; Keddy, 2010; Reddy and Gale, 1994). Threats to wetlands include human factors such as urban development, agriculture, water alterations; river regulation or diversion and construction of dams, weirs and locks on rivers, pollutions; toxic metals, pesticides, eutrophication and natural factors such as prolonged drought, fire or invasion by exotic species (Cronk and Fennessy, 2001; Crosbie et al., 2009).

Many wetlands undergo wet-dry cycles, which are important for wetland sustainability. River regulations and water use can severely change water supply to wetlands. An example for human impact on river systems and wetlands is the MDB, which is the most significant and largest river basin system in Australia (MDBA, 2013). The MDB covers over 1 million km^2, which represents 14% of the area of continental Australia. The MDB comprises of a range of wetlands of high ecosystem value, including rivers, lakes, creeks and floodplains. It is estimated that approximately 0.057 million km^2 of wetlands are found across the MDB and the total number of wetlands with an area of over 1 ha is estimated at 30,000 (MDBA, 2013).

Wetland ecosystems, including those in the MDB system, are strongly affected by river regulations. Ephemeral wetlands disappeared and permanent submerged wetlands emerged as a result of increased river regulation (Gell et al., 2007). In other cases, wetlands dried because of insufficient water supply due to water use by agriculture up-stream.

Banrock station wetland is one of sixteen Ramsar wetlands in the MDB (Fig. 1.1). It is considered as a Ramsar wetland because it fulfils three Ramsar criteria, that is, it (¡) protects two nationally listed species (Southern Bell frog and Regent parrot), (¡¡) provides habitats for migratory water birds, and (¡¡¡) supports biological diversity (Butcher et al., 2009). The site is adjacent to the Lock 3 on the River Murray and covers 1,375 ha.

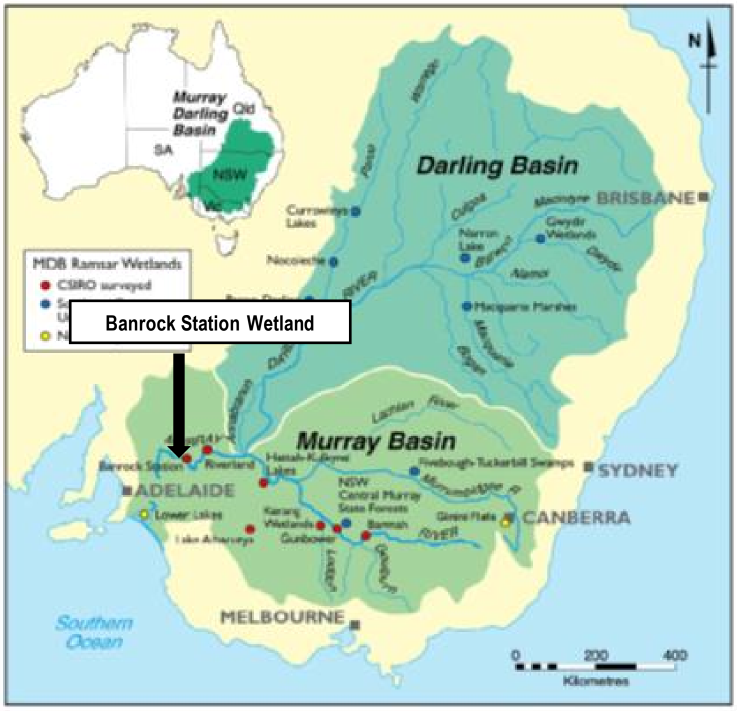


Figure 1.1 The Murray-Darling Basin and Banrock Station Wetland Complex in south-eastern South Australia (from Thomas et al. (2011)).

As with many other wetlands in the MDB, the ecology of the Banrock wetland was strongly influenced by the establishment of Lock 3 in 1925 because it resulted in permanent inundation of the site, which changed its flora and fauna. Since January 2007, managers of Banrock station wetland implemented dry-wet cycles. The dry period was longer than planned because it coincided with natural drought. It lasted for eighteen months until June in 2008 (Butcher et al., 2009).

Dry-wet cycles strongly influence biogeochemistry of ASS. Another important factor is OM. OM can buffer pH and it is also the energy source for microbes involved in various biogeochemical processes in ASS.

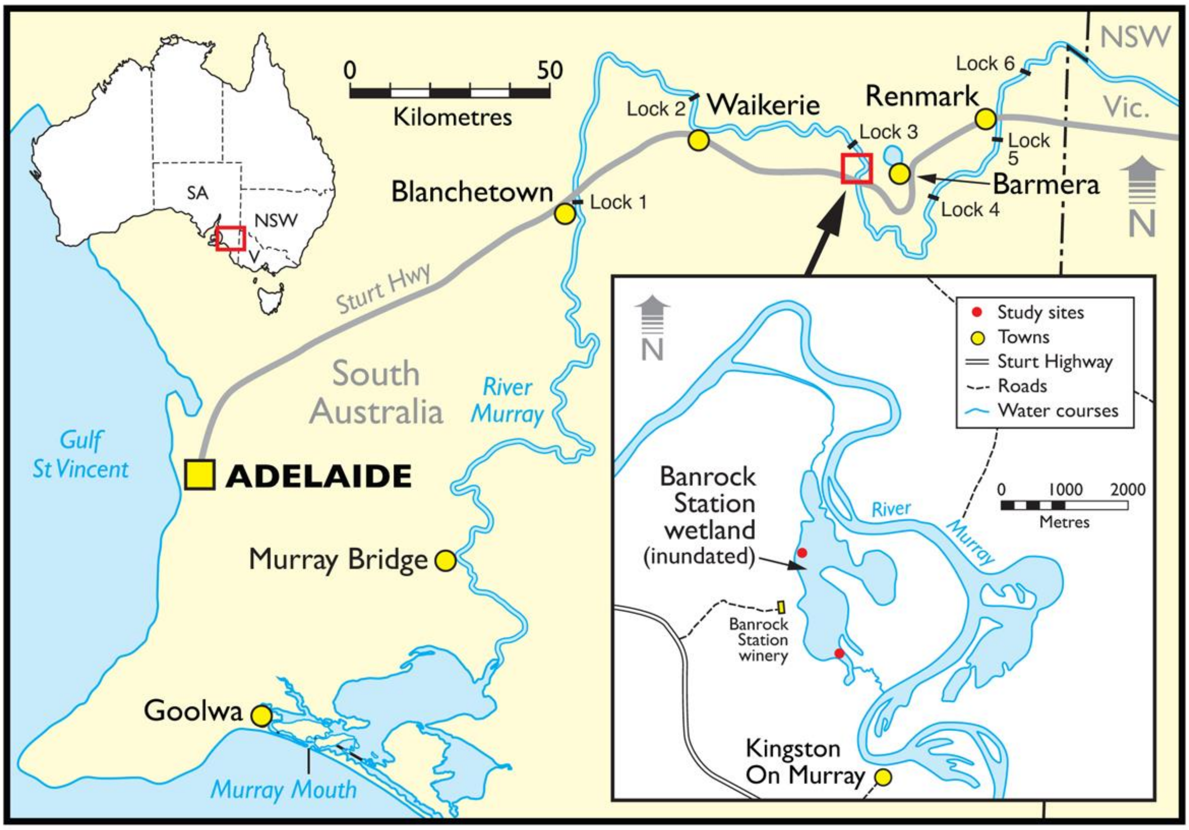


Figure 1.2 *Locality map showing the Banrock Station Wetland Complex (from Fitzpatrick et al. (2015)).*

1.2 Soil organic matter decomposition in wetlands

1.2.1 Soil organic matter

There are several definitions for soil organic matter (SOM). According to Baldock and Broos (2011) , SOM includes all soil organic constituents derived from natural sources. Four fractions of SOM can be differentiated: crop residues that are >2 mm, present in and on the soil; particulate OM (plant residues between 2 mm and 0.053 mm), humus (decomposed materials <0.053 mm bound to soil minerals) and recalcitrant organic C that is resistant to decomposition, mainly charcoal (Hoyle et al., 2011).

Formation of SOM is a fundamental process in ecosystems. Primary production of SOM occurs during photosynthesis, when plants absorb carbon dioxide (CO_2) from the atmosphere and produce complex organic materials using energy from the sun light (Cambardella, 2005).

SOM accumulation can be greater in wetlands than in upland ecosystems because the rate of SOM decomposition is slower under water-logged (anaerobic) conditions (Reddy and DeLaune, 2008).

OM entering the soil contains complex (cellulose, hemicellulose, tannins, lignin, proteins), simple (sugars, amino acids, nucleotide bases) and ether extractable (lipids, waxes, oils) components. Simple constituents are easily decomposable. But, complex materials have to be hydrolysed by extracellular enzymes such as cellulase, protease, which are released by plants, bacteria, fungi (Reddy et al., 2000; Reddy and DeLaune, 2008). Inorganic nutrients such as nitrogen (N) and phosphorous (P) are released during decomposition/mineralisation catalysed by both facultative and obligate anaerobes.

1.2.2 Role of soil organic matter

SOM contributes to a range of functions in soil. Hoyle et al. (2011) classified these functions into three broad groups, physical; chemical and biological functions (Fig. 1.2):

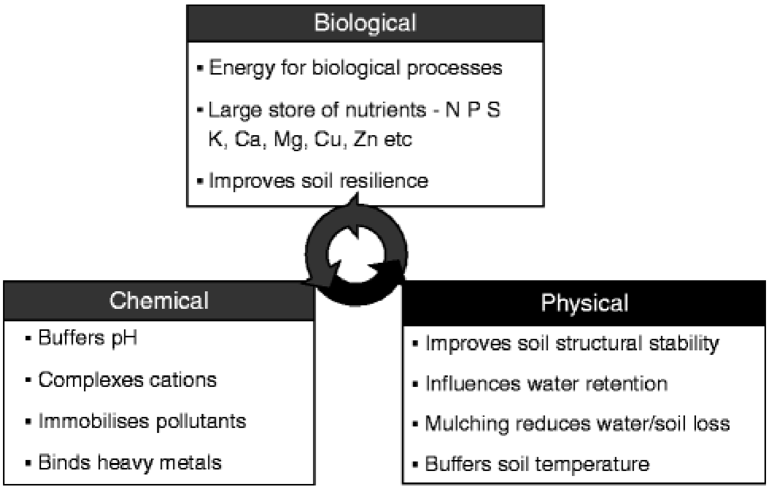


Figure 1.3 *Functions of soil organic matter (from Hoyle et al. (2011)).*

1.2.3 Functions of soil organic matter

These functions are inter-related and improve soil health and crop productivity by improving soil structure, water holding capacity (WHC), buffering temperature and pH, enhancing cation exchange capacity (CEC), immobilising pollutants, binding heavy metals. Moreover, OM provides energy and nutrients for microorganisms while improving soil resilience (Hoyle et al., 2011).

1.2.4 Factors affecting soil organic matter decomposition

Decomposition of SOM is controlled by several factors, e.g., temperature, soil moisture, concentration of O_2 and soil properties. It has been shown that decomposition is greater at higher temperatures in the tropics (25-30°C) than in cooler regions (Parr and Papendick, 1978). Microbial activity increases ten times per degree in the range 5 to 35°C (Cambardella, 2005). But growth and activity of soil microorganisms are inhibited by higher temperatures (Parr and Papendick, 1978). Soil microbes require water for growth and for diffusion of nutrients, enzymes and by-products during decomposition (Parr and Papendick, 1978). Soil properties such as soil texture and pH also play a significant role in OM decomposition (Inglett et al., 2005). Clay and silt bind organic particles to their surfaces whereas sand particles have little binding capacity; binding protects OM from decomposition. Microorganisms differ in pH optimum (Parr and Papendick, 1978). Bacteria and actinomycetes are most active at neutral pH and soil fungi tolerate acidic conditions (Parr and Papendick, 1978). Substrate composition is a major factor controlling the rate of decomposition of SOM (Limpens and Berendse, 2003).

Decomposability of OM depends on its chemical composition, particularly C forms and C/N ratio. As a rule, OM with a high proportion of simple C compounds such as sugars are more rapidly decomposable than those in which complex compounds such as cellulose dominate (Sylvia, 1999). Further, OM with high N concentration (low C/N ratio) is decomposed more rapidly than OM with low N concentration (high C/N ratio) because the former can satisfy the N demand of soil microbes (Tian et al., 1992; Vanlauwe et al., 1996). Therefore OM types may differ in suitability as energy source for sulfate reducers. Most previous studies were carried out with a single OM type.

1.2.5 Organic matter decomposition in wetland soils

There are two distinct layers in wetland soils; (I) aerobic layer where aerobic microorganisms use O_2 as main electron acceptor and (II) an anaerobic layer where other terminal electron acceptors are used (Reddy and DeLaune, 2008).

Eh is a measure of the soil O_2 status by determining electron activity (Reddy and DeLaune, 2008). In aerated soil, the Eh ranges are typically +300 to +500 mV (Reddy and DeLaune, 2008).

Aerobic decomposition, where O_2 is utilised as terminal electron acceptor by heterotrophic organisms, occurs in the aerobic surface layer, in the rhizosphere or during water table fluctuations in wetlands (Equation 1).

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$ (Equation 1)

Anaerobic conditions occur in flooded soil because O_2 diffusion in water is much slower than in air. In aerobic soil, O_2 consumed by roots and soil microbes is replenished by O_2 diffusion from the atmosphere through air-filled pores. However, in flooded soil the rate of O_2 diffusion is not sufficient to compensate O_2 consumption resulting in anaerobic conditions.

Anaerobic decomposition includes fermentation and other microbial processes including Manganese (Mn), Iron (Fe) reduction, denitrification, sulfate reduction and methane formation.

1.3 Biogeochemical processes in wetlands

Anaerobic microorganisms use oxidised compounds; NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}, CO_2 as electron acceptors in the absence of O_2 for the oxidation of OM (McLatchey and Reddy, 1998; Reddy et al., 2000). These alternate electron acceptors supply less energy and therefore anaerobic decomposition is less efficient and slower than aerobic decomposition (Cambardella, 2005; Reddy and DeLaune, 2008). Reduction of NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}, CO_2 is successive with reduction of sulfate occurring only if sufficient OM is available after complete reduction of NO_3^-, Fe^{3+}, Mn^{4+} (Reddy and DeLaune, 2008).

1.3.1 N transformations

In anaerobic conditions NO_3^- is oxidised to NH_3 and NH_4^+. During denitrification, NO_3^- is reduced to NO_2^-, $N_2O_{(gas)}$ and $N_{2\,(gas)}$, which are released to the atmosphere (Equation 2) (Hartig, 2005; Patrick and Reddy, 1976; Reddy et al., 2000):

$NO_3^- \rightarrow NO_2^- \rightarrow N_2O_{(gas)} \rightarrow N_{2\,(gas)}$ (Equation 2)

1.3.2 Iron and manganese oxidation and reduction

Mn and Fe play a significant role in the biogeochemistry of wetlands. Mn and Fe are mainly present as dissolved Mn and Fe derived from rock weathering and biotic reduction. OM complexes and insoluble oxides or hydroxides.

Mn or Fe reducing bacteria use oxidised Mn or Fe compounds such as goethite (FeOOH), hematite (Fe_2O_3), magnetite (Fe_4O_6), siderite ($FeCO_3$) or birnessite (MnO_2) as electron acceptors during OM decomposition while using monomers or organic acids (acetate, lactate, butyrate, propionate) from fermentation as their energy source. The end product is dissolved Mn or Fe (Mn^{2+}or Fe^{2+}) may react with S^{2-} to form pyrite (FeS_2) (Rickard and Morse, 2005). Mn and Fe reduction occurs at Eh of 0 to +100 and +200 to +250 mV respectively.

1.3.3 Sulfate reduction

During sulfate reduction, sulfate (SO_4^{2-}) is reduced to sulfide (S^{2-}). Requirements for sulfate reduction are anaerobic conditions, labile OM, SRB and SO_4^{2-} as an electron acceptor. Sulfate reduction occurs at low Eh (-100 mV). See section 1.4 on ASS for further details on sulfate reduction.

1.3.4 Methane formation in wetlands

At low Eh levels (< -250 mV) (Bell, 1969), methane producing bacteria (methanogens) use substrates such as formic, acetic, propionic, butyric ethanol and CO_2 as energy source and produce methane ($CH_{4(gas)}$) (Hartig, 2005; Ponnamperuma, 1972).

1.4 Acid sulfate soils

Accumulation of sulfidic sediments occurs as a result of sulfate reduction in submerged soils where SRB utilise readily decomposable OM as an energy source and SO_4^{2-} as an electron acceptor during respiration. The produced hydrogen sulfide (H_2S) reacts with dissolved Fe to form sulfide minerals, typically pyrite which is the most stable end-product (Berner, 1984; Luther III, 2005; Reddy and DeLaune, 2008; Rickard and Morse, 2005). When exposed to O_2, sulfidic material may oxidise to produce H_2SO_4 ($pH<4$).

ASS are widely distributed globally, covering 0.13 million km^2 worldwide (Shamshuddin et al., 2004). In Australia, ASS occur on 215,000 km^2 comprising 58,000 and 157,000 km^2 coastal and inland systems, respectively (Fitzpatrick et al., 2008).

1.4.1 Biogeochemical processes in acid sulfate soils

There are two significant biogeochemical processes in ASS, namely, sulfate reduction and sulfide oxidation.

1.4.1.1 Sulfate reduction

Acid volatile (e.g., H_2S, HS^-, S^{2-} and FeS) and non-acid-volatile (FeS_2, elemental sulfur and organic sulfur) products are generated during sulfate reduction. The SO_4^{2-} are the electron acceptors, which oxidise various organic C constituents such as lactate, propionate, acetate etc. These organic constituents present as the electron donors in the wetland sediments. The sulfate reduction requires essential factors: sulfate reducing bacterial population, easily digestible organic C substrates and sulfate concentration (Reddy and DeLaune, 2008).

The sulfate reduction reaction can be formulated as follows (Equation 3) (Reddy and DeLaune, 2008):

$10\ H^+ + SO_4^{2-} + 8\ e^- \rightarrow H_2S + 4\ H_2O$ (Equation 3)

Derived dissolved sulfides (H_2S, HS^-) from sulfate reduction can associate with Fe^{2+} to form iron monosulfides (FeS) (Equation 4) (Benner et al., 1984; Morse et al., 1987):

$H_2S + Fe^{2+} \rightarrow FeS + 2\ H^+$ (Equation 4)

One of the major FeS formed during early diagenesis is hydrotrolite ($FeS.\ nH_2O$), which converts into pyrite during diagenesis. The following reaction represents the pyrite formation (Equation 5) (Reddy and DeLaune, 2008):

$SO_4{}^{2-} \leftrightarrow S^{2-} + Fe^{2+} \leftrightarrow FeS.\ nH_2O \leftrightarrow FeS_2$ (Equation 5)

FeS can be further transferred to gregite (Fe_3S_4) and pyrite (FeS_2) as follows (Reddy and DeLaune, 2008). (Equation 6):

$FeS + S^o \rightarrow Fe_3S_4 + 2\ S^o \rightarrow 3\ FeS_2$ (Equation 6)

1.4.1.2 Sulfide (pyrite) oxidation

It has been researched that molecular O_2 is the principle, initial pyrite oxidant and ferric iron (Fe^{3+}) become the next available, secondary pyrite oxidant in the soil systems (Moses et al., 1987).

Oxidation of pyrite by molecular O_2 represents by the following formula (van Breemen, 1973) (Equation 7):

$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe\ (OH)_3 + 2\ SO_4^{2-} + 4\ H^+$ (Equation 7)

Oxidation of pyrite by Fe^{3+} initiates at pH <4 (Arkesteyn, 1980) and accelerates by iron oxidising bacteria, mainly *Thiobacillus ferrooxidans,* who oxidise ferrous ion (Fe^{2+}) into Fe^{3+} by a factor of 10^6 (Singer and Stumm, 1970). The following reaction represents the pyrite oxidation involving Fe^{3+} (Dent, 1986) (Equation 8):

$2\ FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$ (Equation 8)

1.4.2 Impacts of acid sulfate soils

Products of pyrite oxidation cause very low pH and release of metals/metalloids (mainly Al, As, Co, Cr, Cu, Fe, Mn, Ni, Zn) in-situ and in the surrounding water, particularly in soil with insufficient ANC (Dent and Pons, 1995; Mosley et al., 2014a; Mosley et al., 2014b). Acids and soluble metals have negative effects on aquatic biota, water quality, crop production, human health and infrastructure (Berner, 1984; Dent and Pons, 1995). Another major concern in some ASS environments is formation and oxidation of monosulfidic black ooze (MBO). MBO is black in colour and has a gel-like structure (Ward et al., 2010). It contains FeS, pyritic sulfides and acid volatile sulfur (AVS) enriched with organic material (Bush et al., 2004). FeS is an intermediate product of sulfate reduction. MBO depletes O_2 in the water (deoxygenation), which causes fish kills (Bush et al., 2004) and when oxidized, may also cause acidification of water. Another intermediate products of sulfate reduction is H_2S. H_2S produces noxious odours (Baldwin and Capon, 2011). Sulfur dioxide (SO_2) is derived during pyrite oxidation, it can irritate eyes and throat (Hicks et al., 2008).

The frequency and duration of wetting and drying cycles in wetlands influence sulfur reduction and oxidation, and hence acidification risks and recovery. Stable water levels promote a large build-up of sulfides whereas regular wetting and drying cycles may minimize build-up. However, this requires further research in particular if positive effects of wet-dry cycles can be increased by addition of OM as pH buffer and energy source for microbes or clay-rich materials as pH buffer.

1.5 Aims and objectives of thesis

The general objective of the project reported in this thesis was to investigate the impact of the addition of OM or clay-rich materials to range of inland wetland ASS materials (i.e. hypersulfidic, hyposulfidic and sulfuric materials) on pH changes in reduced and oxidised conditions.

The specific aims were to:

1. Determine the influence of addition of different forms of OM on pH and Eh under submerged/reduced and the following dry/oxidised period in three wetland ASS soils (Chapter 2)
2. Investigate the impact of addition of OM to three wetland ASS on pH changes during wet-dry-wet regime and determine the effect of water content during the dry phase on pH dynamics (Chapter 3)
3. Determine the effect of mixing sulfidic clayey soils with sulfuric sandy soil on pH changes during a submerged/reduced and a following dry/oxidised period and investigate how the pH effect is related to clay soil properties such as clay content, RIS concentration and pHBC (Chapter 4)
4. Determine the effect of OM addition over two successive wet-dry cycles in four ASS (Chapter 5)

The studies were carried out with ASS materials from the Banrock station wetland as representative of a managed wetland in the MDB which now undergoes controlled wet-dry cycles.

