Capacity of organic materials to retain metals and protons released from sulfuric acid sulfate soils

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Dedicated to my family

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ABSTRACT

Acid sulfate soils (ASS) contain the iron sulfide mineral rich in pyrite which is formed under waterlogged or subaqueous conditions. Upon drainage or disturbance, pyrite can be oxidised to produce sulfuric acid which results in soil acidification and metal release. When rewetted due to rainfall or irrigation, oxidised ASS release large amounts of acidity and soluble metals, predominantly Al and Fe, in ground and drainage water that pose a serious risk to ecosystems, agricultural productivity, human health and other assets.

Organic materials have been considered as a low-cost and friendly environment absorbent to reduce acidity and metal concentration in leachate from mine tailings and waste water. However, little is known about the potential of these materials to reduce leaching of protons and metals from sulfuric ASS drainage water and how retention is influenced by properties of the organic materials and form of amendment. Eight organic materials (two plant residues, compost and five biochars produced from a range of food stock sources and varied in production temperature) were used. The aims of this thesis were i) to study the effect of different organic materials on leaching protons and metals from sulfuric soil, ii) to assess the ability of different organic materials to remove protons and metals from ASS drainage water, and iii) to determine maximum capacity to retain proton and metals of a biochar.

In the first experiment, sandy sulfuric soil (pH 3.5), collected from Gilman in the Barker Inlet, South Australia, was used to study i) the effect of organic materials on leaching of protons and metals from the soil and ii) how is this influenced by properties of organic materials and amendment forms. The organic materials were either mixed into the soil or placed as a layer under the soil, at a rate of 15 g C kg^{-1}. Then, the soil columns (30 g soil) were leached four times with reverse osmosis (RO) water. In the unamended soil, 60-90% of total protons, Fe and

Al were released in the first leaching event with only small amounts being released in the three subsequent leachings. Addition of organic materials to the soil increased the pH of the leachate from 0.2 to 2.2 units, and reduced proton and metal leaching by 50-90%. Cumulative retention of protons, Fe and Al was highest in soil amended with eucalypt biochar and wheat biochar produced at 550 ˚C and 450 ˚C, respectively, but low in wheat straw and compost. Retention of Fe and Al was generally greater when mixing organic materials into the soil than when placed as a layer underneath the soil, but there was a little difference between amendment forms in proton retention. Proton retention was positively correlated with C concentration of the material, while Al and Fe retention was positively correlated with percentage of Aryl and O-Aryl groups and negatively correlated with percentage of O-Alkyl and Di-O-Alkyl groups.

Synthetic acid drainage water (pH 3, Al 2 mg L^{-1} and Fe 28 mg L^{-1}) based on the long term average of drainage water in an area dominated by ASS was used to investigate proton and metal retention by organic materials. In this experiment, drainage water was passed through cores which were filled with organic materials at a rate of 1.5 g C per core over four leaching events (45 ml/event). Biochar and compost increased the leachate pH by up to 4 units. Eucalypt and wheat biochar produced at 550 ˚C and 450 ˚C, respectively, had high retention capacity for protons, Al and Fe. The correlation between retention of protons, Al and Fe with properties of organic materials was similar as in the previous experiment. Retention was lower in organic materials with high release of native Al and Fe (compost, wheat straw) than those with low release.

Metal and proton concentration in ASS drainage water can vary substantially. The aim of the third experiment was to study retention capacity at high metal concentrations and assess their subsequent release by uncontaminated water. Drainage water was collected in the field in autumn (pH 3, Al 22 mg L^{-1} and Fe 48 mg L^{-1}). Cores with organic materials at 3.5 g dry wt/core were leached six times with drainage water followed by six leaching events with RO water.

When leached with drainage water, biochar and compost increased the leachate pH by up to 4.5 units and retained almost 100% of added protons. Biochars retained cumulatively over 90 % of added Al and Fe, whereas 50-80% of added Al and Fe was retained in wheat and pea straw. Less than 1% of retained protons and metals were released with subsequent leaching with RO water.

It is well-known that pH plays an important role in metal speciation, solubility and complexation. A batch experiment was conducted to assess the retention capacity of eucalypt biochar produced at 550 ˚C. The biochar was added at 1% (w/v) to solutions with varying concentrations of protons, Al and Fe and shaken for 24 h. In the absence of metals, the biochar had high proton retention, up to 0.035 mmol of acid was adsorbed in the material. The batch experiment with metals was carried out at pH 4 and pH 7 with Fe or Al at 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} M. It showed that the biochar had a high retention capacity for Al and Fe, at high concentrations over 80% of soluble metals was retained. In another experiment, both Al and Fe were added at different ratios, increasing concentrations of one metal did not reduce retention of the other.

It can be concluded that addition of eucalypt biochar and wheat biochar produced at 550 ˚C and 450 ˚C, respectively, can strongly reduce leaching of protons and metals from sulfuric soil and drainage water of acid sulfate soils. The retention of protons and metals to organic materials was strongly correlated with properties of organic materials.

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 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. I certify that no part of this work will, in future, be used in a submission in my name, for any other 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.

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LIST OF PUBLICATIONS

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2. Dang T, Mosley L, Fitzpatrick R, Marschner P (2015) Organic Materials Differ in Ability to Remove Protons, Iron and Aluminium from Acid Sulfate Soil Drainage Water. Water, Air, & Soil Pollution 226(11), 1-13.
3. Dang T, Mosley LM, Fitzpatrick R, Marschner P (2016) Organic materials retain high proportion of protons, iron and aluminium from acid sulphate soil drainage water with little subsequent release. Environmental Science and Pollution Research 23, 23582-23592.

CHAPTER 1

INTRODUCTION AND REVIEW OF LITERATURE

1.1 Introduction

Acid sulfate soils (ASS) are soils containing sulfidic materials or affected by transformations of iron sulfide minerals such as pyrite (Fitzpatrick et al. 2009). Under anaerobic conditions, sulfate is reduced by sulfate reducing bacteria, which reacts with dissolved iron to form iron sulfides. Oxidation of iron sulfides results in formation of sulfuric material (containing sulfuric acid), which if insufficient neutralising capacity is present causes strong acidification of the soils ($pH<4$) and their leachate (Attanandana and Vacharotayan 1986; Dent 1986; Pons 1973).

ASS can be found in coastal, inland, mine and wetland environments (Fitzpatrick and Shand 2009). The global extent of coastal ASS is estimated to be between 10^7 and 10^8 ha (Macdonald et al. 2011; Wim and Mensvoort 2005), but the world extent of inland ASS is unknown. In Australia, the estimated area of ASS is 215,000 km^2, of which coastal ASS occupy 58,000 km^2 and inland ASS 157,000 km^2 (Fitzpatrick et al. (2010).

Acidification of ASS poses an environmental threat for the surrounding environment. Management options for acidified ASS typically include increasing soil pH by liming or stimulation of sulfate reduction. Acid drainage water can also be limed, but may require large amounts to be added, which is costly and can cause environmental problems. Another option for treating acidic drainage water is the use of permeable reactive barriers that bind protons and metals.

In this literature review, the biogeochemistry of ASS is discussed with emphasis on acidification processes. This is followed by an outline of why organic materials could be used in permeable reactive barriers. Lastly, research aims and thesis structure are presented.

1.2 Biogeochemistry of acid sulfate soils

Reduction processes in saturated ASS

Sulfate reduction is a natural process occurring in saturated conditions in many lakes, wetlands, intertidal areas and coastal oceans. Prequisites for sulfate reduction are: presence of sulfate reducing bacteria, sulfate, organic C, iron and pH > 4.5 (Berner 1984; Dent and Pons 1995). If any of these factors is limiting, sulfate reduction is low or does not occur. Sulfate reducers are heterotrophs and require energy derived from organic matter. Initially, bacteria reduce dissolved sulfate to produce H_2S (Berner 1970; Rickard 1973).

$$2H^+ + 2CH_2O + SO_4^{2-} \rightarrow 2\,CO_2 + H_2S + H_2O \qquad (1)$$

H_2S then reacts with Fe^{2+} to precipate FeS, which can be converterted to pyrite. Pyrite formation consumes protons and therefore results in pH increase:

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

$$H_2S + FeS \rightarrow FeS_2 + H_2 \qquad (3)$$

$$4H_2S + 2Fe^{3+} \rightarrow 2FeS_2 + 6H_2O + H_2 \qquad (4)$$

Monosulfides (FeS) are less stable than pyrite, but may accumulate in some ASS environments.

Oxidation processes in dry ASS

When exposed to oxygen upon drainage of previously waterlogged soils, pyrite can be oxidised to produce sulfuric acid but if insufficient acid neutralising capacity is present will result in soil acidification (Attanandana and Vacharotayan 1986; Dent 1986; Pons 1973). Oxidation of monosulfides can also lead to water acidification and can deoxygenate water bodies (Bush et al. 2004). The low pH often induces leaching of major cations, such as Ca^{2+}, Mg^{2+}, dissolution of aluminosilicates, and release of soluble metals and metalloids causing toxicity to plants and microorganisms (Attanandana and Vacharotayan 1986; Dent 1986; Pons 1973; Rabenhorst and

Fanning 2002; Ritchie 1989). In soil with a low acid neutralising capacity (e.g. due to a low carbonate concentration) the pH may drop below 4 (Attanandana and Vacharotayan 1986; Dent 1986) or 2 (Dent and Pons 1995). Pyrite oxidation rate depends on temperature, pH, Eh, surface area of reactant pyrite and soil texture (Bigham and Nordstrom 2000).

Pyrite oxidation is catalysed by bacteria such as *Metallogenium* and *Thiobacillus* genus and results in production of H^+ (Ahern et al. 2004; Otero et al. 2008).

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (5)$$

$$2FeS_2 + 7.5O_2 + 7H_2O \rightarrow 2Fe(OH)_3 + 4SO_4^{2-} + 8H^+ \quad (6)$$

When the pH drops below 4.5 or 4, Fe^{3+} remaining in solution acts as an oxidant to accelerate pyrite oxidation (Ahern et al. 2004; Otero et al. 2008):

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (7)$$

ASS materials can be classified into sulfidic and sulfuric, while the taxonomic terms, potential and actual ASS respectively, have been used in land management for general communication purposes (Fanning 2002). Sulfidic or potential ASS materials contain iron sulfides (pyrite) or monosulfides and are commonly found in waterlogged soil layers. More recently, sulfidic materials have been classified as hypersulfidic material, hyposulfidic material and monosulfidic material in the 2nd edition of the Australian Soil Classification (Isbell and National Committee on Soils and Terrain 2016). When incubated at field capacity, the pH of hypersulfidic material drops substantially either at least 0.5 unit to below pH 4 whereas the pH remains high in hyposulfidic material. Sulfuric material is produced upon oxidation of sulfidic or hypersulfidic material when sulfuric acid is produced from pyrite resulting in acidification (soil pH < 4) (Department of Enviornment and Conservation (DEC) 2008; Fitzpatrick and Shand 2008; Fitzpatrick et al. 2009). Secondary Fe oxy-hydroxy sulfate minerals such as jarosite [$KFe_3(SO_4)_2(OH)_6$] and schwertmannite [$Fe_8O_8(OH)_{8-2x}(SO_4)_x$ with $1 \leq x \leq 1.75$] are commonly found in sulfuric soil materials.

1.3 Acid sulfate soils drainage water

When sulfuric material is rewetted due to rainfall, inundation or irrigation, it can release large amounts of acidity, soluble metals and precipitate iron minerals into ground water and drainage water (Mosley et al. 2014b). In some areas, ASS with sulfuric materials have been drained for over 100 years and still discharging acidity into streams or waterways (Sammut and Lines-Kelly 2000). It was estimated that oxidation of one tonne of iron sulfide materials produces approximately one and half tonnes of sulfuric acid (Sammut and Lines-Kelly 2000). In floodplains in eastern Australia, ASS drainage exported 100 to 300 kg of sulfuric acid per ha per year (Sammut et al. 1996; White et al. 1997). In a 110 ha tropical wetland in East Trinity, Queensland, acid discharge was 700 kg of acid annually (Hicks et al. 2003a).

Drainage water from acidic ASS also contains high amounts of metals that are released due to the low pH. Concentrations of Al, As, Cd, Co, Cr, Cu, Ni, Pb, V and Zn in pore and drainage water have been shown to exceed Australian Water Quality Guidelines (ANZECC 2000) up to 100 fold (Hicks et al. 2003a; Mosley et al. 2014a; Simpson et al. 2008).

Even after several years of re-flooding, previously oxidized hyposulfidic material with sulfuric material can release acidity because iron sulfide oxidation products such as jarosite, natrojarosite, gypsum, schwertmannite or basaluminite (Ahern et al. 2004; Fitzpatrick 2003) store acidity, which can be slowly released upon dissolution. Oxidation of ferrous ion and hydrolysis of ferric ion which are released from ASS oxidation in downstream can generate large amount of acid and cause the depletion of dissolved oxygen in water (Ahern et al. 2004; Hicks et al. 2003b).

1.4 Impact of acid sulfate soils

ASS may pose a serious risk to agricultural productivity, ecosystems, human health and other assets (Baldwin 2009; Ljung et al. 2009) due to low pH and toxicity of metals released.

Plants growing on affected ASS can be stunted and even die leading to loss of agriculture productivity (Department of Environment and Resource Management (DERM) 2011; National Working Party on Acid Sulfate Soils 2000). The main constrains are acidity, salinity, aluminium and iron toxicity, low nutrient and base element contents (Attanandana and Vacharotayan 1986; National Working Party on Acid Sulfate Soils 2000). For example, the elevated iron concentration in submerged ASS inhibited rice growth (Nhung and Ponnamperuma 1966; Ponnamperuma et al. 1955), which was a major impediment to the expansion of rice crops (White et al. 1996). Low P availability can also limit crop growth in ASS (Attanandana et al. 1981). Low yield of rice cultivated on reclaimed ASS have been reported in Indonesia, Malaysia, Philippines, Sri Lanka, Thailand, and Vietnam (Bronswijk et al. 1995; Chaang T et al. 1992; Deturck P et al. 1992; Husson et al. 2000; LiJin 1985; Yampracha et al. 2005). Other crops may also be affected by oxidation of ASS such as sugarcane in Queensland, Australia (Powell and Martens 2005) or oil palm and cocoa seedlings in Malaysia (Auxtero and Shamshuddin 1991; Shamshuddin et al. 2004). Acidification of ASS can decrease animal productivity via a decrease in pasture quality and an increased uptake of aluminium and iron by the grazing animals (Environment Protection Authority (EPA) 2007).

Aquatic organisms are particularly sensitive to any changes in water quality (Ljung et al. 2009), so that the export of acidity in drainage water and metals from ASS to waterway and to groundwater can have severe negative effects on aquatic ecosystems (Cook et al. 2000; Sammut and Lines-Kelly 2000; Sammut et al. 1995). Fish kills are an immediate and recognisable response to acidification events. Fish kills along the Finnish coast due to metals leached and acidity mobilised from ASS occur periodically because of seasonal discharge of acidity and metals (Fältmarsch et al. 2008; Nordmyr et al. 2008; Nyberg et al. 2012). As a result of large scale drainage in ASS areas, massive kills of fish were reported in Malaysia, Senegal, Venezuela and Vietnam in the 1960s (Sammut and Lines-Kelly 2000). Leaking acid and metals into Trinity Inlet (Queensland, Australia) for 30 years resulted in episodic fish kills (Garrett, 1978; Russell, 1980;

Olsen, 1983; Russell and McDougall, 2003). Death and disease of aquatic marine organisms during acid events result from a combination of acidity, low dissolved oxygen and high aluminium concentrations, but may also be due to smothering by iron flocs (Sammut et al., 1996a, b; Cook et al. 2000).

Human health may be affected by elevated metal concentrations in drinking water in areas with a large proportion of oxidized ASS (Fältmarsch et al. 2008; Ljung et al. 2009; Mosley et al. 2014b). An investigation of drinking water of the wells in large areas of oxidized ASS in the Mekong delta found that As and Mn concentrations in drinking water exceeded water quality guidelines (Buschmann et al. 2008).

Due to the large area covered by ASS and their potential impact on the environment, management aimed at minimizing their negative impact is important.

1.5 Remediation and management of acid sulfate soils

Disturbance and oxidation of ASS materials can lead to the release of large amounts of sulfuric acid and soluble metals (Fältmarsch et al. 2008; Hicks et al. 2003b; Mosley et al. 2014b; Mosley et al. 2014c; White et al. 1997). Therefore, remediation and management of ASS preferably should focus on slowing or stopping oxidation of iron sulfide to avoid the formation of sulfuric materials. Options include keeping iron sulfide materials in saturated condition, retaining acidity and oxidation products of oxidised ASS materials on site using a acidity barrier or constructed wetlands, or neutralising sulfuric materials by liming, bioremediation, or flood irrigation control (Baldwin and Fraser 2009; Fitzpatrick and Shand 2009; Hicks et al. 2003b; Johnston et al. 2005; Ray 1985; Sammut and Lines-Kelly 2000).

Soil acidity in ASS with sulfuric material can be neutralized by application of chemical ameliorants such as hydrated lime ($CaOH_2$) or ground limestone $CaCO_3$ (Baldwin and Fraser 2009; Dear et al. 2002; Fitzpatrick and Shand 2009). However, liming may be costly and ineffective, particularly when sulfuric material occurs in large areas or deep soil layers, or has a high clay content (Dear et al. 2002). Limestone may also become coated in gypsum and Fe minerals, reducing its dissolution efficiency (Dear et al. 2002; Hammarstrom et al. 2003).

Addition of organic matter (OM) could be an alternative management technique because OM influences pH changes in reduced and oxidised ASS soils (LiJin 1985; Yuan et al. 2015a). OM increases the pH in submerged soils by stimulating sulfate reduction and minimises acidification in oxidised soils (Berner 1970; Costa and Duarte 2005; Yuan et al. 2015b).

Another management option is amelioration of acidic outflows. This may involve redesign of drainage systems to manage surface waters and reduce drain density or treatment of drains with lime (White et al. 1997). Acidity and metals can also be removed by permeable barriers placed in drainage channels (Regmi et al. 2009; Waite et al. 2003). Materials used in such barriers should have a high capacity to bind protons and metals and retain them even when leached with uncontaminated water, e.g. after disposal. Organic materials have properties that could make them effective barriers for ASS drainage water.

1.6 Sites used in this study

In this project, soil from Gilman, SA was used. The coastal area was previously covered by mangroves and sediments are rich in sulfides. The Gilman site covers approximately 1000 ha and was reclaimed between 1935 and 1954 when bund walls were constructed (Thomas 2010). The bund walls prevent tidal inundation and enhances oxidation of hypersulfidic material, which leads to acidification and is exacerbated by the lack of neutralising material previously supplied by tidal influence. In the 1980s, drainage water pH of less than 3.5 and high concentrations of Al, As, Fe, Pb and Zn in groundwater were then recorded (Pavelic and Dillon 1993). The area is presently under pressure for commercial and industrial development as well as being used for stormwater ponding basins for urban stormwater runoff, and stormwater retention basins that release stormwater to the Barker Inlet at low tide (Thomas 2010).

The other site selected for this project is the Lower Murray Reclaimed Irrigation Area (LMRIA). The sediments in the previous floodplains are sulfide-rich. The LMRIA region occupies 5,200 ha of agricultural land between Mannum and Wellington, which is irrigated by water from the River Murray. When barrages were constructed in the 1930s to prevent seawater ingress into the freshwater lakes downstream, the water level of the river was regulated 1 -1.5 m above the floodplain and levee banks were constructed in the LMRIA. This allowed irrigation of agricultural land behind the levee banks (Mosley et al. 2009). However, due to long and widespread drought in eastern Australia from 2006 to 2010, the water levels in the River Murray fell below -1 m Australian Height Datum (AHD) and irrigation ceased (Fitzpatrick et al. 2012; Mosley et al. 2009). As a consequence, large areas of previously inundated sediments and subaqueous soils were exposed. Pyrite rich materials was oxidised to depths up to 4 m and became acidic (Fitzpatrick et al. 2009). After the end of the drought in 2010 to 2011, the water levels of this region rose back to normal (approx. to 0.75 m AHD). Consequently, the dried and cracked subsoils containing sulfuric materials became inundated and irrigation resumed. But although the soils were saturated, the pH in these soils below ~0.5m to 0.8 m remained low (pH < 4) and the discharged water in the drains had pH 2-5 across the LMRIA (Fitzpatrick et al. 2012). The drainage water also contained high concentrations of soluble metals that exceeded aquatic ecosystem and Australian Drinking water aesthetic and health guidelines (Mosley et al. 2014a).

1.7 Organic materials

Soil organic carbon plays a vital role in the soil system to assist in the functioning many of the physical, chemical and biological processes (Hoyle et al. 2011). Therefore, addition of organic materials in to soil has been proposed as a promising soil amendment approach to increase soil fertility. Organic material addition to acid soil can increase soil pH (Xu et al. 2006), enhance proton binding affinities to soil humic acid (Pedra et al. 2008), and reduce metal mobility(Clemente et al. 2006; Dias et al. 2003; Fest et al. 2008). Furthermore, organic materials have received high attention and are considered as a low-cost and environment-friendly absorbent to remediate waste water (Iakovleva and Sillanpää 2013; Park et al. 2011). Biochar and other organic material have been used to reduce metal concentrations in leachate from mine tailings (Hughes and Gray 2013; Lee et al. 2013; Lindsay et al. 2011) and wastewater (Bhatnagar and Sillanpää 2010; Wan Ngah and Hanafiah 2008; Zhou and Haynes 2010).

The addition of organic materials in the form of manures, sawdust, cattle slurry and biochar has been used to increase the pH and remove metals from acid mine drainage and metal-contaminated soil (Hughes et al. 2013; Zhang et al. 2013). Single or multiple metal adsorption and desorption to organic materials were differed among materials and influenced by a number of factors such as pH environment (Choi et al. 2013; Houben et al. 2013), organic materials properties (Gai et al. 2014; Qian and Chen 2013; Trakal et al. 2014; Uchimiya et al. 2011c), metal speciation (Zhou and Haynes 2010).

Biochar is a carbon-rich product that is produced by pyrolysis of biomass at low or without oxygen supply (Lehmann et al. 2011; Sohi et al. 2010). Biochar composition is affected by composition of the feedstock and pyrolysis temperature and length. Biochar produced at low temperature (450 or 550 ˚C) is often used as soil amendment (Sohi et al. 2010) to increase microbial activity, water holding capacity and nutrient availability (Gomez et al. 2014; Liang et al. 2006; Verheijen et al. 2014). Biochar has been also considered to remediate contaminated soils and to remove heavy metals and others contaminats in aqueous environment (Beesley et al. 2011; Chen et al. 2011; Inyang et al. 2012; Liang et al. 2014; Uchimiya et al. 2010). The effect of biochar addition to soil on immobilization and retention of soluble metals differed among materials (Ahmad et al. 2014; Trakal et al. 2011) and influenced by factors such as physical structure and chemical composition of biochar as well as environmental conditions (Beesley et al. 2011; Chen et al. 2011; Kim et al.

2012; Kookana et al. 2011; Sohi et al. 2010; Trakal et al. 2011; Uchimiya et al. 2011a; Uchimiya et al. 2011c). For example, removal of Cd and Pb from aqueous solution was affected by morphology of the biochar, but more strongly correlated with solution pH (Trakal et al. 2014). Carboxyl and hydroxyl functional groups of biochar play an important role in metal binding (Elaigwu et al. 2014; Lu et al. 2012). Other properties important for metal binding include surface area, pore size, CEC. Biochar produced at low temperature has a high potential for removing inorganic contaminants whereas high temperature biochar with high surface area effectively remove organic contaminants (Ahmad et al. 2014; Tang et al. 2013). Metal sorption also depends on metal composition and concentration (Inyang et al. 2012; Uchimiya et al. 2012; Uchimiya et al. 2011a; Uchimiya et al. 2011b). Thus, selection of organic materials to remediate contaminated soils and water must be made on a case by case basis (Uchimiya et al. 2011c).

Drainage water seeping from adjacent acid sulfate soils (Mosley et al. 2014c; Simpson et al. 2014) differs from acid mine drainage (Sracek et al. 2004) with respect to acidity, sulfate concentration, dominant metals and metal speciation (Hughes et al. 2013; Jeen et al. 2014). Studies in acid mine drainage areas have shown that biochar and other organic amendments can increase the pH and bind metals. But little is known about the potential of these materials to reduce leaching of protons and metals from sulfuric materials in ASS and in adjacent drainage water. Similarly, little is known about how leaching is influenced by properties of the organic materials and whether the protons and metals will be retained on sulfuric materials following leaching with uncontaminated water.

1.8 The aims of this study

As outlined in this literature review, sulfuric materials in ASS can be remediated *in situ* by the application of lime or organic matter. However, these methods can be expensive or ineffective particularly where the sulfuric materials are in deeper soil layers. In such situations, the impact of the drainage water has to be minimised by retention of protons and metals within the soils and drainage channels by organic materials. The aims of this thesis project were:

i) To compare the effect of different organic materials on leaching of protons, Al and Fe from sandy sulfuric soil, and assess how this effect is influenced by the properties of organic materials and their placement in the soil (Chapter 2).

ii) To compare the capacity of different organic materials to remove proton, Al and Fe from ASS drainage water (Chapter 3).

iii) To assess their subsequent release leached by uncontaminated water (Chapter 4), and

iv) To assess eucalypt biochar produced at 550 ˚C for its maximum capacity to retain protons in the absence of metals; and to assess single and competition binding of Al and Fe in pH-controlled solution (Chapter 5).

References

Ahern CR, McElnea AE, Sullivan LA (2004) Acid Sulfate Soils Laboratory Methods Guidelines. Queenland Acid Sulfate Soils Manual 2004. Department of Natural Resources, Nines and Energy, Indooroopilly, Queensland, Australia,

Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage M, Lee SS, Ok YS (2014) Biochar as a sorbent for contaminant management in soil and water: A review Chemosphere 99:19-33

ANZECC (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra

Attanandana T, Vacharotayan S (1986) Acid sulfate soils: Their characteristics, genesis, amelioration and utilization Southeast Asia Studies 24:154-180

Attanandana T, Vacharotayan S, Kyuma K Chemical Characteristics, and Fertility Status of Acid Sulfate Soils of Thailand. In: Dost H, van Breemen N (eds) International Symposium on Acid Sulfate Soils, January 18-30, 1981, Bangkok, Thailand, 1981. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp 137-155

Auxtero EA, Shamshuddin J (1991) Growth of oil palm (Elaeis guineensis) seedlings on acid sulfate soils as affected by water regime and aluminium Plant Soil 137:243-257

Baldwin DS (2009) Knowledge needs to minimise adverse water quality events in the Edward-Wakool river system. Consultancy report for New South Wales office of Water. Murray-Darling Freswater Research Centre,

Baldwin DS, Fraser M (2009) Rehabilitation options for inland waterways impacted by sulfidic sediments - A synthesis Journal of Environmental Management 91:311-319

Beesley L, Moreno-Jiménez E, Gomez-Eyles JL, Harris E, Robinson B, Sizmur T (2011) A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils Environmental Pollution 159:3269-3282

Berner RA (1970) Sedimentary pyrite formation Americal Journal of Science 268:1-23

Berner RA (1984) Sedimentary pyrite formation: An update Geochimica et Cosmochimica Acta 48:605-615

Bhatnagar A, Sillanpää M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review Chemical Engineering Journal 157:277-296

Bigham J, Nordstrom DK (2000) Iron and aluminum hydroxysulfates from acid sulfate waters Reviews in mineralogy and geochemistry 40:351-403

Bronswijk JJB, Groenenberg JE, Ritsema CJ, van Wijk ALM, Nugroho K (1995) Evaluation of water management strategies for acid sulphate soils using a simulation model: A case study in Indonesia Agricultural Water Management 27:125-142

Buschmann J, Berg M, Stengel C, Winkel L, Sampson ML, Trang PTK, Viet PH (2008) Contamination of drinking water resources in the Mekong delta floodplains: Arsenic and other trace metals pose serious health risks to population Environment International 34:756-764

Bush RT, Sullivan LA, Fyfe D, Johnston S (2004) Redistribution of monosulfidic black oozes by floodwaters in a coastal acid sulfate soil floodplain Soil Research 42:603-607

Chaang T, Saari R, Diemont H, A. Y The development of an acid sulfate area in former mangroves in Merbok, Kedah, Malaysia. In: Dent D, van Mensvoort M (eds) Selected papers of the Ho Chi Minh City Symposium on Acid Sulfate Soils, Ho Chi Minh City, Vietnam, 1992. International Institute for Land Reclamation and Improvement, pp 95-102

Chen X, Chen G, Chen L, Chen Y, Lehmann J, McBride MB, Hay AG (2011) Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution Bioresource Technology 102:8877-8884

Choi S-J, Lee B-T, Kim J-Y, Kim K-W (2013) Study on adsorption/desorption of As by mine sludge depending on pH and natural organic matter Geosystem Engineering 16:191-199

Clemente R, Almela C, Bernal MP (2006) A remediation strategy based on active phytoremediation followed by natural attenuation in a soil contaminated by pyrite waste Environmental Pollution 143:397-406

Cook FJ, Hicks W, Gardner EA, Carlin GD, Froggatt DW (2000) Export of Acidity in Drainage Water from Acid Sulphate Soils Marine Pollution Bulletin 41:319-326

Costa MC, Duarte JC (2005) Bioremediation of Acid Mine Drainage Using Acidic Soil and Organic Wastes for Promoting Sulphate-Reducing Bacteria Activity on a Column Reactor Water, Air, & Soil Pollution 165:325-345

Dear SE, Moore NG, Dobos SK, Watling KM, Ahern CR (2002) Soil Management Guidelines. In Queensland Acid Sulfate Soil Technical Manual: (version 3.8). Department of Natural Resources and Mines, Indooroopilly, Queensland,

Dent D (1986) Acid sulphate soils: a baseline for research and development. International Institute for Land Reclamation and Improvement/ILRI, Wageningen, The Netherlands

Dent D, Pons L (1995) A world perspective on acid sulphate soils Geoderma 67:263-276

Department of Enviornment and Conservation (DEC) (2008) What are acid sulfate soils?