The hypotheses were:

(¡) Addition of easily decomposable OM will have a greater effect on pH and redox potential than poorly decomposable OM

(¡¡) Acidification during the dry period will be smaller at high compared to low water content because high water content limits diffusion of oxygen

(¡¡¡) Mixing sulfidic clay soils into ASS will minimise pH changes during wet and dry periods, particularly clay soils with high pH buffer capacity.

1.6 References

Ahern, C., Sullivan, L., McElnea, A., 2004. Laboratory methods guidelines-acid sulfate soils, Queensland Acid Sulfate Soil Technical Manual, Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

Arkesteyn, G, J, M, W., 1980. Pyrite oxidation in acid sulphate soils: The role of miroorganisms. Plant Soil 54(1), 119-134.

Baldock, J, A., Broos, K., 2011. Handbook of Soil Sciences: Properties and Processes, CRC Press, 1-30.

Baldwin, D., Capon, S., 2011. Sulfidic sediments in inland waterways, Waterlines report.

Bell, R., 1969. Studies on the decomposition of organic matter in flooded soil. Soil Biol. Biochem. 1(2), 105-116.

Benner, R., Maccubbin, A., Hodson, R, E., 1984. Anaerobic biodegradation of the lignin and polysaccharide components of lignocellulose and synthetic lignin by sediment microflora. Appl. Environ. Microb. 47(5), 998-1004.

Berner, R, A., 1984. Sedimentary pyrite formation: An update. Geochim. Cosmochim. Acta 48(4), 605-615.

Burton, T, M., Tiner, R, W., 2009. Ecology of Wetlands. in: Likens, G, E. (Ed.,), Encyclopedia of Inland Waters. Academic Press, Oxford, pp. 507-515.

Bush, R, T., Fyfe, D., Sullivan, L, A., 2004. Occurrence and abundance of monosulfidic black ooze in coastal acid sulfate soil landscapes. Aus.Soil Res. 42(6), 609-616.

Butcher, R., Hale, J., Muller, K., Kobryn, H., 2009. Ecological character description for the Banrock Station Wetland Complex. Prepared for Department for the Environment, Water, Heritage and the Arts.

Cambardella, C, A., 2005. Carbon Cycles in Soils: Formation and Decomposition. in: Daniel., H. (Ed.,), Encyclopaedia of Soils in the Environment. Elsevier, Oxford, pp. 170-175.

Cronk, J, K., Fennessy, M, S., 2001. Wetland plants: biology and ecology. CRC press.

Crosbie, R, S., McEwan, K, L., Jolly, I, D., Holland, K, L., Lamontagne, S., Moe, K, G., Simmons, C, T., 2009. Salinization risk in semi-arid floodplain wetlands subjected to engineered wetting and drying cycles. Hydrol. Process. 23(24), 3440-3452.

Dear, S, E., 2002. Soil Management Guidelines, Queensland Acid Sulfate Soil Technical Manual. Department of Natural Resources and Mines.

Dent, D., 1986. Acid sulphate soils: a baseline for research and development. ILRI, Wageningen, Netherlands.

Dent, D, L., Pons, L, J., 1995. A world perspective on acid sulphate soils. Geoderma 67(3–4), 263-276.

Finlayson, C, M., Rea, N., 1999. Reasons for the loss and degradation of Australian wetlands. Wetl. Ecol. Manag. 7(1-2), 1-11.

Fitzpatrick, R., Powell, B., Marvanek, S., 2008. Atlas of Australian acid sulfate soil. in: Fitzpatrick, R. W., Shand, P. (Eds.,), Inland acid sulfate soil systems across Australia, CRC LEME open file report 249, pp. 63-77.

Fitzpatrick, R, W., Shand, P., Merry, R., Marschner, P., Jayalath, N., Grocke, S., 2015. Acid sulfate soil assessment and monitoring of the Banrock Station Wetland (managed wetland- drying cycle). Acid sufate soils centre: ASSC_035 (V12).

Fitzpatrick, R, W., Shand, P., Merry, R, H., 2009. Acid sulfate soils. in: Jennings, J. (Ed.,) Natural History of the Riverland and Murrayland. Royal Society of South Australia, Adelaide, South Australia. pp. 65-111.

Gell, P., Tibby, J., Little, F., Baldwin, D., Hancock, G., 2007. The impact of regulation and salinisation on floodplain lakes: the lower River Murray, Australia. Hydrobiol. 591(1), 135-146.

Hartig, E, K., 2005. Wetlands naturally occurring. in: Daniel, H. (Ed.,), Encyclopedia of Soils in the Environment. Els. Oxford, pp. 328-335.

Hicks, W., Fitzpatrick, R., Shand, P., 2008. Greenhouse Emissions and Toxic Gas Emissions from Soil Organic Matter and Carbonates Associated with Acid Sulfate Soils. in: Fitzpatrick, R. W., Shand, P. (Eds.,), Inland acid sulfate soil systems across Australia, CRC LEME open file report (249), pp.125-135.

Hong-Bo, S., Bao-Shan, C., Jun-Hong, B. 2012. Wetland Ecology in China. Clean-Soil Air Water 40(10), 1011-1014.

Hoyle, F, C., Baldock, J, A., Murphy, D, V., 2011. Soil Organic Carbon-Role in Rainfed Farming Systems. Springer. Netherlands, 339-361.

Inglett, P, W., Reddy, K, R., Corstanje, R. 2005. Aaerobic soils. in: Daniel, H. (Ed.,), Encyclopedia of Soils in the Environment. Els. Oxford, pp.72-78.

IUUS working group WRB, 2014. World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil. http://www.fao.org/3/a-i3794e.pdf. FAO, Rome.

Jha, S., 2004. The Wetland Ecology. Our Nature 2(1), 47-52.

Keddy, P, A., 2010. Wetland ecology: principles and conservation. Cambridge University Press.

Limpens, J., Berendse, F., 2003. How litter quality affects mass loss and N loss from decomposing Sphagnum. Oikos 103(3), 537-547.

Luther III, G, W. 2005. Acid volatile sulfide-a comment. Mar. Chem. 97(3–4), 198-205.

McLatchey, G, P., Reddy, K, R., 1998. Regulation of Organic Matter Decomposition and Nutrient Release in a Wetland Soil. J. Environ. Qual. 27(5), 1268-1274.

MDBA, 2013. Basin environment. http://www.mdba.gov.au/about-basin/basin environment. (accessed 08.08.2013).

Morse, J, W., Millero, F, J., Cornwell, J, C., Rickard, D. 1987. The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. Earth-Sci. Rev. 24(1), 1-42.

Moses, C, O., Nordstrom, D, K., Herman, J, S., Mills, A, L., 1987. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochim. Cosmochim. Acta. 51(6), 1561-1571.

Mosley, L., Zammit, B., Jolley, A., Barnett, L., 2014a. Acidification of lake water due to drought. J Hydrol. 511, 484-493.

Mosley, L, M., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., Baker, A., Fitzpatrick, R, W., 2014 b. Acidification of floodplains due to river level decline during drought. J. Contam. Hydrol. 161, 10-23.

Parr, J, F., Papendick, R, I., 1978. Factors Affecting the Decomposition of Crop Residues by Microorganisms. Crop Residue Management Systems as a special publication. Crop residue mana. 101-129.

Patrick, W., Reddy, K., 1976. Nitrification-denitrification reactions in flooded soils and water bottoms: dependence on oxygen supply and ammonium diffusion. J. Environ. Qual. 5(4), 469-472.

Ponnamperuma, F, N., 1972. The chemistry of submerged soils. Adv. Argon. 24, 29-96.

Ramsar, 2014. Ramsar. http://www.ramsar.org/homepage (accessed 06.05.2016).

Reddy, K., D’Angelo, E., Harris, W., 2000. Biogeochemistry of Wetlands. in: Sumner, M., E. (Ed.,), Handbook of Soil Science. CRC Press, Boca Raton, pp. 89-119.

Reddy, K, R., DeLaune, R, D., 2008. Biogeochemistry of Wetlands: Science and Applications. CRC Press, 2008.

Reddy, K, R., Gale, P, M., 1994. Wetland Processes and Water Quality: A Symposium Overview. J. Environ. Qual. 23(5), 875-877.

Rickard, D., Morse, J., 2005. Acid volatile sulfide: Authors' closing comments. Mar. Chem. 97(3–4), 213-215.

Shamshuddin, J., Muhrizal, S., Fauziah, I., Van R, E., 2004. A Laboratory Study of Pyrite Oxidation in Acid Sulfate Soils. Commun. Soil Sci. Plan. 35(1-2), 117-129.

Singer, P, C., Stumm, W., 1970. Acidic mine drainage: the rate-determining step. Science 167(3921), 1121-1123.

Soil survey staff, 2014. Keys to soil taxonomy. 12th edn. USDA-Natural Resources Conservation Service, Washington, DC.

Sullivan, L, A., Fitzpatrick, R, Bush, R, T., Burton, E, D., Shand, P., Ward, N, J., 2010. The classification of acid sulfate soil materials: further modifications. Southern Cross GeoScience Technical Report, No 310. Southern Cross University, Lismore, NSW, Australia.

Sylvia, D., M., 1999. Principles and applications of soil microbiology. Prentice Hall, Upper Saddle River, N.J.

Thomas, B., Fitzpatrick, R., Shand, P., Simpson, S., Jayalath, N., 2011. Assessment of Acid Sulfate Soil materials in Ramsar wetlands of the Murray-Darling Basin: Banrock Station Wetland Complex, CSIRO, Water for a Healthy Country Flagship Client Report.

Tian, G., Kang, B., Brussaard, L., 1992. Biological effects of plant residues with contrasting chemical compositions under humid tropical conditions-decomposition and nutrient release. Soil Biol. Biochem. 24(10), 1051-1060.

van Breemen, N., 1973. Soil forming processes in acid sulphate soils. in: Dost, H. (Ed.,), Acid sulphate soils. ICRI publication. Wegeningen, Netherlands 18 (1), pp. 66-130.

Vanlauwe, B., Nwoke, O., Sanginga, N., Merckx, R., 1996. Impact of residue quality on the C and N mineralization of leaf and root residues of three agroforestry species. Plant Soil 183(2), 221-231.

Ward, N, J., Bush, R, T., Burton, E, D., Appleyard, S., Wong, S., Sullivan, L, A., Cheeseman, P, J., 2010. Monosulfidic black ooze accumulations in sediments of the Geographe Bay area, Western Australia. Mar. Pollut. Bull. 60(11), 2130-2136.

Yuan, C., Fitzpatrick, R., Mosley, L, M., Marschner, P., 2015a. Amount of organic matter required to induce sulfate reduction in sulfuric material after re-flooding is affected by soil nitrate concentration. J. Environ. Manage. 151, 437-442.

Yuan, C., Fitzpatrick, R., Mosley, L, M., Marschner, P., 2015b. Sulfate reduction in sulfuric material after re-flooding: Effectiveness of organic carbon addition and pH increase depends on soil properties. J. Hazard. Mater. 298, 138-145.

CHAPTER 2. Addition of organic matter influences pH changes in reduced and oxidised acid sulfate soils

Statement of Authorship

Title of Paper	Addition of organic matter influences pH changes in reduced and oxidised acid sulfate soils
Publication Status	☑ Published ☐ Accepted for Publication ☐ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
Publication Details	N. Jayalath, L. M. Mosley, R.W. Fitzpatrick, P. Marschner. 2016. Addition of organic matter influences pH changes in reduced and oxidised acid sulfate soils. Geoderma. 262:125-132.

Principal Author

Name of Principal Author (Candidate)	N. Jayalath		
Contribution to the Paper	Conducted experiment, data analysis and wrote the manuscript		
Overall percentage (%)	70		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	17 May 2016

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	L. M. Mosley		
Contribution to the Paper	Helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	R. W. Fitzpatrick		
Contribution to the Paper	Supervised soil sampling; helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	P. Marschner		
Contribution to the Paper	Supervised development of work, helped in data interpretation, manuscript evaluation, and acted as corresponding author		
Signature		Date	17 May 2016

Geoderma 262 (2016) 125–132

Contents lists available at ScienceDirect

Geoderma

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

Addition of organic matter influences pH changes in reduced and oxidised acid sulfate soils

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 25 March 2015
Received in revised form 8 August 2015
Accepted 10 August 2015
Available online xxxx

Keywords:
Acidification
Amelioration
Organic matter
Oxidation
sulfate reduction

ABSTRACT

Acid sulfate soils (ASS) are wide-spread in coastal and inland wetlands. When sulfidic ASS are exposed to oxygen, sulfuric acid is generated which can threaten wetlands and surrounding ecosystems. Organic matter plays an important role in ASS, as energy source for sulfate reducing bacteria during submergence and by stimulating competition for oxygen between oxidation of iron sulfide and utilisation by decomposers during dry periods. The aim of this study was to assess the effect of organic matter addition, as a potential management strategy, on pH changes in ASS in submerged and dry periods. Three ASS, namely sulfuric, hypersulfidic and hyposulfidic soils, collected from one profile in a wetland were used unamended or amended with 10 g C kg^{-1} as finely ground wheat straw. The soils were exposed to a submerged (wet) period, a dry period, followed by another wet period. In the first wet period (10 weeks), the pH increased only in the amended soils, which was accompanied by a strong decrease in redox potential. To investigate the effect of water content during the dry period on pH, the soils were rapidly dried to 40, 60, 80 or 100% of water holding capacity (WHC) at the start of the dry period. This water content was maintained during the dry period. The pH decrease during the 10 week dry period was greater in amended than in unamended soils and greater at 60, 80 or 100% than at 40% of WHC. At the end of the dry period, the pH was higher in amended than in unamended soils and greater at 40% of WHC than at the higher water contents. In the second wet period (16 weeks), the pH increased only in the amended soils. The pH increase was accompanied by a decrease in redox potential in the amended soils. The water content in the previous dry period did not influence pH in the second wet period in the unamended soils, but in the amended soils, the pH was higher in soils previously maintained at 40% of WHC than that maintained at higher water contents. At the end of the second wet period, the pH was higher in amended than in unamended soils. This study shows the ameliorative effect of organic matter addition in ASS. Organic matter addition can improve energy supply for sulfate reducers which results in an increase in pH during the wet period and lead to a higher pH in the oxidation period. The smaller pH increase and redox potential decrease in amended soils in the second compared to the first wet period suggest that OM decomposition was lower in the second wet period likely because rapidly decomposable compounds had been utilised in the previous wet and dry periods and only recalcitrant OM remained. Therefore OM may have to be added repeatedly for sustained amelioration of ASS.

1. Introduction

Acid sulfate soils (ASS) are soils or sediments that contain sulfidic (typically pyrite, FeS_2) or sulfuric ($pH < 4$) materials. Acid sulfate soils are found in coastal areas as well as inland along rivers and in wetlands in Australia (Fitzpatrick and Shand, 2008; Fitzpatrick et al., 2009) and globally (Shamshuddin et al., 2004). After soil submersion, oxygen is quickly depleted and other oxidised components are used as electron acceptors in anaerobic respiration and reduced according to thermodynamics in the sequence: NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, CO_2 (Borch et al., 2009; Ponnamperuma, 1972). Electron acceptors higher in the sequence retard the reduction of electron acceptors ranked lower (Canfield et al., 1993; Lovley and Phillips, 1987; Ponnamperuma, 1972). Organic matter plays a key role in sulfate reduction because it is required as energy source by sulfate reducing bacteria (Berner, 1984; Pons, 1973). Sulfate from ocean or fresh water can be reduced to H_2S by sulfate-reducing bacteria, most of which are heterotrophs and therefore require organic matter as an energy source (Berner, 1984):

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow 2CO_2 + HS^- + 2H_2O. \qquad (1)$$

The electrons liberated by organic carbon (CH_2O) decomposition reduce sulfate to sulfide (HS^-). The dissolved sulfide reacts with dissolved iron to form particulate iron sulfide (Stumm and Morgan, 1996). Other

---

[*] 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.2015.08.012
0016-7061/© 2015 Elsevier B.V. All rights reserved.

limiting factors for sulfate reduction include sulfate, pH (most sulfate reducers are inactive at pH < 5), presence of other competing electron acceptors, redox potential and temperature (Connell and Patrick, 1969; Ponnamperuma, 1972). H_2S produced reacts with aqueous FeS (FeS_{aq}) to form pyrite (Rickard, 2012).

When exposed to oxygen via drainage or other disturbance, sulfidic materials can oxidise to produce sulphuric materials which threaten the environment through leaching of acidity (Dent and Pons, 1995), release of toxic amounts of metals (Mosley et al., 2014a; Simpson et al., 2010) and deoxygenation (Bush et al., 2004a):

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3\downarrow + 8SO_4^{2-} + 16H^+. \tag{2}$$

Oxygen initiates pyrite oxidation, but in most situations dissolved ferric iron (Fe^{3+}) is the primary oxidant which is reduced to ferrous iron (Fe^{2+}) catalyzed by chemolithotrophic acidophilic iron-oxidising bacteria (Ahern et al., 2004; Emerson et al., 2010; Johnson and Hallberg, 2005). Organic matter could be important in oxidised ASS because it can influence pyrite oxidation through oxygen consumption by OM decomposers, complexation of ferric iron, coating of pyrite (Bronswijk et al., 1993; Bush and Sullivan, 1999; Rigby et al., 2006; Ward et al., 2004), and buffering of the acid generated (Curtin and Trolove, 2013).

Acidification of ASS is of particular concern in wetlands and floodplains, which are already under threat by drainage and reduction in water flow or levels (Bush et al., 2004b; Fitzpatrick et al., 2009; Mosley et al., 2014a, 2014b). Wetlands are important because they provide vital functions in the ecosystem. These functions include maintaining or improving water quality, ground water discharge and recharge (Burton and Tiner, 2009; Jha, 2004), erosion control (Jha, 2004), nutrient cycling and retention (Burton and Tiner, 2009; Jha, 2004; Reddy and Gale, 1994), sediment deposition (Burton and Tiner, 2009), providing habitats for aquatic organisms and wildlife (Burton and Tiner, 2009; Jha, 2004), flood control (Burton and Tiner, 2009), and socio economic benefits such as food/forage production, recreation and tourism. The Murray–Darling Basin (MDB) covers over 1 million km ^{2} which represent 14% of the area of continental Australia (MDBA, 2013). It is estimated that approximately 5.7 million ha of wetlands are found across the MBD with the total number of wetlands with an area >1 ha estimated at 30,000 (MDBA, 2013). Sulfidic material often accumulates in wetlands due to high availability of OM, dissolved sulfate and anoxic conditions associated with prolonged inundation (Hall et al., 2006). According to Baldwin and Fraser (2009) and Lamontagne et al. (2006) frequent wetting and drying cycles could reduce excessive accumulation of sulfidic materials. Baldwin and Capon (2011) and Baldwin and Fraser (2009) suggested that addition of organic matter as a mulch may be a feasible alternative to rehabilitate inland wetlands with sulfuric materials. However, there are no systematic studies on the effect of organic matter addition in ASS exposed to two wet periods separated by a dry period. Moreover, there is little information about the influence of soil water content on acidification during the dry period.

Using ASS from a wetland in the Murray–Darling Basin the aims of this study were to (i) investigate pH changes, sulfate reduction and sulfide oxidation without or with organic matter addition in ASS exposed to a wet–dry–wet regime, and (ii) determine the effect of water content during the dry phase on pH dynamics. We hypothesised that (i) organic matter addition will stimulate pH increase in the wet periods and reduce acidification in the dry period, (ii) the pH decrease during the dry period will be stronger at lower than at high water content because the latter limits oxygen diffusion into the soil.

2. Materials and methods

2.1. Soils

Three soils were collected from different depths in one profile in the Banrock Station Wetland (34°11′50′S, 140°20′20′E), in South Australia (Table 1). The Wetland Complex straddles the boundary of the Mallee Trench and Mallee Gorge geomorphic tracts and is approximately 5–10 m above sea level. At the time of sampling, the soil profile was classified as a Typic Sulfaquept (Soil Survey Staff, 2014), Sulfuric soil in the Australian ASS classification key (Fitzpatrick, 2013) and Hypothionic Gleysol (Drainic, Hypersulfidic) according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). For background information on the landscape and the soils collected from this site during a dry period in 2013 (sample ID RBAc 1.4, 1.5 and 1.7) can be found in Fitzpatrick et al. (2015) (Table 1). The materials were collected from one profile at site RBAc1at different depths (Table 1), namely sulfuric, hypersulfidic and hyposulfidic materials (Sullivan et al., 2010) which are representative of typical soils in this wetland and adjacent wetlands (Fitzpatrick et al., 2009). These three materials were air-dried and sieved to <2 mm and in this experiment the three soils are referred to as soil 1 (sulfuric soil), soil 2 (hypersulfidic soil) and soil 3 (hyposulfidic soil).

The wetland is a Ramsar-listed wetland of international importance and was inundated after construction of Lock 3 on the River Murray. However, the long-lasting drought in Southern Australia during the last decade caused drying of large parts of the wetland. To improve wetland health and sustainability, the wetland now undergoes managed wetting and drying cycles consisting of five months wet and seven months dry. To simulate wet–dry cycles in this study, the three soils were subjected to a wet, a dry, followed by another wet period.

2.2. Experimental design

The experiment consisted of three periods: wet, then dry, followed by another wet period. Thirty g of air-dried soils were placed into 70 mL plastic containers. 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 C kg^{-1} soil and mixed thoroughly into the soils. Soil without addition of wheat straw was used as a control. To initiate the first wet period, reverse osmosis water was added first to saturate the soils which were then mixed thoroughly. Then more water was added so that the soil surface was covered with a 2-

Table 1
Depth, pH, total organic C, total N, maximum water holding capacity (WHC), particle size distribution, acid neutralising capacity (ANC), pH buffer capacity (pHBC), total Fe and reduced inorganic sulphur (RIS) in sulfuric soil 1, hypersulfidic soil 2 and hyposulfidic soil 3 collected in one profile at site RBAa1.

Soil[a]	Depth	Australian ASS classification[b]	pH	Max. WHC	Sand	Silt	Clay	ANC	pHBC	Total organic C	Total N	Total Fe	RIS
	cm		1:1	g g^{-1}		%		% $CaCO_3$			g kg^{-1}		
1	5–20	Sulphuric	4.1	0.08	85	5	10	0.6	13	6	0.4	0.10	0.33
2	20–30	Hypersulfidic	5.3	0.13	85	0	15	0.4	27	8	0.4	0.13	0.79
3	50–65	Hyposulfidic	6.9	0.14	70	7	23	0.2	16	2	0.2	0.32	0.26

[a] See Fitzpatrick et al. (2015) for more background information on Soil 1 (RBAc 1.4), Soil 2 (RBAc 1.5) and Soil 3 (RBAc 1.7),

[b] See Fitzpatrick (2013).

cm thick water layer. The vials were closed and the lids screwed on tightly to minimise entry of air. The water layer was maintained throughout the wet period by adding water if required. The containers were incubated in the dark at 25 °C; pH and redox potential were measured every 2 weeks. There were 16 replicates of each amended and unamended soil. When the pH was stable in most treatments for about 4 weeks (after 10 weeks), the overlying water was removed to start the dry period. The open vials were placed in a fan-forced oven at 30 °C and the soils dried to 100, 80, 60 or 40% of their respective maximum water holding capacity (WHC). After reaching the desired percentage WHC, the vials were removed from the oven and incubated at 25 °C in the dark with lids loose to allow air exchange. During the dry period, the desired percentage of WHC was maintained by weighing the vials regularly and adding water as required. Soil pH was measured every two weeks. After the pH had been stable in most treatments for 2–4 weeks (after 10 weeks), the second wet period was initiated by adding water and mixing as described above for the first wet period. The second wet period lasted until pH and Eh were stable in most treatments for 2–4 weeks (16 weeks).

2.3. Analyses

For determination of initial soil properties, soil pH was determined in a 1:1 soil: water slurry. Total C and N contents of the soils and wheat straw were determined by dry combustion with a LECO Trumac carbon and nitrogen analyser. Soil particle size distribution was determined by a hydrometer method (Gee and Or, 2002) with texture assigned using United States Geological Survey classifications (see website: http://www.nrcs.usda.gov). Maximum water holding capacity (WHC) was determined using a sintered glass funnel connected to a 1 m water column (Ym = −10 k Pa) as described in Haines (1930). Acid neutralising capacity (ANC) was determined by back titration with 1 M HCl as described in Ahern et al. (2004). The percentage water-filled pores during the dry period was calculated using porosity and volumetric water content. Soil pH buffer capacity (pHBC) was determined by titration with 0.05 M HCl and NaOH following the method of Aitken and Moody (1994). Soil reduced inorganic sulphur (mainly pyrite) was determined according to Ahern et al. (2004). Total iron was measured by the method of Zarcinas et al. (1996). At the end of the first wet period, acid volatile sulphur (AVS) was determined as described in Simpson (2001).

During the wet periods, pH and redox potential were determined every two weeks by inserting the probes approximately 1 cm into the soil without removing the water layer. After measurements, the lid was tightly closed. To measure pH during the dry period, the probe was also inserted approximately 1 cm into the soil. After measuring soil pH, the water content was adjusted if necessary and the hole left by the probe backfilled with surrounding soil.

For statistical analysis, the data was subjected to two-way analysis of variance in the first wet period (soil × amendment) and three-way analysis of variance in the dry period and the second wet period (soils × amendment × WHC) (Genstat for Windows 17; VSN International Ltd).

3. Results

Soil 1 had the lowest clay content, soil 3 the highest (Table 1). Soil 3 had lower TOC and total N content and ANC than soils 1 and 2. The reduced inorganic sulphur concentration was highest in soil 2. The pH buffer capacity was greater in soil 2 than the other two soils (Tables 1, 2). Wheat straw addition increased the pH buffering capacity about two fold in all three soils (Table 2).

3.1. First wet period

The initial pH of soil 3 (pH 7) was higher than that of soils 1 and 2 (pH 4–5) (Fig. 1a, Table 1). The pH of the unamended soils decreased over the 10 weeks of the first wet period. This decrease was greater in soil 3 (about 1 unit) than in soils 1 and 2 (about 0.5 units). The pH of the amended soils 1 and 2 increased during the wet period by about 1.5 units to pH 6. The increase was gradual in soil 1, but in soil 2 the pH increased in the first 2 weeks, then remained stable until week 6, after which it increased more strongly to week 10. The pH of amended soil 3 was similar at the start and the end of the wet period, but it changed over time. The pH decreased by about one unit in the first two weeks, then increased by one unit to week 6 after which it remained stable.

Table 2
pH buffer capacity (pHBC) in sulfuric soil 1, hypersulfidic soil 2 and hyposulfidic soil 3 without (−) and with (+) wheat straw.

Soil	Wheat	pHBC
1	−	13
	+	27
2	−	27
	+	44
3	−	13
	+	33

The redox potential of the unamended soils at the end of the wet period was about 100 mV higher than at the start (Fig. 1b). In soil 1, the redox potential steadily increased during the wet period, but in soil 2, it decreased in the first two weeks followed by a steady increase until week 10. The redox potential of unamended soil 3 fluctuated, increasing in the first four weeks, decreasing between weeks 6 and 8, and then increasing again to week 10. At the end of the wet period, the redox potential was lower in soil 3 (200 mV) than in soils 1 and 2 (about 300 mV). The redox potential (Eh) of the amended soils decreased strongly in the first two weeks to about −250 mV and increased gradually from week 4 to week 10 when it was about −120 mV. At the end of the wet period, addition of wheat straw significantly reduced the redox potential and increased the pH in all three soils with a greater difference between amended and unamended soils 1 and 2 than in soil 3 (Table S1).

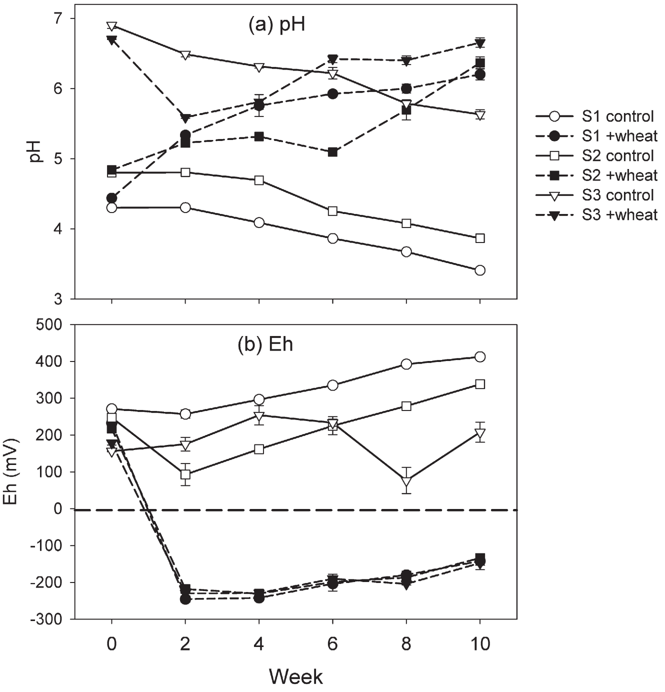


Fig. 1. Soil pH (a) and redox potential, Eh (b) over 10 weeks in the first wet period in sulfuric soil 1, hypersulfidic soil 2 and hyposulfidic soil 3 without (control) and with wheat straw (+wheat) (n = 4).

The AVS concentration at the end of the first wet period was variable among replicates and therefore only few differences among soils or between amended and unamended soils were significant. The AVS concentration was generally higher in soil 2 than in the other two soils, but the only the significant difference was between amended soils 1 and 2 (Table 3). Wheat straw addition did not significantly increase AVS concentration, although the AVS concentration in amended compared to unamended treatments was two-fold higher soils 1 and 3 and 80% higher in soil 2. The black colour (likely monosulphides) was intense in the amended soils whereas it was absent or present in small spots in the unamended soils (data not shown).

3.2. Dry period

At a given percentage of WHC, the percentage air-filled pores were greatest in soil 1 and smallest in soil 3, it was not influenced by addition of wheat straw (Table 4). For example at 80% of WHC, the percentage air-filled pores were 70% in soil 1, 53% in soil 2 but only 27% in soil 3. Approximately half of the pore space was air-filled at 60% of WHC in soil 3 and at 80% of WHC in soil 2. The percentage air-filled pores increased with decreasing water content, with the strongest increase in soil 3 where it increased about six-fold from 100 to 40% of WHC whereas it increased only by about 30% in soil 1.

At the start of the dry period the pH was higher in amended (pH 6–7) than in unamended soils (pH 4–6.5, Fig. 2) with greater differences in soils 1 and 2 than in soil 3. The initial pH differed among adjusted water contents by 0.5 to 1 pH units, being higher at the lower percentage of WHC than at 80 or 100% of WHC. The pH decrease during the oxidation period was greater in amended (1–2.5 units) than unamended soils (0.5–1 units). In amended soils, the decrease was greatest in soil 2 and least in soil 3. The pH deceased gradually in the first 7–8 weeks and then remained stable until week 10 with some fluctuations over time. In all soils without or with wheat amendment, the pH decline in the oxidation period was greater at 100 or 80% of WHC than at 40% of WHC. The differences among water contents were greater in amended than in unamended soils. At the end of the oxidation period, the pH was 0.5 to 1 unit higher in the amended soils in the treatment incubated at 40% of WHC than at the other water contents, but there were no differences in pH among water contents in the unamended soils (Table S2).

3.3. Second wet period

In the second wet period, the pH remained stable in the unamended soils, at pH 3.5 in soils 1 and 2 and at pH 4.5 in soil 3 (Fig. 3a–c). The water content in the previous oxidation period did not influence the pH in the unamended soils. The pH at the start of the second wet period was higher in amended than unamended soils, particularly in soils 2 and 3. In all three soils, the initial pH and the pH in the first six weeks were higher in the treatment that was maintained at 40% of WHC in the previous dry period compared to the other previous water contents. However later, the pH differed little among treatments maintained at different water contents in the previous dry period. In amended soil 1, the pH increased gradually throughout the second wet period, whereas in soil 3, the pH increased until week 6 and then remained stable. In soil 2, the pH of the amended soils remained stable in the second moist period. At the end of the second wet period, the pH was significantly higher in amended than in unamended treatments in soils 1 and 3. In soil 2, the pH did not differ between amended and unamended soils except for a higher pH in the amended soil incubated at 40% of WHC (Table S3) in the previous oxidation period. The water content in the previous oxidation period did not influence the pH in the second wet period except in amended soils 1 and 2 where the pH was higher in soils maintained at 40% of WHC in the previous oxidation period compared to those at 60% of WHC.

Table 3
Acid volatile sulphur (AVS) concentration at the end of the first wet period (week 10) in sulfuric soil 1, hypersulfidic soil 2 and hyposulfidic soil 3 without (−) and with (+) wheat straw. Values followed by different letters are significantly different (n = 4, p ≤ 0.05).

Soil	Wheat	AVS (μmoles/g)
1	−	0.11 a
	+	0.31 ab
2	−	0.40 abc
	+	0.72 c
3	−	0.23 ab
	+	0.52 bc

Table 4
Calculated percentage of air-filled pore space in sulfuric soil 1, hypersulfidic soil 2 and hyposulfidic soil 3 without (−) and with (+) wheat straw during the oxidation period at different percentage water holding capacity (WHC).

% WHC	Wheat	% air-filled pores		
Soil		1	2	3
100	−	63	42	10
	+	61	40	8
80	−	70	53	28
	+	69	52	26
60	−	78	65	46
	+	77	64	45
40	−	85	77	64
	+	85	76	63

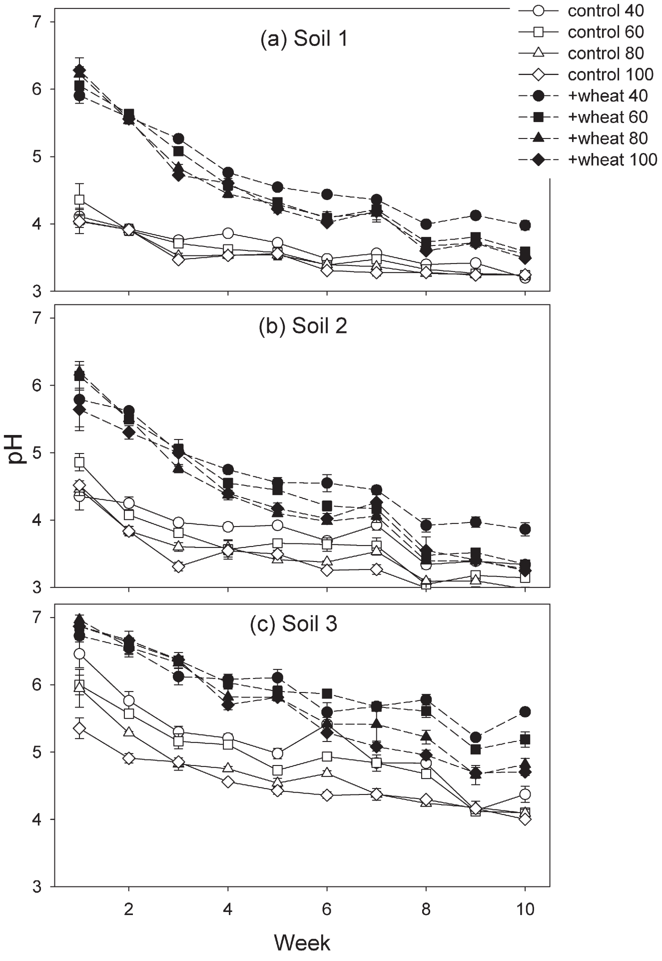


Fig. 2. Soil pH over 10 weeks during the oxidation period in sulfuric soil 1 (a), hypersulfidic soil 2 (b) and hyposulfidic soil 3 (c) without (control) and with wheat straw (+wheat) (n = 4).

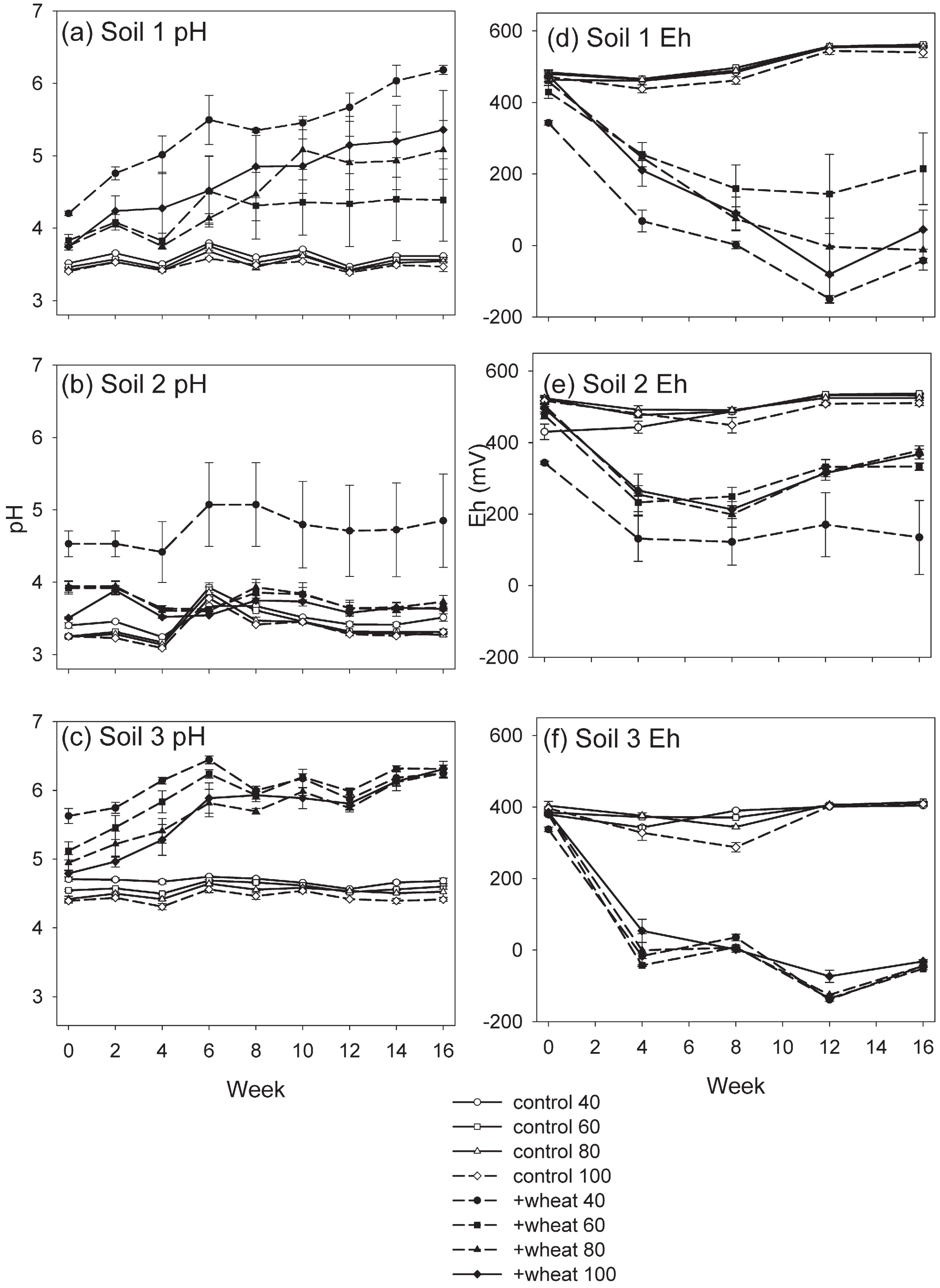


Fig. 3. Soil pH over 10 weeks during the second wet period in sulfuric soil 1 (a, d), hypersulfidic soil 2 (b, e) and hyposulfidic soil 3 (c, f) without (control) and with wheat straw (+wheat) (n = 4). Values in the legend indicate % of WHC during the dry period.

The redox potential of the unamended soils in the second wet period remained stable (soils 2 and 3) or slightly increased (soil 1) (Fig. 3d–f). The water content of the previous oxidation period did not influence the redox potential in the unamended soils. In the amended soil, the redox potential decreased in the first four weeks in soils 2 and 3 and until week 10 in soil 1. After this decrease, the redox potential remained stable until the end of the second wet period. In week 10, redox potential was lower in soils 1 and 3 than in soil 2. In all three soils, the redox potential was lower in amended compared to unamended soils from week 4 until the end of the second wet period. The water content in the previous oxidation period did not influence the redox potential of amended soil 3, but in soils 1 and 2 it was lower in soil previously maintained at 40% of WHC than in treatments maintained at higher water content. At the end of the second wet period, the redox potential was higher in the unamended than in the amended soils with no significant effect of the water content of the previous oxidation period (Table S3).

4. Discussion

This study showed that OM addition to ASS can result in higher pH at the end of the first and second wet period and at the end of the oxidation period. It also showed that low water content during oxidation minimises acidification. Although the experiment was only over 36 weeks, the observed results should also be applicable for longer wet and dry cycles because each period was terminated when pH and redox potential had been stable for several weeks.

4.1. Wet/reducing periods

The pH increase during the wet periods was greater in amended than in unamended soils (Figs. 1a, 3a–c). On the other hand, the redox potential rapidly declined in amended soils and remained lower than in unamended soils throughout the wet periods (Figs. 1b, 3d–f). The latter suggests that the added OM was decomposed, resulting in consumption of oxygen and other terminal electron acceptors (e.g. nitrate) and decrease in redox potential.

A pH increase upon submergence of soils is commonly found, e.g. in paddy soils because most reduction processes consume protons (Ponnamperuma, 1972). After depletion of oxygen, other oxidised components are used as electron acceptors in anaerobic respiration according to thermodynamics in the sequence: NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, CO_2 (Borch et al., 2009; Ponnamperuma, 1972). This pH increase is stimulated by organic matter addition because many microbial groups involved in anaerobic processes are heterotrophs (Furusaka, 1978). The relative importance of the different reduction processes for the pH increase depends redox potential, pH and the concentration of the different electron acceptors (Gotoh and Patrick, 1974; Lovley and Phillips, 1987; Yuan et al., 2015). In soils with sulfidic materials such as those used in this experiment, iron and sulfate reduction likely contribute strongly to the pH increase in the amended soils (Eq. (1); Ponnamperuma, 1972; Wakao and Furusaka, 1976). Decomposition of organic matter can also result in pH increase by decarboxylation of organic acid anions (Yan et al., 1996). Therefore we can accept the first part of the first hypothesis (organic matter addition will stimulate pH increase in the wet periods). Sulfate reduction results in the formation of reduced sulphur species such as monosulphides and pyrite (Berner et al., 1985; Ponnamperuma, 1984). Differences in AVS concentration between amended and unamended soils were not significant due to the high variability among replicates. Nevertheless, OM addition stimulated sulfate reduction because the dark colour (likely monosulphides) was more intense in the amended soils and AVS concentrations were higher in amended soils (Table 3). The stimulation of sulfate reduction by organic matter addition is in agreement with Yuan et al. (2015). The greater sulfide concentration in the amended soils at the end of the first wet period can also explain the strong pH decrease in the following dry period because oxidation of sulfide leads to formation of sulfuric acid (Eq. (2); van Breemen, 1973).

The pH increase in soil 1 was greater in the first than the second wet period and in soil 2, the pH increased only in the first wet period (Figs. 1a and 3a, b). This smaller effect of organic matter addition in second wet periods is likely because a large proportion easily decomposable OM was already decomposed during the first wet period and the following oxidation period. Therefore mainly recalcitrant OM remained in the second wet period. This explanation is corroborated by the smaller decrease in redox potential in soil 2 in the second compared to the first wet period. The smaller pH increase in soils 1 and 2 the second wet period may also be due to the lower pH at the start of the second wet period, particularly in soil 2 where the initial pH in the first wet period was 5.3, but only 3.5–4.5 at the start of the second wet period. The lower pH could inhibit microbial activity in general, but particularly that of sulfate reducers which are inhibited by a pH below 5 (Hao et al., 1996; Ponnamperuma, 1984).