Department of Environment and Resource Management (DERM) (2011) Fact Sheet: L61 - Indentifying acid sulfate soils.

Deturck P, Weerasinghe KDN, Gunarathna DABN, Lexa JP, K. V Rice production on acid sulfate soils of Sri Lanka. In: Dent D, van Mensvoort M (eds) Selected papers of the Ho

Chi Minh City Symposium on Acid Sulfate Soils, Ho Chi Minh City, Vietnam, 1992. International Institute for Land Reclamation and Improvement, pp 137-145

Dias ACB, Pavan MA, Miyazawa M, Zocoler DC (2003) Plant residues: short term effect on sulphate, borate, zinc and copper adsorption by an acid oxisol Brazilian Archives of Biology and Technology 46:199-202

Elaigwu SE, Rocher V, Kyriakou G, Greenway GM (2014) Removal of Pb2+ and Cd2+ from aqueous solution using chars from pyrolysis and microwave-assisted hydrothermal carbonization of Prosopis africana shell Journal of Industrial and Engineering Chemistry

Environment Protection Authority (EPA) (2007) Acid Sulfate Soil Material Guideline: Site contamination-acid sulfate soil materials EPA South Australia EPA 638/07:15

Fältmarsch RM, Aström ME, Vuori K-M (2008) Environmental risks of metals mobilised from acid sulphate soils in Finland: a literature review Boreal environment research 13:444-456

Fanning DS (2002) Acid sulfate soils. Marcel Dekker, New York

Fest EPMJ, Temminghoff EJM, Comans RNJ, van Riemsdijk WH (2008) Partitioning of organic matter and heavy metals in a sandy soil: Effects of extracting solution, solid to liquid ratio and pH Geoderma 146:66-74

Fitzpatrick R (2003) Overview of acid sulfate soil properties, environmental hazards, risk mapping and policy development in Asutralia. Paper presented at the Advances in Regolith, Bentley, W.A,

Fitzpatrick R, Marvanek S, Powell B, Grealish G, Gilkes R (2010) Atlas of Australian Acid Sulfate Soils: recent developments and future priorities. In: Gilkes R, Prakongkep N (eds) Proceedings of the 19th World Congress of Soil Science: Soil solutions for a changing world. Brisbane, Australia, 1-6 August, 2010. Published on DVD; ISBN 987-

0-646-53783-2; http//www.iuss.org; Symposium WG 3.1 Processes in acid sulfate soil materials, pp 24-27

Fitzpatrick R, Shand P (2008) Inland acid sulfate soil systems across Australia. CRC LEME, Perth

Fitzpatrick R, Shand P (2009) Chapter 1: Inland Acid Sulfate Soils in Australia: Overview and Conceptual Models. In: Jennings J (ed) Natural History of the Riverland and Murraylands. Royal Society of South Australia (Inc.), Adelaide, South Australia, pp 6-74

Fitzpatrick R, Shand P, Leyden E, Palmer D, Baker A, Mosley L (2012) Field trip Lower Muray Area Guidebook. 25th National Committee for Acid sulfate Soils, Adelaide, South Australia

Fitzpatrick R, Shand P, Merry R (2009) Chapter 3. Acid Sulfate Soils. In: Jennings J (ed) Natural History of the Riverland and Murraylands. Royal Society of South Australia (Inc.), Adelaide, South Australia, pp 65-111

Gai X, Wang H, Liu J, Zhai L, Liu S, Ren T, Liu H (2014) Effects of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and Nitrate PLoS ONE 9:e113888

Gomez JD, Denef K, Stewart CE, Zheng J, Cotrufo MF (2014) Biochar addition rate influences soil microbial abundance and activity in temperate soils European Journal of Soil Science 65:28-39

Hammarstrom JM, Sibrell PL, Belkin HE (2003) Characterization of limestone reacted with acid-mine drainage in a pulsed limestone bed treatment system at the Friendship Hill National Historical Site, Pennsylvania, USA Applied Geochemistry 18:1705-1721

Hicks W, Fitzpatrick R, Bowman G (2003a) Managing coatal acid sulfate soils: The East Trinity example. Paper presented at the Advances in Regolith, Bentley, W.A, Hicks W, Fitzpatrick RW, Lamontagne S, Rogers S (2003b) Risks of water quality degradation during the remediation of floodplain salinity in the river Murray. Paper presented at the Advances in Regolith,

Houben D, Evrard L, Sonnet P (2013) Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar Chemosphere 92:1450-1457

Hoyle F, Baldock J, Murphy D (2011) Soil Organic Carbon – Role in Rainfed Farming Systems. In: Tow P, Cooper I, Partridge I, Birch C (eds) Rainfed Farming Systems. Springer Netherlands, pp 339-361

Hughes T, Gray NF, Sánchez Guillamón O (2013) Removal of Metals and Acidity from Acid Mine Drainage Using Liquid and Dried Digested Sewage Sludge and Cattle Slurry Mine Water Environ 32:108-120

Hughes TA, Gray NF (2013) Co-treatment of acid mine drainage with municipal wastewater: performance evaluation Environ Sci Pollut Res 20:7863-7877

Husson O, Hanhart K, Phung MT, Bouma J (2000) Water management for rice cultivation on acid sulphate soils in the Plain of Reeds, Vietnam Agricultural Water Management 46:91-109

Iakovleva E, Sillanpää M (2013) The use of low-cost adsorbents for wastewater purification in mining industries Environ Sci Pollut Res 20:7878-7899

Inyang M, Gao B, Yao Y, Xue Y, Zimmerman AR, Pullammanappallil P, Cao X (2012) Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass Bioresource Technology 110:50-56

Isbell R, National Committee on Soils and Terrain (2016) The Australian Soil Classification 2nd Edition. CSIRO publishing, Jeen S-W, Bain JG, Blowes DW (2014) Evaluation of mixtures of peat, zero-valent iron and alkalinity amendments for treatment of acid rock drainage Applied Geochemistry 43:66-79

Johnston SG, Slavich PG, Hirst P (2005) The impact of controlled tidal exchange on drainage water quality in acid sulphate soil backswamps Agricultural Water Management 73:87-111

Kim KH, Kim J-Y, Cho T-S, Choi JW (2012) Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida) Bioresource Technology 118:158-162

Kookana RS, Sarmah AK, Van Zwieten L, Krull E, Singh B (2011) Chapter three - Biochar Application to Soil: Agronomic and Environmental Benefits and Unintended Consequences. In: Donald LS (ed) Advances in Agronomy, vol Volume 112. Academic Press, pp 103-143

Lee SS, Lim JE, El-Azeem SAA, Choi B, Oh S-E, Moon DH, Ok YS (2013) Heavy metal immobilization in soil near abandoned mines using eggshell waste and rapeseed residue Environ Sci Pollut Res 20:1719-1726

Lehmann J, Rillig MC, Thies J, Masiello CA, Hockaday WC, Crowley D (2011) Biochar effects on soil biota – A review Soil Biology and Biochemistry 43:1812-1836

Liang B, Lehmann J, Solomon D, Kinyangi J, Grossman J, O'Neill B, Skjemstad JO, Thies J, Luizão FJ, Petersen J, Neves EG (2006) Black Carbon Increases Cation Exchange Capacity in Soils Soil Sci Soc Am J 70:1719-1730

Liang Y, Cao X, Zhao L, Arellano E (2014) Biochar-and phosphate-induced immobilization of heavy metals in contaminated soil and water: implication on simultaneous remediation of contaminated soil and groundwater Environ Sci Pollut Res 21:4665-4674

LiJin P (1985) Amelioration of an acid sulfate soil in the Philippines: I. The effect of organic and inorganic matter amendments on rice growth and yield in an acid sulfate soil Philippine Journal of Crop Science 10:37-42

Lindsay MBJ, Wakeman KD, Rowe OF, Grail BM, Ptacek CJ, Blowes DW, Johnson DB (2011) Microbiology and Geochemistry of Mine Tailings Amended with Organic Carbon for Passive Treatment of Pore Water Geomicrobiology Journal 28:229-241

Ljung K, Maley F, Cook A, Weinstein P (2009) Acid sulfate soils and human health—A Millennium Ecosystem Assessment Environment International 35:1234-1242

Lu H, Zhang W, Yang Y, Huang X, Wang S, Qiu R (2012) Relative distribution of Pb2+ sorption mechanisms by sludge-derived biochar Water Research 46:854-862

Macdonald BCT, Denmead OT, White I, Byrant G (2011) Gaseous Nitrogen Losses from Coastal Acid Sulfate Soils: A Short-Term Study Pedosphere 21:197-206

Mosley L, Fitzpatrick R, Palmer D, Leyden E, Shand P (2014a) Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought Science of The Total Environment 485–486:281-291

Mosley L, Fleming N, Spencer J (2009) Lower Murray Reclaimed Irrigation Area (LMRIA) Rehabilitation Project environmental monitoring final report. Environment Protection Authority, Adelaide, South Australia,

Mosley L, Palmer D, Leyden E, Cook F, Zammit B, Shand P, Baker A, W. Fitzpatrick R (2014b) Acidification of floodplains due to river level decline during drought Journal of Contaminant Hydrology 161:10-23

Mosley LM, Shand P, Self P, Fitzpatrick R (2014c) The geochemistry during management of lake acidification caused by the rewetting of sulfuric (pH < 4) acid sulfate soils Applied Geochemistry 41:49-61

National Working Party on Acid Sulfate Soils (2000) National strategy for the management of coastal acid sulfate soils. National Working Party in Acid Sulfate Soils,

Nhung M-TM, Ponnamperuma F (1966) Effects of calcium carbonate, manganese dioxide, ferric hydroxide, and prolonged flooding on chemical and electrochemical changes and growth of rice in a flooded acid sulfate soil Soil Science 102:29-41

Nordmyr L, Österholm P, Åström M (2008) Estuarine behaviour of metal loads leached from coastal lowland acid sulphate soils Marine Environmental Research 66:378-393

Nyberg M, Österholm P, Nystrand M (2012) Impact of acid sulfate soils on the geochemistry of rivers in south-western Finland Environ Earth Sci 66:157-168

Otero XL, Ferreira To, Vidal P, Macias F, Chesworth aW (2008) Thionic or Sulfidic soils. Springer Netherlands,

Park JH, Lamb D, Paneerselvam P, Choppala G, Bolan N, Chung J-W (2011) Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils Journal of Hazardous Materials 185:549-574

Pavelic P, Dillon PJ (1993) Dry Creek groundwater study : Final report to MFP Australia. [Canberra]

Pedra F, Plaza C, García-Gil JC, Polo A (2008) Effects of municipal waste compost and sewage sludge on proton binding behavior of humic acids from Portuguese sandy and clay loam soils Bioresource Technology 99:2141-2147

Ponnamperuma FN, Bradfield R, Peech M (1955) Physiological Disease of Rice attributable to Iron Toxicity Nature 175:265-265

Pons LJ (1973) Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In: Dost H (ed) Acid sulphate soils: proceedings of the International Symposium on Acid Sulphate Soils, 13-20 August 1972, Wageningen, the Netherlands.

vol v. 1. International Institute for Land Reclamation and Improvement, Wageningen, Netherlands,

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity Marine Pollution Bulletin 51:149-164

Qian L, Chen B (2013) Dual Role of Biochars as Adsorbents for Aluminum: The Effects of Oxygen-Containing Organic Components and the Scattering of Silicate Particles Environmental Science & Technology 47:8759-8768

Rabenhorst MC, Fanning DS (2002) Acid sulfate soils: Problems. Marcel Dekker, New York

Ray R (1985) Effect of liming on dehydrogenase and rhodanese activity of flooded and nonflooded acid sulfate soils Fertilizer Research 6:193-197

Regmi G, Indraratna B, Nghiem LD (2009) Long-term Performance of a Permeable Reactive Barrier in Acid Sulphate Soil Terrain Water, Air, & Soil Pollution: Focus 9:409-419

Rickard DT (1973) Sedimentary iron sulphide formation. In: Dost H (ed) Acid sulphate soils: proceedings of the International Symposium on Acid Sulphate Soils, 13-20 August 1972, Wageningen, the Netherlands. vol v. 1. International Institute for Land Reclamation and Improvement, Wageningen, Netherlands, pp 28-65

Ritchie G (1989) The chemical behavior of aluminum, hydrogen and manganese in acid soils. In: Robson AD (ed) Soil Acidity and Plant Growth. Academic Press, Sydney, pp 1-60

Sammut J, Lines-Kelly R (2000) An introduction to acid sulphate soils. Natural Heritage Trust, Sydney

Sammut J, Melville MD, Callinan RB, Fraser GC (1995) Estuarine Acidification: Impacts on Aquatic Biota of Draining Acid Sulphate Soils Australian Geographical Studies 33:89-100

Sammut J, White I, Melville M (1996) Acidification of an estuarine tributary in eastern Australia due to drainage of acid sulfate soils Marine and Freshwater Research 47:669-684

Shamshuddin J, Muhrizal S, Fauziah I, Husni MHA (2004) Effects of adding organic materials to an acid sulfate soil on the growth of cocoa (Theobroma cacao L.) seedlings Science of The Total Environment 323:33-45

Simpson S, Fitzpatrick R, Shand P, Angel B, Spadaro D, Merry R, Thomas M (2008) Chapter 3: Acid and Metal Mobilisation Following Rewetting of Acid Sulfate Soils from the River Murray, South Australia: A Rapid Laboratory Method. In: R. F, P. S (eds) Inland acid sulfate soil systems across Australia. vol CRC LEME Open File Report No. 249 (Thematic Volume). CRC LEME, Perth, pp 90-97

Simpson S, Vardanega CR, Jarolimek C, Jolley DF, Angel BM, Mosley LM (2014) Metal speciation and potential bioavailability changes during discharge and neutralisation of acidic drainage water Chemosphere 103:172-180

Sohi SP, Krull E, Lopez-Capel E, Bol R (2010) Chapter 2 - A Review of Biochar and Its Use and Function in Soil. In: Donald LS (ed) Advances in Agronomy, vol Volume 105. Academic Press, pp 47-82

Sracek O, Choquette M, Gélinas P, Lefebvre R, Nicholson RV (2004) Geochemical characterization of acid mine drainage from a waste rock pile, Mine Doyon, Quebec, Canada Journal of contaminant hydrology 69:45-71

Tang J, Zhu W, Kookana R, Katayama A (2013) Characteristics of biochar and its application in remediation of contaminated soil Journal of Bioscience and Bioengineering 116:653-659

Thomas BP (2010) Coastal acid sulfate soil processes in Barker Inlet, South Australia. The Univeristy of Adelaide

Trakal L, Bingöl D, Pohořelý M, Hruška M, Komárek M (2014) Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: Engineering implications Bioresource Technology 171:442-451

Trakal L, Komarek M, Szakova J, Zemanová V, Tlustoš P (2011) Biochar application to metal-contaminated soil: Evaluating of Cd, Cu, Pb and Zn sorption behavior using single-and multi-element sorption experiment Plant Soil Environ 57:372-380

Uchimiya M, Bannon DI, Wartelle LH (2012) Retention of Heavy Metals by Carboxyl Functional Groups of Biochars in Small Arms Range Soil Journal of Agricultural and Food Chemistry 60:1798-1809

Uchimiya M, Chang S, Klasson KT (2011a) Screening biochars for heavy metal retention in soil: Role of oxygen functional groups Journal of Hazardous Materials 190:432-441

Uchimiya M, Klasson KT, Wartelle LH, Lima IM (2011b) Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations Chemosphere 82:1431-1437

Uchimiya M, Lima IM, Klasson KT, Wartelle LH (2010) Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter Chemosphere 80:935-940

Uchimiya M, Wartelle LH, Klasson KT, Fortier CA, Lima IM (2011c) Influence of Pyrolysis Temperature on Biochar Property and Function as a Heavy Metal Sorbent in Soil Journal of Agricultural and Food Chemistry 59:2501-2510

Verheijen FGA, Graber ER, Ameloot N, Bastos AC, Sohi S, Knicker H (2014) Biochars in soils: new insights and emerging research needs European Journal of Soil Science 65:22-27

Waite TD, Desmier R, Melville M, Macdonald B (2003) Chapter 3 - Preliminary Investigation into the Suitability of Permeable Reactive Barriers for the Treatment of Acid Sulfate

Soils Discharge. In: David LN, Stan JM, Christopher CF, James A. DavisA2 - David L. Naftz SJMCCF, James AD (eds) Handbook of Groundwater Remediation using Permeable Reactive Barriers. Academic Press, San Diego, pp 67-104

Wan Ngah WS, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review Bioresource Technology 99:3935-3948

White I, Melville M, Sammut J (1996) Possible impacts of salinewater intrusion floodgate in Vietnam's lower Mekong delta. Paper presented at the Seminar on Environment and Development in Vietnam, December, 6-7, 1996, Australian National University, Australia,

White I, Melville MD, Wilson BP, Sammut J (1997) Reducing acidic discharges from coastal wetlands in eastern Australia Wetlands Ecology and Management 5:55-72

Wim A, Mensvoort MEFv (2005) Acid Sulfate Soils: Distribution and Extent. In: Lal R (ed) Encyclopedia of Soil Science. Second edn. CRC Press, pp 14-19

Xu JM, Tang C, Chen ZL (2006) The role of plant residues in pH change of acid soils differing in initial pH Soil Biology and Biochemistry 38:709-719

Yampracha S, Attanandana T, Sidibe-Diarra A, Yost RS (2005) Predicting the Dissolution of Rock Phosphates in Flooded Acid Sulfate Soils Soil Science Society of America Journal 69:2000-2011

Yuan C, Fitzpatrick R, Mosley LM, Marschner P (2015b) Sulfate reduction in sulfuric material after re-flooding: Effectiveness of organic carbon addition and pH increase depends on soil properties Journal of Hazardous Materials 298:138-145

Yuan C, Mosley LM, 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 Journal of environmental management 151:437-442

Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, Bolan N, Pei J, Huang H (2013) Using biochar for remediation of soils contaminated with heavy metals and organic pollutants Environ Sci Pollut Res 20:8472-8483

Zhou Y-F, Haynes RJ (2010) Sorption of Heavy Metals by Inorganic and Organic Components of Solid Wastes: Significance to Use of Wastes as Low-Cost Adsorbents and Immobilizing Agents Critical Reviews in Environmental Science and Technology 40:909-977

CHAPTER 2

ADDITION OF ORGANINC MATERIAL TO SULFURIC SOIL CAN REDUCE LEACHING OF PROTONS, IRON AND ALUMINIUM

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Addition of organic material to sulfuric soil can reduce leaching of protons, iron and aluminium

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ABSTRACT

Oxidised acid sulfate soils (ASS) with sulfuric horizons (sulfuric soils) can release large amounts of acid and metals, which can be rapidly mobilised when the soils are rewetted or re-flooded. Under flooded conditions, addition of organic materials to ASS has been shown to stimulate microbial sulfate reduction, which results in pH increase. But little is known about the potential of organic materials to reduce leaching of protons and metals from sulfuric soils and how this is influenced by properties of the organic materials and amendment form. Sulfuric material (pH 3.5) was collected from a coastal oxidised ASS at Gillman in the Barker Inlet, South Australia. Eight organic materials (compost, two plant residues and five biochars differing in feed stock and pyrolysis temperature) were applied at 15 g C kg^{-1} in two forms: mixed into or placed as a layer under the sulfuric soil. Twenty grammes of soil (dry weight equivalent) was placed in PVC cores, and the cores were leached four times with 45 ml of reverse osmosis water. In the unamended soil, 70–90% of the total leached protons, Fe and Al were released in the first leaching event with only small amounts being released in the three subsequent leachings. In amended treatments release of protons Fe and Al was lower than in unamended soil, the decrease is referred to as retention. The amount of protons, Fe and Al retained in the amended soil compared to the control was highest in the first leaching. Cumulative retention of protons Fe and Al was highest in the soil amended with eucalypt biochar produced at 550 °C and wheat biochar produced at 450 °C, but low in wheat straw and compost. Leachate pH of the unamended soil was 3.5–4, but up to 6.4 in amended soils. In amended soils, proton retention was positively correlated with C concentration of the materials, while Fe and Al retention was positively correlated with percentage of Aryl and O-Aryl groups and negatively correlated with percentage O-Alkyl, Di-O-Alkyl groups. Generally retention of Fe and Al was greater when organic materials were mixed in the soil than if placed as a layer underneath the soil, but there was little difference between amendment forms in proton retention. We conclude that mixing some biochars, particularly eucalypt biochar produced at 550 °C and wheat biochar produced at 450 °C, can strongly reduce leaching of protons and metals in sulfuric soils whereas wheat straw or compost are less effective.

1. Introduction

Acid sulfate soils (ASS) are wide-spread and occur globally in over 500,000 km^2, mainly in coastal zones (Sullivan et al., 2012). ASS with sulfidic material (Soil Survey Staff, 2014) form under waterlogged or subaqueous conditions and are characterised by sediments or soils rich in iron sulfides, mainly pyrite (Ljung et al., 2009). When exposed to air, e.g. due to natural or artificial drainage, pyrite oxidation leads to release of sulfuric acid (Attanandana and Vacharotayan, 1986; Dent, 1986; Pons, 1973) and formation of ASS with sulfuric horizons (Soil Survey Staff, 2014). In sediments or soils with low pH buffering capacity, the pH can fall below 4 or even 2 (Attanandana and Vacharotayan, 1986; Dent, 1986; Dent and Pons, 1995; Harbison, 1986), which induces release of metals to groundwater systems (Pavelic and Dillon, 1993). Acidity and high metal concentrations reduce plant growth (Bronswijk et al., 1995; Shamshuddin et al., 2014; Yampracha et al., 2005). The acidic leachate from sulfuric ASS ($pH < 4$) can have detrimental effects on ground and surface water quality and damage infrastructure (Baldwin and Fraser, 2009; Ljung et al., 2009). The dominant acid-generating metals in ASS leachates are Fe and Al, but protons are released when the metals hydrolyse (Mosley et al. 2014a).

Remediation of ASS is difficult, particularly when sulfuric material occurs at depth. Liming or controlled flooding may be ineffective or have undesirable side effects (Dear et al., 2002; Mosley et al., 2014a; b).

Organic matter plays an important role in sulfate reduction in ASS by providing energy for sulfate reducers and stimulating pyrite formation (Jayalath et al., 2015; Jayalath et al., 2016; Yuan et al., 2015a; b). Organic materials may also be useful for remediation of sulfuric soils because organic soil amendments such as plant residues, manure, compost or

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biochar can increase the pH of acidic soils (Xu et al., 2006; Yuan and Xu, 2011) and bind metals (Clemente et al., 2006; Dias et al., 2003; Fest et al., 2008; Karami et al., 2011; Walker et al., 2004; Rees et al., 2014) and protons (Pedra et al., 2008). Biochar and other organic materials have also been shown to reduce metal concentrations in leachate from mine tailings (Beesley et al., 2014; Fellet et al., 2011), and waste water (Bhatnagar and Sillanpää, 2010; Wan Ngah and Hanafiah, 2008; Zhou and Haynes, 2010). These studies showed that biochar and other organic amendments can increase the pH and bind metals. But little is known about (a) the potential of these materials to reduce leaching of protons and metals from sulfuric ASS, and (b) how leaching is influenced by properties of the organic materials and amendment form (e.g. mixed into the soil or as a layer under the soil).

Using synthetic drainage water based on drainage water of sulfuric ASS, we showed that passage of the acidic drainage water through various organic materials reduced proton, Fe and Al concentrations (Dang et al., 2015). Retention of protons, Fe and Al was greatest in two biochars and least in compost and wheat straw. The present study expands on these results by investigating if organic materials could also be used to reduce leaching of protons and metals in oxidised ASS; thus when they are in direct contact with the sites where protons and metals are released. A further difference to our previous study is that concentrations of protons and metals varied between leaching events, which is in contrast to the constant concentrations during the five leaching events with synthetic drainage water.

The aims of this experiment were to (i) compare the effect of different organic materials on leaching of protons, Fe and Al from sandy sulfuric soil, and (ii) assess how this effect is influenced by the properties of the organic materials and their placement in the soil. We hypothesised that (i) organic materials will reduce leaching of protons, Fe and Al, but the ability to retain protons and metals will differ among materials, and (ii) leaching of protons, Fe and Al will be reduced to a greater extent when organic materials are mixed in the soil than if placed as a layer under the soil.

2. Materials and methods

2.1. Experimental design

Sulfuric material was collected from between horizons E and B of an oxidised ASS at Gillman (34°49′47.25″S; 138°32′40.24″E) in the Barker Inlet, South Australia near site BG 15 (Thomas, 2010) at 20–80 cm depth (for soil properties see Table 1). The soil profile is classified as Typic Sulfaquept (Soil Survey Staff, 2014), Hyperthionic Gleysol (Drainic, Humic, Hypersulfidic) according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015) and Sulfuric clayey peat soil in accordance with the Australian ASS classification key (Fitzpatrick, 2013). The loss of tidal inundation has caused a lowering of the water table in the estuarine and mangrove swamp environment at Gillman, enabling oxygen to diffuse into sulfidic material, which caused pyrite oxidation and the formation of the peaty sulfuric soil (Thomas, 2010). The area has ponding basins for urban stormwater runoff, which is released to the Barker Inlet at low tides (Thomas, 2010). The sulfuric material was collected at the edge of an exposed drain, which was partly under water at the time of collection. The collected sulfuric material is sandy with white specks of gypsum and pale brown to pale yellow jarosite mottles (Fig. S1, Table S1). The material was air-dried and sieved to 0.5–2 mm.

Table 1
Selected properties of the sulfuric soil material collected at Gillman in the Baker Inlet, South Australia.

pH_w		3.3
Sand	%	91.2
Silt	%	8.0
Clay	%	0.8
Total organic C	$mg\ g^{-1}$	18.9
Total N	$mg\ g^{-1}$	0.9
HCl soluble sulfur	$mg\ g^{-1}$	11.5
KCl soluble sulfur	$mg\ g^{-1}$	1.1
Chromium reducible sulfur[a]	$mg\ g^{-1}$	17
Titratable actual acidity[a]	$mmol\ H^+\ kg^{-1}$	220
Retained acidity[a]	$mmol\ H^+\ kg^{-1}$	1084
Net acidity[a]	$mmol\ H^+\ kg^{-1}$	1462
Acid neutralising capacity[a]	$\%\ CaCO_3^{-1}$	0
Total Fe	$mg\ g^{-1}$	21.9
Total Al	$mg\ g^{-1}$	9.1

[a] From Thomas (2010).

The following organic materials were used: wheat straw, pea straw, compost (from municipal green waste), and five biochars from different feed stocks, produced at 450 °C or 550 °C: poultry biochar 450 °C, poultry biochar 550 °C, wheat biochar 450 °C, wheat biochar 550 °C and eucalypt biochar 550 °C (Table 2). These materials were selected to have a wide range of properties and particularly to test various biochars. The same materials were used in our previous study (Dang et al. 2015). The organic materials were dried, ground and sieved to 0.5–2 mm.

The organic materials were applied at 15 g C kg^{-1} of soil (dry mass basis) in two different ways: mixed with soil or placed as a layer underneath the soil. The control was soil without addition of organic materials. Twenty grammes of soil (dry weight equivalent of unamended soil) was placed in PVC cores (3.7 cm width, 5.0 cm height) with a mesh base (0.75 μm; Australian Filter Specialist Pty Ltd., Huntingwood, NSW). Before adding the soil, Whatman # 42 filter paper was placed on the mesh to minimise loss of soil and organic material during leaching events. There were four replicates per treatment. The cores were leached four times with reverse osmosis (RO) water. At each leaching event a total of 45 ml of water was added per core, in nine aliquots of 5 ml with 5 min between each addition. The total amount of water (45 ml, corresponding to 40 mm water depth) per leaching event was chosen based on preliminary studies to ensure sufficient leachate for the analyses. The 5 min interval was used to minimise pooling of water on the soil surface. After addition of 45 ml, the leachate was collected, its total volume measured, and analysed as described below. Leachate volume was 40 ml in unamended soil and 20–30 ml in amended treatments. Leaching was carried out every seven days for 4 weeks. In the interval between leaching events the cores were kept covered at room temperature; the soil remained moist between leaching events.

Leachate data were expressed as protons (10^{-pH}), Fe and Al retained in the materials for each leaching event and total cumulative retention. Retention per g of soil was calculated as:

(Concentration of element in unamended soil per ml ∗ amount of leachate in ml) − (Concentration of element in amended soil per ml ∗ amount of leachate in ml). This value was divided by the amount of soil per core (20 g) to give retention per g of soil.

2.2. Analyses

Soil texture was determined by the hydrometer method as described by Gee and Or (2002). The pH of the soil and organic materials was measured in a material to water ratio of 1:1 (w/w). Total organic C and total N in the soil and organic materials were measured by dry combustion using a LECO Trumac CN analyser. Total Al and Fe in the soil and organic materials were determined after concentrated nitric acid dissolution (Zarcinas et al., 1996). The extracts were filtered through Whatman #42 filter paper and analysed for Al and Fe by ICP-MS. Extractable sulfur including S_{HCl} and S_{KCl} of the soil were measured by shaking soil with 4 M HCl or 1 M KCl solution at a 1:40 ratio overnight or 4 h on end-over-end shaker (McElnea and Ahern, 2004b). Then the suspension was centrifuged at 3000 ppm for 5 min and the supernatant was filtered through Whatman #42 filter paper. The sulfur concentration in extracts was determined by ICP-AES. Chromium reducible sulfur (Scr), titratable actual acidity, retained acidity and net acidity were measured as described in Sullivan et al. (2004) and McElnea and

Table 2
Properties of organic materials.
From Dang et al. 2015.

	Amount	pH_w	C	N	C/N	ANC	CEC	Surface area	Total Al	Total Fe
	(g $core^{-1}$)		(mg g^{-1})			(% $CaCO_3$)	(cmol(+) kg^{-1}	(m^2 g^{-1})	(mg g^{-1})	
Wheat straw	3.51	5.5	427.3	4.3	100	0.03	15.6	0.8	0.2	0.2
Pea straw	3.41	6.3	439.9	8.8	50	0.4	43.4	0.9	0.4	0.3
Compost	5.31	8.2	282.6	20.2	14	7.5	53.9	4.0	9.4	8.9
Poultry 450	3.16	7.7	475.0	16.8	28	4.8	44.9	1.2	2.1	2.9
Poultry 550	4.03	9.6	372.0	16.6	22	7.1	50.9	7.9	2.9	3.7
Wheat 450	2.83	8.4	529.2	23.4	23	2.5	54.8	1.1	1.7	2.6
Wheat 550	3.89	9.0	385.2	14.2	27	6.7	51.0	6.1	1.8	2.2
Eucalypt 550	2.72	7.5	551.6	5.6	98	3.8	39.3	2.5	3.8	19.8

Ahern (2004a). McElnea and Ahern (2004a) define retained acidity as the 'less available' existing acidity that may be released by hydrolysis of relatively insoluble sulfate salts (such as jarosite, natrojarosite, and other iron and aluminium hydroxy sulfates) is included. Such compounds do not necessarily require oxygen to hydrolyse and produce acidity, however for jarosite and natrojarosite, the rate at which acid is released is likely to be limited by their extremely low solubility. Retained acidity will be released more slowly than the titratable actual acidity.

Acid neutralising capacity (ANC) expressed as $CaCO_3$ equivalent was determined by the rapid titration method as described in Ahern et al. (2004). Briefly 1.0 g of each finely ground organic material was placed into a 250 mL flask with 50 mL of deionised water and 25 ml of standardised 0.1 M HCl. The suspensions were boiled on a hotplate for 2 min, then allowed to cool to room temperature. The unreacted acid in the flask was titrated with standardised 0.1 M NaOH to pH 7.

Net acidity is calculated as:

Net acidity = potential sulfidic acidity + titratable actual (soluble) acidity + retained acidity) − acid neutralising capacity.

Surface area was analysed by nitrogen gas adsorption method and calculated as described by Brunauer et al. (1938). The organic materials were degassed overnight at a vacuum of 10–5 kPa prior to measuring nitrogen adsorption. Biochar samples were degassed at 200 °C; plant residues and compost at ambient temperature. Nitrogen gas adsorption was measured at 77 K using a Belsorp-max gas adsorption apparatus. Ultra high purity (>99.9%) helium and nitrogen were used for dead-space measurements and adsorption experiments, respectively.

Cation exchange capacity (CEC) was determined after Rayment and Lyons (2011). The organic materials were extracted with 0.1 M NH_4Cl at a 1:30 *w*/*w* ratio in an end over end shaker for 1 h. The extracts were centrifuged at 3000 rpm for 10 min the supernatant filtered through Whatman # 42 filter paper. The solution was analysed by inductively coupled plasma mass spectroscopy (ICP-MS).

Chemical groups of organic materials were measured by solid-state ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy as described in Smernik and Oades (2000) and McBeath et al. (2014) for organic matter and biochar, respectively.

The pH of the leachate was measured immediately after collection. The leachates were filtered through a 0.45 μm nitrocellulose membrane filter before measuring Al and Fe by ICP-AES. Proton, Fe and Al concentration of the leachate was multiplied by leachate volume to calculate the amount of protons, Fe and Al leached. Retention in treatments with organic materials was calculated by subtracting amounts of protons, Fe and Al leached in soil with amendments from that in unamended soil.

2.3. Statistical analyses

Data was analysed by two-way ANOVA with organic materials and amendment type (mixed or layer) as fixed factors. Correlations between retention and properties of organic materials were calculated in SPSS.

Differences between means were compared by Duncan analysis ($P \leq 0.05$) using GenStat 15th edition (VSN Int. Ltd, UK). Linear correlations between proton, Fe and Al retention and organic material properties were calculated with SPSS 20th edition.

3. Results

3.1. Soil properties

The pH of the dried sulfuric Gillman soil was 3.3, which indicates that pyrite oxidation had occurred in the field (Table 1). The soil was very sandy (91% sand) and had no measurable acid neutralising capacity, which explains why pyrite oxidation led to such a low pH. There was a high concentration of HCl soluble S compared to KCl soluble S (Table 1). The soil had a high net acidity.

This high titratable and retained acidity indicates that the soil has a large store of acidity, which could be released when rewetted (Fig. S1).

3.2. Properties of organic materials

The pH of the organic materials ranged from 9.6 in Poultry 550 to 5.5 in wheat straw (Table 2). The organic C concentration was lowest in compost and highest in Eucalypt 550. Total N concentration was lowest in wheat straw and highest in Wheat 450. The C/N ratio was highest in wheat straw and lowest in compost. The ANC was highest in compost and lowest in wheat straw. The CEC was lowest in wheat straw and highest in Wheat 450 and compost. The surface area was lowest in the two straws (wheat and pea) and highest in Poultry 550 where it was eight times higher than in the straws. Total Fe and Al were highest in Eucalypt 550 followed by compost and lowest in the two straws.

The two plant residues (wheat and pea straw) had the lowest percentage of Aryl, O-Aryl and Ketone-C and the highest percentage of O-Alkyl and Di-O-Alkyl-C (Table S2). Compost had the highest percentage of Alkyl-C.

3.3. Retention of protons, Al and Fe

In the unamended soil, 67, 71 and 90% of the total leached protons, Fe and Al were released in the first leaching event, respectively (Tables 3, S4, S5). Compared to the first leaching event, proton release in the second leaching event was only 25% and about 10% in the third

Table 3
Proton, Fe and Al release when passing reverse osmosis water through Gillman soil without amendment over four leaching events and cumulative release.

	Leaching event				Cumulative release
	1	2	3	4	
Proton (μg $core^{-1}$)[a]	22 ± 2	5 ± 0	3 ± 0	2 ± 0	33 ± 2
Fe (μg $core^{-1}$)	784 ± 63	64 ± 16	111 ± 17	138 ± 22	1097 ± 101
Al (μg $core^{-1}$)	3096 ± 228	92 ± 22	95 ± 15	145 ± 30	3428 ± 258

[a] 1 μMol H^+ = 1.

and fourth events. Cumulative Fe and Al leached represented 0.25 and 1.9% of total Fe and Al in the soil.

In all leaching events, the leachate pH from the amended soils was higher than of unamended soil (Table S3). The pH increase ranged from 0.2 to 2.2 units and was smaller in the first compared to following leaching events. The pH increase was greater in biochar amended soils than in soils with the straws. For a given material, the pH of the leachate was greater when it was placed as a layer under the soil than if mixed into the soil.

In amended soils, proton release was between 5 and 97% of that in the unamended soil (Table 4), with greater reduction when organic materials were placed as a layer than when mixed into the soil. When mixed into the soil, the release of protons relative to the unamended soil was smaller in the first than the following leaching events. With organic material as a layer on the other hand, the percentage release relative to unamended soil was lower in leaching events 2–4 than in the first leaching event, except for wheat straw.

In amended soils, proton retention was greatest in the first leaching event (Fig. 1A, B, Tables S6, S7). Compared to the first leaching event, retention was 70–80% lower in the second leaching event and then decreased by a further 50% from the second to the third leaching event. Proton retention in the first and second leaching was greatest in Wheat 450 followed by Eucalypt 550 and low in compost. Cumulative proton retention was greatest in Wheat 450, followed by Eucalypt 550, it was lowest in wheat straw and compost (Fig. 1C, Tables S6, S7). Amendment form (mixed or as layer under the soil) had little effect on cumulative proton retention except with wheat straw where it was greater when placed as layer under the soil than if mixed into the soil (Fig. 1C).

Iron retention was generally greatest in the first leaching event (Fig. 2A, B, Tables S8, S9). Exceptions were wheat and pea straw mixed into the soil where Fe retention was negative in the first leaching event (i.e. more Fe was released than in the unamended soil). Iron retention was low in the subsequent leaching events and for the layer treatments there was net release of Fe in some leachings, for example in the third event for compost and Wheat 550. When the organic materials were mixed into the soil, Fe retention in the first leaching event was greatest in Wheat 450 followed by Poultry 450 whereas it was greatest in Poultry 550 and Eucalypt 550 when the organic material was placed as a layer under the soil. In the mixed treatment, cumulative Fe retention was greatest with Poultry 450 followed by Wheat 450 (Fig. 2C, Tables S8, S9). There was net cumulative Fe release in the two straws. When the organic materials were placed as a layer, cumulative Fe retention was high in pea straw, the two poultry biochars and Eucalypt 550; it was low in compost and Wheat 550. Except for the two straws, cumulative Fe retention was 20–30% greater when organic materials were mixed into the soil than if placed as layer.

In the first leaching event, the Al concentration in the leachate of the soil alone exceeded Australian water quality guidelines (77 compared to 55 mg L^{-1}, ANZECC 2000)(Table S5). All organic materials reduced the Al concentrations in the first leachate below 55 mg L^{-1} with least reduction by the two straws. Compost and biochars reduced Al concentrations in the first leaching event by 70 to >90% when mixed and by about 50 to 80% when placed as a layer. In the following leaching events, leachate Al concentrations were low in all treatments. In the third and fourth leaching event, addition of some organic materials increased Al concentration compared to Gillman soil alone, but concentrations remained below 10 mg L^{-1}.

Table 4
Release of protons from Gilman soil with organic materials mixed or as a layer.

	Mixed				Layer			
Leaching event	1	2	3	4	1	2	3	4
Protons	%							
Wheat straw	48	27	19	22	24	31	35	42
Pea Straw	28	19	13	16	24	1	1	1
Compost	4	2	2	2	6	0	0	0
Poultry 450	20	12	12	14	31	7	4	3
Poultry 550	5	4	4	4	17	1	1	3
Wheat 450	19	15	12	13	25	6	2	1
Wheat 550	11	8	8	7	19	0	0	1
Eucalypt 550	28	17	18	19	34	17	6	7

The data is expressed as percentage in Gilman soil alone.

Aluminium retention was greatest in the first leaching event and very low in subsequent leaching events (Fig. 3A, B, Tables S10, S11). In the first leaching event, Al retention was greatest in Wheat 450 followed by Poultry 450 and Eucalypt 550. It was lowest in wheat straw and compost where it was about 40% lower than in Wheat 450. When placed as a layer under the soil, Al retention was greatest in Poultry 550 and Eucalypt 550 and lowest in wheat straw and compost where it was 30% lower than with the two biochars. Cumulative Al retention was about 30% greater when mixed compared to placement as layer (Fig. 3C, Tables S10, S11).

3.4. Correlations between retention and material properties

In general, correlations between proton, Fe and Al retention and properties of the organic materials were stronger in the first leaching event than for cumulative retention (Tables S12-17). Proton retention was positively correlated with C content of the organic materials (Tables S12, S13). When the organic materials were mixed into the soil, proton retention was also positively correlated with O-Aryl and Ketone-C, but negatively correlated with alkyl and Di-O-Alkyl C. Iron retention in both mixed and layer treatments was negatively correlated with O-Alkyl and Di-O-Alkyl-C, but positively correlated with percentage Aryl, O-Aryl and Ketone-C as well as with Al retention (Tables S14, S15). Aluminium retention was positively correlated with Aryl and O-Aryl-C and negatively with Alkyl and O-Alkyl-C (Tables S16, S17). However, these correlations were mainly due to the large differences in Alkyl and Aryl content of the straws on the one hand and the biochars on the other. When comparing only biochars, the relationship between Fe and Al retention and C groups was different. For example, Wheat 450 and Poultry 450 had the highest Fe and Al retention (Figs. 2, 3) and they also had the highest percentage O-Alkyl and lowest percentage Aryl groups among biochars. Thus there appeared to be a positive correlation of Fe and Al retention with O-Alkyl and a negative correlation with Aryl-C.

4. Discussion

The organic materials used in this experiment differed in their capacity to retain protons, Fe and Al in leached sulfuric soil. Retention was greatest in biochars Wheat 450, Eucalypt 550, Poultry 450 and to a lesser extent in Poultry 550. Retention was lowest in wheat straw and compost. This is in agreement with our earlier study where the same organic materials were leached with synthetic ASS drainage water (pH 3.5, high in Fe and Al) (Dang et al., 2015). In that study retention of protons, Fe and Al was greatest in Eucalypt 550 and Wheat 450 and lowest in compost and wheat straw. The results of this study confirm the first hypothesis (organic materials will reduce leaching of protons, Fe and Al, but the ability to bind protons and metals will differ among materials). This retention capacity, may in part, be due to retention of water in amended soil. Leachate volume of amended soils was 25–50% lower than in unamended soils. However compared to unamended soil, leachate pH was up to 2 units higher and Fe and Al concentrations in the first leaching event 50 to >90% lower in leachates of amended treatments. This suggests that proton and metal leaching was reduced by binding to organic materials. Differences in capacity to bind metals has been shown for biochars differing in feedstocks or pyrolysis temperature (e.g., Qian and Chen, 2013a, b; Uchimiya et al. 2011 a, b; Trakal et al. 2014). Binding of metals is thought to be related to various mechanisms. For example ion exchange, which results in very

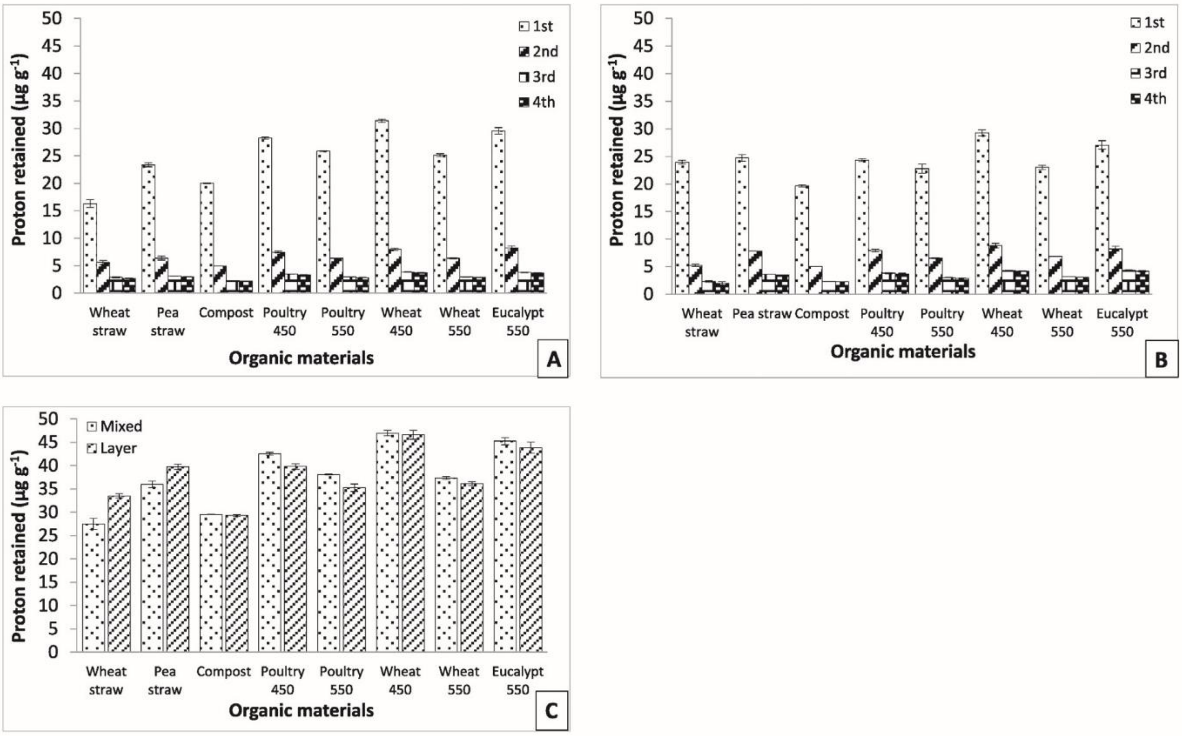

Fig. 1. Proton (1 μMol H^+ = 1 μg) retention per leaching event in Gillman soil with organic materials mixed (A) or as layer under the soil (B); and cumulative proton retention (C) relative to Gillman soil alone (n = 4, vertical line represents standard error).

strong binding (Trakal et al., 2014). Carbon functional groups (carboxyl, carbonyl, hydroxyl) can bind metals (Qian and Chen, 2013a; Uchimiya et al., 2011a; Uchimiya et al., 2011b). In agreement with this, Fe and Al retention were positively correlated with percentage Akyl/O-Akyl and Aryl/O-Aryl-C in the organic materials used this study. Metals can also bind to silica particles in biochar (Qian and Chen, 2013b). In the present study, leachate pH was increased from around pH 3–4 in unamended soil to >6 in amended soils after the first leaching event. An

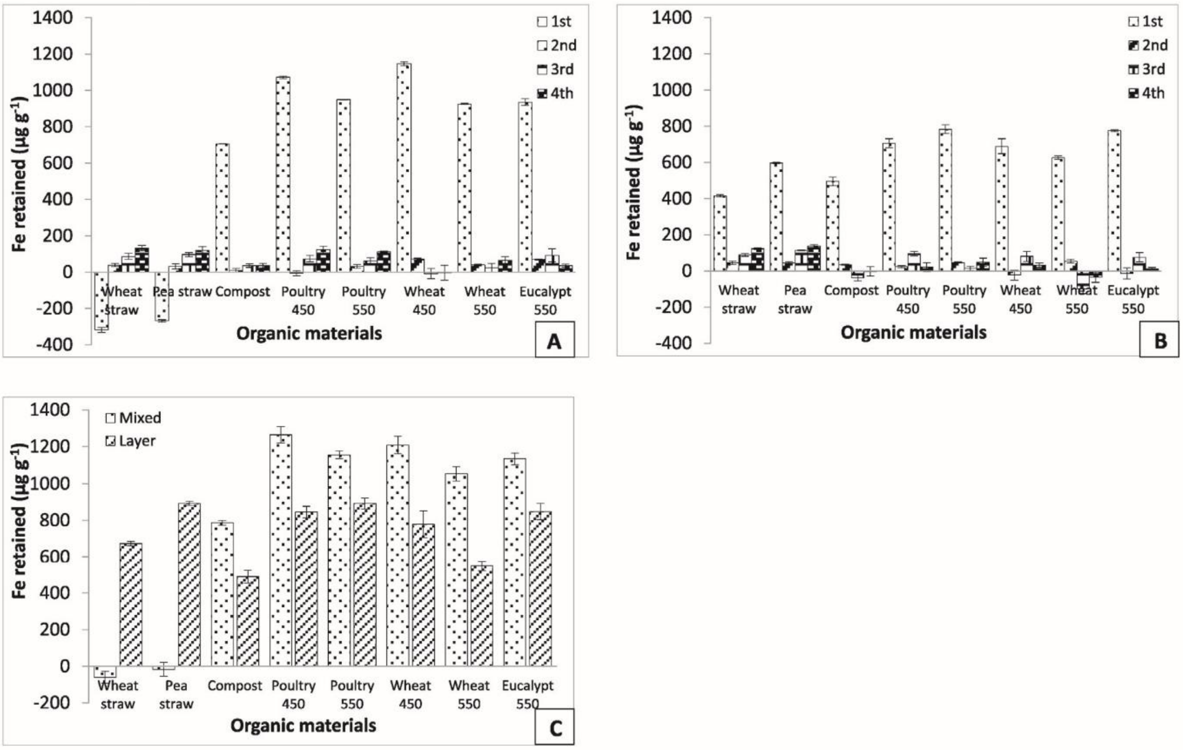

Fig. 2. Fe retention per leaching event in Gillman soil with organic materials mixed (A) or as layer under the soil (B); and cumulative proton retention (C) relative to Gillman soil alone (n = 4, vertical line represents standard error).

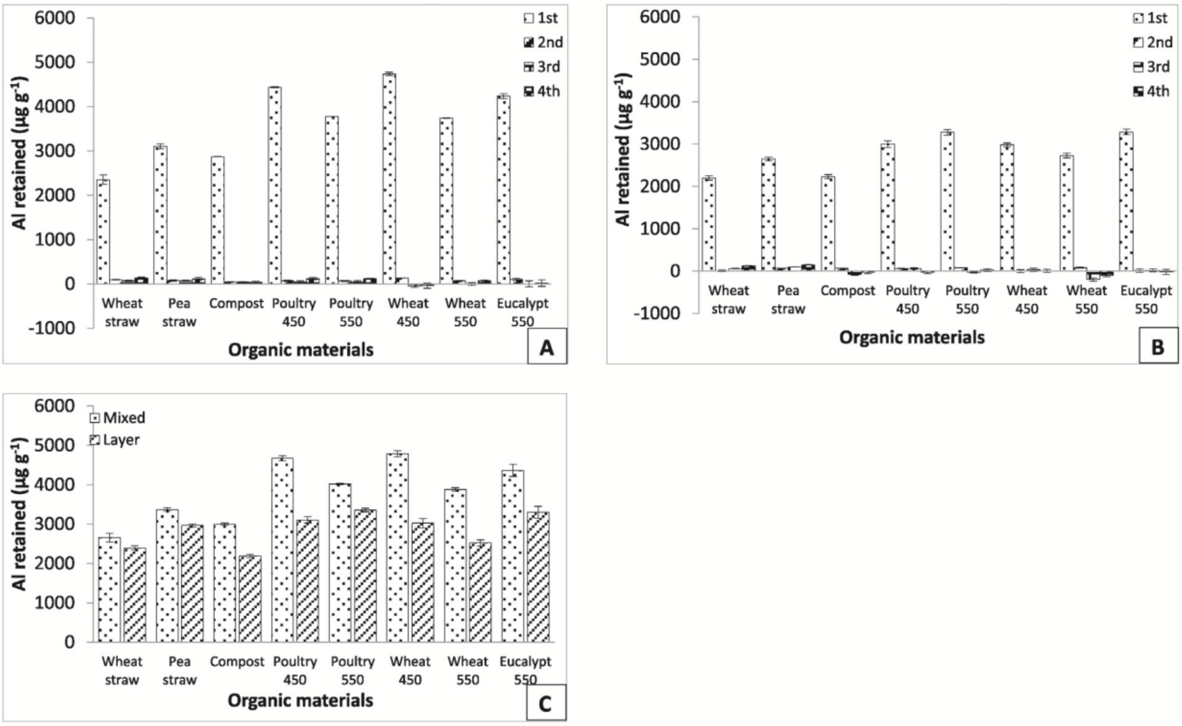

Fig. 3. Al retention per leaching event in Gillman soil with organic materials mixed (A) or as layer under the soil (B); and cumulative proton retention (C) relative to Gillman soil alone (n = 4, vertical line represents standard error).

increase in soil pH after addition of organic materials was also reported in other studies (e.g. Houben et al., 2013, Yuan and Xu 2011). This can reduce metal solubility and increase the ability of organic materials to bind metals. Metal binding to organic materials is pH dependent, increasing from low pH (pH 2) to pH 5 because the negative surface charge increases and metal precipitation can occur at higher pH (Houben et al., 2013; Qian and Chen, 2013b). In our study, the pH of the leachate was higher when the organic material was placed as a layer under the soil compared to the treatment where the organic material was mixed into the soil. This may be related to the greater retention of Fe and Al in the latter. Positively charged ions compete for negatively charged binding sites, thus preferential binding of Fe and Al may reduce proton retention. Another possible indirect effect of mixed organic materials on proton and metal retention is that organic materials induced changes in binding capacity by the soil, e.g. by changing the pH.

In this study, cumulative Fe and Al retention was greater with biochars than the two straws and compost. As well as the differences in functional groups for proton and metal binding discussed above, this could be due to greater release of soluble organic compounds from the straws and compost. Soluble organic carbon compounds can mobilise metals and increase leaching (Ahmad et al., 2014; Beesley et al., 2014). The release of soluble organic carbon may be aided by microbial decomposition of the straw and compost whereas biochars are poorly decomposable. Soluble organic carbon release and metal mobilisation has been shown for compost and biochars produced at low temperatures (about 400–500 °C) (Beesley et al., 2014) whereas biochars produced at 700 °C released little soluble organic C (Ahmad et al., 2014). However in the present study, retention in soils amended with wheat or poultry biochars tended to be greater with biochars produced at 450 °C compared to 550 °C. Increased metal availability in plant residue amended soil has been explained by the pH decrease induced by nitrification (Xu et al., 2006). Protons produced in nitrification may also explain why the pH increase of the leachate in straw amended soils compared to the unamended Gillman soil was smaller than in soils with biochar.

Nevertheless, mobilisation of metals by soluble organic carbon may explain the higher Fe and Al concentrations in leaching events 3 and 4 compared to the unamended Gillman soil. However, this increase in Fe and Al concentration in the later leaching events was small compared to the strong decrease relative to unamended Gillman soil in the first leaching events. Thus amendment with all organic materials resulted in net Fe and Al retention compared to Gillman soil alone.

The main difference in organic C composition between the biochars produced at 450 and 550 °C was that Wheat 450 and Poultry 450 had higher O-Alkyl-C and lower Aryl-C proportions than Wheat 550 and Poultry 550. This suggests that O-Alkyl-C played an important role in metal binding to biochars. The lack of correlation with other properties such as CEC, ANC and surface area which have been shown to be important in binding of cations (Beesley et al., 2011; Pedra et al., 2008) may be due to the limited range of values for these properties in the materials used here.