The pH increase in soil 3 in the first wet period was small because the initial pH was already high (6.9) (Fig. 1a). Thus, although sulfate reduction occurred as indicated by the black colour and the higher AVS concentration compared to the unamended soils (Table 3), the pH did not further increase. However, the pH increased strongly in the second wet period where the initial pH was lower (pH 5.0–5.5, Fig. 3c). As a result of the different pH dynamics in the first and second wet periods, the final pH of soil 3 was similar in the first and second periods. The higher microbial activity in the second wet period in this soil compared to soils 1 and 2 may also be due to the more favourable pH at the start of the second wet period (pH > 5) compared to pH < 5 in soils 1 and 2.

In the unamended soils, the pH decreased by about one unit in the first wet period and remained unchanged in the second wet period (Figs. 1a, 3a–c). This was accompanied by a slightly increasing or stable redox potential in the first and second wet period (Figs. 1b and 3d–f). The lack of decrease in redox potential in the unamended soils suggests low microbial activity as a result of low amounts and availability of native OM. Thus, microbial processes that increased the pH in the amended soils such as iron and sulfate reduction were slower in unamended soils. However, fermentation seems to have occurred because the pH decreased in the first wet period indicating that native OM availability was higher than in the second wet period. Fermentation products such as acetic, propionic or butyric acid (Tsutsuki and Ponnamperuma, 1987) can result in a pH decrease (Bell, 1969; Yamane and Sato, 1964). The slight increase in redox potential in the unamended soils is likely due to insertion and removal of the pH and redox probes. Oxygen entry by insertion and removal of probes will also have occurred in the amended soils, but the higher microbial activity rapidly utilised the oxygen resulting in a low redox potential.

4.2. Dry/oxidising period

As expected, the pH decreased during the oxidation period (Fig. 2) which can be explained by oxidation of iron sulfide which results in formation of sulfuric acid (Eq. (2); van Breemen, 1973; Pons, 1973). At a given percentage of WHC, the proportion of air-filled pores was smaller in soil 3 than in soils 1 and 2 (Table S3). For example at 60% of WHC, the percentage air-filled pores was 78, 65 and 46% in soils 1, 2 and 3, respectively. The lower proportion of air-filled pores in soil 3 can be explained by its higher clay content (23%) compared to soils 1 and 2 (10 and 15%) (Table 1). A higher clay content results in a greater proportion of small pores compared to lighter-textured soils (Voroney and Heck, 2015). As soils dry, small pores hold water more tightly than larger pores and thus remain water-filled when larger pores are drained (Voroney and Heck, 2015), thereby reducing oxygen diffusion (Bronswijk et al., 1993). Reduced oxygen diffusion into soil 3 can explain the smaller pH decrease compared to the other two soils which had a lower clay content (Fig. 1). Additionally, the initial reduced inorganic sulphur concentration was lower in soil 3 than in the other two soils (Table 1). Thus, there was less iron sulfide that could be oxidised.

Despite differences in percentage air-filled pore space at a given percentage of WHC, the pH decrease was smaller at 40% than at 60–100% of WHC in all three soils (Fig. 2). The pH decrease was greater in amended than in unamended soils; therefore we decline the second part of our first hypothesis (organic matter addition will reduce acidification in the dry period). The stronger pH decrease in amended soils can be explained by the stimulation of sulfate reduction by OM addition in the first wet period. This resulted in a higher pH and also a higher concentration of iron sulfide which could be oxidised.

In the soils used here, oxidation occurred at 40–100% of WHC. If oxygen limited oxidation, the pH decrease would be greater at lower percentage of WHC because of the greater proportion of air-filled pores. But this was not the case in this study where the pH decrease was smaller at 40% of WHC than at 60–100% of WHC (Fig. 2). Thus, our second hypothesis (the pH decrease during the dry period will be stronger at lower than at high water content because the latter limits oxygen diffusion into the soil) has to be declined. The stronger pH decrease at 60–100% of WHC indicates that sufficient oxygen entered the soils for sulfide oxidation. It should be noted that the strong pH decrease at 100% of WHC even in soil 3 where only 10% of pores were air-filled (Table 4) could also be due to the experimental design. Firstly, the soil layer was thin (approximately 1.5 cm) which would maximise oxygen penetration into the soil. Secondly, oxygen may have entered the soil during or shortly after the fortnightly pH measurements. The hole remaining after removal of the pH probe was quickly back-filled, but this disturbance may have introduced oxygen into the soil.

The smaller pH decrease at 40% of WHC indicates that low water availability limited Fe sulfide oxidation. Low water availability decreases microbial activity (Liang et al., 2003) and pyrite oxidation (Chandra and Gerson, 2011; Fennemore et al., 1998). Fennemore et al. (1998) showed that pyrite oxidation is lower in arid environments than under controlled conditions at high humidity. The effect of low water content may be particularly pronounced in the present study where the soils were quickly dried to the target water content at the end of the first wet period (within a few hours). In the field, drying will be slower and therefore the period in which sufficient water is still available for sulfide oxidation will be longer. Therefore the effect of water content on sulfide oxidation in the field is likely to be smaller than in the present study.

We had hypothesised that the pH decrease during the oxidation period would be smaller in amended than in unamended soils because OM amendment increases pH buffer capacity (Curtin and Trolove, 2013) (Table 2) and by competition for oxygen by microbes decomposing OM (Bronswijk et al., 1993; Rigby et al., 2006). However, this was not the case in the present study where the pH decrease was greater in the amended soils. This is likely due to stimulation of sulfate reduction by OM addition in the first wet period. Therefore more sulfide could be oxidised in the dry period compared to unamended soils and the pH at the start of the oxidation period was higher (Figs. 1, 2). Despite the stronger pH decrease in amended soils, the pH was higher at the end of the oxidation period than in the unamended soils. As discussed above, this higher pH can, at least partly explain the stronger pH increase in the second wet period in amended soils.

5. Conclusion

Biochemical processes and controlling factors in ASS are well understood. But there is little information about the influence of organic matter addition on pH and redox potential in soils exposed to two wet periods which are separated by a dry period. Natural and managed wetting and drying cycles occur in many wetlands and floodplains and our study provides important information on the effects of this on acid sulfate soils and the role of organic matter. It showed that although OM stimulates iron sulfide formation in the wet periods, it minimises acidification during dry periods. The study also showed that rapid drying to ≤40% of WHC minimises sulfide oxidation and soil acidification during dry periods. The smaller effect of OM addition in the second compared to the first wet period suggests that easily decomposable OM was utilised in the previous wet and dry period. Therefore OM may have to be added repeatedly for sustained amelioration of ASS in the field, but our results indicate that an annual amendment is sufficient. The small particle size of the added OM and its thorough mixing into the soil in our experiments will have maximised OM availability to microbes. In the field where OM added may be in larger particle size and placed more localised (e.g. in furrows), it is likely to be less effective. The higher pH induced by OM addition could improve plant establishment and growth which would act as organic C source and could minimise the need for OM amendment in the long run.

Acknowledgement

We thank the wetland manager, Christophe Tourenq of Banrock Station for allowing us to collect the soils in the Banrock Station wetland complex.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2015.08.012.

References

Ahern, C., Sullivan, L., McElnea, A., 2004. Laboratory Methods Guidelines—Acid Sulfate Soils, Queensland Acid Sulfate Soil Technical Manual. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia (www.nrw.qld.gov.au/land/ass).

Aitken, R., Moody, P., 1994. The effect of valence and Ionic-strength on the measurement of pH buffer capacity. Aust. J. Soil Res. 32, 975–984.

Baldwin, D., Capon, S., 2011. Sulfidic sediments in inland waterways. Waterlines Report.

Baldwin, D.S., Fraser, M., 2009. Rehabilitation options for inland waterways impacted by sulfidic sediments — a synthesis. J. Environ. Manag. 91, 311–319.

Bell, R., 1969. Studies on the decomposition of organic matter in flooded soil. Soil Biol. Biochem. 1, 105–116.

Berner, R.A., 1984. Sedimentary pyrite formation: an update. Geochim. Cosmochim. Acta 48, 605–615.

Berner, R., De Leeuw, J., Spiro, B., Murchison, D., Eglinton, G., 1985. Sulphate reduction, organic matter decomposition and pyrite formation [and discussion]. Philos. Trans. R. Soc. A 315, 25–38.

Borch, T., Kretzschmar, R., Kappler, A., Cappellen, P.V., Ginder-Vogel, M., Voegelin, A., Campbell, K., 2009. Biogeochemical redox processes and their impact on contaminant dynamics. Environ. Sci. Technol. 44, 15–23.

Bronswijk, J., Nugroho, K., Aribawa, I., Groenenberg, J., Ritsema, C., 1993. Modeling of oxygen transport and pyrite oxidation in acid sulphate soils. J. Environ. Qual. 22, 544–554.

Burton, T.M., Tiner, R.W., 2009. Ecology of wetlands. In: Likens, G.E. (Ed.), Encyclopedia of Inland Waters. Academic press, Oxford, pp. 507–515.

Bush, R.T., Sullivan, L.A., 1999. Pyrite micromorphology in three Australian Holocene sediments. Aust. J. Soil Res. 37, 637–654.

Bush, R.T., Fyfe, D., Sullivan, L.A., 2004a. Occurrence and abundance of monosulfidic black ooze in coastal acid sulfate soil landscapes. Aust. J. Soil Res. 42, 609–616.

Bush, R.T., Sullivan, L.A., Ward, N.J., 2004b. The response of partially oxidised acid sulfate soil materials to anoxia. Aust. J. Soil Res. 42, 515–525.

Canfield, D.E., Thamdrup, B., Hansen, J.W., 1993. The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. Geochim. Cosmochim. Acta 57, 3867–3883.

Chandra, A.P., Gerson, A.R., 2011. Pyrite (FeS_2) oxidation: a sub-micron synchrotron investigation of the initial steps. Geochim. Cosmochim. Acta 75, 6239–6254.

Connell, W.E., Patrick, W.H., 1969. Reduction of sulfate to sulfide in waterlogged soils. Soil Sci. Soc. Am. J. 33 (5), 711–715.

Curtin, D., Trolove, S., 2013. Predicting pH buffering capacity of New Zealand soils from organic matter content and mineral characteristics. Aust. J. Soil Res. 51, 494–502.

Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. Geoderma 67, 263–276.

Emerson, D., Fleming, E.J., McBeth, J.M., 2010. Iron-oxidizing bacteria: an environmental and genomic perspective. Annu. Rev. Microbiol. 64 (1), 561–583.

Fennemore, G.G., Neller, W.C., Davis, A., 1998. Modeling pyrite oxidation in arid environments. Environ. Sci. Technol. 32, 2680–2687.

Fitzpatrick, R.W., 2013. Demands on soil classification and soil survey strategies: special-purpose soil classification systems for local practical use. In: Shahid, S.A., Taha, F.K., Abdelfattah, M.A. (Eds.), Developments in Soil Classification, Land Use Planning and Policy Implications: Innovative Thinking of Soil Inventory for Land Use Planning and Management of Land Resources. Springer Science + Business Media, Dordrecht, pp. 51–83.

Fitzpatrick, R., Shand, P., 2008. Inland acid sulfate soils: overview and conceptual models. In: Fitzpatrick, R., Shand, P. (Eds.), Inland acid sulfate soil systems across Australia. CRC LEME Open File Report 249, pp. 6–74 (http://www.clw.csiro.au/acidsulfatesoils/ass-book.html).

Fitzpatrick, R.W., Shand, P., Merry, R.H., 2009. Acid sulfate soils. In: Jennings, J.T. (Ed.), Natural History of the Riverland and Murraylands. Royal Society of South Australia (Inc.), Adelaide, South Australia, pp. 65–111.

Fitzpatrick, R.W., Shand, P., Merry, R.H., Marschner, P., Jayalath, N., Grocke, S., 2015. Acid sulfate soil assessment and monitoring of the Banrock Station wetland. Acid Sulfate Soils Report No ASSC_035 (https://www.adelaide.edu.au/directory/robert.fitzpatrick?dsn=directory.file;field=data;id=33074;m=view).

Furusaka, C., 1978. Introduction to microbiology of a paddy soil. J. Agric. Chem. Soc. Jpn. 52, R151–R158.

Gee, G.W., Or, D., 2002. Particle-size analysis. In: Dane, J.H., Topp, C.G. (Eds.), Methods of Soil Analysis: Physical Methods 4, pp. 255–293.

Gotoh, S., Patrick, W.H., 1974. Transformation of iron in a waterlogged soil as influenced by redox potential and pH. Soil Sci. Soc. Am. J. 38, 66–71.

Haines, W.B., 1930. Studies in the physical properties of soil. V. The hysteresis effect in capillary properties, and the modes of moisture distribution associated therewith. J. Agric. Sci. 20, 97–116.

Hall, K.C., Baldwin, D.S., Rees, G.N., Richardson, A.J., 2006. Distribution of inland wetlands with sulfidic sediments in the Murray–Darling Basin, Australia. Sci. Total Environ. 370, 235–244.

Hao, O.J., Chen, J.M., Huang, L., Buglass, R.L., 1996. Sulfate-reducing bacteria. Crit. Rev. Environ. Sci. Technol. 26, 155–187.

IUSS Working Group WRB, 2014. World reference base for soil resources 2014. World Soil Res. Report 106. FAO, Rome (http://www.fao.org/3/a-i3794e.pdf).

Jha, S., 2004. The wetland ecology. Our Nat. 2, 47–52.

Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Sci. Total Environ. 338 (1–2), 3–14.

Lamontagne, S., Hicks, W.S., Fitzpatrick, R.W., Rogers, S., 2006. Sulfidic materials in dryland river wetlands. Mar. Freshw. Res. 57, 775–788.

Liang, C., Das, K.C., McClendon, R.W., 2003. The influence of temperature and moisture contents regimes on the aerobic microbial activity of a biosolids composting blend. Bioresour. Technol. 86, 131–137.

Lovley, D.R., Phillips, E.J., 1987. Competitive mechanisms for inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments. Appl. Environ. Microbiol. 53, 2636–2641.

MDBA, 2013. Basin environment. http://www.mdba.gov.au/about-basin/basin-environment (accessed 08.08.2013).

Mosley, L., Zammit, B., Jolley, A., Barnett, L., 2014a. Acidification of lake water due to drought. J. Hydrol. 511, 484–493.

Mosley, L.M., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., Baker, A., Fitzpatrick, R.W., 2014b. Acidification of floodplains due to river level decline during drought. J. Contam. Hydrol. 161, 10–23.

Ponnamperuma, F.N., 1972. The chemistry of submerged soils. Adv. Agron. 29–96.

Ponnamperuma, F.N., 1984. Effects of flooding on soils. In: Kozlowski, T.T. (Ed.), Flooding and Plant Growth, pp. 9–45.

Pons, L., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In: Dost, H. (Ed.), Acid sulphate soils. Proc. 1st Int. Symp., ILRI Publ 18, 13–20 August 1972, Wageningen, The Netherlands vol. 1, pp. 3–27.

Reddy, K.R., Gale, P.M., 1994. Wetland processes and water quality: a symposium overview. J. Environ. Qual. 23, 875–877.

Rickard, D., 2012. Chapter 6 — sedimentary pyrite. In: Rickard, D. (Ed.)Developments in Sedimentology vol. 65. Elsevier, pp. 233–285.

Rigby, P.A., Dobos, S., Cook, F.J., Goonetilleke, A., 2006. Role of organic matter in framboidal pyrite oxidation. Sci. Total Environ. 367, 847–854.

Shamshuddin, J., Muhrizal, S., Fauziah, I., Van Ranst, E., 2004. A laboratory study of pyrite oxidation in acid sulfate soils. Commun. Soil Sci. Plant Anal. 35, 117–129.

Simpson, S.L., 2001. A rapid screening method for acid-volatile sulfide in sediments. Environ. Toxicol. Chem. 20, 2657–2661.

Simpson, S.L., Fitzpatrick, R.W., Shand, P., Angel, B.M., Spadaro, D.A., Mosley, L., 2010. Climate-driven mobilisation of acid and metals from acid sulfate soils. Mar. Freshw. Res. 61, 129–138.

Soil Survey Staff, 2014. Keys to Soil Taxonomy. 12th edn. USDA-Natural Resources Conservation Service, Washington, DC.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters. 3rd ed. John Wiley & Sons, Inc., New York (1022 pp.).

Sullivan, L.A., Fitzpatrick, R.W., Bush, R.T., Burton, E.D., Shand, P., Ward, N.J., 2010. The classification of acid sulfate soil materials: further modifications. Southern Cross GeoScience Technical Report No. 310 (http://scu.edu.au/geoscience/index.php/55#2010).

Tsutsuki, K., Ponnamperuma, F.N., 1987. Behavior of anaerobic decomposition products in submerged soils: effects of organic material amendment, soil properties, and temperature. Soil Sci. Plant Nutr. 33, 13–33.

van Breemen, N., 1973. Soil forming processes in acid sulphate soils. In: Dost, H. (Ed.), Acid Sulphate Soils. ICRI publi. 18, 1973, Wageningen, The Netherlands vol. 1, pp. 66–130.

Voroney, R.P., Heck, R.J., 2015. The soil habitat. In: Paul, E.A. (Ed.)Soil Microbiology, Ecology and, Biochemistry 4, pp. 15–39.

Wakao, N., Furusaka, C., 1976. Influence of organic matter on the distribution of sulfate-reducing bacteria in a paddy-field soil. Soil Sci. Plant Nutr. 22.

Ward, N.J., Sullivan, L.A., Bush, R.T., 2004. Soil pH, oxygen availability, and the rate of sulfide oxidation in acid sulfate soil materials: implications for environmental hazard assessment. Aust. J. Soil Res. 42, 509–514.

Yamane, I., Sato, K., 1964. Decomposition of glucose and gas formation in flooded soil. Soil Sci. Plant Nutr. 10, 35–41.

Yan, F., Schubert, S., Mengel, K., 1996. Soil pH increase due to biological decarboxylation of organic anions. Soil Biol. Biochem. 28, 617–624.

Yuan, C., Mosley, L.M., Fitzpatrick, R., Marschner, P., 2015. Amount of organic matter required to induce sulfate reduction in sulfuric material after re-flooding is affected by soil nitrate concentration. J. Environ. Manag. 151, 437–442.

Zarcinas, B.A., McLaughlin, M.J., Smart, M.K., 1996. The effect of acid digestion technique on the performance of nebulization systems used in inductively coupled plasma spectrometry. Commun. Soil Sci. Plant Anal. 27, 1331–1354.

CHAPTER 3. Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions

Statement of Authorship

Title of Paper	Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions.
Publication Status	☑ Published ☐ Accepted for Publication ☐ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
Publication Details	Nilmini Jayalath, Rob W. Fitzpatrick, Luke Mosley, Petra Marschner 2016. Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions. Journal of Soils and Sediments.16:518-526.

Principal Author

Name of Principal Author (Candidate)	Nilmini Jayalath		
Contribution to the Paper	Conducted experiment, data analysis and wrote the manuscript		
Overall percentage (%)	75		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	17 May 2016

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);
ii. permission is granted for the candidate in include the publication in the thesis; and
iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Rob W. Fitzpatrick		
Contribution to the Paper	Helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	Luke Mosley		
Contribution to the Paper	Supervised soil sampling; helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	Petra Marschner		
Contribution to the Paper	Supervised development of work, helped in data interpretation, manuscript evaluation, and acted as corresponding author		
Signature		Date	17. May 2016

Jayalath, N., Fitzpatrick, R.W., Mosley, L. & Marschner, P. (2016). Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions.
Journal of Soils and Sediments, *16*(2), 518-526.

CHAPTER 4. Addition of clayey soils with high net negative acidity to sulfuric sandy soil can minimise pH changes during wet and dry periods

Statement of Authorship

Title of Paper	Addition of clayey soils with high net negative acidity to sulfuric sandy soil can minimise pH changes during wet and dry periods
Publication Status	☑ Published ☐ Accepted for Publication ☐ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
Publication Details	N. Jayalath, L. M. Mosley, R.W. Fitzpatrick, P. Marschner (2016). Addition of clayey soils with high net negative acidity to sulfuric sandy soil can minimise pH changes during wet and dry periods. Geoderma. 269:153-159.

Principal Author

Name of Principal Author (Candidate)	N. Jayalath		
Contribution to the Paper	Conducted experiment, data analysis and wrote the manuscript		
Overall percentage (%)	75		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	17 May 2016

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	L. M. Mosley		
Contribution to the Paper	Helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	R. W. Fitzpatrick		
Contribution to the Paper	Supervised soil sampling; helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	P. Marschner		
Contribution to the Paper	Supervised development of work, helped in data interpretation, manuscript evaluation, and acted as corresponding author		
Signature		Date	17. May 2016

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
0016-7061/© 2016 Elsevier B.V. All rights reserved.

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.

was absent or very low in unamended soils and increased when amended with 20 g residue kg^{-1}. The organic C concentration of plant residues is about 50%, therefore a rate of 10 g C kg^{-1} is equivalent to 20 g residue kg^{-1}. The added wheat residue was finely ground and carefully mixed into the soil. This may not be possible in the field, but was done in this experiment to maximise accessibility to soil microbes.

Each treatment was replicated four times. To initiate the wet period, reverse osmosis (RO) water was added followed by thorough soil mixing. More water was added so that the soil surface was covered by a water layer of 2 cm, which was maintained throughout the wet period. Then the vials were closed tightly to minimise entry of air and incubated at 25 °C in the dark. Soil pH and redox potential (Eh) were measured fortnightly during the wet period, which lasted for 14 weeks. This duration was chosen because pH and redox potential became stable after 8–10 weeks.

To initiate the dry period, the overlying water was removed and the vials placed in a fan–forced oven at 30 °C for 24 h to reach a water content of 100% of maximum water holding capacity (WHC), which was maintained during the dry period by weighing the vials regularly and adding water if required. This water content was used based on a previous study (Jayalath et al., 2015b) where acid sulfate soils were incubated at 40–100% of WHC. Acidification was maximal at 100% WHC, and significantly lower at 40% WHC indicating water limitation. This is in agreement with previous studies (Chandra and Gerson, 2011; Fennemore et al., 1998), which showed that pyrite oxidation can be reduced in dry conditions because of lack of sufficient moisture. The vials were closed loosely and incubated at 25 °C in the dark. Soil pH was measured immediately after the soils had reached 100% WHC (week 0) and then weekly for 10 weeks. The pH stabilised after the 6–8 weeks.