Oxidation of sulfidic material generates large amounts of acidity, which can solubilise metals (Attanandana and Vacharotayan, 1986; Dent and Pons, 1995) and can be released upon rewetting (Burton et al., 2008; Simpson et al., 2008). The unamended Gillman soil released the largest amounts of protons, Fe and Al in the first leaching event (Table 3). This can be explained by flushing of accumulated soluble acidity (i.e. the protons and metals comprising titratable actual acidity) from sulfuric soils when they are first rewet. Release in subsequent leaching events was much lower likely due to the dissolution and release of protons and metals retained in insoluble sulfate minerals (jarosite, Table 1 and Supplementary material), which is slow (Ahern et al., 2004). Correspondingly, retention of protons, Fe and Al by the organic materials was highest in the first leaching event with the exception of wheat and pea straw mixed into the soil where there was net release of Fe in the first leaching event.

Generally, retention of Fe and Al was greater when the organic materials were mixed with soil than when they were placed as a layer under the soil. When the organic materials are mixed with soil, there is a high likelihood that protons, Fe and Al released during oxidation come in close contact with and therefore are retained by the organic materials. When the organic materials are placed as a layer underneath the soil, protons, Fe and Al released are only temporarily in contact with the organic materials as the leachate passes through. This and the speed by which the leaching solution passes the layer would limit the contact between metals with the organic materials. Further, preferential flow may occur during passage through the layer of organic materials, which would reduce the proportion of organic material in close contact with the leaching solution.

For proton retention, there were no clear differences between the layer and mixed treatments, which suggests that the limited time of contact of the leaching solution in the layer treatment is sufficient for binding of protons. Therefore the second hypothesis (leaching of protons, Fe and Al will be reduced to a greater extent when organic materials are mixed into the soil than if placed as a layer under the soil) is true only for Fe and Al and only for the biochars and compost, not the two straws. The hypothesis has to be declined for protons because there were no consistent differences between the two application types.

5. Conclusion

The results show that amendment with biochars could be considered as remediation option for sulfuric soils because of their capacity to bind protons and metals, particularly Eucalypt 550 and Wheat 450 biochars. The higher pH and lower Fe and Al concentrations compared to unamended sulfuric soil would reduce the impact of ASS with sulfuric horizons on ground and surface water. Proton and particularly Fe and Al released from unamended soil were much greater in the first than the following leaching events. Relative to the unamended soil, Fe and Al concentrations in the leachate of amended soils were much lower in the first leaching event, but did not differ from the unamended soils in subsequent leaching events. This indicates that protons, Fe and Al bound to organic materials in the first leaching event strongly bound and released to only a very limited amount in subsequent leaching events. Further research could investigate the effect of application rates and types of biochars for different types of acid sulfate soils with sulfuric horizons.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2016.02.012.

References

Ahern, C.R., McElnea, A.E., Sullivan, L.A., 2004. Acid neutralising capacity, carbonate and alkali cation methods. In: Ahern, C.R., McElnea, A.E., Sullivan, L.A. (Eds.), Acid Sulfate Soils Laboratory Methods Guidelines. Department of Natural Resources Nines and Energy, Indooroopilly, Queensland, Australia.

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19–33.

ANZECC, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.

Attanandana, T., Vacharotayan, S., 1986. Acid sulfate soils: their characteristics, genesis, amelioration and utilization. Southeast Asia Stud. 24 (2), 154–180.

Baldwin, D.S., Fraser, M., 2009. Rehabilitation options for inland waterways impacted by sulfidic sediments — a synthesis. J. Environ. Manag. 91 (2), 311–319.

Beesley, L., Inneh, O.S., Norton, G.J., Moreno-Jimenez, E., Pardo, T., Clemente, R., Dawson, J.J.C., 2014. Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. Environ. Pollut. 186 (0), 195–202.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T., 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environ. Pollut. 159 (12), 3269–3282.

Bhatnagar, A., Sillanpää, M., 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. Chem. Eng. J. 157 (2–3), 277–296.

Bronswijk, J.J.B., Groenenberg, J.E., Ritsema, C.J., van Wijk, A.L.M., Nugroho, K., 1995. Evaluation of water management strategies for acid sulphate soils using a simulation model: a case study in Indonesia. Agric. Water Manag. 27 (2), 125–142.

Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60 (2), 309–319.

Burton, E.D., Bush, R.T., Sullivan, L.A., Johnston, S.G., Hocking, R.K., 2008. Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. Chem. Geol. 253 (1–2), 64–73.

Clemente, R., Almela, C., Bernal, M.P., 2006. A remediation strategy based on active phytoremediation followed by natural attenuation in a soil contaminated by pyrite waste. Environ. Pollut. 143 (3), 397–406.

Dang, T., Marschner, P., Mosley, L., Fitzpatrick, R., 2015. Organic materials differ in ability to remove protons, iron and aluminium from acid sulfate soil drainage water. Water Air Soil pollut. 226 (11), 1–13.

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: (version 3.8). Department of Natural Resources and Mines, Indooroopilly, Queensland.

Dent, D., 1986. Acid Sulphate Soils: A Baseline for Research and Development. International Institute for Land Reclamation and Improvement/ILRI, Wageningen, The Netherlands.

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

Dias, A.C.B., Pavan, M.A., Miyazawa, M., Zocoler, D.C., 2003. Plant residues: short term effect on sulphate, borate, zinc and copper adsorption by an acid oxisol. Braz. Arch. Biol. Technol. 46 (2), 199–202.

Fellet, G., Marchiol, L., Delle Vedove, G., Peressotti, A., 2011. Application of biochar on mine tailings: effects and perspectives for land reclamation. Chemosphere 83 (9), 1262–1267.

Fest, E.P.M.J., Temminghoff, E.J.M., Comans, R.N.J., van Riemsdijk, W.H., 2008. Partitioning of organic matter and heavy metals in a sandy soil: effects of extracting solution, solid to liquid ratio and pH. Geoderma 146 (1–2), 66–74.

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. Springer Netherlands, pp. 51–83.

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 Science Society of America, Madison, WI.

Harbison, P., 1986. Mangrove muds: a source and sink for trace metals. Mar. Pollut. Bull. 17, 246–250.

Houben, D., Evrard, L., Sonnet, P., 2013. Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. Chemosphere 92 (11), 1450–1457.

IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014, Update 2015. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. FAO, Rome.

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

Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N.W., Beesley, L., 2011. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. J. Hazard. Mater. 191 (1–3), 41–48.

Ljung, K., Maley, F., Cook, A., Weinstein, P., 2009. Acid sulfate soils and human health—a millennium ecosystem assessment. Environ. Int. 35 (8), 1234–1242.

McBeath, A.V., Smernik, R.J., Krull, E.S., Lehmann, J., 2014. The influence of feedstock and production temperature on biochar carbon chemistry: a solid-state 13C NMR study. Biomass Bioenergy 60 (0), 121–129.

McElnea, A.E., Ahern, C.R., 2004a. Actual acidity method. In: McElnea, A.E., Ahern, C.R. (Eds.), Acid Sulfate Soils Laboratory Methods Guidelines. Department of Natural Resources Nines and Energy, Indooroopilly, Queensland, Australia.

McElnea, A.E., Ahern, C.R., 2004b. Sulfur-various extraction techniques. In: McElnea, A.E., Ahern, C.R. (Eds.), Acid Sulfate Soils Laboratory Methods Guidelines. Department of Natural Resources Nines and Energy, Indooroopilly, Queensland, Australia.

Mosley, L., Fitzpatrick, R., Palmer, D., Leyden, E., Shand, P., 2014a. Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the lower Murray River after a severe drought. Sci. Total Environ. 485–486 (0), 281–291.

Mosley, L.M., Shand, P., Self, P., Fitzpatrick, R., 2014b. The geochemistry during management of lake acidification caused by the rewetting of sulfuric ($pH < 4$) acid sulfate soils. Appl. Geochem. 41 (0), 49–61.

Pavelic, P., Dillon, P.J., 1993. Dry Creek groundwater study. Final report to MFP Australia (1875753060, Canberra).

Pedra, F., Plaza, C., García-Gil, J.C., Polo, A., 2008. Effects of municipal waste compost and sewage sludge on proton binding behavior of humic acids from Portuguese sandy and clay loam soils. Bioresour. Technol. 99 (7), 2141–2147.

Pons, L.J., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In: Dost, H. (Ed.), Acid Sulphate Soils: Proceedings of the International Symposium on Acid Sulphate Soils, 13–20 August 1972, Wageningen, The Netherlands. International Institute for Land Reclamation and Improvement, Wageningen, Netherlands.

Qian, L., Chen, B., 2013a. Dual role of biochars as adsorbents for aluminum: the effects of oxygen- rees, F. containing organic components and the scattering of silicate particles. Environ. Sci. Technol. 47 (15), 8759–8768.

Qian, L., Chen, B., 2013b. Interactions of aluminum with biochars and oxidized biochars: implications for the biochar aging process. J. Agric. Food Chem. 62 (2), 373–380.

Rayment, G.E., Lysons, D.J., 2011. Soil Chemical Methods—Australia. 3. CSIRO publishing, Victoria.

Rees, F., Simonnot, M.O., Morel, J.L., 2014. Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. Eur. J. Soil Sci. 65 (1), 149–161.

Shamshuddin, J., Elisa Azura, A., Shazana, M.A.R.S., Fauziah, C.I., Panhwar, Q.A., Naher, U.A., 2014. Chapter three — properties and management of acid sulfate soils in Southeast Asia for sustainable cultivation of rice, oil palm, and cocoa. In: Donald, L.S. (Ed.), Advances in Agronomy. Academic Press, pp. 91–142.

Simpson, S., Fitzpatrick, R., Shand, P., Angel, B., Spadaro, D., Merry, R., Thomas, M., 2008. Chapter 3: acid, metal and nutrient mobilisation following rewetting of acid sulfate soils from the river Murray, South Australia: a rapid laboratory method. In: Fitzpatrick, R., Shand, P. (Eds.), Inland Acid Sulfate Soil Systems Across Australia. CRC LEME, Perth, pp. 90–97.

Smernik, R.J., Oades, J.M., 2000. The use of spin counting for determining quantitation in solid state 13C NMR spectra of natural organic matter: 1. Model systems and the effects of paramagnetic impurities. Geoderma 96 (1–2), 101–129.

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

Sullivan, L., Bush, R., Burton, E., Ritsema, C., van Mensvoort, M., 2012. Acid sulfate soils. In: Huang, P.M., Li, Y., Sumner, M.E. (Eds.), Handbook of Soil Sciences: Resource Management and Environmental Impacts. CRC Press, Boca Raton, FL, pp. 21.21–21.26.

Sullivan, L.A., Bush, R.T., Lancaster, G., Clark, M., Lin, C., Saenger, P., 2004. Chromium reducible sulfur. In: McElnea, A.E., Ahern, C.R. (Eds.), Acid Sulfate Soils Laboratory Methods Guidelines. Department of Natural Resources, Nines and Energy, Indooroopilly, Queensland, Australia.

Thomas, B.P., 2010. Coastal Acid Sulfate Soil Processes in Barker Inlet, South Australia, the Univeristy of Adelaide. Adelaide, South Australia 9368 pp.).

Trakal, L., Bingöl, D., Pohořelý, M., Hruška, M., Komárek, M., 2014. Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: engineering implications. Bioresour. Technol. 171 (0), 442–451.

Uchimiya, M., Klasson, K.T., Wartelle, L.H., Lima, I.M., 2011a. Influence of soil properties on heavy metal sequestration by biochar amendment: 2. Copper desorption isotherms. Chemosphere 82 (10), 1438–1447.

Uchimiya, M., Wartelle, L.H., Klasson, K.T., Fortier, C.A., Lima, I.M., 2011b. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. J. Agric. Food Chem. 59 (6), 2501–2510.

Walker, D.J., Clemente, R., Bernal, M.P., 2004. Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. Chemosphere 57 (3), 215–224.

Wan Ngah, W.S., Hanafiah, M.A.K.M., 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour. Technol. 99 (10), 3935–3948.

Xu, J.M., Tang, C., Chen, Z.L., 2006. The role of plant residues in pH change of acid soils differing in initial pH. Soil Biol. Biochem. 38 (4), 709–719.

Yampracha, S., Attanandana, T., Sidibe-Diarra, A., Yost, R.S., 2005. Predicting the dissolution of Rock phosphates in flooded acid sulfate soils. Soil Sci. Soc. Am. J. 69 (6), 2000–2011.

Yuan, C., Fitzpatrick, R., Mosley, L.M., Marschner, P., 2015a. Sulfate reduction in sulfuric material after re-flooding: effectiveness of organic carbon addition and pH increase depends on soil properties. J. Hazard. Mater. 298 (0), 138–145.

Yuan, C., Mosley, L.M., Fitzpatrick, R., Marschner, P., 2015b. 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 (0), 437–442.

Yuan, J.H., Xu, R.K., 2011. The amelioration effects of low temperature biochar generated from nine crop residues on an acidic ultisol. Soil Use Manag. 27 (1), 110–115.

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 (5–8), 1331–1354.

Zhou, Y.-F., Haynes, R.J., 2010. Sorption of heavy metals by inorganic and organic components of solid wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents. Crit. Rev. Environ. Sci. Technol. 40 (11), 909–977.

Supplementary data

Figures S1: Pale brown to yellow jarosite mottles in sandy Gilman soil

Table S1: Soil profile description[1] and soil classification

Horizon	Depth (cm)	Description	Sulfuric horizon/sulfidic material[2]	Soil class[2]	Australian ASS identification key[3]
Oe	0-5	Brown to greyish brown silty loam	Sulfuric	Typic Sulfaquept	Sulfuric clayey peat soil
A	5-15	Greyish brown clay loam	Sulfuric		
E	15-40	Pale yellow silty clay with brown mottles	Sulfuric		
B	40-110	Greyish brown sandy with pale brown mottles of jarosite	Sulfuric		

[1] Soil collected at site BG15 as descriped in Thomas (2010)

[2] Acid sulfate soil horizon and material (Soil Survey Staff, 2014)

[3] Australian acid sulfate soil classification (Fitzpatrick, 2013)

Table S2: Carbon groups of organic materials based on NMR spectroscopy (from Dang et al. 2015).

	Alkyl	N-Alkyl/ Methoxyl	O-Alkyl	Di-O-Alkyl	Aryl	O-Aryl	Amide/ Carboxyl	Ketone
	% of organic C detected							
Wheat straw	4.8	4.3	61.3	14.1	7.4	3.2	4.1	0.7
Pea Straw	6.8	5.6	59.4	12.8	7.2	2.8	4.7	0.6
Compost	20.3	8.9	31.2	7.7	16.1	6.1	8.2	1.5
Poultry 450	9.2	5.5	26.6	8.2	34.3	9.9	4.1	2.2
Poultry 550	10.4	2.8	5.1	4.1	61.7	10.4	3.3	2.1
Wheat 450	15.3	5.2	14.9	5.2	39.2	10.9	6.2	3.1
Wheat 550	13.2	3.9	5.6	3.7	52.9	12.9	4.5	3.3
Eucalypt 550	10.3	3.1	4.5	3.6	57.5	13.6	4.3	3.2

Table S3. pH of leachates after passing reverse osmosis water through Gillman soil with organic materials mixed into the soil or placed as a layer underneath the soil over 4 leaching events. Letter indicate significant differences (Duncan analysis, P≤ 0.05)

	Leaching event							
	1		2		3		4	
	Mixed	Layer	Mixed	Layer	Mixed	Layer	Mixed	Layer
Gillman alone	3.26 ± 0.03		3.87 ± 0.03		4.21 ± 0.02		4.22 ± 0.03	
Wheat straw	3.45 ± 0.02 a	3.75 ± 0.02 cd	4.16 ± 0.07 ab	4.08 ± 0.04 a	4.64 ± 0.07 ab	4.37 ± 0.05 a	4.58 ± 0.03 ab	4.31 ± 0.07 a
Pea Straw	3.69 ± 0.02 bc	3.76 ± 0.04 cd	4.33 ± 0.09 abc	5.73 ± 0.12 g	4.78 ± 0.03 abc	6.10 ± 0.22 hij	4.73 ± 0.04 ab	5.85 ± 0.09 f
Compost	4.54 ± 0.03 h	4.40 ± 0.08 g	5.22 ± 0.06 f	6.22 ± 0.09 h	5.73 ± 0.10 fgh	6.62 ± 0.07 k	5.76 ± 0.13 ef	6.41 ± 0.06 g
Poultry 450	3.84 ± 0.01 de	3.65 ± 0.01 bc	4.50 ± 0.06 bcd	4.83 ± 0.18 de	4.84 ± 0.02 abc	5.60 ± 0.27 efg	4.79 ± 0.07 abc	5.81 ± 0.34 ef
Poultry 550	4.42 ± 0.02 g	3.94 ± 0.09 e	5.02 ± 0.05 ef	5.61 ± 0.21 g	5.34 ± 0.05 def	6.21 ± 0.38 ijk	5.32 ± 0.06 de	5.81 ± 0.36 ef
Wheat 450	3.86 ± 0.02 de	3.75 ± 0.02 cd	4.41 ± 0.06 abc	5.05 ± 0.27 ef	4.84 ± 0.08 abc	5.85 ± 0.19 ghi	4.83 ± 0.06 bcd	5.95 ± 0.12 fg
Wheat 550	4.08 ± 0.03 f	3.86 ± 0.03 de	4.71 ± 0.07 cde	6.09 ± 0.10 h	5.02 ± 0.05 bcd	6.37 ± 0.08 jk	5.08 ± 0.04 bcd	6.12 ± 0.25 fg
Eucalypt 550	3.69 ± 0.02 bc	3.61 ± 0.03 b	4.37 ± 0.08 abc	4.39 ± 0.12 abc	4.65 ± 0.04 ab	5.21 ± 0.16 cde	4.65 ± 0.03 ab	5.26 ± 0.23 cd

Table S4. Fe concentration (mg L^{-1}) of leachates after passing reverse osmosis water through Gillman soil with organic materials mixed into the soil or placed as a layer underneath the soil over 4 leaching events. Letter indicate significant differences (Duncan analysis, $P \leq 0.05$)

	Leaching event							
	1		2		3		4	
	Mixed	Layer	Mixed	Layer	Mixed	Layer	Mixed	Layer
	Fe concentration (mg L^{-1})							
Gillman alone	19.59 ± 1.6		1.61 ± 0.4		2.78 ± 0.4		3.45 ± 0.6	
Wheat straw	33.5 ± 0.3 k	16.4 ± 0.2 i	1.9 ± 0.3 ab	1.6 ± 0.3 ab	2.5 ± 0.6 ab	2.5 ± 0.3 ab	2.3 ± 0.5 a	2.6 ± 0.2 a
Pea Straw	32.2 ± 0.1 j	12.6 ± 0.1 h	2.1 ± 0.5 ab	1.7 ± 0.2 ab	2.3 ± 0.4 a	1.7 ± 0.1 a	2.8 ± 0.7 ab	2.2 ± 0.2 a
Compost	1.2 ± 0.0 ab	8.6 ± 0.8 e	2.8 ± 0.5 bcd	1.4 ± 0.1 ab	3.7 ± 0.6 abc	7.6 ± 0.9 ef	5.0 ± 0.7 bcd	7.1 ± 1.4 de
Poultry 450	3.6 ± 0.1 c	11.3 ± 0.5 g	3.4 ± 0.4 cd	2.5 ± 0.2 abc	3.3 ± 0.6 abc	2.6 ± 0.4 ab	3.0 ± 0.6 ab	6.2 ± 0.8 cde
Poultry 550	0.5 ± 0.0 a	5.0 ± 0.7 d	2.0 ± 0.4 ab	1.3 ± 0.1 a	3.0 ± 0.7 abc	5.0 ± 0.4 cd	2.4 ± 0.2 a	4.9 ± 0.9 bcd
Wheat 450	4.3 ± 0.2 cd	13.0 ± 0.8 h	1.2 ± 0.1 a	3.9 ± 0.8 d	5.8 ± 0.8 de	3.3 ± 0.8 abc	7.0 ± 1.2 de	6.0 ± 0.3 cde
Wheat 550	2.1 ± 0.1 b	9.8 ± 0.2 f	1.7 ± 0.2 ab	1.1 ± 0.4 a	4.6 ± 1.0 bcd	9.4 ± 1.0 f	4.4 ± 0.8 abc	8.2 ± 1.1 e
Eucalypt 550	9.3 ± 0.3 ef	12.2 ± 0.1 gh	1.3 ± 0.1 a	3.6 ± 0.8 cd	3.1 ± 1.0 abc	3.5 ± 0.7 abc	5.9 ± 0.2 cde	6.6 ± 0.2 cde

Table S5. Al concentration (mg L^{-1}) of leachates after passing reverse osmosis water through Gillman soil with organic materials mixed into the soil or placed as a layer underneath the soil over 4 leaching events. Letter indicate significant differences (Duncan analysis, $P \leq 0.05$)

	Leaching event							
	1		2		3		4	
	Mixed	Layer	Mixed	Layer	Mixed	Layer	Mixed	Layer
	Al concentration (mg L^{-1})							
Gillman alone	77.4 ± 5.7		2.3 ± 0.6		2.4 ± 0.4		3.6 ± 0.7	
Wheat straw	48.3 ± 2.4 i	51.9 ± 1.3 j	1.3 ± 0.2 ab	4.3 ± 0.6 c	2.2 ± 0.7 ab	2.5 ± 0.4 ab	2.4 ± 0.6 ab	2.8 ± 0.2 abc
Pea Straw	32.9 ± 1.3 f	43.2 ± 1.0 gh	2.0 ± 0.6 ab	2.3 ± 0.1 ab	2.2 ± 0.5 ab	1.3 ± 0.0 a	3.3 ± 0.9 abcd	2.2 ± 0.3 a
Compost	1.7 ± 0.1 a	24.5 ± 1.6 e	2.2 ± 0.6 ab	1.0 ± 0.1 ab	2.6 ± 0.7 ab	8.8 ± 1.0 d	5.3 ± 1.2 bcdef	8.8 ± 1.9 fg
Poultry 450	10.1 ± 0.3 c	40.2 ± 1.6 g	2.3 ± 0.5 ab	2.6 ± 0.2 b	3.2 ± 0.8 abc	2.7 ± 0.5 ab	3.5 ± 0.8 abcd	8.0 ± 1.1 efg
Poultry 550	1.3 ± 0.1 a	14.7 ± 1.7 d	1.9 ± 0.4 ab	1.4 ± 0.1 ab	2.4 ± 0.7 ab	5.8 ± 0.6 c	2.4 ± 0.3 ab	6.3 ± 1.2 bcdef
Wheat 450	13.2 ± 0.7 cd	46.6 ± 0.9 hi	0.7 ± 0.1 a	4.6 ± 1.1 c	6.1 ± 1.0 c	3.8 ± 1.1 abc	8.4 ± 1.7 efg	6.9 ± 1.0 def
Wheat 550	5.9 ± 0.2 b	32.2 ± 1.5 f	1.8 ± 0.3 ab	1.5 ± 0.5 ab	5.0 ± 1.2 bc	12.4 ± 1.6 e	4.6 ± 0.8 abcde	10.9 ± 1.6 g
Eucalypt 550	27.0 ± 0.9 e	44.1 ± 1.2 h	1.8 ± 0.6 ab	4.2 ± 1.0 c	4.7 ± 1.7 bc	4.2 ± 1.0 abc	6.7 ± 2.1 cdef	7.8 ± 1.7 efg

Table S6. Proton retention (µMol g^{-1}) in Gilman soil mixed with organic materials over four leaching events with RO water (n=4). Values followed by different letters are significantly different ($P \leq 0.05$)

	Leaching event				Cumulative retention
	1	2	3	4	
Organic materials	Proton retention (µMol g^{-1})				
Wheat straw	16.3 ± 0.7 a	5.6 ± 0.4 a	2.9 ± 0.1 b	2.7 ± 0.1 b	27.5 ± 1.2 a
Pea Straw	23.4 ± 0.4 c	6.4 ± 0.4 b	3.2 ± 0.03 c	3.0 ± 0.1 c	36.0 ± 0.7 c
Compost	20.0 ± 0.1 b	4.9 ± 0.02 a	2.3 ± 0.01 a	2.2 ± 0.01 a	29.5 ± 0.1 b
Poultry 450	28.2 ± 0.2 e	7.5 ± 0.2 c	3.5 ± 0.03 d	3.3 ± 0.1 d	42.5 ± 0.3 e
Poultry 550	25.9 ± 0.1 d	6.4 ± 0.03 b	3.0 ± 0.01 b	2.9 ± 0.02 bc	38.1 ± 0.1 d
Wheat 450	31.4 ± 0.3 g	8.0 ± 0.2 cd	3.8 ± 0.1 e	3.7 ± 0.1 d	47.0 ± 0.6 f
Wheat 550	25.1 ± 0.3 d	6.4 ± 0.1 b	3.0 ± 0.03 b	2.9 ± 0.02 bc	37.3 ± 0.3 cd
Eucalypt 550	29.6 ± 0.6 f	8.3 ± 0.3 d	3.8 ± 0.1 e	3.6 ± 0.1 d	45.2 ± 0.8 f

Table S7. Proton retention (µMol g^{-1}) in Gilman soil with organic materials as layer over four leaching events with RO water (n=4). Values followed by different letters are significantly different ($P \leq 0.05$)

	Leaching event				Cumulative retention
	1	2	3	4	
Organic materials	Proton retention (µMol g^{-1})				
Wheat straw	23.9 ± 0.4 bc	5.3 ± 0.2 a	2.3 ± 0.1 a	2.0 ± 0.3 a	33.5 ± 0.4 b
Pea Straw	24.8 ± 0.6 c	7.8 ± 0.02 c	3.6 ± 0.01 c	3.5 ± 0.01 c	39.7 ± 0.6 d
Compost	19.7 ± 0.2 a	5.1 ± 0.00 a	2.4 ± 0.00 a	2.3 ± 0.00 a	29.3 ± 0.2 a
Poultry 450	24.4 ± 0.3 bc	7.9 ± 0.2 c	3.8 ± 0.1 c	3.7 ± 0.1 c	39.8 ± 0.6 d
Poultry 550	22.8 ± 0.8 b	6.5 ± 0.1 b	3.0 ± 0.04 b	2.9 ± 0.04 b	35.3 ± 0.8 bc
Wheat 450	29.3 ± 0.5 e	8.8 ± 0.4 d	4.3 ± 0.04 d	4.2 ± 0.02 d	46.6 ± 0.9 f
Wheat 550	23.0 ± 0.4 b	6.9 ± 0.00 b	3.2 ± 0.00 b	3.1 ± 0.01 b	36.1 ± 0.4 c
Eucalypt 550	27.1 ± 0.8 d	8.2 ± 0.5 cd	4.3 ± 0.11 d	4.2 ± 0.1 d	43.8 ± 1.2 e

Table S8. Fe retention (µg g^{-1}) in Gilman soil mixed with organic materials over four leaching events with RO water (n=4). Values followed by different letters are significantly different (P≤ 0.05)

	Leaching event				Cumulative retention
	1	2	3	4	
	Fe retention (µg g^{-1})				
Wheat straw	-318.3 ± 12.5 a	38.8 ± 9.1 b	86.3 ± 16.5 bc	132.4 ± 13.3 d	-60.9 ± 33.2 a
Pea Straw	-267.3 ± 5.9 b	31.9 ± 15.4 b	97.2 ± 11.7 abc	120.6 ± 20.3 cd	-17.7 ± 37.9 a
Compost	706.5 ± 1.4 c	8.7 ± 8.9 ab	35.9 ± 11.0 c	35.3 ± 12.6 ab	786.4 ± 12.5 b
Poultry 450	1072.3 ± 7.1 e	-6.2 ± 13.6 a	73.2 ± 17.6 bc	124.3 ± 19.0 cd	1263.7 ± 45.1 e
Poultry 550	949.1 ± 1.3 d	31.2 ± 9.9 b	62.1 ± 17.0 bc	111.7 ± 4.3 cd	1154.0 ± 21.4 cd
Wheat 450	1147.2 ± 11.0 f	72.8 ± 5.2 c	-8.9 ± 27.5 a	-3.8 ± 40.8 a	1207.3 ± 48.1 de
Wheat 550	925.8 ± 3.0 d	39.4 ± 5.0 b	24.2 ± 24.8 ab	64.8 ± 21.3 bc	1054.2 ± 38.5 c
Eucalypt 550	935.8 ± 19.2 d	70.1 ± 3.0 c	92.0 ± 36.3 bc	35.8 ± 8.6 ab	1133.7 ± 30.2 cd

Table S9. Fe retention (µg g^{-1}) in Gilman soil with organic materials as layer over four leaching events with RO water (n=4). Values followed by different letters are significantly different (P≤ 0.05)

	Leaching event				Cumulative retention
	1	2	3	4	
	Fe retention (µg g^{-1})				
Wheat straw	415.3 ± 6.6 a	45.3 ± 9.3 b	88.8 ± 7.5 c	123.8 ± 4.5 c	673.2 ± 12.4 b
Pea Straw	596.7 ± 3.9 c	43.6 ± 5.8 b	113.9 ± 2.5 c	138.4 ± 7.1 c	892.5 ± 10.7 c
Compost	495.6 ± 23.8 b	34.4 ± 2.6 b	-37.8 ± 16.2 b	-3.0 ± 26.0 ab	489.2 ± 34.6 a
Poultry 450	705.6 ± 24.8 d	23.7 ± 5.6 ab	95.1 ± 12.6 c	21.1 ± 25.0 ab	845.6 ± 31.7 c
Poultry 550	783.1 ± 24.1 e	46.9 ± 2.7 b	14.5 ± 10.8 b	48.2 ± 22.1 b	892.7 ± 29.4 c
Wheat 450	688.8 ± 41.2 d	-22.8 ± 27.6 a	80.8 ± 27.6 c	31.8 ± 12.1 b	778.5 ± 73.7 bc
Wheat 550	626.6 ± 9.3 c	53.5 ± 10.0 b	-97.7 ± 26.7 a	-33.6 ± 28.7 a	548.8 ± 26.9 a
Eucalypt 550	776.1 ± 4.9 e	-14.1 ± 30.2 a	75.6 ± 25.9 c	10.7 ± 8.5 ab	848.2 ± 43.9 c

Table S10. Al retention (µg g^{-1}) Gilman soil mixed with organic materials over four leaching events with RO water (n=4). Values followed by different letters are significantly different ($P \leq 0.05$)

	Leaching event				Cumulative retention
	1	2	3	4	
	Al retention (µg g^{-1})				
Wheat straw	2352.5 ± 101.5 a	93.2 ± 7.0 b	71.7 ± 18.9 b	139.8 ± 16.9 b	2657.2 ± 112.5 a
Pea Straw	3103.3 ± 56.6 b	75.9 ± 16.2 ab	74.0 ± 15.6 b	115.1 ± 27.3 b	3368.4 ± 40.7 c
Compost	2873.8 ± 3.0 c	45.1 ± 10.9 a	41.5 ± 12.9 ab	37.2 ± 21.7 ab	2997.6 ± 28.3 b
Poultry 450	4434.7 ± 13.0 f	72.5 ± 16.2 ab	48.2 ± 23.9 ab	118.0 ± 25.5 b	4673.3 ±63.8 f
Poultry 550	3776.5 ± 2.6 d	66.6 ± 10.8 ab	57.8 ± 17.0 b	119.6 ± 6.6 b	4020.4 ± 21.7 d
Wheat 450	4737.7 ± 37.0 g	136.6 ± 4.7 c	-45.9 ± 33.4 a	-38.8 ± 58.7 a	4789.7 ± 76.3 f
Wheat 550	3743.5 ± 8.5 d	72.3 ± 7.4 ab	-5.1 ± 29.6 ab	67.9 ± 21.5 ab	3878.6 ± 42.8 d
Eucalpt 550	4236.4 ± 52.2 e	102.8 ± 22.6 bc	2.7 ± 64.3 ab	21.1 ± 76.9 ab	4363.1 ± 154.5 e

Table S11 Al retention (μg g^{-1}) in Gilman soil with organic materials as layer over four leaching events with RO water (n=4). Values followed by different letters are significantly different (P≤ 0.05)

	Leaching event				Cumulative retention
	1	2	3	4	
	Al retention (μg g^{-1})				
Wheat straw	2197.7 ± 54.6 a	8.7 ± 18.5 ab	63.7 ± 10.1 d	127.20± 4.7 cd	2397.3 ± 54.9 ab
Pea Straw	2648.8 ± 43.9 b	68.3 ± 2.8 bc	100.7 ± 1.5 d	149.4 ± 8.6 d	2967.2 ± 43.3 c
Compost	2228.8 ± 46.0 a	67.1 ± 1.9 bc	-76.2 ± 19.4 b	-28.5 ± 35.4 ab	2191.2 ± 35.7 a
Poultry 450	2999.1 ± 78.2 c	64.4 ± 7.6 bc	63.8 ± 16.8 d	-24.7 ± 33.3 ab	3102.6 ± 80.2 cd
Poultry 550	3277.4 ± 63.4 d	79.2 ± 3.5 c	-26.9 ± 13.9 bc	24.1 ± 29.8 bc	3353.8 ± 47.5 d
Wheat 450	2978.8 ± 46.8 c	-1.2 ± 36.9 a	33.7 ± 38.8 cd	11.1 ± 35.5 ab	3022.3 ± 115.6 c
Wheat 550	2731.2 ± 56.8 b	80.4 ± 13.4 c	-195.7 ± 40.9 a	-94.6 ± 40.6 a	2521.2 ± 77.7 b
Eucalypt 550	3283.0 ± 67.2 d	15.1 ± 38.1 abc	20.7 ± 36.0 cd	-18.6 ± 62.7 ab	3300.3 ± 149.8 d

Table S12. Correlation between proton retention in organic materials mixed with Gilman acid sulfate soil with their properties in the first and cumulative leaching events.

	1. Leaching event			Cumulative retention		
	Equation	R square	P (95%)	Equation	R square	P (95%)
C	y = 0.0376x + 8.7299	0.4317	0.077	y = 0.0606x + 11.67	0.5806	0.028
N	y = 0.2874x + 21.052	0.1558	0.333	y = 0.2906x + 33.899	0.0824	0.490
C/N ratio	y = -0.0364x + 26.647	0.064	0.545	y = -0.0244x + 38.993	0.0149	0.774
ANC	y = 0.3071x + 23.734	0.0324	0.670	y = 0.1238x + 37.377	0.0027	0.902
CEC	y = 0.2245x + 15.066	0.3276	0.138	y = 0.2448x + 27.062	0.2015	0.564
Surface area	y = 0.0387x + 24.876	0.0004	0.961	y = -0.2265x + 38.581	0.0077	0.837
Alkyl	y = 0.1931x + 22.816	0.0359	0.653	y = 0.1123x + 36.618	0.0063	0.852
N-Alkyl/Methoxyl	y = -0.8533x + 29.187	0.1074	0.429	y = -1.3914x + 44.721	0.1479	0.347
O-Alkyl	y = -0.8533x + 29.187	0.4906	0.053	y = -0.1889x + 42.812	0.4021	0.091
Di-O-Alkyl	y = -0.8481x + 31.292	0.4852	0.055	y = -1.0559x + 45.726	0.3893	0.098
Aryl	y = 0.1542x + 19.67	0.4661	0.062	y = 0.2012x + 30.938	0.4107	0.087
O-Aryl	y = 0.9183x + 16.983	0.588	0.026	y = 1.2207x + 27.235	0.5379	0.038
Amide/Carboxyl	y = -0.4472x + 27.198	0.0193	0.743	y = -0.8995x + 42.316	0.0404	0.633
Ketone	y = 3.5823x + 17.517	0.6004	0.024	y = 4.7867x + 27.893	0.5549	0.034

Table S13. Correlation between proton retained on organic materials placed as a layer under Gilman acid sulfate soil with their properties in firstand and cumulative leaching events.

	1. Leaching event			Cumulative retention		
	Equation	R square	P (95%)	Equation	R square	P (95%)
C	y = 0.031x + 10.94	0.8871	0.000	y = 0.0594x + 12.327	0.859	0.001
N	y = -0.0242x + 24.691	0.0033	0.891	y = 0.0318x + 37.588	0.0015	0.927
C/N ratio	y = 0.0257x + 23.191	0.0967	0.453	y = 0.0251x + 36.885	0.0243	0.712
ANC	y = -0.5349x + 26.556	0.2967	0.162	y = -0.7347x + 41.041	0.1478	0.347
CEC	y = -0.0125x + 24.912	0.0031	0.895	y = 0.0669x + 35.066	0.0232	0.719
Surface area	y = -0.5371x + 26.007	0.252	0.205	y = -0.8736x + 40.705	0.176	0.301
Alkyl	y = -0.1509x + 26.063	0.0662	0.537	y = -0.1944x + 40.218	0.029	0.687
N-Alkyl/Methoxyl	y = -0.6559x + 27.581	0.1916	0.278	y = -1.1546x + 43.696	0.1568	0.331
O-Alkyl	y = -0.0205x + 24.893	0.0276	0.695	y = -0.0704x + 39.859	0.0859	0.481
Di-O-Alkyl	y = -0.1098x + 25.174	0.0245	0.712	y = -0.3954x + 40.96	0.0841	0.486
Aryl	y = 0.0304x + 23.309	0.0547	0.578	y = 0.0865x + 35.035	0.117	0.407
O-Aryl	y = 0.2281x + 22.369	0.1095	0.424	y = 0.6037x + 32.757	0.2026	0.263
Amide/Carboxyl	y = -0.4377x + 26.515	0.0558	0.572	y = -0.8222x + 42.074	0.052	0.587
Ketone	y = 1.1064x + 22.049	0.1729	0.306	y = 2.653x + 32.486	0.2625	0.194

Table S14. Correlation between Fe retention in on organic materials mixed with Gilman acid sulfate soil with their properties in first and cumulative leaching events.

	1. Leaching event			Cumulative retention		
	Equation	R square	P (95%)	Equation	R square	P (95%)
C	y = 1.0937x + 170.46	0.0262	0.702	y = 1.2255x + 284.64	0.0386	0.641
N	y = 56.561x - 132.21	0.4323	0.076	y = 47.703x + 160.54	0.3612	0.115
C/N ratio	y = -8.735x + 1040.4	0.2643	0.192	y = -7.3759x + 1149.9	0.2213	0.239
ANC	y = 141.99x + 60.827	0.4961	0.051	y = 129.24x + 284.41	0.4827	0.056
CEC	y = 32.432x - 790.38	0.4898	0.053	y = 28.249x - 434.18	0.4364	0.075
Surface area	y = 90.998x + 364.63	0.1717	0.307	y = 85.926x + 551.4	0.1797	0.295
Alkyl	y = 70.871x - 156.08	0.3465	0.125	y = 56.93x + 172.49	0.2626	0.194
N-Alkyl/Methoxyl	y = -32.765x + 804.84	0.0113	0.802	y = -50.477x + 1063.1	0.0316	0.673
O-Alkyl	y = -22.942x + 1242.1	0.8206	0.002	y = -21.367x + 1372.2	0.836	0.001
Di-O-Alkyl	y = -128.73x + 1599.7	0.8009	0.003	y = -118.79x + 1697.1	0.8009	0.003
Aryl	y = 20.964x - 80.17	0.6173	0.021	y = 20.216x + 116.88	0.6741	0.012
O-Aryl	y = 124.43x - 441.79	0.7735	0.004	y = 117x - 205.74	0.8032	0.003
Amide/Carboxyl	y = 40.882x + 442.53	0.0116	0.800	y = 5.5628x + 787.69	0.0003	0.97
Ketone	y = 471.74x - 340.88	0.746	0.006	y = 433.5x - 89.839	0.7398	0.006
Proton	y = 89.649x - 1596.9	0.5789	0.029	y = 55.499x - 1287.6	0.5007	0.05
Al	y = 0.593x - 1524.8	0.6807	0.012	y = 0.5753x - 1396	0.6705	0.013

Table S15. Correlation between Fe retained on organic materials placed as a layer under Gilman acid sulfate soil with their properties in first and cumulative leaching events

	1. Leaching event			Cumulative retention		
	Equation	R square	P (95%)	Equation	R square	P (95%)
C	y = 0.7104x + 328.48	0.2281	0.231	y = 1.1145x + 263.7	0.3827	0.102
N	y = 4.1587x + 578.9	0.0482	0.601	y = -4.708x + 810.69	0.0421	0.626
C/N ratio	y = -0.7122x + 668.3	0.0363	0.652	y = 0.9304x + 703.85	0.0422	0.626
ANC	y = 15.316x + 573.07	0.1191	0.402	y = -19.399x + 825.75	0.1303	0.380
CEC	y = 5.1062x + 410.15	0.2505	0.207	y = -0.84x + 783.23	0.0046	0.873
Surface area	y = 16.167x + 586.36	0.1118	0.418	y = -11.618x + 781.74	0.0394	0.638
Alkyl	y = 0.7235x + 627.8	0.0007	0.949	y = -18.807x + 958.37	0.3432	0.127
N-Alkyl/Methoxyl	y = -36.652x + 816.02	0.293	0.166	y = -42.63x + 955.51	0.2702	0.187
O-Alkyl	y = -4.2525x + 746.85	0.5817	0.028	y = -0.1451x + 749.87	0.0005	0.960
Di-O-Alkyl	y = -23.409x + 809.78	0.5464	0.036	y = 0.7689x + 740.38	0.0004	0.962
Aryl	y = 4.9092x + 466.41	0.6983	0.010	y = 1.6082x + 690.55	0.0511	0.590
O-Aryl	y = 23.714x + 429.06	0.5796	0.028	y = 2.5839x + 723.54	0.0047	0.872
Amide/Carboxyl	y = -34.271x + 804.75	0.1676	0.314	y = -63.206x + 1057.4	0.3886	0.099
Ketone	y = 79.587x + 469.83	0.438	0.074	y = -5.52x + 757.61	0.0014	0.929
Proton	y = 19.864x + 152.1	0.1932	0.276	y = 17.333x + 87.028	0.3798	0.104
Al	y = 0.305x - 215.93	0.9765	0.000	y = 0.3318x - 201.83	0.8267	0.002

Table S16. Correlation between Al retained on organic materials mixed with Gilman acid sulfate soil with their properties in the first and cumulative leaching events

	1. Leaching event			Cumulative retention		
	Equation	R square	P (95%)	Equation	R square	P (95%)
C	y = 5.8652x + 1118.6	0.3893	0.098	y = 5.6864x + 1382.2	0.4106	0.087
N	y = 55.717x + 2892.8	0.2167	0.245	y = 48.43x + 3179	0.1837	0.289
C/N ratio	y = -7.168x + 3982.7	0.0919	0.465	y = -6.2961x + 4129.3	0.0796	0.498
ANC	y = 66.238x + 3385.3	0.0558	0.573	y = 55.115x + 3617.2	0.0433	0.621
CEC	y = 35.712x + 2078	0.3068	0.154	y = 31.231x + 2462.4	0.2632	0.193
Surface area	y = 7.58x + 3634.1	0.0006	0.954	y = 4.1312x + 3830.9	0.0002	0.973
Alkyl	y = 35.959x + 3251.4	0.0461	0.610	y = 21.647x + 3599.2	0.0187	0.747
N-Alkyl/Methoxyl	y = -128.23x + 4287.2	0.0898	0.471	y = -137.37x + 4518.3	0.1156	0.410
O-Alkyl	y = -25.308x + 4317.2	0.5159	0.045	y = -22.922x + 4441.2	0.4748	0.059
Di-O-Alkyl	y = -140.23x + 4698.5	0.491	0.053	y = -125.37x + 4774.4	0.4403	0.073
Aryl	y = 25.515x + 2776.1	0.4724	0.060	y = 23.891x + 3018.4	0.4647	0.063
O-Aryl	y = 156.51x + 2291.7	0.6322	0.018	y = 143.5x + 2591.5	0.5963	0.025
Amide/Carboxyl	y = -71.93x + 4011.6	0.0185	0.748	y = -105.46x + 4362.9	0.0446	0.616
Ketone	y = 610.83x + 2382.2	0.6461	0.016	y = 549.75x + 2695.9	0.5872	0.027
Proton	y = 161.03x - 367.7	0.9598	0.000	y = 107.66x - 235.19	0.9299	0.000

Table S17. Correlation between Al retained on organic materials placed as a layer under Gilman acid sulfate soil with their properties in first, second and cumulative leaching events

	1. Leaching event			cumulative retention		
	Equation	R square	P (95%)	Equation	R square	P (95%)
C	y = 2.702x + 1623.6	0.3143	0.148	y = 3.1247x + 1504.5	0.4006	0.092
N	y = 7.5738x + 2689.2	0.0152	0.771	y = -1.3756x + 2875.9	0.0005	0.959
C/N ratio	y = -0.8683x + 2832.5	0.0051	0.866	y = 0.7526x + 2822.8	0.0037	0.887
ANC	y = 34.787x + 2650.3	0.0585	0.564	y = -5.3142x + 2878.8	0.0013	0.932
CEC	y = 12.456x + 2242.3	0.142	0.358	y = 6.5x + 2569.5	0.0369	0.649
Surface area	y = 44.261x + 2657.3	0.0798	0.498	y = 10.264x + 2825.5	0.0041	0.880
Alkyl	y = -7.6314x + 2879.2	0.0079	0.834	y = -28.834x + 3182.5	0.1074	0.428
N-Alkyl/Methoxyl	y = -140.99x + 3485.7	0.413	0.086	y = -139.45x + 3542	0.3851	0.101
O-Alkyl	y = -13.09x + 3134.4	0.5251	0.042	y = -8.0371x + 3066.6	0.1887	0.282
Di-O-Alkyl	y = -70.908x + 3319.6	0.4776	0.058	y = -8.0371x + 3066.6	0.1566	0.332
Aryl	y = 15.834x + 2246.2	0.692	0.010	y = 11.59x + 2456.7	0.3534	0.120
O-Aryl	y = 75.123x + 2137.7	0.5541	0.034	y = 47.901x + 2439	0.2147	0.248
Amide/Carboxyl	y = -136.93x + 3467.5	0.2548	0.202	y = -162.56x + 3657.6	0.3423	0.128
Ketone	y = 250.28x + 2270.6	0.4127	0.086	y = 140.05x + 2564.6	0.1232	0.394
Proton	y = 75.612x + 951.25	0.2667	0.190	y = 53.15x + 835.99	0.4756	0.058

CHAPTER 3

ORGANIC MATERIALS DIFFER IN ABILITY TO REMOVE PROTONS, IRON AND ALUMINIUM FROM ACID SULFATE SOIL DRAINAGE WATER

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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	15/02/2017

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.

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Organic Materials Differ in Ability to Remove Protons, Iron and Aluminium from Acid Sulfate Soil Drainage Water

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Abstract Drainage water from acid sulfate soils with sulfuric material has high concentrations of protons and dissolved metals which can have detrimental effects on the surrounding ecosystems. Liming is expensive; therefore, alternative methods are needed. Organic materials such as plant residues, compost or biochars can bind protons and metals but have not been evaluated with respect to remediation of acid drainage water from acid sulfate soils. In this study, eight organic materials (compost, two straws and five biochars differing in feed stock and production temperature) were placed in small PVC cores at 1.5 g C/core and synthetic acid drainage water (pH 3, 28 mg Fe/l and 2 mg Al/l, properties based on long-term averages of drainage water from sulfuric acid sulfate soils) was applied in four leaching events. Mallee biochar produced at 550 °C and wheat biochar produced at 450 °C had high retention capacity for protons, Fe and Al. Retention was low in compost and wheat straw. Retention of protons was positively correlated with organic C concentration of the materials. Retention of Fe and Al was correlated with percentage alkyl, aryl and ketone groups. Other properties such as release of native Fe and Al and amount of material per core could explain differences in ability of organic materials to retain protons, Fe and Al. We conclude that some organic materials such as mallee biochar produced at 550 °C and wheat biochar produced at 450 °C could be used to remediate acidic drainage water.

Keywords Aluminium · Biochar · Drainage water · Iron · Proton · Retention

1 Introduction

Acid sulfate soils (ASS) contain iron sulphides such as pyrite which is formed under water-logged conditions. When exposed to oxygen upon drainage, pyrite can be oxidised to produce sulfuric acid, which results in soil acidification (Attanandana and Vacharotayan 1986; Dent 1986; Pons 1973) and sequential metal release (Astrom 1998). The low pH induces leaching of nutrients, such as Ca and Mg, and release of soluble metals causing toxicity to plants and microorganisms (Attanandana and Vacharotayan 1986; Dent 1986; Pons 1973; Rabenhorst and Fanning 2002; Ritchie 1989). In material with low acid neutralising capacity (e.g. low carbonate concentration), the pH may drop below four (Attanandana and Vacharotayan 1986; Dent 1986) or two (Dent and Pons 1995). Acid sulfate soils occur in a wide range of environments such as coastal zones as well as inland including rivers and stream channels, lakes, wetlands and mine sites

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(EPHC and NRMMC 2011; Fitzpatrick and Shand 2008a). Globally, they are found in up to 24 million ha (Sullivan 2004), occupying extensive areas in South-East Asia, Western Africa, Australia, Latin America and Europe (Österholm et al. 2012). The total ASS area in Australia is 215,000 km^2, of which 157,000 km^2 is inland and 58,000 km^2 is coastal (Fitzpatrick et al. 2009).

ASS may pose a serious risk to ecosystems, agricultural productivity, human health and other assets due to low pH and toxicity of metals released when they are oxidised (Baldwin 2009; DERM 2011; Fitzpatrick and Shand 2008; Ljung et al. 2009; Simpson et al. 2008b). It is estimated that this damage due to poor acid sulfate soil management amounts to a \$10 billion legacy in Australia alone (Fitzpatrick 2003).

Long drought periods such as Australia's recent "millennium" drought resulted in large areas of previously inundated sediments and subaqueous soils being exposed and oxidised. For example, approximately 3500 ha of sulphidic material were exposed in subsoils of the Lower Murray Reclaimed Irrigation Area (LMRIA) due to falling groundwater levels and lack of irrigation during this period (Mosley et al. 2014a). Pyrite-rich material was oxidised to depths up to 4 m (Fitzpatrick et al. 2009), and surface water and groundwater became acidic (Mosley et al. 2014c). Even now, after several years of flood irrigation, drainage water and groundwater have low pH and high concentrations of dissolved metals that exceeded Australian Drinking water guidelines, and Al and Fe are precipitated in drainage channels (Mosley et al. 2014a; Simpson et al. 2008a; Simpson et al. 2014). Addition of hydrated lime ($CaOH_2$) or limestone ($CaCO_3$) to neutralise acid drainage water is very expensive. In addition, lime-based neutralising materials may not be available in many locations or costly to transport to the acid-affected site. Therefore, it is important to find alternative methods to remediate acidic drainage water.

Organic material addition to soil in the form of plant residues, manure or compost can increase the pH of acid soils (Xu et al. 2006) and bind metals (Clemente et al. 2006; Dias et al. 2003; Fest et al. 2008; Karami et al. 2011; Walker et al. 2004) and protons (Pedra et al. 2008). Biochar and other organic material have been used to reduce metal concentrations in leachate from mine tailings (Beesley et al. 2014; Fellet et al. 2011) and wastewater (Bhatnagar and Sillanpää 2010; Wan Ngah and Hanafiah 2008; Zhou and Haynes 2010). In studies with single or multiple metals, organic materials were shown to differ in Pb, Cd, As, Cu, Zn and Ni adsorption and desorption (Arcibar-Orozco et al. 2014; Choi et al. 2013; Houben et al. 2013; Kołodyńska et al. 2012; Trakal et al. 2014). Organic materials, for example, manures, sawdust and cattle slurry, have been used to increase the pH and remove metals from acid main drainage (Henze and Comeau 2008; Hughes and Gray 2013, Hughes et al. 2013; Jeen et al. 2014; Zhang and Wang 2014). In most cases, metal and acidity removal from acid mine drainage was studied in batch or column experiments (Hughes and Gray 2013; Hughes et al. 2013; Jeen et al. 2014; Kijjanapanich et al. 2012; Zhang and Wang 2014) after addition of lime or sulfate-reducing bacteria. This will alter the chemical environment within the organic materials. Drainage water from acid sulfate soils (Mosley et al. 2014a; Mosley et al. 2014b; Simpson et al. 2014) differs from acid mine drainage (Sracek et al. 2004) with respect to acidity, sulfate concentration, dominant metals and metal speciation (Hughes and Gray 2013; Jeen et al. 2014). This may influence metal and proton binding. Further, little is known about the relationship between proton and metal binding and properties of the organic materials.

The aim of this study was to compare the ability of different organic materials to remove protons and Al and Fe from ASS drainage water. We hypothesised that (i) passage of acidic ASS drainage water through organic materials will increase pH and reduce metal concentrations and (ii) the effect of the organic materials will differ depending on their properties such as acid neutralising capacity, cation exchange capacity and organic C composition.

2 Materials and Methods

2.1 Experimental Design

Synthetic drainage water was prepared based on long-term average properties of LMRIA drainage water according to Mosley et al. (2014a): in milligrams per liter Fe 28, Al 2, Mn 2, Na 1380, Ca 922, K 43, Mg 170, SO_4 5110 and Cl 567. The pH of the solution was adjusted to pH 3.0 with concentrated H_2SO_4.

The following organic materials were used: wheat straw, pea straw, compost (from municipal green waste) and five biochars from different feed stocks, produced at

450 or 550 °C: poultry biochar 450 °C, poultry biochar 550 °C, wheat biochar 450 °C, wheat biochar 550 °C and mallee (eucalyptus-dominated vegetation typical for semi-arid areas of southern Australia) biochar 550 °C (Table 1).

The organic materials were ground and sieved to 0.5–2 mm and placed in PVC cores (3.7 cm width, 5.0 cm height) with a mesh base (0.75 μm; Australian Filter Specialist Pty Ltd., Huntingwood, NSW) at 1.5 g C/core. Before adding the organic materials, filter paper Whatman #42 was placed on the mesh to minimise loss of materials during the leaching events. There were four replicates per organic material. The cores were leached four times with the synthetic drainage water. Controls were leached with reverse osmosis (RO) water (one replicate per organic material). At each leaching event, a total of 45 ml solution was added per core, in nine aliquots of 5 ml with 5 min between each addition. The total amount of solution (45 ml) per leaching event was chosen based on preliminary studies to ensure sufficient leachate for the analyses. The 5-min interval between additions was considered sufficient to allow interaction of the solution with the organic material. After addition of 45 ml, the leachate was collected and the total volume was measured and analysed as described below. Leaching was carried out every 7 days. In the interval between leaching events, the organic materials were left undisturbed at room temperature. The materials lost water through evaporation, but remained moist.

2.2 Analyses

The pH of the organic materials was measured in a material to water ratio of 1:1 (*w*/*w*). Total organic C and total N were measured by dry combustion using a LECO Trumac CN analyser.

Acid neutralising capacity (ANC) expressed as $CaCO_3$ equivalent was determined by the rapid titration method as described in Ahern et al. (2004). Briefly, 1 g of finely ground organic material was placed into a 250-ml flask with 50 ml of deionised water and 25 ml of standardised 0.1 M HCl. The suspensions were boiled on a hotplate for 2 min and then allowed to cool to room temperature. The unreacted acid in the flask was titrated with standardised 0.1 M NaOH to pH 7.

Surface area was analysed by nitrogen gas adsorption method and calculated as described by Brunauer et al. (1938). The organic materials were degassed overnight at a vacuum of 10^{-5} kPa prior to measuring nitrogen adsorption. Biochar samples were degassed at 200 °C, plant residues and compost at ambient temperature. Nitrogen gas adsorption was measured at 77 K using a Belsorp-max gas adsorption apparatus. Ultra high purity (>99.999 %) helium and nitrogen were used for dead space measurements and adsorption experiments, respectively.

Cation exchange capacity (CEC) was determined after Rayment and Lysons (2011). The organic materials were extracted with 0.1 M NH_4Cl at a 1:30 *w*/*w* ratio in an end-over-end shaker for 1 h. The extracts were centrifuged at 3000 rpm for 10 min, the supernatant filtered through Whatman #42 filter paper. The solution was analysed by inductively coupled plasma mass spectroscopy (ICP-MS).

Total Al and Fe in the organic materials were determined after acid dissolution (Zarcinas et al. 1996). The extracts were filtered through Whatman #42 filter paper and analysed for Al and Fe by ICP-MS.

Chemical groups of organic materials were measured by solid-sate ^{13}C nuclear magnetic resonance (NMR)

Table 1 Properties of organic materials

	Amount (g/core)	pH_w	C (mg/g)	N	C/N	ANC (% $CaCO_3$)	CEC $cmol_c$/kg	Surface area (m^2/g)	Total Al (mg/g)	Total Fe
Wheat straw	3.5	5.5	427	4.3	100	0.03	15.6	0.8	0.2	0.2
Pea Straw	3.4	6.3	440	8.8	50	0.4	43.4	0.9	0.4	0.3
Compost	5.3	8.2	283	20.2	14	7.5	53.9	4.0	9.4	8.9
Poultry 450	3.2	7.7	475	16.8	28	4.8	44.9	1.2	2.1	2.9
Poultry 550	4.0	9.6	372	16.6	22	7.1	50.9	7.9	2.9	3.7
Wheat 450	2.8	8.4	529	23.4	23	2.5	54.8	1.1	1.7	2.6
Wheat 550	3.9	9.0	385	14.2	27	6.7	51.0	6.1	1.8	2.2
Mallee 550	2.7	7.5	552	5.6	98	3.8	39.3	2.5	3.8	19.8

spectroscopy as described in Smernik and Oades (2000) and McBeath et al. (2014) for organic matter and biochar, respectively.