2.3. Analyses

The following initial soil properties were determined. Soil pH was determined in a 1:1 soil: water slurry. Total C and N of the soils and the wheat straw were determined by dry combustion with a LECO Trumac C and N analyzer. Soil particle size distribution was determined by the hydrometer method (Gee and Or, 2002) and soil texture was classified using the United States Geological Survey textural triangle (see website: http://www.nrcs.usda.gov). Maximum water holding capacity was determined using a sintered glass funnel connected to a 1 m water column (−10 k Pa) according to Haines (1930). Acid neutralising capacity (ANC) was determined as described in Ahern et al. (2004). The percentage of air filled pore space during the dry period was calculated as:

$$\text{Porosity} = \text{bulk density}/2.65 \tag{2}$$

Using the volumetric water content the % water-filled pore space was calculated. Then

$$\text{air} - \text{filled pore space} = 100 - \text{water} - \text{filled pore space} \tag{3}$$

Soil pH buffer capacity (pHBC) was determined following Aitken and Moody (1994). Reduced inorganic sulfur (RIS) (mainly FeS_2, pyrite, also includes metastable FeS) was measured as chromium reducible sulfur (Ahern et al., 2004) at the start and the end of the experiment. Net acidity was calculated according to Eq. (1) (Ahern et al., 2004).

To determine soil pH and Eh during the wet period, the pH and Eh probes were inserted to a depth of about 1 cm into the soil without removing the overlying water. During the dry period, the pH electrode was also inserted into the soil to a depth of about 1 cm. After measurements, the holes made by the electrodes were back-filled with surrounding soil and more water was added if necessary before lids were replaced.

After confirming that the data was normally distributed and random, it was subjected to repeated measures two-way analysis of variance (ANOVA) [proportion of clay soil in mixes (0–100) × type of clay soil] in wet and dry periods (Genstat for Windows 17; VSN International Ltd).

3. Results

The sulfuric sandy soil had the highest percentage sand (85%) and the lowest pH (pH 4.1), WHC, total organic C, total N, total Fe concentration, no measurable ANC and positive net acidity (Table 1). Among the clay soils, the pH was lower in NA-8 than the other two soils (Table 1). NA-334 had the highest ANC, pH buffer capacity and RIS concentration and the greatest (most negative) net acidity (−334 mol H^+ $tonne^{-1}$). The clay content was highest in NA-54; this soil had the highest total Fe concentration and a negative net acidity of −54 mol H^+ $tonne^{-1}$. NA-8 had the lowest ANC, pH buffer capacity and RIS concentration; with a negative net acidity of only −8 mol H^+ $tonne^{-1}$ (Table 1).

Due to the differences in clay concentration among clay soils, the mixtures also differed in clay concentration (Table S2). For example, in the mixtures with 50% clay soil, the clay concentration ranged from 19% with NA-8 to 36% with NA-54.

The pH buffer capacity of the soil treatments was lowest in the sulfuric soil alone and increased with proportion of clay in the mixture (Table S2) with a greater increase in the clay treatments with NA-334 than the other two clay soils. Compared to sulfuric soil alone, the pH buffer capacity of the mixture with 50% clay was two to three-fold higher.

3.1. Wet period

The initial soil pH was lower in the sulfuric soil alone than in treatments with clay soils (Fig. 1). In sulfuric soil alone, the pH increased by about two pH units from the start of the wet period (pH 4) to week 14 (pH 6), with a greater increase in the first six weeks than later.

The pH changed less in the treatments with clay soils. In the mixtures of sulfuric soil and NA-334 (Fig. 1a, Table S4), the initial pH was about three units higher than sulfuric soil alone. In all treatments with NA-334, the pH dropped by about 0.5 units in the first two weeks and then remained stable. In week 14, the pH of the treatments with NA-334 was about 0.5 units higher than in sulfuric soil alone (Table S5).

The initial pH of the treatments with NA-54 was 1.5 to 3 units higher than in sulfuric soil alone (Fig. 1b). Among NA-54 treatments, the initial pH was lowest in the mixture with 25% NA-54 (pH 5.6) and highest with 75–100% NA-54 (pH 7.0). In the first two weeks of the wet period, the pH increased by about two units in sulfuric soil alone and by about one unit with 25% NA-54. With 50% NA-54, the pH decreased slightly in the first two weeks, whereas the decrease was greater in the treatments with higher proportion of NA-54, by about one unit with 75% NA-54 and by two units with NA-54 alone. From week 2 to week 6 the pH increased in all treatments, with the greatest increase in NA-54 alone. After week 8, the pH was stable and similar in all treatments.

The initial pH of sulfuric sandy soil alone was 1–2 units lower than in treatments with NA-8 (Fig. 1c). Among the treatments with NA-8, the initial pH increased with clay concentration from pH 5.1 to 5.8. The pH increased in the first six weeks in all treatments with the greatest increase in the sulfuric soil alone and the smallest with 75 or 100% NA-8. The pH was stable after week 8 and did not differ among treatments (Tables S4, S5).

In all soils, the redox potential decreased in the first two weeks, followed by an increase from week 4 to week 8, after which the Eh decreased again to week 12 and then increased (Fig. 2a–c, Tables S4, S5). The changes in redox potential were greater in the first eight weeks than later. There were no clear differences among treatments of sulfuric soil with NA-54 or NA-8. But the redox potential was lower in week 4 in

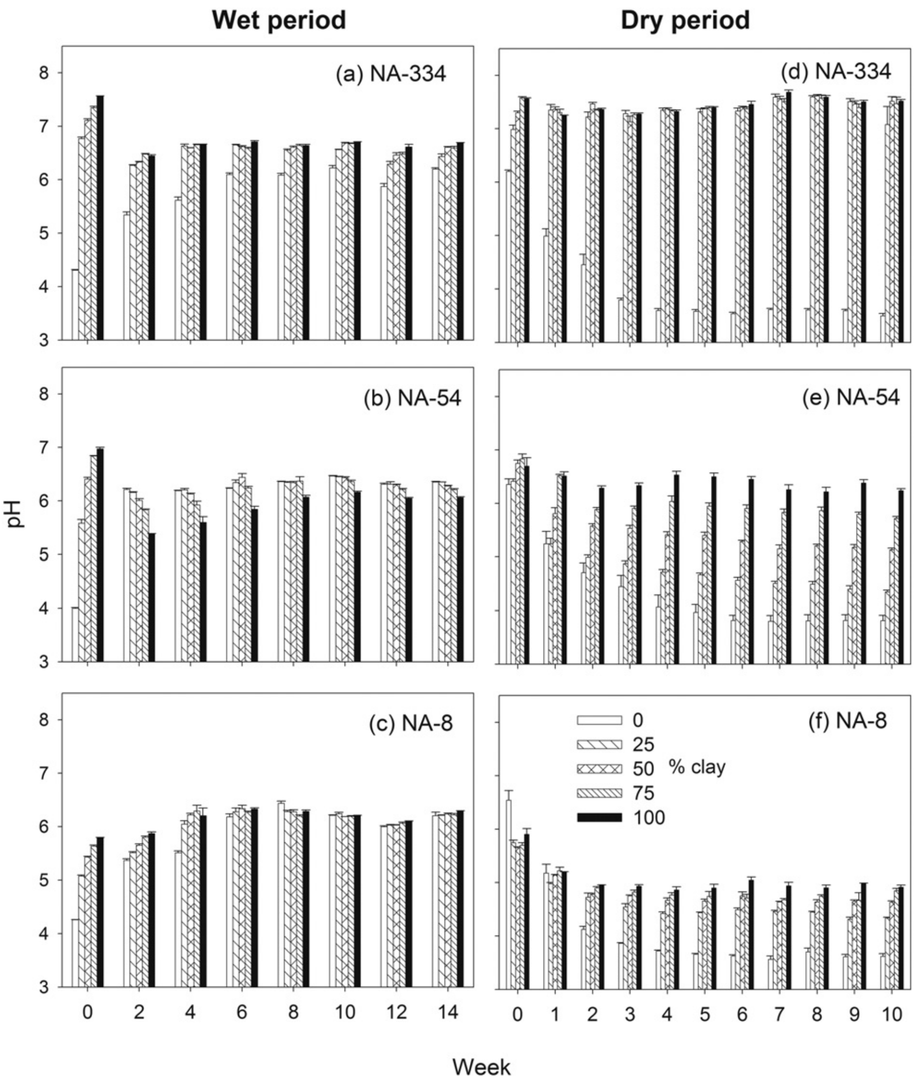


Fig. 1. Soil pH in wet (a to c) and following dry period (d to f) in sandy sulfuric soil alone (0% clay soil), sulfuric soil mixed with 25, 50 or 75% (w/w) of three hyposulfidic clay soils NA-334 (a, d), NA-54 (b, e), NA-8 (c, f) or hyposulfidic clay soils alone (100% clay soil) during the wet period (n = 4, vertical bars indicate standard error). All treatments had 10 g C kg^{-1} wheat straw added.

sulfuric soil alone than in treatments with NA-334 (Fig. 2a). In week 14, redox potential varied little among treatments.

In all soils, the extent of black material, likely monosulfides (FeS), increased during the wet period, with no apparent differences among treatments (data not shown).

3.2. Dry period

The percentage of air-filled pores was highest in sulfuric soil alone and decreased with proportion of clay soil in the mixes (Table S6). Among clay soils, it was higher in mixtures with NA-334 than the other two clay soils.

The pH after drying to 100% of WHC (initial pH of the dry period) was 0.5–1 units lower in sulfuric soil alone (pH 6.2) than the treatments with NA-334, and 0.5 units lower than in mixtures with ≥50% NA-54 (Fig. 1d and e, Table S5). However the initial pH of treatments with NA-8 was 1–1.5 units lower than sulfuric soil alone (Fig. 1f). During the dry period, the pH of sulfuric soil alone decreased to about pH 4 in the first six weeks and then stabilised. In contrast, the pH of treatments with NA-334 remained between pH 7 and 7.5 (Fig. 1d) or decreased by up to one pH unit in treatments with NA-8 (Fig. 1f). In treatments with NA-54, the pH change during the dry period depended on the clay concentration (Fig. 1e). The pH decreased only by about 0.5 units with 75 or 100% NA-54. However in the treatments with a lower proportion of NA-54, the pH decrease was greater, by one unit in the treatment with 50% NA-54, and by more than 1.5 units with 25% NA-54.

At the end of the dry period (week 10), the pH was lowest in sulfuric soil alone (pH 3.5–3.8) (Table S7). The pH was above 7 in all treatments with NA-334 and ranged between 4.3 and 4.9 in the treatments with NA-8. In mixtures with NA-54, the pH in week 10 ranged between 4.4 and 6.2, increasing with clay soil proportion.

The initial RIS concentration was 15-fold greater in NA-334 than in sulfuric soil and NA-54 and 30-fold greater than in NA-8 (Table 1). In the soil mixes, the RIS concentration at the start of the experiment increased with increasing proportion of NA-334 (Table 2). In contrast, the RIS concentration in treatments with NA-54 and NA-8 was lower than in sulfuric soil alone and was little affected by proportion clay soil. In general, the RIS concentration was lower at the end of the dry period than at the start of the experiment, with the decrease ranging from 0.02 g kg^{-1} in NA-8 alone to 0.95 g kg^{-1} in NA-334 alone. During the dry period, the RIS concentration decreased by 0.13 g kg^{-1} in the sulfuric soil alone, by 0–0.7 g kg^{-1} in all treatments with NA-54 and

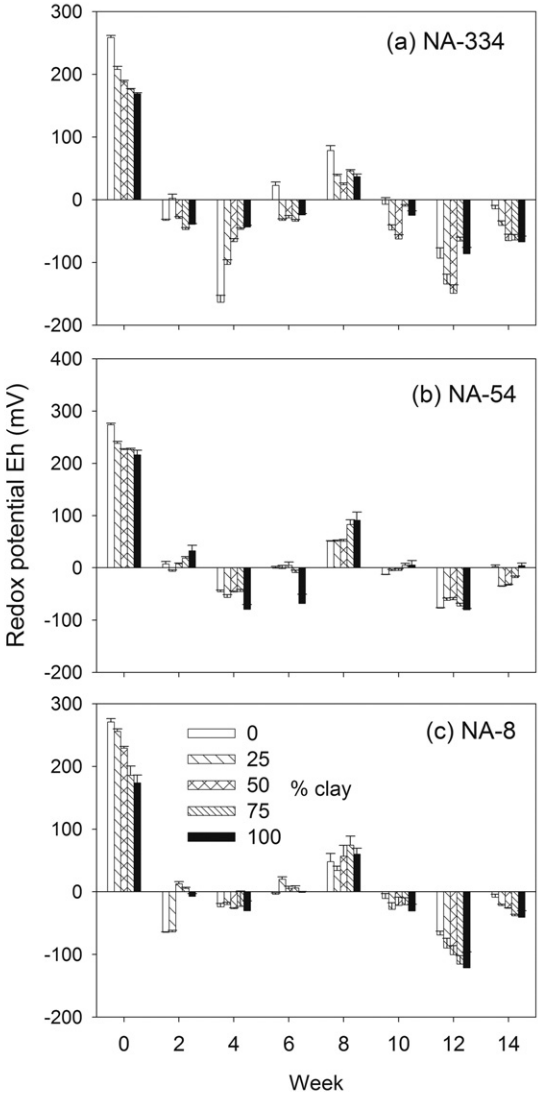


Fig. 2. Soil redox potential in sandy sulfuric soil alone (0% clay soil), sulfuric soil mixed with 25, 50 or 75% (w/w) of three hyposulfidic clay soils NA-334 (a), NA-54 (b), NA-8 (c) or hyposulfidic clay soils alone (100% clay soil) during the dry period ($n = 4$, vertical bars indicate standard error). All treatments had 10 g C kg^{-1} wheat straw added.

NA-8 and by 0.28–0.95 g kg^{-1} in treatments with NA-334. However, the percentage decrease in RIS concentration during the dry period was smaller in all clay soil treatments than in sulfuric soil alone (0–38% compared to 50–60% in clay soil treatments). The smallest percentage decrease occurred in the NA-8 treatments (0–30%).

Table 2
Reduced inorganic sulfur concentration in sandy sulfuric soil alone (0% clay soil), sulfuric soil mixed with 25, 50 or 75% (w/w) of three hyposulfidic clay soils (NA-334, NA-54, NA-8) or hyposulfidic clay soils alone (100% clay soil) at the beginning of the incubation experiment and at the end of the dry period ($n = 1$). All treatments had 10 g C kg^{-1} wheat straw added.

	Reduced inorganic sulfur (g kg^{-1})									
	Initial					End (dry period)				
	Proportion of clay soil									
Clay soil	0	25	50	75	100	0	25	50	75	100
NA-334	0.23	0.73	1.72	2.06	2.95	0.09	0.45	1.00	1.50	2.00
NA-54	0.23	0.14	0.14	0.17	0.17	0.10	0.14	0.09	0.17	0.10
NA-8	0.23	0.14	0.10	0.10	0.13	0.11	0.10	0.10	0.10	0.11

4. Discussion

This study showed that addition of hyposulfidic clay soils with negative net acidity to a sulfuric soil can minimise pH changes during the wet and dry periods. In two of the three clay soils, a proportion of 25% in the mixtures with sulfuric soil was sufficient to stabilise the pH. We can confirm the first hypothesis (clay soils with high pH buffer capacity and negative net acidity will minimise pH changes during the wet and dry period), but the second hypothesis (acidification during the dry period will be greater with higher initial RIS concentrations in the soil mixtures) has to be declined because acidification during the dry period was not directly related to RIS concentration.

4.1. Wet period

After inundation, the redox potential decreased sharply because of oxygen consumption by heterotrophic microbes decomposing the added wheat straw. After oxygen depletion, other terminal electron acceptors such as NO_3^-, Fe^{+3} and SO_4^{-2} are used (Ponnamperuma, 1984). Organic matter addition stimulates these processes because they are in most cases catalysed by heterotrophic microbes (Furusaka, 1978). These changes in redox potential in the first weeks after submergence are typical of soils when organic matter has been added. When an aerobic soil is submerged, its Eh decreases during the first few days and reaches a minimum; then it increases, attains a maximum, and decreases again asymptotically to a value characteristic of the soil, after 8–12 weeks of submergence (Ponnamperuma, 1972, 1984; Motorura, 1962; Yamane and Sato, 1968). The rapid initial decrease of Eh is due to oxygen consumption by microbes decomposing readily available C. Then Mn(IV) and Fe(III) oxides are reduced, buffering Eh as electrons are accepted (e.g. for Mn: $MnO_2 + 2e^- + 4\,H^+ <-> Mn^{2+} + 2H_2O$). However, when this buffer capacity is saturated, oxygen consumption by microbes decomposing organic C leads to another Eh decrease.

The redox potential followed the same pattern in all soils indicating that mixing of clay soils with a sulfuric soil did not influence redox processes during the wet period.

Decomposition of the added wheat straw and redox processes consume protons (Ponnamperuma, 1984; Yan and Schubert, 2000). The contribution of the different reduction processes to pH increase depends on various factors, e.g. concentration of the different electron acceptors, redox potential and pH range (Gotoh and Patrick, 1974; Lovley and Phillips, 1987; Yuan et al., 2015a,b). In ASS, a pH increase during the wet period is likely to be mainly due Fe and sulfate reduction (Berner et al., 1985), as indicated by the appearance of black material, likely FeS. In sulfuric soil alone, the pH increased by about two units in the first eight weeks of the wet period (Fig. 1). The pH increase is in agreement with Yuan et al. (2015b) who showed for a range of sulfuric soils that organic C addition was necessary to stimulate sulfate reduction and the concomitant pH increase. However, a large pH increase occurred only in the sulfuric soil alone, which can be explained its low pH buffer capacity (Tables 1, S2). In the other treatments, the greater pH buffer capacity minimised the pH increase (Tables 1, S2). Further, the initial pH was higher in the clay treatments than in sulfuric soil alone (Fig. 1). Among the three clay soils, the changes in pH during the wet period were smallest with NA-334 and only occurred in the first two weeks, which can be explained by its high pH buffer capacity and high negative net acidity (-334 mol H^+ $tonne^{-1}$).

4.2. Dry period

The pH decrease during the dry period was greatest in sulfuric soil alone, where the pH decreased from 6.5 to about 4 within six weeks (Fig. 2). Above pH 5 the pH decrease may be due to nitrification (Cai et al., 2014). However, it is unlikely that protons generated by nitrification played an important role in the pH decrease in this experiment because the ammonium concentration in the soils in the Banrock wetland is low (7–15 mg kg^{-1}, Jayalath et al., 2015b). Cai et al. (2014) found that even at high fertiliser addition rates (80 mg N kg^{-1}) nitrification resulted only in a pH decrease of about 0.5 units in a Ferralic Cambisol. Therefore in the soils used here the contribution of nitrification to the pH decrease is likely to be small. In this study, the pH decrease can be mainly explained by oxidation of pyrite (FeS_2) present in the soil at the start of the experiment (Ahern et al., 2004; Emerson et al., 2010; Johnson and Hallberg, 2005), and new FeS_2 and FeS formed in the preceding wet period (Pons, 1973; van Breemen, 1973) according to the following equation:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \quad (4)$$

The large pH decrease in the sulfuric sandy soil can be explained by its low pH buffer capacity (Tables 1, S2). In contrast, there was little or no pH decrease during the dry period in the clay soil treatments (Fig. 2), which can be explained by two factors. Firstly, the lower percentage air-filled pore space in the clay soil treatments compared to sulfuric soil alone (Table S4) will have reduced oxygen diffusion into the soil and oxidation of sulfides. Secondly, compared to sulfuric soil alone, all clay soils had greater negative net acidity, acid neutralising capacity and pH buffer capacity (Tables 1, S2), which will minimise pH decrease when protons are generated. However, the pattern of pH change during the dry period differed among the three clay soils.

Treatments with NA-334 had the highest initial pH and the pH remained stable throughout the dry period (Fig. 2a). However, the treatments with NA-334 also had the highest RIS concentration and the greatest absolute decrease in RIS concentration during experimental period among clay soil treatments (decrease in RIS ranged from 0.28 and 0.95 g kg^{-1}, Table 2). The decrease in RIS concentration indicates that pyrite was oxidised, which may have been facilitated by the high proportion air-filled pore space in the treatments with NA-334 compared to the other clay soils (Table S4). Thus, although protons were generated, the pH remained unchanged which can be explained by the greater negative net acidity, acid neutralising capacity and pH buffer capacity of NA-334 (Tables 1 and 2). NA-334 had a lower clay concentration than NA-54, but its net negative acidity, acid neutralising capacity and pH buffer capacity were greater, which could be due to the higher silt fraction in NA-334 contributing to pH buffer capacity.

The pH at the start of the dry period was lower in the treatments with NA-8 than sulfuric soil alone (Fig. 2c). However, during the dry period, the pH decreased in the treatments with NA-8 by only 0.5 units and from week 2 onwards, it was higher than in the sulfuric soil alone. This small pH decrease with NA-8 can be explained by its low RIS concentrations (Table 2) and the small change in RIS concentrations during the experiment (0–0.12 g kg^{-1}, Table 2). This suggests limited proton generation by sulfide oxidation, which may have been aided by the low proportion of air-filled pores in treatments with NA-8 (Table S4). Thus the pH remained stable despite the low pH buffer capacity and acid neutralising capacity of NA-8 (Tables 1, S2).

In the treatments with NA-334 and NA-8, the proportion of the clay soil in the mixtures had very little effect on pH. The small effect of the proportion of these two clay soils may be due to pH buffer capacity in case of NA-334 or low RIS concentration and pyrite oxidation in treatments with NA-8.

In contrast in treatments with NA-54, the pH changes during the dry period depended on the proportion of clay soil, with the greatest pH changes occurring in the mixture with 25% NA-54 and the least with NA-54 alone (Fig. 2b). NA-54 had the highest clay concentration, but compared to NA-334 its acid neutralising capacity, pH buffer capacity and negative net acidity were lower (Tables 1, 2). RIS concentration and the absolute decrease in RIS concentration during the experiment were slightly greater in NA-54 compared to NA-8. Thus more acid was generated than in NA-8, but the ability to buffer the pH was lower in NA-54. With increasing proportion of NA-54, the percentage air-filled pore space and thus potential for sulfide oxidation and proton generation decreased whereas the pH buffer capacity increased (Tables S3, S5).