The pH of the leachate was measured immediately after collection. The leachates were filtered through a 0.45-µm filter before measuring Al and Fe by ICP-MS.

2.3 Statistical Analyses

Leachate data were expressed as protons (10^{-pH}), Fe and Al retained in the materials for each leaching event and total cumulative retention. Retention per core was calculated as

(Concentration of element in added solution per ml × amount of added solution in ml)−(Concentration of element in leachate per ml × amount of leachate in ml). This value was divided by the amount of organic material per core to give retention per gram of material.

Cumulative retention is the sum of retention in the four leaching events. The data were analysed by one-way ANOVA for each leaching event separately and for cumulative retention. Differences between means were compared by Duncan analysis ($P \leq 0.05$) using GenStat 15th edition (GenStat 2013). Linear correlations between proton, Fe and Al retention and organic material properties were calculated with SPSS 20th edition. The correlations were calculated for the first leaching event and cumulative retention of the first and second leaching events.

3 Results

3.1 Properties of Organic Materials

Wheat biochar 550 had the highest pH (9.0), wheat straw the lowest (7.5; Table 1). For poultry litter and wheat biochar, the pH was lower in biochar produced at 450 compared to 550 °C. The organic C concentration was highest in mallee biochar and lowest in compost. Since the amount of material was 2.5 g C/core, the amount per core was lowest for mallee 550 and highest for compost. Poultry litter and wheat biochar produced at 550 °C had a lower organic C concentration than that produced at 450 °C. Wheat biochar 450 and compost had a higher total N concentration than the other organic materials. Total N concentration was lowest in wheat straw followed by mallee biochar and pea straw. Total N concentration was not affected by production temperature in poultry litter and wheat biochar. The C/N ratio ranged from 14 to 100; it was highest in wheat straw and lowest in compost. Among the organic materials, compost had the highest ANC, wheat straw the lowest. For poultry litter and wheat straw, biochar produced at 450 °C had a lower ANC than that produced at 550 °C. The CEC was higher in wheat 450 and compost than in the other organic materials; it was lowest in wheat straw. The temperature at which the biochar was produced had no consistent effect on CEC. The two straws (wheat and pea) had the lowest surface area. Surface area was highest in poultry 550 where it was eight times higher than in the straws. Biochar produced at 550 °C had a 6–7-fold higher surface area than biochar produced at 450 °C. The Al and Fe concentrations were low in the two straws and high in compost and mallee 550.

The two plant residues (wheat and pea straw) had the highest percentage of O-alkyl and di-O-alkyl groups and the lowest percentage of aryl, O-aryl and ketone (Table 2). Compost had the highest percentage of alkyl groups. Poultry litter and wheat biochar produced at 450 °C had higher percentages of N-alkyl and O-alkyl,

Table 2 Carbon groups of organic materials based on NMR spectroscopy

	Alkyl % of organic C detected	N-Alkyl/methoxyl	O-Alkyl	Di-O-alkyl	Aryl	O-Aryl	Amide/carboxyl	Ketone
Wheat straw	4.8	4.3	61.3	14.1	7.4	3.2	4.1	0.7
Pea Straw	6.8	5.6	59.4	12.8	7.2	2.8	4.7	0.6
Compost	20.3	8.9	31.2	7.7	16.1	6.1	8.2	1.5
Poultry 450	9.2	5.5	26.6	8.2	34.3	9.9	4.1	2.2
Poultry 550	10.4	2.8	5.1	4.1	61.7	10.4	3.3	2.1
Wheat 450	15.3	5.2	14.9	5.2	39.2	10.9	6.2	3.1
Wheat 550	13.2	3.9	5.6	3.7	52.9	12.9	4.5	3.3
Mallee 550	10.3	3.1	4.5	3.6	57.5	13.6	4.3	3.2

but lower percentages of aryl and O-aryl than biochar produced at 550 °C.

3.2 Leaching with Synthetic Drainage Water

The leachate volume was higher in the first leaching event than in the following events (Table S1). At a given leaching event, leachate volume was lower in wheat and pea straw than in the other organic materials. It was highest in the two poultry biochars and mallee 550. For example, only 11 % of the added solution was retained in the first leaching event in the poultry biochars compared to 44 % in wheat and pea straw.

In the first leaching event, passage through compost, poultry 550 and wheat 550 increased the pH from pH 3 (added solution) to about 7, whereas poultry 450, wheat 450 and mallee 550 increased the pH only to 4.5–5 (Table 3). Compost was the only organic material that consistently increased the pH of the leached solution to above pH 7. For most other materials, the pH increase was greater in the first two leaching events than the third and fourth events.

Proton retention was greatest in the first leaching event and lowest in the fourth leaching event (Fig. 1a, Table S2). Differences in proton retention among leaching events were greatest in wheat straw and smallest in compost. At the first leaching event, proton retention was lowest with compost and highest in mallee 550. Cumulative proton retention was lowest in compost followed by wheat straw and highest in wheat 450 and mallee 550 (Tables 4 and S2). In wheat 450, proton retention was nearly 2-fold higher than in compost.

Iron retention was greatest in the second leaching event and lowest in the last leaching event (Fig. 2a, Table S3). In all leaching events, Fe retention was lowest in wheat straw and highest in wheat 450. Cumulative Fe retention was lowest in wheat straw and highest in wheat 450 with retention being more than 2-fold greater in the latter than in wheat straw (Tables 4 and S3).

Aluminium retention was greatest in the second leaching event (Fig. 3a, Table S4). In the first leaching event, Al was only retained in wheat and pea straw whereas the other organic materials released more Al than was added. Release of Al in the first leaching event was greatest in mallee 550 and smallest in compost. But in the following leaching events, there was net Al retention in most organic materials. The exception was wheat straw with net Al release in the fourth leaching event. Cumulative Al retention was highest in pea straw, followed by wheat 450 and mallee 550; it was lowest in poultry 550 (Tables 4 and S4). Compared to poultry 550, Al retention was 3-fold higher in wheat 450 and mallee 550 and 5-fold higher in pea straw.

Retention of protons in the four leaching events and cumulative retention expressed as percentage of added ranged between 61 and 100 % (Table 5). Cumulative proton retention was lower in wheat straw (82 % of added) than the other organic materials (92–100 %). Iron and Al retention in percentage of added was lower than of protons (0–99 %) and was lower for Al than for Fe. Cumulative Al retention was highest in pea straw

Table 3 Measured pH and pH difference to added solution after leaching with synthetic drainage water over four leaching events through organic materials

Leaching event	1		2		3		4	
	Measured pH	Difference to added solution	Measured pH	Difference to added solution	Measured pH	Difference to added solution	Measured pH	Difference to added solution
Wheat straw	5.07±0.02 b	2.11±0.02 b	4.41±0.2 a	1.42±0.10 a	3.40±0.07 a	0.4±0.03 a	3.09±0.04 a	0.06±0.02 a
Pea Straw	5.43±0.12 c	2.47±0.12 c	7.76±0.09 c	4.77±0.05 c	6.98±0.15 f	3.98±0.07 f	5.94±0.50 e	2.91±0.25 e
Compost	7.15±0.13 e	4.19±0.06 e	7.38±0.04 c	4.39±0.02 c	7.28±0.05 f	4.28±0.02 f	7.08±0.07 f	4.05±0.03 f
Poultry 450	4.92±0.47 b	1.96±0.24 b	4.51±0.32 a	1.52±0.16 a	4.40±0.41 c	1.4±0.20 c	4.49±0.47 c	1.46±0.23 c
Poultry 550	6.99±0.11 de	4.03±0.05 de	6.56±0.29 b	3.57±0.15 b	6.18±0.38 f	3.18±0.19 f	6.29±0.24 e	3.26±0.12 e
Wheat 450	4.77±0.17 ab	1.81±0.08 ab	6.19±0.08 b	3.20±0.04 b	5.02±0.37 d	2.02±0.18 d	5.37±0.17 d	2.34±0.08 d
Wheat 550	6.68±0.14 e	3.72±0.07 e	6.28±0.44 b	3.29±0.22 b	5.72±0.36 e	2.72±0.18 e	5.98±0.46 e	2.95±0.23 e
Mallee 550	4.58±0.18 a	1.62±0.09 a	4.27±0.35 a	1.28±0.18 a	3.84±0.31 b	0.84±0.17 b	3.93±0.07 b	0.90±0.04 b

Within a column, values followed by different letters are significantly different ($P \leq 0.05$)

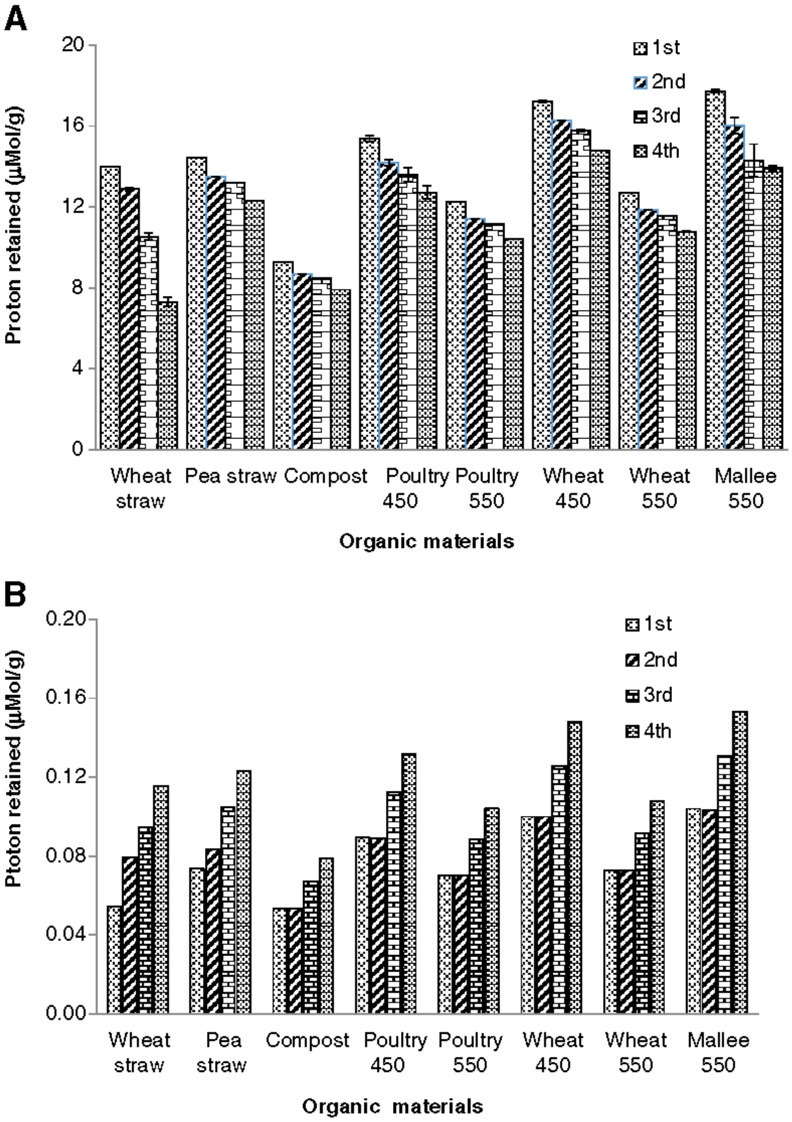


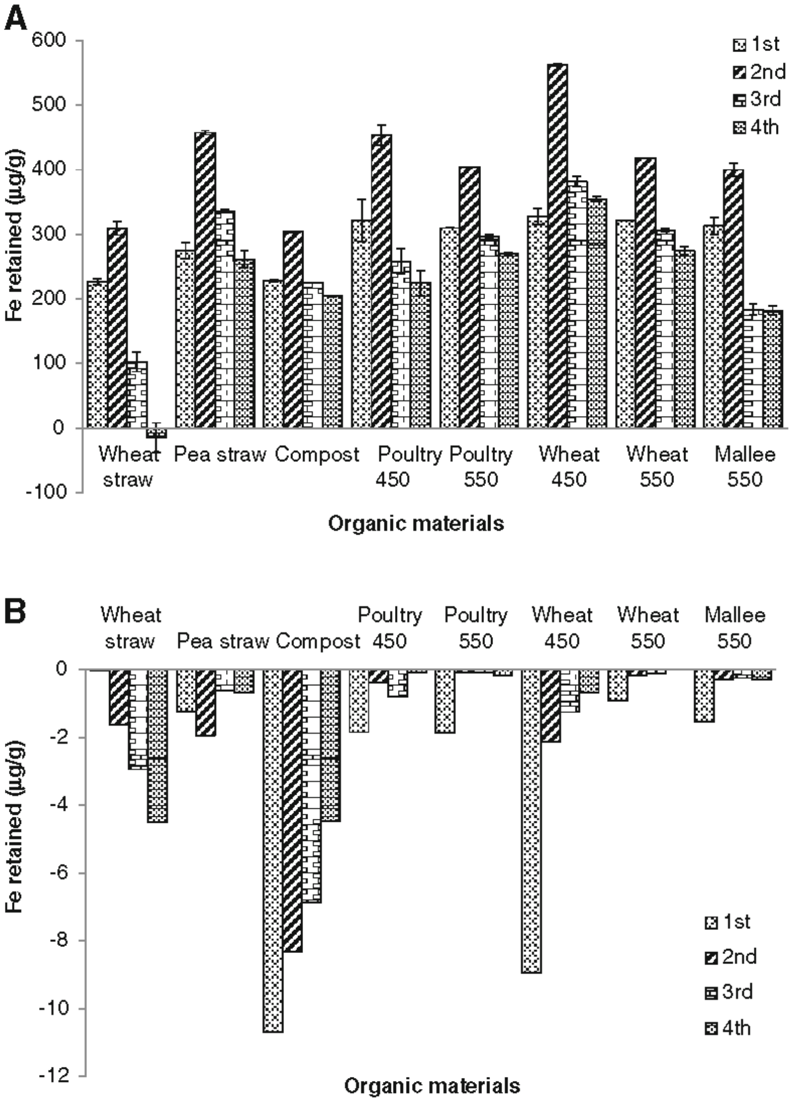
Fig. 1 Proton retention in organic materials leaching with synthetic drainage water (**a**) and RO water (**b**) after four leaching events (for drainage water *n*=4, *vertical line* represents standard error) (for RO water *n*=1)

Table 4 Cumulative proton, Fe and Al retention in organic materials after four leaching events with synthetic drainage water or RO water

Organic materials	Proton (µmol/g)		Fe (µg/g)		Al (µg/g)	
	Drainage	RO	Drainage	RO	Drainage	RO
Wheat straw	44.7±0.4 b	0.3	624±20 a	−9	7.5±1.3 ab	−6.2
Pea Straw	53.5±0.0 d	0.4	1329±27 d	−4	23.0±1.0 d	−6.2
Compost	34.4±0.0 a	0.3	962±2 b	−30	8.5±0.3 b	−18.1
Poultry 450	55.9±0.1 e	0.4	1259±86 d	−3	7.0±1.8 ab	−11.2
Poultry 550	45.2±0.0bc	0.3	1281±5 d	−2	43±0.5 a	−9.2
Wheat 450	64.1±0.0 g	05	1626±7 e	−13	14.3±0.8 c	−10.7
Wheat 550	46.9±0.0 c	0.4	1320±9 d	−1	9.3±0.7 b	−7.5
Mallee 550	62.0±1.2 f	05	1078±30 c	−2	13.1±2.0 c	−11.7

Within a column, values followed by different letters are significantly different ($P \leq 0.05$)

Fig. 2 Iron retention in organic materials leaching with synthetic drainage water (**a**) and RO water (**b**) after four leaching events (for drainage water n=4, *vertical line* represents standard error) (for RO water n=1)



(70 % of added) and low in the two poultry biochars and wheat straw. Wheat straw also had the lowest percentage cumulative Fe retention (42 %).

Proton retention in the first leaching event and cumulative proton retention in the first and second leaching events was significantly ($P<0.05$) positively correlated with C content of the organic materials, but not correlated with any other measured property (Table S5).

Iron retention in the first leaching event was positively correlated with percentage aryl, O-aryl and ketone but negatively correlated with Al retention and solution retained (Table S6). Cumulative Fe in the first and second leaching event retention was positively correlated with C content of the organic materials and proton retention ($P<0.1$).

Aluminium retention in the first leaching event and cumulative Al retention in the first and second leaching were positively correlated with amount of solution retained and percentages O-alkyl, di-O-alkyl but negatively correlated with percentages of aryl, O-aryl and ketone (Table S7). Cumulative Al retention was negatively correlated with ANC.

3.3 Leaching with RO Water

The organic materials were leached with RO water to assess release of native protons, Fe and Al.

Overall proton retention from RO water was about two orders of magnitude lower than with acid drainage solution (Fig. 1b, Table 4). When leached with RO water (pH 5.2), the organic materials retained protons in all

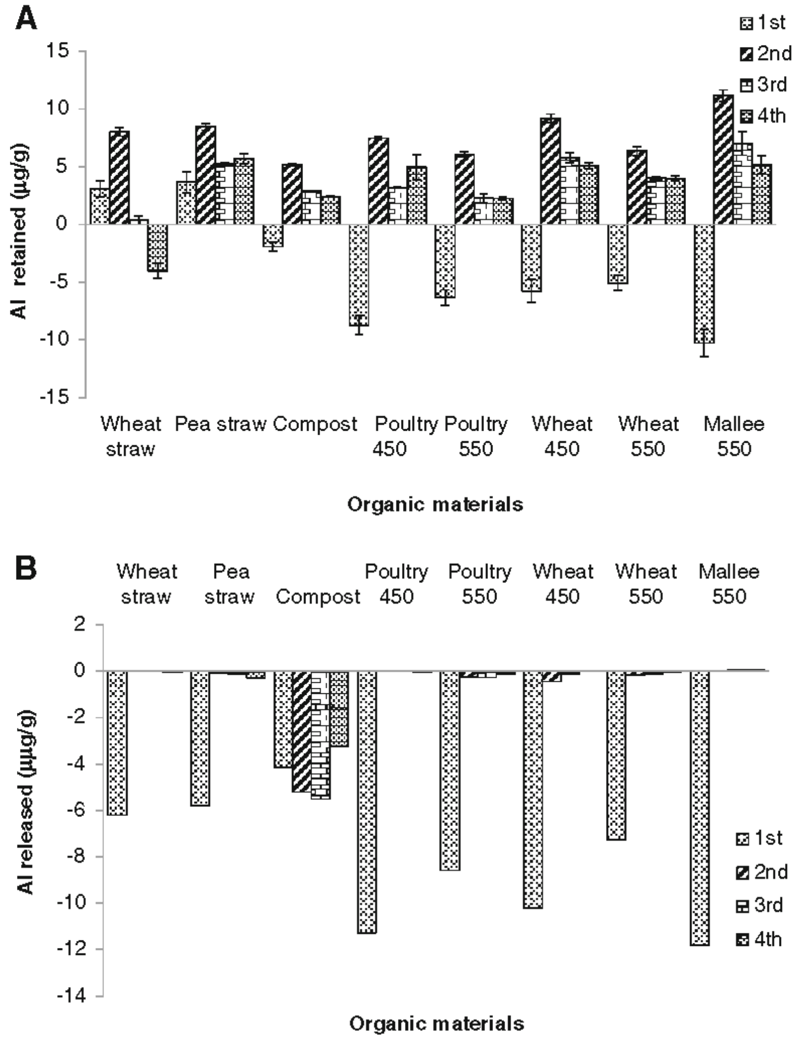


Fig. 3 Aluminium retention in organic materials leaching with synthetic drainage water (**a**) and RO water (**b**) after four leaching events (for drainage water $n=4$, *vertical line* represents standard error) (for RO water $n=1$)

Table 5 Retention of protons, Fe and Al in percentage of added in synthetic ASS drainage water for four leaching events and cumulative retention

	% Protons retained					% Fe retained					% Al retained				
Leaching event	1	2	3	4	Cumulative	1	2	3	4	Cumulative	1	2	3	4	Cumulative
Wheat straw	100	98	82	61	86	63	67	30	0	42	42	79	5	0	23
Pea straw	100	100	100	100	100	75	96	95	81	87	48	81	67	80	70
Compost	100	100	100	100	100	97	99	99	98	98	0[a]	77	58	53	40
Poultry 450	98	97	95	96	97	81	88	68	64	77	0	67	38	65	20
Poultry 550	100	100	100	100	100	100	100	99	99	99	0	69	34	38	15
Wheat 450	99	100	99	100	99	74	98	89	91	89	0	74	61	59	36
Wheat 550	100	100	100	100	100	100	100	99	97	99	0	70	59	64	32
Mallee 550	98	95	86	90	92	68	67	41	45	56	0	86	72	58	32

[a] Zero indicates no retention or net release of Al or Fe

leaching events with lower retention in the first two leaching events than the fourth leaching event (Table 4). In the first leaching event, proton retention was low in wheat straw and compost and high in wheat 450 and mallee 550. Cumulative proton retention was highest in mallee 550 and wheat 450 and lowest in compost; it was about 2-fold higher in mallee 550 and wheat 450 than in compost (Table 4).

All organic materials released small amounts of Fe when leached with RO water (Fig. 2b), but the release was about 100-fold lower than Fe retention after leaching with synthetic drainage water (Fig. 2a, Table 4). In the first three leaching events with RO water, Fe release was greatest from compost and lowest in wheat 550. Cumulative Fe release was greatest in compost and lowest in wheat 550 and 3- to 15-fold greater in compost than the other organic materials (Table 4).

All organic materials except compost released most Al in the first leaching event; only small amounts of Al were released in the subsequent leaching events (Fig. 3b). Compost released less Al in the first leaching than the other organic materials, but these release rates were maintained in the following leaching events. Cumulative release of Al with RO water was in the same order of magnitude as cumulative retention with synthetic drainage water (Table 4). Cumulative Al release in compost was 3-fold greater than the two straws and 40–60 % higher than the other organic materials (Table 4).

4 Discussion

This study confirmed our first hypothesis that passage of acidic ASS drainage water through organic material will increase the pH and reduce metal concentrations, but only partially confirmed the second hypothesis because the differences in ability of the organic materials to retain protons, Fe and Al was correlated with organic C composition, but not with acid neutralising capacity, and only cumulative Fe retention was positively correlated with cation exchange capacity.

4.1 Effect of Number of Leaching Events with Synthetic Drainage Water

Proton retention decreased with increasing number of leaching events, and Fe and Al retention was also lowest at the fourth leaching event (Figs. 1, 2 and 3). This decrease was strongest in wheat straw. The decrease in retention suggests approach of saturation of the retention capacity of the organic materials, particularly wheat straw which had low ANC and CEC. Nevertheless, cumulative retention in the organic materials was 86–100 % of added protons (Table 5).

Fe and Al retention was greatest at the second leaching event (Figs. 2 and 3). Compared to the first leaching event, 10–18 % more of the added solution was retained in the second leaching event. Therefore, the higher Fe and Al retention in the second leaching may not be due to binding or precipitation but through retention of the Fe and Al-containing synthetic drainage water in the material. The larger leachate volume and lower metal retention in the first leaching event could be due to preferential flow through larger pores which would also reduce the contact time of the added solution with the organic materials. The solution retained after the first leaching event would cause swelling, and the interval between first and second leaching events would have allowed the materials to settle in the cores resulting in a more uniform pore size distribution in the following leaching events. This would increase the contact of the added solution with the organic materials and thus liquid retention and likelihood of binding or precipitation in the second to fourth leaching events. Leaching volume was similar in the second to fourth leaching event, but Fe and Al retention was lower in the third and fourth than in the second leaching event (Figs. 2 and 3, Table 5). This suggests saturation of metal retention capacity, as the binding sites on the organic materials were increasingly occupied. Despite the decrease in retention in the third and fourth leaching events, cumulative Fe and Al retention was on average 42 and 81 % of added, respectively (Table 5).

For Fe and Al, the lower retention in the first leaching event with synthetic drainage water (Figs. 2 and 3) may also be due to native Fe and Al release by the organic materials as seen in the leaching with RO water. However, release of native Fe upon leaching with RO water was small compared to retention of added Fe with synthetic drainage water, suggesting that the material itself was not a significant source and there was net Fe retention. The high Fe release from compost can be explained by its high total Fe concentration (Table 1). The compost used here was made from garden waste and municipal green waste which would contain soil particles. These inorganic components accumulate during compost production because of the loss of organic mass via respiration (Park et al. 2011). Although the total Fe concentration was higher in mallee 550 than in compost (Table 1), release of Fe was high only in compost. This may be explained by at least two factors. Firstly, due to its lower C concentration, the amount of compost per core (5.31 g/core) was about twice as high than that of mallee 550 which had a higher C concentration (2.72 g/core) (Table 1). Since the Fe concentration was 2-fold higher in mallee 550 than in compost, the amount of Fe per core was similar for the two organic materials. Secondly, Fe in compost may be more soluble than in mallee 550 because decomposition products such as organic acids can chelate Fe and thereby increase its solubility (Jansen et al. 2002). Pyrolysis used for biochar production, on the other hand, reduces metal solubility (He et al. 2010).

For Al, release of native Al with RO water was of similar magnitude as Al retention after passage of synthetic drainage water resulting in net Al release except in the two straws. In most organic materials, this release of native Al was greater in the first than in the subsequent leaching events with RO water. The low release of native Al in subsequent leaching events with RO water explains net Al retention in leaching events 2–4 with synthetic drainage water. Net Al retention even occurred in compost where larger amounts of Al were released in leaching events 2–4 when RO water was added. The high Al release from compost can be explained by its high total Al concentration (Table 1). The sustained Al release from compost suggests that Al in the compost was progressively released. Chelating compounds produced during composting may have increased Al solubility (Jansen et al. 2002). This is in contrast to the other organic materials which had lower Al concentrations, where Al release was low after the first leaching event.

4.2 Correlations Between Retention and Properties

Proton retention was positively correlated with C content of the organic materials t (Table S6). The amount of C per core was the same for all materials; therefore, the amount of materials with high C content was less per core than for materials with low C content (Table 1). The positive correlation between proton retention and C content of the organic materials could be due to better contact of the added solution with the organic materials when the amount per core was low. With large amounts of material per core, the added solution may only get in contact with a proportion of the materials because of uneven wetting. There was no correlation between C content and leachate amount (data not shown).

Correlations between Fe retention in the first leaching event and measured properties were generally low (Table S6). Iron retention was positively correlated with the percentage of aryl, O-aryl and ketone groups in the materials. Metals can bind to aromatic carbon structures (aryl and O-aryl) and ketones (Chaberek and Martell 1959; Uchimiya et al. 2012). Only in the first leaching event, Fe retention was negatively correlated with Al retention which is most likely due to the fact that Al was released by most organic materials in the first leaching event whereas Fe was retained. A further mechanism of Fe retention may be precipitation as a result of the increase pH of the solution (Lee et al. 2002; Spiteri et al. 2006). Cumulative Fe retention of the first and second leaching events was positively correlated with C content and proton retention (Table S6). The latter suggests that the higher pH induced by proton retention during the passage of the drainage water through the materials may have induced precipitation of Fe as Fe solubility decreases with increasing pH (Colombo et al. 2014).

Retention of Al in the first leaching event was positively correlated with volume of solution retained (Table S7). This can be explained by the high liquid retention capacity of the two straws which were the only materials with net Al retention in the first leaching event. Net Al retention occurred although the two straws released Al in the first leaching event when RO water was added (Fig. 3). Thus, despite release of native Al, retention of the added synthetic drainage water minimised Al loss by leaching. Aluminium retention in the first leaching event and cumulative retention were positively correlated with percentage of di-O-alkyl and O-alkyl groups but negatively correlated with proportion of aryl, O-aryl and ketone groups in the materials. Aluminium can bind to di-O-alkyl groups (Qian and Chen 2013a, b) and replace protons on carboxyl groups (Qian and Chen 2013b). However, the strong positive correlation between Al retention and solution retained in the first leaching event suggests that liquid retention was the main mechanism for net Al retention in that leaching event.