The data of this study suggest that for clay soils with high pH buffer capacity and negative net acidity (NA-334), a proportion of 25% clay soil (approximately 20% clay) can prevent acidification in the dry period even if the RIS concentration of the clay soil is high. The soil solution, minerals and exchange complex all have the capacity to neutralise soil acidity. Acid neutralising capacity (ANC) measurement incorporates these buffering mechanisms as the method involves addition of standardised HCl followed by back titration with standardised NaOH to pH 7. Net acidity is calculated according to Eq. (1) and also takes into account the soil's acidification potential. Our results suggest that net acidity is particularly useful in determining the potential of clay soils to ameliorate sulfuric sandy soils whereas RIS concentration of the clay soil is less important. Net acidity could be used to calculate how much clay soil will be required to achieve neutralisation. For a net acidity in mixed soil of zero, the positive net acidity of the acid soil has to be equal to the negative net acidity of the clay soil × fraction clay soil of the mixed soil. For example, if net acidities of sulfuric soil $= 100$ and of clay soil $= -500$, then a clay soil fraction of 0.2 is required.

5. Conclusion

It can be concluded that large changes in pH during wet and dry periods in sulfuric soils can be minimised by mixing with clay soils. In agreement with our previous studies (Jayalath et al., 2015a; Yuan et al., 2015b), organic matter addition stimulated sulfate reduction and lead to a pH increase in treatments where the pH at the start of the wet period is low. However, organic matter addition at the start of the experiment did not prevent acidification of the sulfuric sandy soil in the dry period in this study. Reduction of acidity in acid sulfate soils by organic matter addition relies on decomposition of the added organic matter to stimulate sulfate reduction during the wet period and proton consumption during the dry period. Therefore a sustained effect may require repeated addition of organic matter. In contrast, addition of clay soil could be a once-off amelioration strategy for pH stabilisation of sulfuric soils, especially in wetlands where clay soils occur immediately adjacent to sulfuric soils. When wetlands dry out, precipitation of alkalinity of surface water can lead to a pH increase. However Reid and Mosley (2016) studied alkaline wetlands in Southeast Australia also connected to the River Murray and found that even there, Ca concentrations remained low during periods of high evaporation (Reid and Mosley, 2016). Therefore it is unlikely that precipitation of alkalinity in surface waters could increase the soil pH in the Banrock Station Wetland, which emphasises the importance of amelioration strategies such as that presented in this study to minimise acidification. Field experiments are required to test how long mixing with clay soils is effective in reducing acidity. The pH stabilisation by clay soil addition to sulfuric soil in this experiment may also be due to the fine grinding of both the sulfuric and clay soils and the thorough mixing of the two soils. This will have maximised the effect of the clay soils in binding protons and buffering the pH. The effect may be smaller in the field where after mixing the clay and sulfuric soils, the clay soil may be in clods of varying size and unevenly distributed.

Acknowledgements

We thank the wetland manager, Christophe Tourenq of Banrock Station for permitting us to collect soils in the Banrock Station wetland complex.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2016.01.040.

References

Ahern, C.R., McElnea, A.E., Sullivan, L.A., 2004. Acid Sulfate Soils Laboratory Methods Guidelines. Queensland Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

Aitken, R., Moody, P., 1994. The effect of valence and ionic-strength on the measurement of pH buffer capacity. Aust. J. Soil Res. 32 (5), 975–984.

Batty, L.C., Younger, P.L., 2004. The use of waste materials in the passive remediation of mine water pollution. Surv. Geophys. 25, 55–67.

Berner, R., De Leeuw, J., Spiro, B., Murchison, D., Eglinton, G., 1985. Sulphate reduction, organic matter decomposition and pyrite formation–discussion. Philos. Trans. R. Soc. Lond. A 315 (1531), 25–38.

Burton, T.M., Tiner, R.W., 2009. Ecology of wetlands. In: Likens, G.E. (Ed.), Encyclopedia of Inland Waters. Academic Press, Oxford, pp. 507–515.

Cai, Z.J., Wang, B.R., Xu, M.G., Zhang, H.M., Zhang, L., Gao, S.D., 2014. Nitrification and acidification from urea application in red soil (Ferralic Cambisol) after different long-term fertilization treatments. J. Soils Sediments 14, 1526–1536.

Chandra, A.P., Gerson, A.R., 2011. Pyrite (FeS_2) oxidation: a sub-micron synchrotron investigation of the initial steps. Geochim. Cosmochim. Acta 75, 6239–6254.

Dear, S.E., Moore, N.G., Dobos, S.K., Watling, K.M., Ahern, C.R., 2002. Soil management guidelines. Queensland Acid Sulfate Soil Technical Manual. Department of Natural Resources and Mines, Indooroopilly, Queensland, Australia.

Dent, D.L., 1986. Acid Sulphate Soils: a Baseline for Research and Development 39. ILRI, Wageningen, The Netherlands.

Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. Geoderma 67 (3–4), 263–276.

Emerson, D., Fleming, E.J., McBeth, J.M., 2010. Iron-oxidizing bacteria: an environmental and genomic perspective. Annu. Rev. Microbiol. 64 (1), 561–583.

Fennemore, G.G., Neller, W.C., Davis, A., 1998. Modeling pyrite oxidation in arid environments. Environ. Sci. Technol. 32 (18), 2680–2687.

Fitzpatrick, R., 2013. Demands on soil classification and soil survey strategies: special purpose soil classification systems for local practical use. In: Shahid, S.A., Taha, F.K., Abdelfattah, M.A. (Eds.), Developments in Soil Classification, Land Use Planning and Policy Implications: Innovative Thinking of Soil Inventory for Land Use Planning and Management of Land Resources. Springer, Netherlands, pp. 51–83.

Fitzpatrick, R., Marvanek, S., Shand, P., Merry, R., Thomas, M., Raven, M., 2008. Acid sulfate soil maps of the River Murray below Blanchetown (Lock 1) and Lakes Alexandrina and Albert when water levels were at pre-drought and current drought conditions. CSIRO Land and Water Science Report 12/08.

Fitzpatrick, R.W., Shand, P., Merry, R.H., 2009. Acid sulfate soils. In: Jennings, J.T. (Ed.), Natural History of the Riverlands and Murraylands. Royal Society of South Australia (Inc.), Adelaide, South Australia, pp. 65–111.

Fitzpatrick, R.W., Shand, P., Merry, R.H., Marschner, P., Jayalath, N., Grocke, S., 2015. Acid sulfate soil assessment and monitoring of the Banrock Station wetland. Acid Sulfate Soils Report No ASSC_035 (https://www.adelaide.edu.au/directory/robert.fitzpatrick?dsn=directory.file;field=data;id=33074;m=view).

Fraser, M.A., Baldwin, D.S., Rees, G.N., Silvester, E.J., Whitworth, K.L., 2012. Rehabilitation options for inland waterways impacted by sulfidic sediments — field trials in a south-eastern Australian wetland. J. Environ. Manag. 102, 71–78.

Furusaka, C., 1978. Introduction to microbiology of a paddy soil. J. Agric. Chem. Soc. Jpn. 52, R151–R158.

Gee, G.W., Or, D., 2002. Particle-size analysis. In: Dane, J.H., Topp, C.G. (Eds.), Methods of Soil Analysis: Part 4 Physical Methods. Soil Sci. Soc. Am., pp. 255–293.

Gotoh, S., Patrick, W.H., 1974. Transformation of iron in a waterlogged soil as influenced by redox potential and pH. Soil Sci. Soc. Am. J. 38, 66–71.

Haines, W.B., 1930. Studies in the physical properties of soil. V. The hysteresis effect in capillary properties, and the modes of moisture distribution associated therewith. J. Agric. Sci. 20 (01), 97–116.

Hall, K.C., Baldwin, D.S., Rees, G.N., Richardson, A.J., 2006. Distribution of inland wetlands with sulfidic sediments in the Murray–Darling Basin, Australia. Sci. Total Environ. 370 (1), 235–244.

Isbell, R.F., National Committee on Soils and Terrain, 2016. The Australian Soil Classification. Second Edition. CSIRO Publishing, Clayton, Victoria, Australia.

IUSS Working Group WRB, 2014. World reference base for soil resources 2014. World Soil Res. Report 106. FAO, Rome (http://www.fao.org/3/a-i3794e.pdf).

Jayalath, N., Fitzpatrick, R.W., Mosley, L., Marschner, P., 2015a. Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions. J. Soils Sediments 16, 518–526.

Jayalath, N., Mosley, L.M., Fitzpatrick, R.W., Marschner, P., 2015b. Addition of organic matter influences pH changes in reduced and oxidized acid sulfate soils. Geoderma 262, 125–132.

Jha, S., 2004. Wetland ecology. Our Nat. 2 (1), 47–52.

Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Sci. Total Environ. 338, 3–14.

Johnston, S.G., Keene, A.F., Bush, R.T., Burton, E.D., Sullivan, L.A., 2009. Remediation of coastal acid sulfate soils by tidal inundation: effectiveness and geochemical implications. Proc. of 18th NSW Coastal Conference, Ballina, NSW.

Lovley, D.R., Phillips, E.J., 1987. Competitive mechanisms for inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments. Appl. Environ. Microbiol. 53, 2636–2641.

Mosley, L., Zammit, B., Jolley, A., Barnett, L., 2014a. Acidification of lake water due to drought. J. Hydrol. 511, 484–493.

Mosley, L.M., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., Baker, A., Fitzpatrick, R.W., 2014b. Acidification of floodplains due to river level decline during drought. J. Contam. Hydrol. 161, 10–23.

Motorura, S., 1962. Effect of organic matters on the formation of ferrous iron in soils. Soil Sci. Plant Nutr. 8 (1), 20–29.

Ponnamperuma, F.N., 1972. The chemistry of submerged soils. Adv. Agron. 24, 29–96.

Ponnamperuma, F.N., 1984. Effects of flooding on soils. In: Kozlowski, T.T. (Ed.), Flooding and Plant Growth. Academic Press, Inc., Orlando, Florida, United States of America, pp. 9–45.

Pons, L., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In: Dost, H. (Ed.), Acid sulphate soils. Proc. Int. Symp. Acid sulphate soils 1st. ILRI Publ 18, Wageningen, The Netherlands 1, pp. 3–27.

Ramsar Convention, 1998. Banrock Station Wetland Complex. https://rsis.ramsar.org/ris/1221.

Reddy, K.R., Gale, P.M., 1994. Wetland processes and water quality: a symposium overview. J. Environ. Qual. 23 (5), 875–877.

Reid, R.J., Mosley, L.M., 2016. Comparative contributions of solution chemistry, microbial metabolism and aquatice photosynthesis to the development of high pH in ephemeral wetlands in South East Australia. Sci. Total Environ. 542, 334–343.

Skousen, J.G., Sexstone, A., Ziemkiewicz, P.F., 2000. Acid mine drainage control and treatment. In: Barnhisel, R.I., Darmody, R.G., Daniels, W.L. (Eds.), Reclamation of drastically disturbed lands. American Society of Agronomy, Madison, pp. 131–168.

Soil Survey Staff, 2014. Keys to Soil Taxonomy. United States Department of Agriculture Natural Resources Conservation Service, Washington D.C.

Sullivan, L.A., Fitzpatrick, R., Bush, R.T., Burton, E.D., Shand, P., Ward, N.J., 2010. The classification of acid sulfate soil materials: further modifications. Southern Cross GeoScience Technical Report. Southern Cross University, Lismore, NSW, Australia.

van Breemen, N., 1973. Soil forming processes in acid sulphate soils. In: Dost, H. (Ed.), Acid sulphate soils. ICRI publ 18, Wageningen, The Netherlands 1, pp. 66–130.

Yamane, I., Sato, K., 1968. Initial rapid drop of oxidation–reduction potential in submerged air-dry soils. Soil Sci. Plant Nutr. 14 (2), 68–72.

Yan, F., Schubert, S., 2000. Soil pH changes after application of plant shoot materials of faba bean and wheat. Plant Soil 220 (1-2), 279–287.

Younger, P.L., Ananda, J., Elliot, A., Wood, R., Amos, P., Daugherty, A.J., Martin, A., Bowden, L., Aplin, A.C., Johnson, D.B., 2003. Passive treatment of acidic mine waters in subsurface-flow systems: exploring RAPS and permeable reactive barriers. Land Contam. Reclam. 11, 127–135.

Yuan, C., Mosley, L.M., Fitzpatrick, R., Marschner, P., 2015a. Amount of organic matter required to induce sulfate reduction in sulfuric material after re-flooding is affected by soil nitrate concentration. J. Environ. Manag. 151, 437–442.

Yuan, C., Fitzpatrick, R., Mosley, L.M., Marschner, P., 2015b. Sulfate reduction in sulfuric material after re-flooding: effectiveness of organic carbon addition and pH increase depends on soil properties. J. Hazard. Mater. 298, 138–145.

CHAPTER 5. Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive wet-dry cycles

Statement of Authorship

Title of Paper	Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive wet-dry cycles
Publication Status	☐ Published ☐ Accepted for Publication ☐ Submitted for Publication ☑ Unpublished and Unsubmitted work written in manuscript style
Publication Details	N. Jayalath, Rob Fitzpatrick, Luke M. Mosley, Petra Marschner. Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive wet-dry cycles.

Principal Author

Name of Principal Author (Candidate)	N. Jayalath		
Contribution to the Paper	Conducted experiment, data analysis and wrote the manuscript		
Overall percentage (%)	80		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	17 May 2016

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);
ii. permission is granted for the candidate in include the publication in the thesis; and
iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Rob Fitzpatrick		
Contribution to the Paper	Helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	Luke M. Mosley		
Contribution to the Paper	Supervised soil sampling; helped to evaluate and edit the manuscript		
Signature		Date	17 May 2016

Name of Co-Author	Petra Marschner		
Contribution to the Paper	Supervised development of work, helped in data interpretation, manuscript Evaluation.		
Signature		Date	17. May 2016

Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive wet-dry cycles.

N. Jayalath[1, 2], Rob Fitzpatrick[3], Luke M. Mosley[3], Petra Marschner[2*]

[1] CSIRO Land and Water, Private Bag No. 2, Glen Osmond, SA, 5064, Australia

[2] School of Agriculture, Food & Wine, The University of Adelaide, Adelaide SA 5005, Australia

[3]Acid Sulfate Soils Centre, The University of Adelaide, Adelaide SA 5005, Australia

(*) Corresponding author:

e-mail: petra.marschner@adelaide.edu.au

Tel +61 8 8313 7379

Fax +61 8 8313 6511

Abstract

Acid sulfate soils (ASS) are wide-spread in wetlands and experience distinct biogeochemical changes in wet and dry periods. During wet periods, under reducing conditions, sulfate reduction can result in an increase in pH whereas dry periods induce sulfide and ferrous iron oxidation, which may result in acidification which poses a threat to the environment. The present incubation experiment was carried out to determine the effect of organic matter (OM) over two successive wet-dry cycles in four ASS.

Four soils differing in clay content (10, 15, 23, 38% referred to as C10, C15, C23 and C38) were collected in a managed wetland complex (Banrock Station, South Australia). The experiment was conducted over 24 weeks with each wet and each dry period lasting 6 weeks. The soils were unamended or amended with 10 g C kg^{-1} finely ground wheat straw. During the wet periods, the soils were maintained under a layer of water, in the dry periods they were kept at 100% of water holding capacity (WHC).

The soil pH increased in both wet periods, particularly in amended soils with low clay content (C10 and C15). The redox potential (Eh) decreased more strongly in amended soils than in unamended soils and became negative from week 2 onwards whereas the Eh stayed positive in unamended soils except C38.

In the dry periods, the pH decreased more strongly in amended soils than in unamended soils, particularly in C10 and C15. Changes in pH during wet and dry periods were greater in soils with low clay content (C10, C15) than those with high clay content (C23, C38). The effect of wheat straw addition on pH at the end of wet and dry periods did not differ between the two wet-dry periods, with a higher pH in amended than unamended soils.

This study showed that wheat straw addition maintains its ameliorative effect on soil pH for at least two wet-dry cycles, but the pH ameliorative effect depends on clay content, being greater in soils with low clay content. The effectiveness of this method would have to be tested under field conditions, particularly where wet and dry periods continue for longer periods.

Keywords: acid sulfate soils; amelioration; clay content; organic C; pH; redox potential; wet-dry cycles

Introduction

Wetlands experience wet and dry periods that influence both vegetation and soil properties. In flooded conditions, soils become anaerobic triggering processes such as fermentation, denitrification, iron, manganese and sulfate reduction and methanogenesis (Reddy and Delaune 2008). Sulfate reduction is a particularly important process in wetlands because it can lead to formation of acid sulfate soils. ASS are soils in which sulfuric acid (H_2SO_4) may be produced in amounts that have a lasting effect on main soil characteristics (Pons 1973). Sulfate, dissolved in the pore and overlying water, is used as an electron acceptor by sulfate reducing bacteria, which require decomposable OM as an energy source. Sulfides can react with dissolved iron to form iron mono-(FeS) and di-sulfide (pyrite, FeS_2) via various mechanisms (Rickard and Luther 2007).

When ASS dry, pyrite may be oxidized, which can induce severe acidification in soils with insufficient acid neutralising capacity (ANC) and formulated as follows (Equation 1) (Fitzpatrick 2013, Fitzpatrick et al. 2009):

$4\ FeS_2 + 15\ O_2 + 14\ H_2O \rightarrow 4\ Fe(OH)_3 + 8\ SO_4^{2-} + 16\ H^+$ (Equation 1)

The low pH together with acidification-induced metal release can have detrimental effects on both on surface and groundwater, biota and infrastructure (Berner 1985, Dent 1986, Dent and Pons 1995, van Breemen 1973). Management strategies aimed at preventing or minimizing acidification include liming or inundation. However, they may not be practically possible or economic and can be ineffective (Johnston et al. 2009).

After inundation, the pH may increase as a result of sulfate reduction which consumes protons (Ponnamperuma 1972). However, this is often not the case, even when the pH is raised to levels above that inhibiting sulfate reducers (Jayalath et al. 2015, Yuan et al. 2015a). This suggests that other factors are limiting sulfate reduction. Sulfate reducers are heterotrophs, and therefore require available organic carbon. Addition of decomposable OM stimulates sulfate reduction under flooded conditions and has also been shown to minimize acidification in dry ASS (Jayalath et al. 2015, 2016a, Yuan et al. 2015a). However, amelioration of ASS through OM addition relies, at least partly, on OM decomposition. Thus, its effect may diminish with time as less and less of the added OM remains. In our previous studies (Jayalath et al. 2015, 2016a, Yuan et al. 2015a), ASS were exposed to only one or two wet periods separated by a dry period. It is not clear if the initially added OM can also minimize acidification in a second dry period. Understanding the effectiveness of OM in ameliorating ASS over time is important because it informs scheduling of OM additions.

The aim of this study was to determine the effect of OM added at the start of the experiment on pH in two successive wet-dry cycles and how this is related to soil properties such as clay content and pH buffer capacity (pHBC). We hypothesised that (¡) the change in soil pH is greater in soils with low compared to high clay content because the latter have a greater pHBC, and (¡¡) the effect of OM addition on soil pH (stimulating pH increase in the wet period and minimizing pH decrease in the dry period compared to the unamended soil) is greater in the first than the second wet-dry cycle.

Materials and Methods

Soils

The soils were collected in the Banrock Station wetland, South Australia (34°1150S, 140°2020E), which is a Ramsar designated wetland of international importance. Acid sulfate soils are wide-spread in the wetland which was permanently inundated from 1925 after the construction of Lock 3 on the River Murray. From 2001 to 2009, southern Australia experienced a severe drought during which large parts of the wetland dried and water tables lowered. As a consequence, pyrite was oxidised leading to sulfuric soils (pH < 4) (Fitzpatrick et al. 2015). With the aim of improving wetland health, the wetland managers introduced 6-monthly wet-dry periods. The four soils were collected from two different soil profiles during a dry period in 2013 (Fitzpatrick et al. 2015) (Tables S1). Soil profile 1 (RBAc-01) was at the edge of the wetland 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 (IUUS working group WRB 2014). The second profile (RBAc-06) was located closer to the lower lying lakebed. It is classified as a Hyposulfidic soils in the Australian ASS classification key (Fitzpatrick 2013) and Oxygleyic Gleysol (Drainic, Hyposulfidic) in the World Reference Base for Soil Resources (IUUS working group WRB 2014). The soils were air-dried and stored until the start of the experiment. Based on their clay content, the soils are referred to as C13, C15, C23 and C38 (Table 1).

Experimental design

The experiment comprised of two wet (reduced) and dry (oxidised) cycles, with each period lasting 6 weeks. Thirty grams of soil (dry weight equivalent), sieved to < 2 mm, was placed in 70 ml plastic vials and mixed thoroughly with mature wheat straw at 10 g of C kg $^{-1}$ (total organic Carbon -TOC) 423 g kg^{-1}, C/N 108, ANC 0.3 % $CaCO_3$ equivalent, finely ground and sieved to < 2 mm). Controls without wheat straw were mixed in a similar manner. This C addition rate was selected based on earlier studies in our group in which sulfuric soils were incubated submerged (Yuan et al. 2015a). In those studies, addition of 20 g residue kg^{-1} increased sulfate reduction compared to the unamended control. The organic C concentration of plant residues is about 50%, therefore a rate of 10 g C kg^{-1} is equivalent to 20 g residue kg^{-1}. There were four replicates per treatment and soil. To initiate the wet period, reverse osmosis water was added to the vials followed by thorough mixing. Then, more water was added until the soil surface was covered by a 2 cm water layer, which was maintained throughout the wet period. After closing the lids tightly, the vials were incubated in the dark at 25℃. Soil pH and the Eh were measured fortnightly. To initiate the dry period, the overlying water was removed and the soils dried in a fan forced oven at 30℃ until a water content equivalent to 100% WHC was reached. The required drying time depended on the clay content of the soil, ranging from about 3 h in C10 to 24 h in C38. This water content was maintained by weight throughout the dry period by adding water if required. In previous studies, we found that 100% WHC provides sufficient moisture and oxygen for pyrite oxidation, whereas oxidation is inhibited at 40% WHC (Jayalath et al. 2016a). This is in agreement with previous studies (Chandra and Gerson 2011, Fennemore et al. 1998), which showed that pyrite oxidation can be reduced in dry conditions because of lack of sufficient moisture. To ensure adequate gas exchange, the lids were only placed loosely on the vials. Soil pH was measured fortnightly.