Binding of metals in ASS drainage water by organic materials in the field may be more variable than in the present study. ASS drainage water in the field may contain dissolved organic matter (e.g. humic acids) which can bind metals (Kerndorff and Schnitter 1980; Nystrand and Oesterholm 2013) and thereby reduce metal binding to organic materials. Therefore, the data on metal sorption in our study, where the synthetic drainage water did not contain organic substances, may be an overestimation of metal binding. Further, acidity, metal and organic C concentrations (dissolved, colloidal and particulate) of ASS drainage water in the field are highly variable both in time and in space (Astrom and Bjorklund 1996; Nystrand and Österholm 2013). The pH of the drainage water could influence binding of metals to organic materials because metal binding increases as pH increases due to reduced competition between proton-binding sites on the organic materials (Kerndorff and Schnitzer 1980; Gundersen and Steinies 2003).

5 Conclusion

All organic materials used in this study retained protons, Fe and Al from the synthetic drainage water with low pH and high Fe and Al concentrations suggesting that they may be suitable materials for barriers in drainage channels to reduce the negative impact of ASS drainage water on the environment. However, the organic materials differed in their ability to retain protons, Fe and Al. The amount of material per core and thus its C concentration appears to be very important with respect to proton, Fe and Al retention. Smaller amounts of material per core may allow better contact of the added solution with the material and may also reduce release of native protons, Fe and Al. Another important factor influencing Fe and Al retention is the release of native Fe and Al.

Among the organic materials used in this study, mallee 550 and wheat 450 had high retention capacity for protons, Fe and Al. Retention was low in compost and wheat straw. Further studies are required to investigate how strong the retention is, that is how much of the retained protons, Fe and Al could be released in subsequent leaching events which may be influenced by the pH, organic matter content and/or ionic composition of the added water. For the field application, materials with high retention, low bioavailability but also low release of retained protons and metals are desirable.

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References

Ahern, C. R., McElnea, A. E., & Sullivan, L. A. (2004). Acid neutralising capacity, carbonate and alkali cation methods. In C. R. Ahern, A. E. McElnea, & L. A. Sullivan (Eds.), *Acid sulfate soils laboratory methods guidelines*. Queensland, Australia: Department of Natural Resources, Nines and Energy, Indooroopilly.

Arcibar-Orozco, J., Rangel-Mendez, J., & Diaz-Flores, P. (2014). Simultaneous adsorption of Pb(II)-Cd(II), Pb(II)-phenol, and Cd(II)-phenol by activated carbon cloth in aqueous solution. *Water, Air, and Soil Pollution, 226*(1), 1–10.

Astrom, M. (1998). Mobility of Al, Co, Cr, Cu, Fe, Mn, Ni and V in sulphide-bearing fine-grained sediments exposed to atmospheric O-2: an experimental study. *Environmental Geology, 36*, 219–226.

Astrom, M., & Bjorklund, A. (1996). Hydrogeochemistry of a stream draining sulfide-bearing postglacial sediments in Finland. *Water, Air, and Soil Pollution, 89*, 233–246.

Attanandana, T., & Vacharotayan, S. (1986). Acid sulfate soils: their characteristics, genesis, amelioration and utilization. *Southeast Asia Studies, 24*(2), 154–180.

Baldwin, D. S. (2009). *Knowledge needs to minimise adverse water quality events in the Edward-Wakool river system. Consultancy report for New South Wales office of Water. Murray-Darling Freswater Research Centre.*

Beesley, L., Inneh, O. S., Norton, G. J., Moreno-Jimenez, E., Pardo, T., Clemente, R., et al. (2014). Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. *Environmental Pollution, 186*, 195–202.

Bhatnagar, A., & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. *Chemical Engineering Journal, 157*(2–3), 277–296.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society, 60*(2), 309–319.

Chaberek, S., & Martell, A. E. (1959). *Organic sequestering agents: a discussion of the chemical behavior and applications of metal chelate compounds in aqueous systems*. New York: Wiley.

Choi, S.-J., Lee, B.-T., Kim, J.-Y., & Kim, K.-W. (2013). Study on adsorption/desorption of As by mine sludge depending on pH and natural organic matter. *Geosystem Engineering, 16*(3), 191–199.

Clemente, R., Almela, C., & Bernal, M. P. (2006). A remediation strategy based on active phytoremediation followed by natural attenuation in a soil contaminated by pyrite waste. *Environmental Pollution, 143*(3), 397–406.

Colombo, C., Palumbo, G., He, J. Z., Pinton, R., & Cesco, S. (2014). Review on iron availability in soil: interaction of Fe minerals, plants, and microbes. *Journal of Soils and Sediments, 14*, 538–548.

Dent, D. (1986). *Acid sulphate soils: a baseline for research and development*: International Institute for Land Reclamation and Improvement/ILRI, Wageningen.

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

DERM. (2011). *Indentifying acid sulfate soils* (Fact sheet L61).

Dias, A. C. B., Pavan, M. A., Miyazawa, M., & Zocoler, D. C. (2003). Plant residues: short term effect on sulphate, borate, zinc and copper adsorption by an acid oxisol. *Brazilian Archives of Biology and Technology, 46*(2), 199–202.

EPHC and NRMMC. (2011). *National guidancee for the management of acid sulfate soils in inland aquatic ecosystems*. Canbera: ACT.

Fellet, G., Marchiol, L., Delle Vedove, G., & Peressotti, A. (2011). Application of biochar on mine tailings: effects and perspectives for land reclamation. *Chemosphere, 83*(9), 1262–1267.

Fest, E. P. M. J., Temminghoff, E. J. M., Comans, R. N. J., & van Riemsdijk, W. H. (2008). Partitioning of organic matter and heavy metals in a sandy soil: effects of extracting solution, solid to liquid ratio and pH. *Geoderma, 146*(1–2), 66–74.

Fitzpatrick, R. W. (2003). *Overview of acid sulfate soil properties, environmental hazards, risk mapping and policy development in Asutralia*. Paper presented at the Advances in Regolith, Bentley.

Fitzpatrick, R., & Shand, P. (2008). Chapter 1: inland acid sulfate soils in Australia: overview and conceptual models. In R. Fitzpatrick & P. Shand (Eds.), *Inland acid sulfate soil systems across Australia* (CRC LEME Open File Report 249, pp. 6–74). Perth: CRC LEME.

Fitzpatrick, R., Shand, P., & Merry, R. (2009). Chapter 3. Acid sulfate soils. In J. Jennings (Ed.), *Natural History of the Riverland and Murraylands* (pp. 65–111). Adelaide, South Australia: Royal Society of South Australia (Inc.).

Gundersen, P., & Steinnes, E. (2003). Influence of pH and TOC concentration on Cu, Zn, Cd, and Al speciation in rivers. *Water Research, 37*, 307–318.

He, Y., Zhai, Y., Li, C., Yang, F., Chen, L., Fan, X., et al. (2010). The fate of Cu, Zn, Pb and Cd during the pyrolysis of sewage sludge at different temperatures. *Environmental Technology, 31*(5), 567–574.

Henze, M., & Comeau, Y. (2008). Wastewater characterization. In M. Henze, M. C. M. van Loosdrecht, G. A. Ekama, & D. Drdjanovic (Eds.), *Biological wastewater treatment: principles, modelling and design* (pp. 33–52). London: IWA Publishing.

Houben, D., Evrard, L., & Sonnet, P. (2013). Beneficial effects of biochar application to contaminated soils on the bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (Brassica napus L.). *Biomass and Bioenergy, 57*, 196–204.

Hughes, T., & Gray, N. F. (2013). Removal of metals and acidity from acid mine drainage using municipal wastewater and activated sludge. *Mine Water and the Environment, 32*(3), 170–184.

Hughes, T., Gray, N. F., & Sánchez Guillamón, O. (2013). Removal of metals and acidity from acid mine drainage using liquid and dried digested sewage sludge and cattle slurry. *Mine Water and the Environment, 32*(2), 108–120.

Jansen, B., Nierop, K. G., & Verstraten, J. M. (2002). Influence of pH and metal/carbon ratios on soluble organic complexation of Fe (II), Fe (III) and Al (III) in soil solutions determined by diffusive gradients in thin films. *Analytica Chimica Acta, 454*(2), 259–270.

Jeen, S.-W., Bain, J. G., & Blowes, D. W. (2014). Evaluation of mixtures of peat, zero-valent iron and alkalinity amendments for treatment of acid rock drainage. *Applied Geochemistry, 43*, 66–79.

Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N. W., & Beesley, L. (2011). Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. *Journal of Hazardous Materials, 191*(1–3), 41–48.

Kerndorff, H., & Schnitzer, M. (1980). Sorption of metals on humic acid. *Geochimica Et Cosmochimica Acta, 44*, 1701–1708.

Kijjanapanich, P., Pakdeerattanamint, K., Lens, P. N. L., & Annachhatre, A. P. (2012). Organic substrates as electron donors in permeable reactive barriers for removal of heavy metals from acid mine drainage. *Environmental Technology, 33*(23), 2635–2644.

Kołodyńska, D., Wnętrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapiński, W., & Hubicki, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal, 197*, 295–305.

Lee, G., Bigham, J. M., & Faure, G. (2002). Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Applied Geochemistry, 17*(5), 569–581.

Ljung, K., Maley, F., Cook, A., & Weinstein, P. (2009). Acid sulfate soils and human health—a Millennium Ecosystem Assessment. *Environment International, 35*(8), 1234–1242. doi.

McBeath, A. V., Smernik, R. J., Krull, E. S., & Lehmann, J. (2014). The influence of feedstock and production temperature on biochar carbon chemistry: a solid-state 13C NMR study. *Biomass and Bioenergy, 60*, 121–129.

Mosley, L., Fitzpatrick, R., Palmer, D., Leyden, E., & Shand, P. (2014a). Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. *Science of the Total Environment, 485–486*, 281–291.

Mosley, L., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., et al. (2014b). Acidification of floodplains due to river level decline during drought. *Journal of Contaminant Hydrology, 161*, 10–23.

Mosley, L., Zammit, B., Jolley, A. M., & Barnett, L. (2014c). Acidification of lake water due to drought. *Journal of Hydrology, 511*, 484–493.

Nystrand, M. I., & Österholm, P. (2013). Metal species in a Boreal river system affected by acid sulfate soils. *Applied Geochemistry, 31*, 133–141.

Osterholm, P., Yli-Halla, M., & Edén, P. (2012). *7th International Acid Sulfate Soil Conference, Vaasa, Finland 2012 Towards Harmony between Land Use and the Environment*. Vaasa, Finland: Geological Survey of Findland, Guide 56.

Park, J. H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., & Chung, J.-W. (2011). Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *Journal of Hazardous Materials, 185*(2–3), 549–574.

Pedra, F., Plaza, C., García-Gil, J. C., & Polo, A. (2008). Effects of municipal waste compost and sewage sludge on proton binding behavior of humic acids from Portuguese sandy and clay loam soils. *Bioresource Technology, 99*(7), 2141–2147.

Pons, L. J. (1973). Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In H. Dost (Ed.), *Acid sulphate soils: proceedings of the International Symposium on Acid Sulphate Soils, 13–20 August 1972, Wageningen, the Netherlands* (Vol. v. 1). Wageningen: International Institute for Land Reclamation and Improvement.

Qian, L., & Chen, B. (2013a). Dual role of biochars as adsorbents for aluminum: the effects of oxygen-containing organic components and the scattering of silicate particles. *Environmental Science & Technology, 47*(15), 8759–8768.

Qian, L., & Chen, B. (2013b). Interactions of aluminum with biochars and oxidized biochars: implications for the biochar aging process. *Journal of Agricultural and Food Chemistry, 62*(2), 373–380.

Rabenhorst, M. C., & Fanning, D. S. (2002). Acid sulfate soils: problems. In R. Lal (Ed.), *Encyclopedia of soil science* (2nd ed., pp. 29–32). New York: Marcel Dekker.

Rayment, G. E., & Lysons, D. J. (2011). *Soil chemical methods-Australia* (Vol. 3). Victoria: CSIRO publishing.

Ritchie, G. (1989). The chemical behavior of aluminum, hydrogen and manganese in acid soils. In A. D. Robson (Ed.), *Soil Acidity and Plant Growth* (pp. 1–60). Sydney: Academic Press.

Simpson, S., Fitzpatrick, R., Shand, P., Angel, B., Spadaro, D., Merry, R., et al. (2008a). *Acid, metal and nutrient mobilisation following rewetting of acid sulfate soils in the Lower Murray* (CSIRO Land and Water report number CLW27/08 Prepared for the South Australian Environmental Protection Agency).

Simpson, S., Fitzpatrick, R., Shand, P., Angel, B., Spadaro, D., Merry, R., et al. (2008b). Chapter 3: acid and metal mobilisation following rewetting of acid sulfate soils from the River Murray, South Australia: a rapid laboratory method. In F. R., & S. P. (Eds.), *Inland acid sulfate soil systems across Australia* (pp. 90–97, Vol. CRC LEME Open File Report No. 249 (Thematic Volume)). Perth: CRC LEME.

Simpson, S., Vardanega, C. R., Jarolimek, C., Jolley, D. F., Angel, B. M., & Mosley, L. M. (2014). Metal speciation and potential bioavailability changes during discharge and neutralisation of acidic drainage water. *Chemosphere, 103*, 172–180.

Smernik, R. J., & Oades, J. M. (2000). The use of spin counting for determining quantitation in solid state 13C NMR spectra of natural organic matter: 1. Model systems and the effects of paramagnetic impurities. *Geoderma, 96*(1–2), 101–129.

Spiteri, C., Regnier, P., Slomp, C. P., & Charette, M. A. (2006). pH-dependent iron oxide precipitation in a subterranean estuary. *Journal of Geochemical Exploration, 88*(1), 399–403.

Sracek, O., Choquette, M., Gélinas, P., Lefebvre, R., & Nicholson, R. V. (2004). Geochemical characterization of acid mine drainage from a waste rock pile, Mine Doyon, Quebec, Canada. *Journal of Contaminant Hydrology, 69*(1), 45–71.

Sullivan, L. (2004). Preface: sustainable management of acid sulfate soil. *Soil Research, 42*(6), I-I.

Trakal, L., Bingöl, D., Pohořelý, M., Hruška, M., & Komárek, M. (2014). Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: engineering implications. *Bioresource Technology, 171*, 442–451.

Uchimiya, M., Bannon, D. I., & Wartelle, L. H. (2012). Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. *Journal of Agricultural and Food Chemistry, 60*(7), 1798–1809.

Walker, D. J., Clemente, R., & Bernal, M. P. (2004). Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere, 57*(3), 215–224.

Wan Ngah, W. S., & Hanafiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology, 99*(10), 3935–3948.

Xu, J. M., Tang, C., & Chen, Z. L. (2006). The role of plant residues in pH change of acid soils differing in initial pH. *Soil Biology and Biochemistry, 38*(4), 709–719.

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. *Communications in Soil Science and Plant Analysis, 27*(5–8), 1331–1354.

Zhang, M., & Wang, H. (2014). Organic wastes as carbon sources to promote sulfate reducing bacterial activity for biological remediation of acid mine drainage. *Minerals Engineering, 69*, 81–90.

Zhou, Y. -F., & Haynes, R. J. (2010). Sorption of heavy metals by inorganic and organic components of solid wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents. *Critical Reviews in Environmental Science and Technology, 40*, 909–977.

Supplementary data

Table S1: leachate volume in four leaching events after addition of 45 ml synthetic drainage water to different organic materials.

Leaching event	1	2	3	4
	leachate volume (ml core^{-1})			
Wheat straw	25	20	20	20
Pea Straw	25	20	20	20
Compost	30	23	25	25
Poultry 450	40	32	35	35
Poultry 550	40	32	35	35
Wheat 450	35	25	25	25
Wheat 550	35	25	25	25
Mallee 550	40	35	35	35

Table S2: Proton retention over four leaching events and cumulative leaching after passage of synthetic drainage water through different organic materials. Values in a column followed by different letters are significantly different ($P\leq 0.05$).

Leaching event	1	2	3	4	Cumulative
	Protons retained (µMol g^{-1})				
Wheat straw	14.0 ± 0.0 d	12.9 ± 0.1 c	10.5 ± 0.2 b	7.3 ± 0.2 a	44.7 ± 0.4 b
Pea Straw	14.4 ± 0.0 e	13.5 ± 0.0 d	13.2 ± 0.0 d	12.3 ± 0.0 d	53.5 ± 0.0 d
Compost	9.3 ± 0.0 a	8.7 ± 0.0 a	8.5 ± 0.0 a	7.9 ± 0.0 b	34.4 ± 0.0 a
Poultry 450	15.4 ± 0.1 f	14.2 ± 0.2 e	13.6 ± 0.4 de	12.7 ± 0.3 e	55.9 ± 1.0 e
Poultry 550	12.2 ± 0.0 b	11.4 ± 0.0 b	11.2 ± 0.0 bc	10.4 ± 0.0 c	45.2 ± 0.0 bc
Wheat 450	17.2 ± 0.0 g	16.3± 0.0 f	15.8 ± 0.1 f	14.8 ± 0.0 g	64.1 ± 0.0 g
Wheat 550	12.7 ± 0.0 c	11.8 ± 0.0 b	11.5 ± 0.0 c	10.8 ± 0.0 c	46.9 ± 0.0 c
Mallee 550	17.7 ± 0.1 h	16.0 ± 0.4 f	14.3 ± 0.8 e	13.9 ± 0.1 f	62.0 ± 1.18 f

Table S3: Fe retention over four leaching events and cumulative leaching after passage of synthetic drainage water through different organic materials. Values in a column followed by different letters are significantly different ($P \leq 0.05$).

Leaching event	1	2	3	4	Cumulative
	Fe retention (μg g^{-1})				
Wheat straw	226 ± 5 a	309 ± 11 a	102 ± 15 a	-14 ± 23 a	624 ± 20 a
Pea Straw	274 ± 13 b	457 ± 3 c	336 ± 2 f	262 ± 13 d	1329 ± 27 d
Compost	228 ± 1 a	304 ± 48 a	225 ± 0 c	205 ± 1 bc	962 ± 2 b
Poultry 450	322 ± 33 c	454 ± 15 c	258 ± 20 d	225 ± 19 c	1259 ± 86 d
Poultry 550	310 ± 11 bc	404 ± 9 b	297 ± 3 e	270 ± 2 d	1281 ± 5 d
Wheat 450	328 ± 12 c	563 ± 2 d	382 ± 8 g	354 ± 4 e	1626 ± 7 e
Wheat 550	321 ± 12 c	419 ± 8 b	306 ± 3 e	274 ± 6 d	1320 ± 9 d
Mallee 550	313 ± 13 bc	400 ± 10 b	183 ± 9 b	182 ± 7 b	1078 ± 30 c

Table S4 Al retention over four leaching events and cumulative leaching after passage of synthetic drainage water through different organic materials. Values in a column followed by different letters are significantly different (P≤ 0.05).

Leaching event	1	2	3	4	Cumulative
	Al retention (µg g^{-1})				
Wheat straw	3.1 ± 0.7 f	8.0 ± 0.4 c	0.4 ± 04 a	-4.0 ± 0.7 a	7.5 ± 1.3 ab
Pea Straw	3.7 ± 0.9 f	8.5 ± 0.3 cd	5.2 ± 0.1 de	5.7 ± 0.4 d	23.0 ± 1.0 d
Compost	-1.9 ± 0.1 d	5.2 ± 0.13 a	2.9 ± 0.1 bc	2.4 ± 0.1 bc	8.5 ± 0.3 b
Poultry 450	-8.7 ± 0.1 ab	7.5 ± 0.1 c	3.2 ± 0.1 bc	5.0 ± 1.1 d	7.0 ± 1.8 ab
Poultry 550	-6.4 ± 0.2 bc	6.1 ± 0.2 ab	2.3 ± 0.4 b	2.3 ± 0.1 b	4.3 ± 0.5 a
Wheat 450	-5.8 ± 0.4 c	9.2 ± 0.4 d	5.8 ± 0.4 ef	5.1 ± 0.2 d	14.3 ± 0.8 c
Wheat 550	-5.1 ± 0.4 c	64 ± 0.4 b	4.0 ± 0.2 cd	4.0 ± 0.2 cd	9.3 ± 0.7 b
Mallee 550	-10.3 ± 0.5 a	11.2 ± 0.3 f	7.0 ± 1.0 f	5.2 ± 0.8 d	13.1 ± 2.0 c

Table S5: Correlation between proton retention in the first leaching event and cumulative retention of first and second leaching events in organic materials and their properties.

	1. Leaching event			Cumulative retention of first and second leaching event		
	Equation	R^2	P (95%)	Equation	R^2	P (95%)
C	y = 0.03x + 0.52	0.99	0.00	y = 0.06x + 1.31	0.99	0.00
N	y = -0.1x + 15.49	0.06	0.55	y = -0.17x + 29.57	0.05	0.59
C/N ratio	y = 0.04x + 12.44	0.22	0.24	y = 0.07x + 24.18	0.20	0.27
ANC	y = -0.52x + 16.24	0.30	0.16	y = -0.99x + 31.30	0.31	0.15
CEC	y = -0.04x + 16.04	0.04	0.63	y = -0.08x + 30.55	0.03	0.67
Surface area	y = -0.57x + 15.87	0.31	0.15	y = -1.09x + 30.56	0.31	0.15
Alkyl	y = -0.23x + 16.72	0.17	0.31	y = -0.43x + 32.06	0.16	0.32
N-Alkyl/Methoxyl	y = -0.71x + 17.61	0.25	0.21	y = -1.33x + 33.77	0.24	0.22
O-Alkyl	y = -0.02x + 14.54	0.02	0.75	y = -0.03x + 28.00	0.02	0.75
Di-O-Alkyl	y = -0.07x + 14.65	0.01	0.80	y = -0.14x + 28.23	0.01	0.80
Aryl	y = 0.03x + 13.09	0.06	0.57	y = 0.06x + 25.29	0.06	0.57
O-Aryl	y = 0.23x + 12.12	0.12	0.40	y = 0.43x + 23.46	0.12	0.41
Amide/Carboxyl	y = -0.68x + 17.45	0.15	0.35	y = -1.26x + 33.40	0.14	0.37
Ketone	y = 0.98x + 12.08	0.15	0.35	y = 1.87x + 23.32	0.15	0.35
Solution retained	y = -0.13x + 15.57	0.09	0.47	y = -0.31x + 33.02	0.12	0.44

Table S6: Correlation between Fe retention in the first and second leaching event and cumulative retention of first and second leaching events in organic materials and their properties.

	1. Leaching event			Cumulative retention of first and second leaching event		
	Equation	R^2	P (95%)	Equation	R^2	P (95%)
C	y = 0.0003x + 0.18	0.31	0.14	y = 0.87x + 327.93	0.41	0.09
N	y = 0.003x + 0.26	0.10	0.45	y = 7.05x + 607.34	0.16	0.32
C/N ratio	y = -0.0003x + 0.31	0.08	0.49	y = -1.13x + 755.11	0.11	0.43
ANC	y = 0.004x + 0.28	0.06	0.63	y = -2.01x + 712.23	0.00	0.91
CEC	y = 0.002x + 0.22	0.27	0.20	y = 4.75x + 493.99	0.26	0.20
Surface area	y = 0.003x + 0.28	0.05	0.66	y = -3.71x + 715.39	0.01	0.84
Alkyl	y = 0.0003x + 0.29	0.001	0.99	y = 0.40x + 699.52	0.00	0.97
N-Alkyl/Methoxyl	y = -0.01x + 0.35	0.28	0.18	y = -20.85x + 806.42	0.11	0.42
O-Alkyl	y = -0.001x + 0.32	0.54	0.05	y = -2.37x + 765.76	0.21	0.25
Di-O-Alkyl	y = -0.007x + 0.34	0.51	0.07	y = -13.33x + 802.98	0.21	0.25
Aryl	y = 0.002x + 0.24	0.61	0.03	y = 2.60x + 614.21	0.23	0.23
O-Aryl	y = 0.008x + 0.22	0.66	0.02	y = 15.63x + 567.61	0.30	0.16
Amide/Carboxyl	y = -0.01x + 0.34	0.15	0.33	y = -17.01x + 787.75	0.05	0.60
Ketone	y = 0.03x + 0.23	0.63	0.03	y = 66.08x + 566.05	0.36	0.12
Proton	y = 0.008x + 0.17	0.31	0.14	y = 15.15x + 291.65	0.44	0.07
Al	y = -0.006x + 0.27	0.57	0.05	y = -8.27x + 735.64	0.12	0.39
Solution retained	y = -0.005x + 0.35	0.61	0.03	y = -9.46x + 810.4	0.26	0.28

Table S7: Correlation between Al retention in the first and second leaching event and cumulative retention of first and second leaching events in organic materials and their properties.

	1. Leaching event			Cumulative retention of first and second leaching event		
	Equation	R^2	P (95%)	Equation	R^2	P (95%)
C	y = -0.02x + 5.87	0.15	0.35	y = -0.002x + 4.81	0.00	0.93
N	y = -0.24x - 0.65	0.10	0.44	y = -0.37x + 8.86	0.25	0.21
C/N ratio	y = 0.03x - 5.09	0.03	0.68	y = 0.06x + 0.97	0.19	0.28
ANC	y = -0.98x + 0.10	0.31	0.15	y = -1.38x + 9.50	0.64	0.02
CEC	y = -0.18x + 3.96	0.20	0.27	y = -0.23x + 13.83	0.33	0.14
Surface area	y = -0.58x - 2.13	0.09	0.46	y = -1.00x + 6.90	0.28	0.18
Alkyl	y = -0.31x - 0.41	0.09	0.47	y = -0.47x + 9.09	0.21	0.26
N-Alkyl/Methoxyl	y = 0.90x - 8.33	0.11	0.42	y = 0.48x + 1.49	0.03	0.67
O-Alkyl	y = 0.19x - 8.95	0.77	0.004	y = 0.19x - 1.16	0.78	0.004
Di-O-Alkyl	y = 1.05x - 11.74	0.71	0.01	y = 1.05x - 3.94	0.72	0.01
Aryl	y = -0.20x + 2.84	0.72	0.01	y = -0.19x + 10.22	0.66	0.02
O-Aryl	y = -1.13x + 5.93	0.85	0.001	y = -1.03x + 12.81	0.72	0.01
Amide/Carboxyl	y = 0.53x - 6.55	0.03	0.70	y = 0.20x + 2.82	0.00	0.88
Ketone	y = -4.02x + 4.47	0.72	0.01	y = -3.57x + 11.28	0.58	0.03
Proton	y = -0.69x + 5.76	0.14	0.37	y = -0.02x + 4.25	0.00	0.97
Solution retained	y = 0.78x - 12.68	0.94	0.000	y= 0.73x - 9.62	0.69	0.002

CHAPTER 4

ORGANIC MATERIALS RETAIN HIGH PROPORTION OF PROTONS, IRON AND ALUMINIUM FROM ACID SULFATE SOIL DRAINAGE WATER WITH LITTLE SUBSEQUENT RELEASE

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Name of Principal Author	Tan Dang		
Contribution to the Paper	Performed experiment, analyses of leachate, data analysis and interpretation, wrote 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	15/02/2017

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.

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RESEARCH ARTICLE

Organic materials retain high proportion of protons, iron and aluminium from acid sulphate soil drainage water with little subsequent release

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Abstract When previously oxidised acid sulphate soils are leached, they can release large amounts of protons and metals, which threaten the surrounding environment. To minimise the impact of the acidic leachate, protons and metals have to be retained before the drainage water reaches surrounding waterways. One possible amelioration strategy is to pass drainage water through permeable reactive barriers. The suitability of organic materials for such barriers was tested. Eight organic materials including two plant residues, compost and five biochars differing in feedstock and production temperature were finely ground and filled into PVC cores at 3.5 g dry wt/core. Field-collected acidic drainage water (pH 3, Al 22 mg L^{-1} and Fe 48 mg L^{-1}) was applied in six leaching events followed by six leaching events with reverse osmosis (RO) water (45 mL/event). Compost and biochars increased the leachate pH by up to 4.5 units and had a high retention capacity for metals. The metal and proton release during subsequent leaching with RO water was very small, cumulatively only 0.05–0.8 % of retained metals and protons. Retention was lower in the two plant residues, particularly wheat straw, which raised leachate pH by 2 units only in the first leaching event with drainage water, but had little effect on leachate pH in the following leaching events. It can be concluded that organic materials and particularly biochars and compost have the potential to be used in acid drainage treatment to remove and retain protons and metals.