Analyses

Initial soil properties

Soil pH was measured in a 1:1, soil: water slurry. Total C and Nitrogen (N) of soils and wheat straw were determined by dry combustion with a LECO Trumac C and N analyser. Soil particle size distribution was determined by the hydrometer method (Gee and Or 2002). Maximum WHC was determined using a sintered glass funnel connected to a 1 m water column (-10 k Pa) according to Haines (1930). ANC was determined as described in Ahern and McElnea (2004). The percentage of air filled pore space during the dry period was calculated using porosity and volumetric water content. Soil pHBC was determined following Aitken and Moody (1994). Available N was extracted by shaking soil with 2 M KCl (potassium chloride) solution at a soil: solution ratio of 1:5 for one hour at 200-300 rpm. The suspension was filtered through Whatman filter paper No. 42. Ammonium was measured colorimetrically at 685 nm as described by Willis et al. (1996). Nitrate in the 2 M KCl extracts was determined at 540 nm using a modification of Miranda et al. (2001) as described in Cavagnaro et al. (2006). Reduced inorganic sulfur (RIS) (mainly

FeS_2, pyrite) was measured as chromium reducible sulfur (Ahern and McElnea 2004) at the start and the end of the experiment.

During the experiment

Soil pH and Eh were measured during the wet periods by insertion of the electrodes directly into the inundated soil to about 1 cm depth. Similarly, the pH in the dry period was measured by insertion of the pH electrode into the dry soil to a depth of about 1 cm. After measurement, the hole made by the electrode was closed using surrounding soil, and water was added if required. Measurement of pH and redox potential was non-destructive, thus the same vial was measured throughout the experiment.

For statistical analysis, initial soil properties and pH and redox data at the end of each period were subjected to two-way analysis of variance (ANOVA) with fixed factors soil and amendment treatment (GenStat for Windows 17, VSN International Ltd).

Results

Soil properties

Soil C10 had the lowest pH (4.1), WHC, clay content and total Fe (iron) concentration and no measurable ANC (Table 1). Soil C15 had the highest ANC and RIS content. Although the clay content of C23 was twice as high as in C10, the two soils had a similar low pHBC. Soil C23 had the highest pH (6.9) and the lowest TOC content. WHC, clay content, total organic nitrogen (TON) and Fe concentrations were highest in C38.

The pHBC in amended soils was 2-3 fold greater than in unamended soils (Table S2). Ammonium N was the dominant inorganic N form at the start of the experiment in all soils (Table S3). In unamended soils, the ammonium concentration was lowest in C23 and highest in C38. Addition of wheat straw increased the ammonium concentration in all soils.

First wet period

The initial pH was lowest in C15 and highest in C38, but in a given soil did not differ between amendment treatments (Figure 1). The pH of unamended C10, C15 and C23 remained stable during the six weeks of the first wet period, but increased in the first two weeks by 0.5 unit in C38. The pH of the amended soils increased during the first wet period with the strongest pH increase in C15 (2 units) and very small increases in C23 and C38 (< 0.5 units). From week 2 onwards, the pH was >1 unit higher in amended than unamended C10 and C15. In C23, the pH of the amended treatment was higher than the unamended control only in weeks 4 and 6, by 0.5 and 1 unit, respectively. In C38, the pH of unamended and amended treatments did not differ except in week 2 when it was approximately 0.5 units higher in the unamended control. At the end of the first wet period, the pH was > 2 units higher in amended compared to unamended C10 and C15 (pH 5.6 and 5.7, respectively), but, was only 0.7 units higher in amended C23 and did not differ between amended and unamended treatments in C38 (Table S3).

At the start of the first wet period, the Eh was similar in all four soils (Figure 2). In unamended C10 and C15, the Eh slightly increased whereas it dropped below zero in the first two weeks in amended treatments and stayed at this level until week 6. In unamended C23, the Eh was stable until week 4 and then dropped to close to zero in week 6. In amended C23, the Eh decreased to below zero in the first four weeks and then remained stable. In C38, the Eh in amended and unamended treatments decreased to below zero in the first two weeks and then decreased slightly until week 6. At the end of the first wet period, there were large differences in Eh between amended and unamended treatments in C10, C15 and C23, but the two amendment treatments did not differ in Eh in C38.

First dry period

The percentage of air-filled pores at 100% WHC was greatest in C10 (68%) followed by C15 (50%) and C38 (46%), and lowest in C23 (32%) (Table S5). The pH at the start of the first dry period of amended C10 and C15 soils was 6 and 5, respectively, about two units higher than in unamended treatments (Figure 1). In C23, the initial pH of the amended soil was about one unit higher (pH about 6) than in the unamended treatment, whereas there was no difference between amendment treatments in C38 (pH about 6). In amended C10, C15 and C38, the strongest pH decrease occurred in the first two weeks whereas in C23, the pH decrease was gradual throughout the first dry period. The pH in the unamended C10, C15 and C23 changed little in the first dry period. At the end of the first dry period, the pH was 0.2-0.5 units higher in amended C10 and C15, but did not differ between amended and unamended C23. In C38, changes in pH during the dry period were similar in amended and unamended treatments. In the first two weeks, the pH decreased by about one unit followed by a smaller pH decrease until week 6. At the end of the first dry period, the pH did not differ between amended and unamended treatments (Table S6).

Second wet period

The pH at the start of the second wet period was higher in amended and unamended soils except in C23 (Figure 1). The pH was highest in C38 and lowest in C15. In unamended C10, C15 and C23, the pH changed little during the second wet period. But the pH increased in amended C10 and C15 by two units and in C23 by one unit by the end of the wet period. In C38, the pH increased by about 0.5 units in amended and unamended treatments but was 0.4 units higher in amended than unamended soil at the end of the second wet period. Compared to the end of the first wet period, the pH at the end of the second wet period in unamended C10 and C23 was about 0.3 units higher, did not differ in C15 and was 0.7 units lower in C38. In amended soils, the pH at the end of the second wet period was about 0.5 units lower in C10 and C15, 0.7 units higher in C23 and did not differ in C38. Nevertheless, the pH was higher in amended than unamended treatments at the end of the second wet period.

The initial Eh in the second wet period was similar in all soils and did not differ between amended and unamended treatments (Figure 2). In all soils, the Eh decreased more strongly in amended than unamended treatments. In unamended C10, the Eh decreased slowly in the first four weeks and then more rapidly from week 4 to week 6. The Eh decreased gradually in unamended C15 and C 23, but the Eh decrease was very small in C15 (< 100 mV), whereas Eh decreased by about 300 mV in unamended C23. In unamended C38, the Eh decreased by about 250 mV in the first two weeks and then remained just below zero until the end of the second wet period. In all amended soils, the Eh decreased more strongly in the first two weeks than later with a greater decrease in C10 and C23 (by about 500 mV) than in the other two soils. At the end of the second wet period, Eh was 150-200 mV lower in amended than unamended treatments (Table S4). Compared to the end of the first wet period, the Eh was lower in all amended soils at the end of the second wet period.

Second dry period

The pH at the start of the second dry period was about 1.5 units higher in amended compared to unamended C10, C15 and C23, but was only slightly higher in C38 (Figure 1). The pH changed little in unamended C10, but decreased by 0.5 to 1 unit in the other unamended soils. In amended C15, C23 and C38, the pH decreased by about 1 to 1.5 units in the first two weeks and then stabilised. At the end of the second dry period compared to the unamended treatments, the pH was 0.9, 0.6 and 0.4 units higher in amended C10, C15 and C23, respectively (Table S6). There was no difference in final pH between amended and unamended C38. In amended soils compared to the end of the first dry period, the pH was 0.1 to 0.6 units higher at the end of the second dry period. Compared to the start of the experiment, the pH at the end of the second dry period was about 0.5 units lower in all unamended soils and amended C38, but did not differ in amended C10, C15 and C23.

The RIS concentration at the start and the end of the experiment was very low in C10, C23 and C38 (Table S7). In C15, which had a much higher RIS concentration at the start of the experiment than the other soils the RIS concentration decreased by a factor of 3-6 during the experiment, with the stronger decrease in the unamended than the amended treatment.

The initial KCl and HCl-extractable S concentrations were highest in C10 and lowest in C38 (Table S8). The concentration of KCl extractable S was greater than that of HCl-S. Both KCl and HCl-extractable S concentrations decreased by 50% or more during the experiment, except HCl extractable S in C38, which decreased only by about 25%.

Discussion

This experiment confirmed our earlier studies that addition of organic C to ASS stimulates a pH increase during the wet period, which in turn results in a higher pH at the end of the dry period (Jayalath et al. 2015, 2016a). However, the present study adds new information to the previous work by demonstrating that the ameliorative effect of OM addition prevails for at least two wet-dry cycles and its effect is dependent on the clay content of the ASS.

The results confirm the first hypothesis because the pH increase in amended soils in both wet and dry periods was greater in soils with low (C10 and C15) compared to high clay content (C38). This could be due to the pHBC of clay (Dent 1986, Lottermoser 2010). However, measured pHBC was similar in C10 and C23 although the clay content was more than two-fold greater in C23. It is likely that the higher TOC content of C10 (6 compared to 2 g kg^{-1} in C23) also contributed to the measured pHBC. It is unclear why, nevertheless, the pH changes during the experiment were greater in C10 than C23. The smaller pH change in amended C23 and particularly C38 compared to C10 and C15 can be explained by the pHBC of the clay, but may also be due to reduced accessibility of the added OM to soil microbes. Clay surfaces can bind native OM (Baldock 2007, Lützow et al. 2006) and thereby reducing its accessibility to soil microbes which has also been shown for added OM (Shi and Marschner 2013, Yuan et al. 2015b). Compared to C23 and particularly C38, in soils with low clay content (C10 and C15), a larger proportion of the added OM would be accessible to decomposers in general, but also sulfate reducers, resulting in a stronger pH increase in the wet period.

The observed changes in pH were clearly related to the added wheat straw because the pH in the unamended soils changed little during the experiment. Unamended C10, C15 and C23 remained strongly acidic and unamended C38 stayed moderately acidic.

The pH increase in amended soils in the two wet periods was accompanied by appearance of black material, likely monosulfides, suggesting reduction of sulfate which consumes protons (Ponnamperuma 1972, Reddy and Delaune 2008). Reduction of Fe and manganese also consumes protons and may have contributed to the pH increase. These reduction reactions are catalysed by anaerobic heterotrophic microbes that require organic C as energy source. The stronger decrease in Eh in amended C10, C15 and C23 compared to unamended treatments in the wet periods confirms depletion of oxygen and other terminal electron acceptor by heterotrophic microbes consuming the added wheat straw and inducing reducing conditions. The exception was C38, where the decrease in Eh was similar in amended and unamended treatments. This may be due to the higher native TOC content in this soil compared to the others (Table 1), providing sufficient organic C available to heterotrophic microbes despite the high clay content.

The pH decrease in the dry periods can be explained by sulfide oxidation. Oxygen is the primary oxidant of pyrite, which leads to proton release, and pyrite oxidation is expresses as follows (Equation 2) (Pons 1973, van Breemen 1973):

$FeS_2 + 15\ O_2 + 14\ H_2O \rightarrow 4\ Fe\ (OH)_3 + 8\ SO_4^{2-} + 16\ H^+$ (Equation 2)

Protons are also generated by oxidation of FeS, which represent by the following formula (Equation 3 and 4) (Smith 2004):

$4\ FeS + 8\ O_2 \rightarrow 4\ Fe^{2+} + 4\ SO_4^{2-}$ (Equation 3)

$4\ Fe^{2+} + O_2 + \rightarrow 8\ H^+ + 4\ Fe\ (OH)_3$ (Equation 4)

Oxygen initiates oxidation, but at the low pH common in ASS, dissolved ferric iron (Fe^{3+}) becomes the primary oxidant e.g., Johnson and Hallberg (2005).

In aerobic soils, nitrification can also induce acidification, but it is unlikely that nitrification contributed to the pH decrease in the dry periods in our soils because the initial ammonium concentration and total N content are low in the soils used in this experiment (Tables S3). The pH decrease during the dry period was greater in amended than unamended soils, except in C38 where it did not differ between amendment treatments. The greater pH decrease is related to the higher pH at the start of the dry period in amended soils and may also be due to oxidation of FeS_2 and FeS, with the latter apparent only in amended soils. The strong pH decrease in amended soils during dry periods indicates that the increase in pH and pHBC induced by wheat straw addition (Table S2) did not prevent re-acidification, but reduced the extent of acidification relative to the unamended soils.

In a previous study (Jayalath et al. 2016b) soil C10 was mixed with different proportions of clayey soils (clay content 38-75%) with a range of net negative acidity (-8 to – 338 moles H^+ $tonne^{-1}$). After addition of OM at the same rate as in the present experiment, the soil mixes were exposed to one wet-dry cycle. Clay soil addition minimized acidification in the dry period and the ameliorative effect was greater in clay soils with high net negative acidity. This indicates that in soils with high clay content, clay can buffer pH by binding protons. However, in that study, soils with a higher clay content than the present study were used and soils were only exposed to one wet-dry cycle.

The second hypothesis, that is, the effect of OM addition on soil pH is greater in the first than the second wet-dry cycle, has to be declined because the pH changes in the second wet and dry periods were similar or greater than in the first.

The pH increase induced by wheat addition in the second wet period was similar (C15) or greater (C10, C23, C38) than in the first wet period. The decrease in Eh in amended soils also did not differ between first and second wet period. This indicates that sufficient OM remained to be utilised by oxygen-consuming heterotrophs and reducing microbes in the second wet period. It is also possible that there were more sulfate reducers present at the start of the second wet period than at the start of the first because they multiplied in the first wet period. The greater pH increase in the second wet period cannot be due to a more favourable initial pH for sulfate reduction because the initial pH was similar (C10) or lower (C15, C23, C38) in the second compared to the first wet period.

In the first dry period the pH of amended soils dropped by 2-3 units and by the end of the first dry period, the pH was only slightly higher in amended than unamended soils. In the second dry period the pH decrease in amended soils was smaller (0.5 – 1.5 units) than in the first dry period and the pH at the end was 0.4 to 0.9 units higher in amended C10, C15 and C23 than unamended treatments. There are several possible explanations for the smaller pH decrease in the second dry period. The more decomposed OM compared to the first dry period may have had a greater pHBC (Beldin et al. 2007). This more decomposed OM or microbial metabolites may have chelated dissolved Fe^{3+} (Bronswijk et al. 1993) generated during pyrite oxidation and thus prevent it from oxidizing pyrite. It is also possible that aerobic microbes stimulated in the first dry period were still present at the start of the second dry period. Oxygen consumption by the greater biomass could limit sulfide oxidation.

The wet and dry periods in this experiment were only for 6 weeks each, which may be shorter than would occur in many natural or managed wetlands. This duration was selected because we had found in previous experiments with soils from the Banrock wetland that the main changes in pH and Eh in wet and dry periods occurred in the first six weeks (Jayalath et al. 2015, 2016a). A longer duration of wet-dry cycles will likely lead to stronger decomposition of the added OM, potentially reducing the ability to sustain the ameliorative effects over multiple cycles.

The initial pyrite concentrations as indicated by RIS values was low in all soils except C15 (Table 1). It was low in all soils at the end of the experiment. This indicates that although wheat straw addition stimulated sulfate reduction, this did not lead to an accumulation of pyrite during the experiment, likely due to oxidation in the dry period. Pyrite accumulation would be undesirable because it would increase the acidification risk upon oxidation.

Conclusion

Wheat straw addition appears to be a suitable strategy to reduce acidification in ASS during repeated wet-dry periods. The effect of wheat straw on pH and Eh did not diminish in the second wet-dry cycle suggesting that the ameliorative effect lasts for at least two cycles. This would need to be confirmed in the field during wet and dry periods. A factor that may reduce the effectiveness in the field compared to that in this experiment is the particle size of the added wheat straw and the extent of mixing with the soil. In this study, the wheat straw was finely ground and mixed thoroughly with the soils. This will not be possible in the field where the particles of the added OM are likely to be larger and mixing with the soil rather limited. On the other hand, soils may dry completely during prolonged dry periods which would reduce pyrite oxidation rates and thus acidification.

Acknowledgment

We thank the wetland manager, Dr Christophe Tourenq of Banrock Station for permitting us to collect the soils in the Banrock Station wetland complex.

References

Ahern, C., Sullivan, L., McElnea A., 2004. Laboratory methods guidelines-acid sulfate soils, Queensland Acid Sulfate Soil Technical Manual, Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

Aitken, R., Moody, P., 1994. The effect of valence and Ionic-strength on the measurement of pH buffer capacity. Aust. J. Soil Res. 32, 975-984.

Baldock, J., 2007. Composition and Cycling of Organic Carbon in Soil. In: Marschner, P., Rengel, Z. (Eds.,), Nutrient Cycling in Terrestrial Ecosystems. Soil Biol. Springer Berlin Heidelberg, pp. 1-36.

Beldin, S. I., Caldwell, B, A., Sollins, P., Sulzman, E, W., Lajtha, K., Crow, S, E., 2007. Cation exchange capacity of density fractions from paired conifer/grassland soils. Biol. Fert. Soils, 43, 837-841.

Berner, R, A., De leewuw, J., Spiro, B., Murchison, D., Eglinton, G., 1985. Sulphate Reduction, Organic Matter Decomposition and Pyrite Formation-Discussion. Philos. T. Roy. Soc. A, 25-38.

Bronswijk, J., Nugroho, K., Aribawa, I., Groenenberg, J., Ritsema, C., 1993. Modeling of oxygen transport and pyrite oxidation in acid sulphate soils. J. Environ. Qual, 22, 544-554.

Cavagnaro, T., Jackson, L., Six, J., Ferris, H., Goyal, S., Asami, D., Scow, K., 2006. Arbuscular mycorrhizas, microbial communities, nutrient availability, and soil aggregates in organic tomato production. Plant Soil, 282, 209-225.

Chandra, A, P., Gerson, A., 2011. Pyrite (FeS2) oxidation: a sub-micron synchrotron investigation of the initial steps. Geochim. Cosmochim. Acta, 75, 6239-6254.

Dent, D, L., 1986. Acid sulphate soils : a baseline for research and development. ILRI, Wageningen, Netherlands. P 39.

Dent, D, L., Pons, L, J., 1995. A world perspective on acid sulphate soils. Geoderma, 67, 263-276.

Fennemore, G., Neller, W., Davis, A., 1998. Modeling pyrite oxidation in arid environments. Environ. Sci. Technol, 32, 2680-2687.

Fitzpatrick, R., Shand, P., Merry, R., 2009. Acid Sulfate Soils. In: Natural History of the Riverland and Murraylands. Jennings, J, T. (Ed.,), Royal Society of South Australia, Adelaide, South Australia. pp. 65-111.

Fitzpatrick, R., 2013. Demands on Soil Classification and Soil Survey Strategies: Special purpose soil classification systems for local practical use. In: Shahid, S, A., Taha, F, K., Abdelfattah, M, A. (Eds.,), Developments in Soil Classification, Land Use Planning and Policy Implications: Innovative Thinking of Soil Inventory for Land Use Planning and Management of Land Resources. Springer-Verlag, London. pp. 51-83.

Fitzpatrick, R., Shand, P., Merry, R., Marschner, P., Jayalath, N., Grocke, S., 2015. Acid sulfate soil assessment and monitoring of the Banrock Station Wetland (managed wetland- drying cycle). Acid sufate soils centre: ASSC_035 (V12).

Gee, G, W., Or, D., 2002. Particle-Size Analysis. In: Dane, J, H., Topp, C, G. (Eds.,), Methods of Soil Analysis: Physical Methods 4, SSSA Book Series. J. Soil Sci. Soc. Am, pp. 255-293.

Haines, W, B., 1930. Studies in the physical properties of soil. V. The hysteresis effect in capillary properties, and the modes of moisture distribution associated therewith. J. Agric. Sci, 20, 97-116.

IUUS working group WRB., 2014. World Reference Base for Soil Resources: international soil classification system for naming soils and creating legends for soil maps. World Soil Res Report ,106 , FAO, Rome. http://www.fao.org/3/a-i3794e.pdf.

Jayalath, N., Fitzpatrick, R, W., Mosley, L., Marschner, P., 2015. Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions. J. Soils Sediments, 16, 518-526.

Jayalath, N., Fitzpatrick, R, W., Mosley, L., Marschner, P,. 2016a. Addition of organic matter influences pH changes in reduced and oxidised acid sulfate soils. Geoderma, 262, 125-132.

Jayalath, N., Fitzpatrick, R, W., Mosley, L., Marschner, P., 2016b. Addition of clayey soils with high net negative acidity to sulfuric sandy soil can minimize pH changes during wet and dry periods. Geoderma, 269, 153-159.

Johnson, D, B., Hallberg, K, B., 2005. Acid mine drainage remediation options: a review. Sci. Total Environ. , 338, 3-14.

Johnston,S, G., Keene, A, F., Bush, R, T., Burton, E, D., Sullivan, L, A., 2009. Remediation of coastal acid sulfate soils by tidal inundation: effectiveness and geochemical implications, 18th NSW Coastal Conference, Ballina, NSW.

Lottermoser, B., 2010. Mine Wastes: Characterization, Treatment and Environmental Impacts. 3 rd edn Springer Science & Business media, Springer-Verlag, Berlin Heidelberg.

Lutzow, M., Kogel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions- a review. Eur. J Soil Sci. 57(2), 426-445.

Miranda, K, M., Espey, M, G., Wink, D, A., 2001. A rapid simple spectrophotometric method for simultaneous determination of nitarte and nitrite. Nitric Oxide, 5, 62-71.

Ponnamperuma, F, N., 1972. The chemistry of submerged soils. Adv Agro, 24, 29-96.

Pons, L., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils, Proc. Int. Symp. Acid sulphate soils 1st. ILRI Publ, pp. 3-27.

Reddy, K, R., DeLaune, R, D., 2008. Biogeochemistry of Wetlands: Science and Applications. CRC press, 2008.

Rickard, D., Luther, G.W., 2007. Chemistry of Iron Sulfides. Chem. Rev. 107(2), 514-562.

Shi, A., Marschner, P., 2013. Addition of a clay subsoil to a sandy top soil alters CO2 release and the interactions in residue mixtures. Sci. Total Environ. 465, 248-254.

Smith, J., 2004. Chemical changes during oxidation of iron monosulfide-rich sediments. Soil Res. 42 (6), 659-666.

Soil survey staff 2014. Keys to soil taxonomy. 12th edn. USDA-Natural Resources Conservation Service, Washington.

van Breemen, N., 1973. Soil forming processes in acid sulphate soils. In: Dost H (ed.,), acid sulphate soils ICRI publi. 18, 1973, Wegeningen, The Netherlands. 1, pp. 66-130.

Yuan C., Mosley, L, M., Fitzpatrick, R., Marschner, P., 2015a. Amount of organic matter required to induce sulfate reduction in sulfuric material after re-flooding is affected by soil nitrate concentration. J Environ Manage, 51, 437-442.

Yuan C., Fitzpatrick, R., Mosley, L, M., Marschner, P., 2015b. Sulfate reduction in sulfuric material after re-flooding: effectiveness of organic carbon addition and pH increase depends on soil properties. J. Hazard Mater. 298, 138-145.

Table 1. Collection depth, pH, total organic C, total N, maximum water holding capacity (WHC), particle size distribution, acid neutralising capacity (ANC) pH buffer capacity (pHBC), Total Fe and reduced inorganic sulfur (RIS) in soils C10, C15, C23 and C38.

Soil profile	Soil	Australian ASS Classification[1]	Depth	pH	Max. WHC	Sand	Silt	Clay	ANC	pHBC m mole kg^{-1} pH^{-1}	Total organic C	Total N	Total Fe	RIS
			cm	1:1	g g^{-1}		%		% $CaCO_3$				g kg^{-1}	
1	C10	sulfuric	5-20	4.1	0.08	85	5	10	0	13	6	0.4	96	<0.05
1	C15	Hypersulfidic	20-30	5.3	0.13	85	0	15	0.4	27	8	0.4	134	0.28
1	C23	Hyposulfidic	50-65	6.9	0.14	70	7	23	0.2	13	2	0.2	324	<0.05
2	C38	Hyposulfidic	0-1.5	5.9	0.23	58	4	38	0.2	70	22	2.1	557	<0.05

[1] See Fitzpatrick (2013) and Fitzpatrick et al. (2015). For further details about classification, see Table S1.

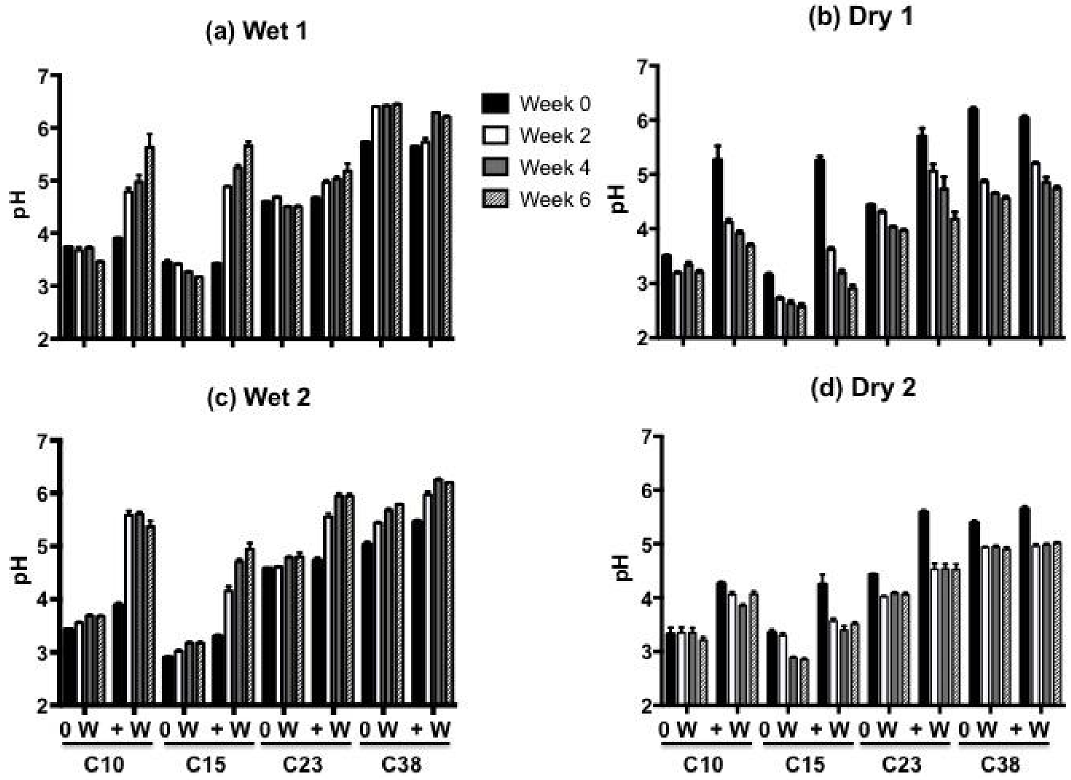
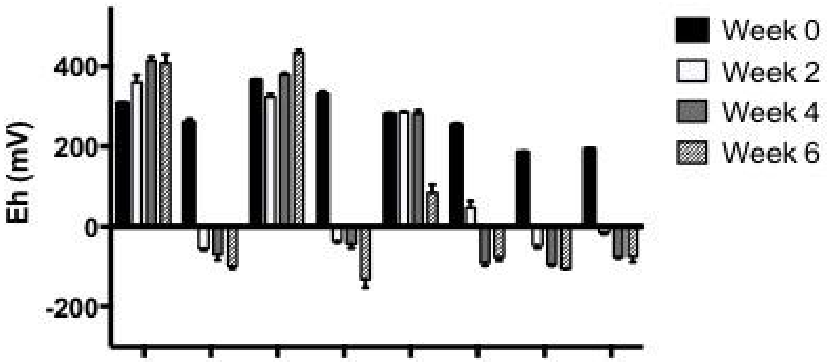


Fig. 1. pH of soils C10, C15, C23 and C38 without and with 10 g C kg^{-1} as wheat straw in first wet (a), first dry (b), second wet (c) and second dry period (d) (n=4).

(a) Wet 1



(b) Wet 2

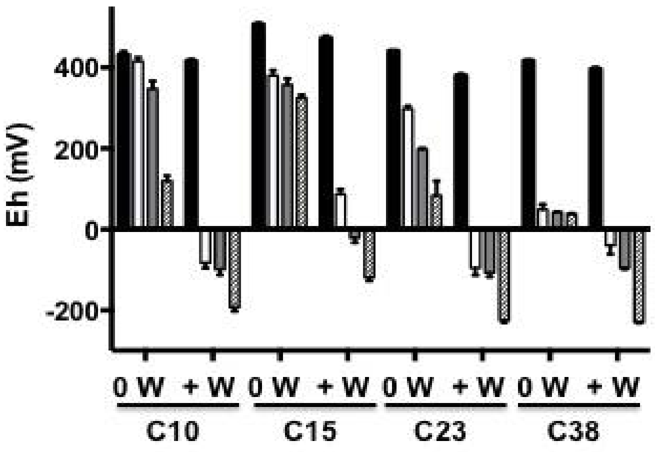


Fig.2. Redox potential (Eh) of soils C10, C15, C23 and C38 without and with 10 g C kg^{-1} as wheat straw in first (a) second (b) wet period (n=4).

Table S1. Classification of profiles from which the soils used in the study were taken.

Profile	Australian ASS Classification[1]	Soil Taxonomy[2]	World Reference Base[3]
RBA c 1	Sulfuric soil	Typic Sulfaquept	Hypothionic Gleysol (Drainic, Hypersulfidic)
RBA c 6	Hyposulfidic clay[4]	Typic Hydraquent	Oxygleyic Gleysol (Drainic, Hyposulfidic)

[1] Fitzpatrick (2013) and Fitzpatrick et al. (2015).

[2] Acid sulfate soil profile classification used in Soil Taxonomy (Soil Survey Staff, 2014)

[3] IUSS Working Group WRB (2014): World Reference Base for Soil Resources 2014. World Soil Res. Report 106, FAO, Rome. http://www.fao.org/3/a-i3794e.pdf

[4] By definition, 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 (IUUS working group WRB 2014) that adequately describes these hyposulfidic clayey soils as being acid sulfate soils because they do not qualify as having "sulfidic material" as defined in Soil Taxonomy and (ii) the term "hyposulfidic material" does not exist in Soil Taxonomy. Consequently, these hyposulfidic clayey soils are classified as Typic Hydraquents in Soil Taxonomy.

Table S2. pH buffer capacity (pHBC) of soils C10, C15, C23 and C38 without (-) and with (+) 10 g C kg^{-1} as wheat straw.

Soil	Wheat	pHBC
C10	-	13
	+	27
C15	-	27
	+	44
C23	-	13
	+	33
C38	-	70
	+	132

Table S3. Initial NO_3^- and NH_4^+ concentrations in soils C10, C15, C23 and C38 without (-) and with (+) 10 g C kg^{-1} as wheat straw.

		mg N kg^{-1}	
		NO_3^-	NH_4^+
Soil	Wheat		
C10	-	0.3	9.3
	+	0.3	14.5
C15	-	0.3	12.2
	+	0.3	12.7
C23	-	0.3	5.8
	+	0.3	7.3
C38	-	0.4	13.9
	+	0.4	15.7

Table S4. pH and Eh in soils C10, C15, C23 and C38 without (-) and with (+) 10 g C kg^{-1} as wheat straw at the end of the first and second wet periods (6 weeks each). Within each period, values followed by different letters are significantly different (n=4, P≤ 0.05).

		Wet 1		Wet 2	
Soil	Wheat	pH	Eh (mV)	pH	Eh (mV)
C10	-	3.46 a	414 d	3.68 b	120 d
	+	5.63 c	-70 ab	5.37 d	-193 ab
C15	-	3.17 a	380 d	3.17 a	325 e
	+	5.66 cd	-44 b	4.95 c	-120 b
C23	-	4.50 b	282 c	4.80 c	83 cd
	+	5.18 c	-92 a	5.94 ef	-225 a
C38	-	6.45 e	-95 a	5.79 e	39 c
	+	6.21 de	-77ab	6.20 f	-230 c

Table S5. Calculated percentage of air filled pores in soil soils C10, C15, C23 and C38 at the end of the first and second dry periods (6 weeks).

	Percentage of air filled pores
Soil	Dry period
C10	68
C15	50
C23	32
C38	46

Table S6. pH in soils C10, C15, C23 and C38 without (-) and with (+) 10 g C kg^{-1} as wheat straw at the end of the first and second dry periods (6 weeks). In each dry period, values followed by different letters are significantly different (n=4, P≤ 0.05).

		Dry 1	Dry 2
Soil	Wheat	pH	
C10	-	3.2 b	3.2 b
	+	3.7 c	4.1 d
C15	-	2.6 a	2.9 a
	+	2.9 b	3.5 c
C23	-	4.0 cd	4.1 d
	+	4.2 d	4.5 e
C38	-	4.6 e	4.9 f
	+	4.7 e	5.0 f

Table S7. Reduced inorganic sulfur (RIS) concentration in soils C10, C15, C23 and C38 without (-) and with (+) 10 g C kg^{-1} as wheat straw at the beginning of the experiment and at the end of the second dry period (n=1).

		RIS (g kg^{-1}) in soil	
Soil	Treatment	Initial	End of dry period
C10	control	<0.05	<0.05
	Wheat	0.06	0.05
C15	control	0.28	0.05
	wheat	0.28	0.09
C23	control	<0.05	<0.05
	wheat	<0.05	<0.05
C38	control	<0.05	<0.05
	wheat	<0.05	<0.05

Table S8. HCl-S and KCl-S concentration in soils C10, C15, C23 and C38 without (-) and with (+) 10 g C kg^{-1} as wheat straw at the beginning of the experiment and the end of the second dry period.

		Initial	End	Initial	End
		HCl-S		KCl-S	
Soil	Wheat	mg S g^{-1}			
C10	-	1.5	0.3	1.8	0.7
	+	1.4	0.5	1.8	0.8
C15	-	1.0	0.8	1.5	1.0
	+	1.0	0.2	1.5	1.2
C23	-	1.2	0.4	1.9	0.8
	+	1.2	0.6	1.6	0.7
C38	-	0.4	0.3	0.8	0.3
	+	0.4	0.3	0.8	0.3

CHAPTER 6. Conclusions and future work

Conclusions and future work

In environments such as wetlands that are exposed to wet-dry cycles, ASS can pose a threat to the environment as they can acidify in the dry period and may remain acidic when rewetted. On the other hand, wet-dry cycles are important for sustainable management of wetland flora and fauna.

OM plays an important role in the biogeochemistry of ASS as an energy source for sulfate reducers and pH buffer (Berner, 1984; Ponnamperuma, 1972; Reddy and DeLaune, 2008). Previous studies showed that OM addition to oxidized ASS can enhance sulfate reduction under reducing conditions (Michael et al., 2015; Yuan et al., 2015b). When sulfidic ASS are exposed to O_2, OM addition can minimise acidification (Yuan et al., 2015b; Yuan et al., 2015a). These studies were carried out over either a single wet period or a single dry period. However, to maximise the beneficial effects of OM additions in ASS, particularly those exposed to wet-dry cycles, more information is required about (¡) the influence of OM composition on pH during wet periods, (¡¡) effect of water content during the dry period on pH, and (¡¡¡) the duration of the OM effect during successive wet-dry cycles.

It may be possible to enhance the beneficial effect of OM addition in ASS by combining it with other management options. Wetland soils can have clay-rich layers at depth, which may provide buffer capacity when added to sulfuric sandy top soil because clay minerals have a high CEC and could therefore bind protons (Ahern et al., 2004). However, studies are needed to assess how the capacity to buffer the pH is influenced by clay soil properties and how much clay soil has to be added to a sulfuric sandy soil to increase the pH sustainably.

The experiments described in this thesis addressed these knowledge gaps.

The experiment described in Chapter 2 confirmed that addition of wheat straw to ASS increased soil pH and lowered Eh compared to unamended soil during a wet period, but also showed that OM addition minimised acidification in the following dry period. Although there was no measurable increase in sulfide with OM addition, it is likely that sulfate and other reduction reactions (e.g. nitrate, Fe oxides) were stimulated by OM and contributed to the pH increase. Further, the initial OM addition stimulated pH increase in the second wet period, but to a lesser extent than in the first. Water content during the dry period influenced acidification. The soils acidified less at 40% of maximum WHC than at higher water contents. This suggests that O_2 diffusion into the soil was sufficient to induce sulfide oxidation at water contents > 40% of maximum WHC. But at 40% of maximum WHC, water limited pyrite oxidation. This suggests that rapid drying to very low water contents can minimize acidification during dry periods. In wetland management, this may be achieved by initialising dry periods in hot and dry weather and draining the wetland quickly. In the other experiments described in this thesis, the water content during the dry period was maintained at 100% of maximum WHC to maximize acidification potential.

Decomposability of OM depends on its chemical composition, particularly C forms and C/N ratio. As a rule, OM with a high proportion of simple C compounds such as sugars are more rapidly decomposable than those in which complex compounds such as cellulose dominate (Sylvia, 1999). Further, OM with high N concentration (low C/N ratio) is decomposed more rapidly than OM with low N concentration (high C/N ratio) because the former can satisfy the N demand of soil microbes (Tian et al., 1992; Vanlauwe et al., 1996). Therefore, OM types may differ in suitability as an energy source for sulfate reducers. Most previous studies were carried out with a single OM type. In the experiment described in Chapter 3, 10 g C kg^{-1} was added as glucose, wheat straw, pea straw or Phragmites litter (C/N of plant residues 109, 58 and 28, respectively). The three ASS materials were exposed to one wet-dry cycle. During the wet period, all OM types induced a drop in Eh compared to the unamended control, but only the plant residues increased the pH by up to 2 pH units. In the following dry period, the pH decreased over time in the residue-amended soils whereas it remained stable in the control and the glucose-amended soils. However, at the end of the dry period, the pH in the residue amended soils was 0.5-1 unit higher than in the control. These results suggest that glucose is not a suitable OM amendment in ASS, probably because it is rapidly decomposed by soil microbes that grow more rapidly than sulfate reducers. The plant residues on the other hand provide a more sustained C source because they are decomposed more slowly. The effect of the plant residues on soil pH did not differ greatly, but Phragmites amended soil generally had the highest pH which suggests that low C/N residues are particularly useful amendments for management of wetland ASS.

In the experiment described in Chapter 4, a sulfuric sandy soil was mixed with three hyposulfidic clay soils (with clay contents ranging between 38 and 72% and net negative acidity from 8 to 334 moles H^+ tonne $^-$) to give clay soil proportions of 0, 25, 50, 75 and 100 (% dry soil). 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. At the end of the wet period, the pH was similar in all treatments. 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 results indicate that 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. Therefore, clay soils with high negative net acidity could be used to ameliorate acidity in acid sulfate soils with sulfuric materials. If such clay soils are present in the deeper soil horizons within the wetland, they could be mixed into sulfuric topsoil by delving or spading. Another option may be using clay soils from the surrounding areas. However, field studies are needed to assess if such profound changes to the soil profile are economical and do not have other undesirable effects, e.g. on water relations.

The experiment in Chapter 5 was conducted to explore the influence of OM addition on soil pH over two consecutive wet-dry cycles in a range of soils differing in clay content. Four soils differing in clay content (10, 15, 23, 38% referred to as C10, C15, C23 and C38), unamended or amended with 10 g C kg^{-1} finely ground wheat straw, were exposed to two wet-dry cycles with each wet and each dry period lasting 6 weeks. In OM amended soils, the pH increased in both wet periods and decreased in the dry periods, with greater changes in the soils with low clay content (C10 and C15). The effect of wheat straw addition on pH at the end of wet and dry periods did not differ between the two wet-dry periods, but was greater in soils with low clay content. This suggests that OM addition will be most effective in minimising acidification in soils with inherently low clay content (i.e., low pHBC), but will also lead to higher pH compared to unamended soils in soils with higher clay content.

The series of incubation experiments described in this thesis showed that OM addition could be used to minimise acidification in ASS exposed to wet-dry cycles. But they also suggested that the effect of OM depends on OM composition as well as soil properties such as clay content and net negative acidity whereas sulfide concentration appears to be less important.

However, the laboratory-based studies in this thesis also had a number of limitations in terms of the applicability of the results for ASS management, specifically:

1. The incubation studies set up to maximise the effect of OM and clay soil addition by using finely ground soil and OM. To be more realistic larger OM particles could be mixed only into the top soil layer only to mimic tillage or as a strip placed deeper in the soil

2. The experiments were conducted only with soils from one wetland which are unlikely to be representative of the wide range of ASS in other wetlands. Future studies could include similar experiments with soils from a range of wetlands differing in clay content, net negative acidity and reduced sulfur concentration

3. A limitation of the pH and Eh measurements was that they were carried out only fortnightly and by insertion of the probes which may have altered redox conditions in the soil. Future studies could use in-situ pH and Eh probes linked to data loggers for detailed monitoring under undisturbed conditions

4. Another aspect that was not investigated in this thesis was if the ameliorative effect of OM addition was related to changes in microbial community composition and/or gene expression, particularly those of sulfate reducers. Future studies could study abundance and composition of genes involved in sulfate reduction such as *dsrAB* gene using real-time PCR (He et al., 2010) or microarray (He et al., 2007) in soils with and without OM addition.

5. Further laboratory incubation studies could provide more detailed information about mechanisms involved in the ameliorative effect of OM addition in ASS. However, to test if this is also a realistic ASS management option, field experiments should be conducted accompanied by economic and ecological analyses for comparison to other more conventional treatments such as limestone addition. These

experiments could initially be limited to ASS with properties which maximise the effect of OM addition and the most effective OM types. Later, they could be expanded to other ASS.

References

Ahern, C., Sullivan, L., McElnea, A., 2004. Laboratory methods guidelines-acid sulfate soils, Queensland Acid Sulfate Soil Technical Manual,Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

Berner, R, A., 1984. Sedimentary pyrite formation: An update. Geochim. Cosmochim. Acta 48(4), 605-615.

He, J.-Z., Liu, X.-Z., Zheng, Y., Shen, J.-P., Zhang, L.-M. 2010. Dynamics of sulfate reduction and sulfate-reducing prokaryotes in anaerobic paddy soil amended with rice straw. Biol. Fertil. Soils 46(3), 283-291.

He, Z., Gentry, T, J., Schadt, C, W., Wu, L., Liebich, J., Chong, S, C., Huang, Z., Wu, W., Gu, B., Jardine, P., Criddle, C., Zhou, J., 2007. GeoChip: a comprehensive microarray for investigating biogeochemical, ecological and environmental processes. ISME Journal 1(1), 67-77.

Michael, P, S., Fitzpatrick, R., Reid, R., 2015. The role of organic matter in ameliorating acid sulfate soils with sulfuric horizons. Geoderma 255–256, 42-49.

Ponnamperuma, F, N., 1972. The chemistry of submerged soils. Adv. Agron. 24, 29-96.

Reddy, K, R., DeLaune, R, D., 2008. Biogeochemistry of Wetlands: Science and Applications. CRC Press, 2008.

Sylvia, D, M. 1999. Principles and applications of soil microbiology. Prentice Hall, Upper Saddle River, N.J.

Tian, G., Kang, B., Brussaard, L., 1992. Biological effects of plant residues with contrasting chemical compositions under humid tropical conditions-decomposition and nutrient release. Soil Biol. Biochem. 24(10), 1051-1060.

Vanlauwe, B., Nwoke, O., Sanginga, N., Merckx, R., 1996. Impact of residue quality on the C and N mineralization of leaf and root residues of three agroforestry species. Plant Soil 183(2), 221-231.

Yuan, C., Mosley, L, M., Fitzpatrick, R., Marschner, P., 2015a. Amount of organic matter required to induce sulfate reduction in sulfuric material after re-flooding is affected by soil nitrate concentration. J. Environ. Manag. 151, 437-442.

Yuan, C., Fitzpatrick, R., Mosley, L, M., Marschner, P., 2015b. Sulfate reduction in sulfuric material after re-flooding: Effectiveness of organic carbon addition and pH increase depends on soil properties. J. Hazard. Mater. 298, 138-145.