Keywords Acid sulphate soils · Aluminium · Biochar · Drainage water · Iron · Organic materials · pH

Introduction

Under constant waterlogged conditions, iron sulphides such as pyrite (FeS_2) are formed, particularly in the presence of abundant organic material and sulphate (Dent and Pons 1995). Such soils are referred to as acid sulphate soils. Upon removal of water from the soil profile by evaporation or drainage pyrite, it can be oxidised and release sulfuric acid and ferrous iron (Fe^{+2}) via the following reaction (Bronswijk et al. 1993):

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+.$$

The ferrous iron can subsequently be oxidised to Fe^{+3} which at low pH (<4) can rapidly oxidise additional pyrite. Such soils can become sulfuric (pH <4) if insufficient neutralising capacity (e.g. carbonate) is present. This acidification can cause the release of aluminium, manganese and other metals into pore water (Simpson et al. 2008, 2014). Drainage water and runoff from sulfuric acid sulphate soils can have severe negative impacts on aquatic ecosystems, agriculture and infrastructure (Fältmarsch et al. 2008; Ljung et al. 2009; Mosley et al. 2014a, b; Shamshuddin et al. 2014).

Acid sulphate soils (ASS) with sulfuric material (pH <4) are widespread in the Lower Murray Reclaimed Irrigation Area (LMRIA) in South Australia, which comprises 5500 ha of agricultural land (Fitzpatrick et al. 2009, 2012). Irrigation is

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mainly by flood irrigation with water from the adjoining River Murray. The water is returned to the river by an extensive network of drainage channels. With adequate water supply, the soils remain under reduced conditions at depth and are sulfidic. Southern Australia experienced a long extreme drought between 2006 and 2010, which resulted in falling groundwater levels and a lack of irrigation water in the LMRIA. Approximately 3500 ha of sulfidic ASS was exposed and oxidised even to 4 m depth during this period (Fitzpatrick et al. 2009; Mosley et al. 2014a). One common remediation strategy for sulfuric soils is to neutralise acidity by liming (e.g. Powell and Martens 2005). However, large amounts of lime may be required, which is costly and may have negative side effects on the environment (Fraser et al. 2012; Vahedian et al. 2014). Organic materials play an important role as energy source of sulphate and other reducing bacteria (Berner 1984; Dent and Pons 1995). Recently, it has been shown that addition of organic materials can stimulate sulphate reduction, which consumes protons (Jayalath et al. 2016; Michael et al. 2015; Yuan et al. 2015a, b) and can also reduce acidification during oxidation of ASS (Jayalath et al. 2016).

Since late 2010, water levels recovered and these oxidised areas are again irrigated. Irrigation mobilised soil acidity and caused surface water acidification and precipitation of mainly schwertmannite and traces of jarosite in drainage channels and groundwater (Fitzpatrick et al. 2012). High acidity and soluble metal concentrations that exceeded Australian drinking water quality guidelines were reported for the drainage water even several years after the end of the drought (Mosley et al. 2014a; Simpson et al. 2014). Using artificial drainage water based on long-term average composition of ASS drainage water in the LMRIA, we showed that passage through organic materials such as compost and biochars reduced leaching of acidity and dissolved metals (Dang et al. 2016). Other studies also reported the removal of acidity and dissolved metals in acid mine drainage wastewater by organic materials (Beesley et al. 2014; Bhatnagar and Sillanpää 2010; Fellet et al. 2011; Zhou and Haynes 2010). Biochars, plant residues and municipal wastes have been used to remediate heavy metal-contaminated soil and groundwater (Liang et al. 2014) and to treat acid mine drainage water (Choi and Lee 2015; Hughes and Gray 2013; Westholm et al. 2014). Absorption capacity differed among organic materials and depended on metal speciation and dominant metals (Choi et al. 2013; Hughes et al. 2013; Yang et al. 2014).

In our previous study (Dang et al. 2015), organic materials were leached with synthetic drainage water based on long-term observation (June 2011–May 2013) of the composition of LMRIA drainage water according to Mosley et al. (2014a). Acidity and metal speciation of drainage water may vary seasonally (Macdonald et al. 2007; Mosley et al. 2014a, b; Simpson et al. 2014). Therefore, retention of protons and metals in the materials when leached with uncontaminated water after repeated addition of acidic drainage water is important for application in drainage channels as well as after removal of the organic materials from the barriers. If the disposed materials leach contaminants, for example following rainfall events if spread on land, this could result in negative impacts on waterways.

The aim of this study was to (i) determine the capacity of organic materials that have received repeated applications of acid drainage water to retain protons, Fe and Al, and (ii) assess their release when subsequently leached with uncontaminated water. We hypothesised that organic materials with high retention capacity for protons, Al and Fe would also release little in the subsequent leaching.

Materials and methods

Experimental design

Acid sulphate soil drainage water was collected from a drainage channel in the LMRIA near Mobilong (35° 06′ 18″ S 139° 16′ 29″ °E) in April 2015 after the first rains at the end of summer (Table 1, Fig. S1).

The same eight organic materials as in our previous study (Dang et al. 2015) were used, including plant residues (wheat straw and pea straw), compost made from municipal green waste and five biochars from different feed stocks produced by pyrolysis in a low-oxygen environment at 450 or 550 °C: poultry litter biochar 450 °C, poultry litter biochar 550 °C, wheat straw biochar 450 °C, wheat straw biochar 550 °C and mallee wood biochar 550 °C. Mallee is a semiarid woodland in southern Australia; feedstock for the mallee biochar included wood from various eucalyptus species. Residues and compost were dried at 40 °C, then all organic materials were ground and sieved to 0.5–2 mm.

The organic materials were filled into PVC cores (radius 1.85 cm and height 5 cm) with a mesh bottom as described by Dang et al. (2015) at 3.5 g dry weight/core. The cores were leached six times with either the LMRIA acid drainage water or reverse osmosis (RO) water. At each leaching event, a total of 45 mL water was added per core, in nine aliquots of 5 mL in 5 min between each addition. The total amount of solution (45 mL) per leaching event was chosen based on our previous study to ensure sufficient leachate for the analyses. The 5-min interval between additions was considered sufficient to allow interaction of the solution with the organic materials. After the addition of 45 mL, the leachate was collected, and the total volume was measured and analysed as described below. Leaching was carried out every 7 days. Between leaching events, the organic materials were left undisturbed at room temperature. The materials lost water through evaporation, but remained moist. To assess the release of native protons,

Table 1 Composition of LMRIA drainage water

Parameter	Unit	Concentration	WQG[a]
pH_w		*3.15*	6.5–9.0
Acidity	mg L^{-1} $CaCO_3$	326	NV
Alkalinity	mg L^{-1} $CaCO_3$	0	NV
Al	mg L^{-1}	*21.8*	0.0005/0.055
Ca	mg L^{-1}	472	NV
Cl	mg L^{-1}	4270	NV
Dissolved organic C	mg L^{-1}	13.3	NV
Fe	mg L^{-1}	47.9	NV
K	mg L^{-1}	64.8	NV
Mg	mg L^{-1}	538	NV
Mn	mg L^{-1}	*5.1*	1.9
Ni	mg L^{-1}	*0.39*	0.028
Na	mg L^{-1}	2820	NV
SO_4	mg L^{-1}	3944	NV
Zn	mg L^{-1}	*0.197*	0.020

Values are set in italic when exceeding WQG

[a] WQG (water quality guideline)—trigger value for 95 % species protection applicable to freshwaters of hardness 30 mg $CaCO_3$ L^{-1} from ANZECC (2000). For Al, WQG is for waters with pH <6.5/pH >6.5. NV—no WQG exists. Hardness-adjusted WQGs for Ni and Zn applicable to fresh waters (ANZECC, 2000)

Al and Fe, the organic materials were also leached six times with RO water (one replicate). The leaching experiment with drainage water included two phases. In the first phase, the cores were leached with LMRIA acid drainage water (Table 1) to assess retention of protons, Al and Fe from the drainage water in materials (aim 1). In the second phase, the cores that had received LMRIA acid drainage water were leached with RO water to evaluate the release of protons, Al and Fe from the materials (aim 2). The leachate was collected and analysed as described below.

Analyses

The pH of the organic materials was measured in a material to water ratio of 1:1 (*w/w*). Total organic C and total N were measured by dry combustion using a LECO Trumac CN analyser. Acid neutralising capacity (ANC) expressed as $CaCO_3$ equivalent was measured by the rapid titration method as described by Ahern et al. (2004). Briefly, 1.0 g of each finely ground organic material was placed into a 250-mL flask with 50 mL of deionised water and 25 mL of standardised 0.1 M HCl. The suspensions were boiled on a hotplate for 2 min then allowed to cool to room temperature. The unreacted acid in the flask was titrated with standardised 0.1 M NaOH to pH 7.

Surface area of the organic materials was analysed by the nitrogen gas adsorption method and calculated as described by Brunauer et al. (1938). The organic materials were degassed overnight at a vacuum of 10^{-5} kPa prior to measuring nitrogen adsorption. Biochar samples were degassed at 200 °C; plant residues and compost at ambient temperature. Nitrogen gas adsorption was measured at 77 K using a Belsorp-max gas adsorption apparatus. Ultra high purity (>99.999 %) helium and nitrogen were used for dead-space measurements and adsorption experiments, respectively.

Cation exchange capacity (CEC) was determined after Rayment and Lyons (2011). The organic materials were extracted with 0.1 M NH_4Cl at a 1:30 *w/w* ratio in an end-over-end shaker for 1 h. The extracts were centrifuged at 3000 rpm for 10 min, and the supernatant was filtered through Whatman #42 filter paper. The solution was analysed by inductively coupled plasma mass spectroscopy (ICP-MS).

Acid extractable Al and Fe in the organic materials were determined after acid dissolution (Zarcinas et al. 1996). The extracts were filtered through Whatman #42 filter paper and analysed for Al and Fe by ICP-MS.

Chemical groups of organic materials were measured by solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy as described by Smernik and Oades (2000) and McBeath et al. (2014) for organic matter and biochar, respectively.

Following hot peroxide digestion, acidity of the LMRIA drainage water was measured by titration to pH 8.3 at 25 °C. Alkalinity was measured by titration to pH 4.5 (APHA 2005). Ca, Mg, Na and K were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) with a ferricyanide method used for Cl [method 4500-Cl-E, APHA (2005)]. Dissolved metals were measured by ICP-MS. Dissolved organic carbon was measured by high-temperature combustion and infrared detection of evolved CO_2 [method 5310B, APHA (2005)].

The pH of the leachate was measured immediately after collection. The leachates were filtered through a 0.45-μm filter and acidified with nitric acid (2 % *v/v*) before measuring Al and Fe by ICP-OES.

Statistical analyses

Leachate data of retention phase were expressed as protons (10^{-pH}), and Al and Fe retained in the materials for each leaching event and total cumulative retention. Retention per gram material per leaching event was calculated as follows: [(concentration of element in added solution per mL * amount of added solution in mL) − (concentration of element in leachate per mL * amount of leachate in mL)] / amount of organic material (g) per core. Cumulative retention was the sum of retention in the six leaching events.

Proton, Fe and Al release in the second phase (leaching with RO water) was calculated per gram material per leaching event as follows: (concentration of element in leachate per mL * amount of leachate in mL) / the amount of organic material per core. Cumulative release was the sum of release from each leaching event. Release was also expressed in percentage of Al and Fe retained in the first phase (Release of element per g material / cumulative retention of element per g material at the end of phase 1) * 100.

The data were analysed by one-way ANOVA for each leaching event separately and for cumulative retention and release. Where ICP-MS values were below detection limit, zero was used for statistical analyses. Differences between means were compared by Duncan analysis ($P \leq 0.05$) using GenStat 15th edition (VSN Int. Ltd., UK).

Results

Composition of LMRIA drainage water

The collected LMRIA drainage water was very acidic (pH 3.15, acidity 326 mg L^{-1} as $CaCO_3$) and had high metal concentrations (Table 1), many of which exceed Australian water quality guidelines (ANZECC 2000). Acidity and metal concentrations were also higher than the long-term average drainage water composition reported by Mosley et al. (2014a, b). The reddish brown colour shown in Fig. S1 comes from precipitates of schwertmannite which commonly form in the drainage water at pH between 3 and 4.5. Protons, along with the high concentrations of dissolved Al, Fe and Mn, contribute to acidity in the drainage water as described by Kirby and Cravotta (2005) and Mosley et al. (2014a). Protons are generated in the soil and drainage water from pyrite oxidation, which also releases dissolved Fe. Other metals such as Al and Mn are dissolved from other minerals in the soil due to proton-driven dissolution.

Properties of organic materials

Organic materials in the form of plant residues (wheat straw and pea straw) had neutral pH (5.5 and 6.3), whereas compost and biochars were alkaline (Table S1). Organic C content varied among materials, and it was lowest in compost and highest in mallee 550. Plant residues had lower total N concentration and higher C/N ratio than compost and biochars except mallee 550. The ANC was lowest in plant residues and highest in compost. The CEC was highest in compost and lowest in wheat straw. Surface area was low in plant residues and highest in biochar produced at 550 °C. Total Al and Fe concentrations were highest in compost and mallee and lowest in wheat straw. Chemical functional groups in the organic materials were expressed as percentage of organic C detected (Table S2). The proportions of alkyl, aryl, O-aryl and ketone C groups were higher in compost and biochar than in plant residues; plant residues had the highest percentage of O-alkyl and di-O-alkyl C groups.

Leaching with RO water only

To assess the release of native protons, Fe and Al from organic materials, they were leached six times with RO water (pH 5.5). All organic materials increased leachate pH with the smallest increase in wheat straw (Fig. 1b). The pH increase was smallest in the first leaching event and greatest in the fourth leaching event except in pea straw where it was greatest in the second leaching event. The highest leachate pH was about 7 in wheat straw, 7.8 in pea straw and above 8 in the other materials. Native Al was released (negative retention), with greater cumulative release in compost, poultry 550 and wheat 450 than in the other organic materials, and it was lowest in wheat straw (Table 2). Leachate Al concentrations were generally <0.1 mg L^{-1}. The two straws and compost released more Fe than the biochars; however, Fe concentrations were generally <0.1 mg L^{-1} (Table S8). Cumulative Fe release was highest in compost and lowest in wheat 550 (Table 2).

Leaching phase 1 (with LMRIA acid drainage water)

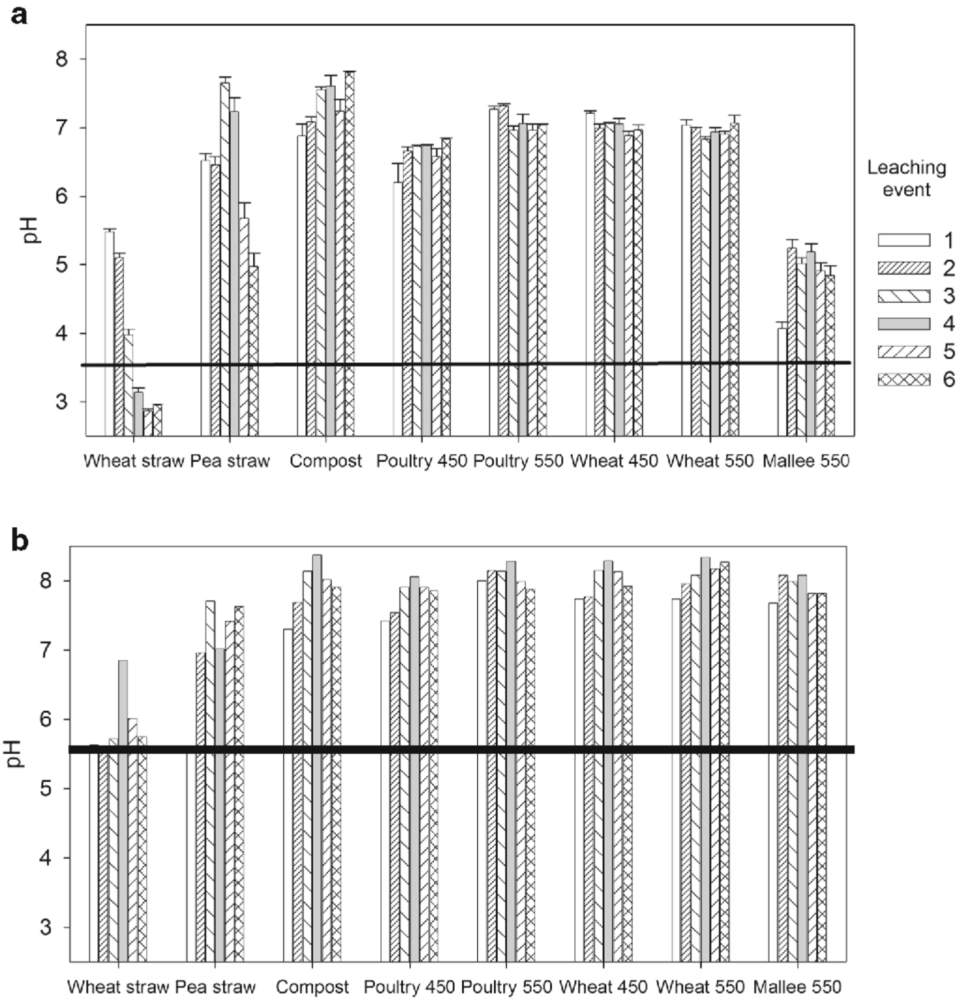
The organic materials retained between 10 and 20 mL of the added LMRIA water at each leaching event (Table S3). The leachate volume was lower in the first leaching event than in the following events. The largest amount of leachate was collected in the second leaching event with the highest volume in the poultry biochars. In the following leaching events, around 20–30 % of added LMRIA water was retained in biochars, compost and wheat straw whereas pea straw retained 35–45 %.

Leachate pH was generally higher than that of the added LMRIA water (pH 3.15) except in the last two leaching events in wheat straw (Fig. 1a). Compared to the other organic materials, the pH increase was smaller in wheat straw and mallee 550, which increased the pH by about 1.5 units. In wheat straw, the pH increase was greatest in the first leaching event whereas in mallee 550, it was smaller in the first than the following leaching events. Compost and most biochars (except mallee 550) increased leachate pH in all leaching events by about 3 units, to pH 6–7. Leachate pH was higher in compost than in biochars. In pea straw, leachate pH was higher in the first four leaching events than in the last two.

Proton retention per leaching event was consistently high in compost, and most biochars with 100 % of added protons retained in the materials (Fig. 2a). Retention decreased with the number of leaching events in wheat straw whereas in mallee 550, it increased from the first to the third leaching event and then remained high. Cumulative proton retention in wheat straw was about half of that of the other organic materials (Fig. 1b).

The Al concentration in the leachates was always higher in wheat straw than in compost and the biochars

Fig. 1 pH of leachates of different organic materials over six leaching events compared to the pH of the added solution. **a** LMRIA water added (pH 3.15). **b** RO water added (pH 5.5). *Thick horizontal lines* are pH of the added solution (*n* = 4 for LMRIA water; *vertical lines* represent standard error)



except for the second leaching event where it was similar as in mallee 550 (Table S6). In compost and most biochars (except mallee 550), Al concentrations in leachates were around 1 mg L^{-1}. Retention of Al decreased with the number of leaching events with LMRIA water in wheat straw where it was always lower than in the other organic materials which had similar retention (Fig. 2b). In the last two leaching events, retention by wheat straw was only about half of that in the other organic materials. In mallee 550, Al retention increased from the first to the third leaching event and then stabilised at about 270 μg g^{-1}, which was similar as in the other biochars and in

Table 2 Al released in micrograms per gram and as percentage of Al retention in organic materials after the addition of RO water over six leaching events to different organic materials that were previously leached with LMRIA water six times in the first three leaching events with RO water and cumulative over six leaching events

Leaching event	1		2		3		Cumulative	
	Al released (μg g^{-1})	%	(μg g^{-1})	%	(μg g^{-1})	%	(μg g^{-1})	%
Wheat straw	88 ± 5a	8.2	2.9 ± 0.7a	0.27	1.05 ± 0.33a	0.10	93.29 ± 5.58a	8.65
Pea straw	36 ± 6b	2.3	2.6 ± 0.3a	0.16	1.64 ± 0.27b	0.10	47.65 ± 4.48b	2.98
Compost	0c	0	0.1 ± 0.05b	0.03	0.31 ± 0.12c	0.11	2.10 ± 0.41c	0.78
Poultry 450	0c	0	0b	0	0.04 ± 0.01c	0.00	0.41 ± 0.12c	0.03
Poultry 550	0c	0	0b	0	0.11 ± 0.05c	0.01	0.40 ± 0.09c	0.02
Wheat 450	0c	0	0b	0	0.32 ± 0.12c	0.02	1.33 ± 0.19c	0.08
Wheat 550	0c	0	0b	0	0.11 ± 0.03c	0.01	0.65 ± 0.24c	0.04
Mallee 550	0c	0	0b	0	0.14 ± 0.06c	0.01	0.74 ± 0.24c	0.05

Within columns, values followed by different letters are significantly different (Duncan test, $P \leq 0.05$)

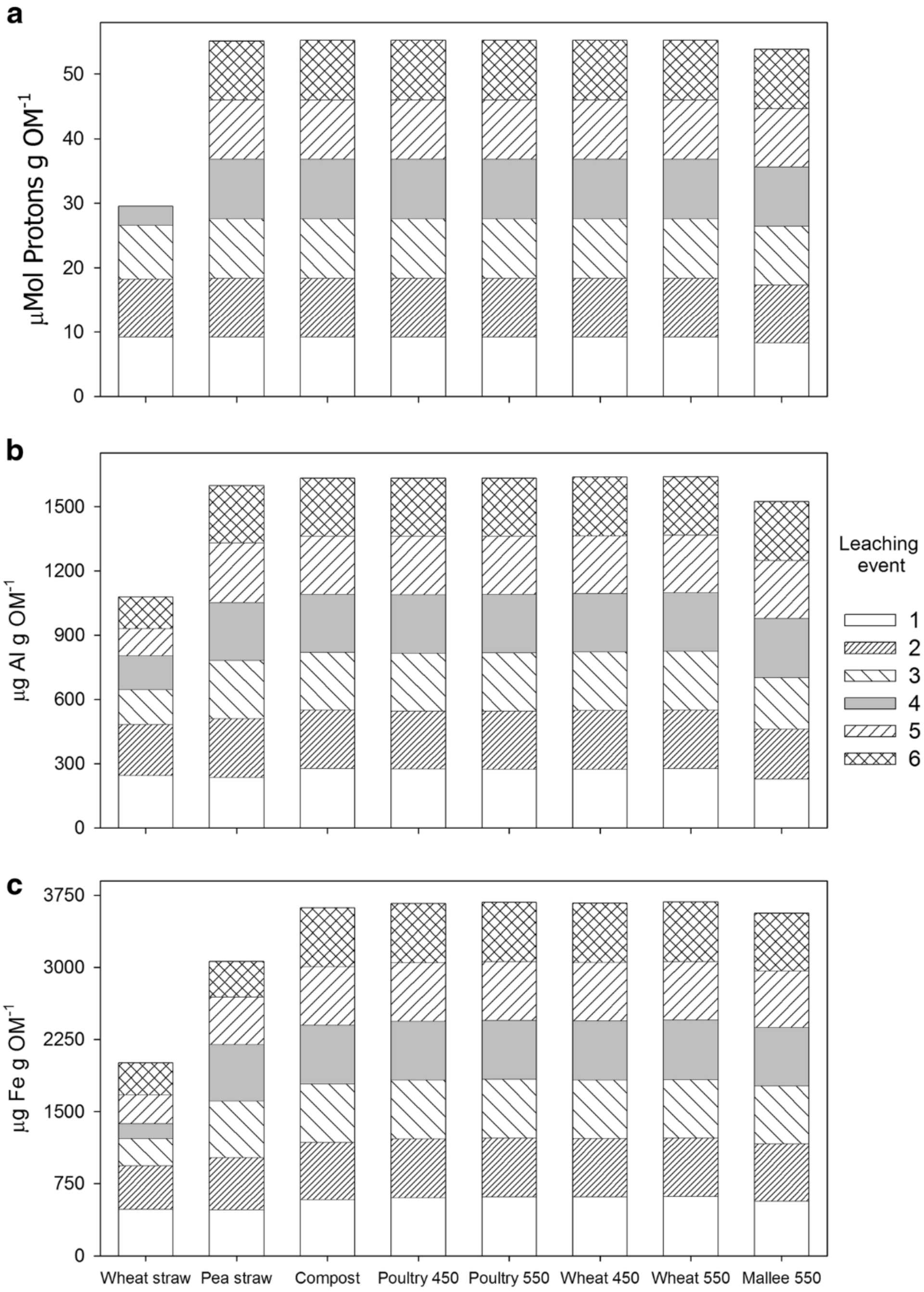


Fig. 2 Retention of protons (**a**), Al (**b**) and Fe (**c**) by organic materials in six leaching events with LMRIA water (*n* = 4)

compost, and is >97 % of the added Al (Table S4). The other biochars and compost retained >97 % in all leaching events. Cumulative Al retention in pea straw, compost and all biochars was about 1.5-fold greater than in wheat straw (Fig. 2b).

The Fe concentration in the leachates was 5–40-fold higher in wheat and pea straw than in the other organic materials (Table S7). In compost, poultry 450 and mallee 550, the Fe concentration was highest in the first leaching event. Iron retention was lowest in wheat straw followed by pea straw (Fig. 2c). In the first two leaching events, Fe retention in mallee 550 was lower than in the other biochars, but retention did not differ among biochars and compost from the fourth leaching event onwards. Between 92 and 100 % of the added Fe was retained by biochars and compost compared to 50–80 % in wheat straw (Table S4). Cumulative Fe retention was lowest in wheat straw, followed by pea straw (Fig. 2c). Cumulative Fe retention in compost and all biochars was about 1.8-fold greater than in wheat straw.

Leaching phase 2 (with RO water)

After leaching with LMRIA water six times, the organic materials were leached six times with RO water to determine the capacity of the organic materials to retain protons, Al and Fe accumulated from the LMRIA water. Passage of RO water through wheat straw resulted in a pH decrease compared to that of the applied RO water (5.5) by between 0.5 and more than 1.5 units (Fig. 3). Leaching of pea straw with RO water also decreased the pH by about 1 unit in the first two leaching events, but from the third leaching event onwards, the pH was about 1.5 units higher than the applied RO water. Passage through compost and biochars increased the pH compared to the applied RO water by up to 2.5 units with the smallest pH increase in the first leaching event and the greatest increase in the fourth. The pH increase was generally greatest in compost and smallest in mallee 550.

Leachate Al concentrations were very low (often below the detection limit of 0.001 mg L^{-1}) in biochars and compost (Table S9). They were highest in the two straws, particularly in the first leaching event with RO water. Cumulative Al release in the biochars was less than 0.1 % of Al accumulated during the previous leaching with LMRIA water (Table 2). It was also low in compost (0.8 % of retained) whereas pea straw released 3 % and wheat straw 9 % of retained Al.

Iron concentrations in the leachate after application of RO water remained below 0.2 mg L^{-1} in all biochars, and it was slightly higher in compost and pea straw and significantly higher in wheat straw (Table S10). In the two straws, Fe concentrations were highest in the first leaching event, 16 and 3 mg L^{-1} for wheat and pea straw. The biochars released less than 0.2 % of Fe accumulated in the previous leaching with LMRIA water (Table 3). Release from compost was also very low (0.3 %), whereas pea straw released 1.7 % and wheat straw 12 % of previously accumulated Fe.

Discussion

This study showed that all organic materials tested and particularly compost and biochars had a high retention capacity for protons, Al and Fe when leached repeatedly with ASS drainage water, which was highly acidic and had high concentrations of Fe and Al. Further, only a very small proportion of accumulated protons, Al and Fe was released when organic materials were subsequently leached with RO water. To our knowledge, this is the first study that has assessed the capacity of organic materials to retain protons, Al and Fe from field-collected ASS drainage water when subsequently leached with uncontaminated (RO) water.

Previous studies with organic materials and acidic media can provide explanations for the findings of this study. The greater pH increase in compost and biochars compared to plant residues is likely due to their higher ANC (Table S1). The ANC of biochar is thought to play an important role in pH neutralisation of acid drainage via alkalinity from $CaCO_3$ dissolution (Mosley et al. 2015). Dissolved alkalinity content depends on biochar feedstock, which may explain the smaller pH increase in poultry 450 and mallee 550 compared to the other biochars. For example, wood-based biochars such as mallee 550 have been shown to have lower alkalinity than biochars from other feedstocks (Liu et al. 2015). In other studies, the pH increase induced by organic materials has been explained by humic compounds formed during the composting process (McCartney and Wichuk 2010), which have high proton-binding affinity (Pedra et al. 2008). Biochar can contain water soluble humification products, which contribute to their proton-binding capacity (Zhang et al. 2014).

Metal retention in organic materials may be due to adsorption, surface precipitation, complexation and fixation and has been shown to vary among organic materials (e.g. Bhatnagar and Sillanpää 2010; Zhou and Haynes 2010). Metals can be bound to lignin and tannin in plant

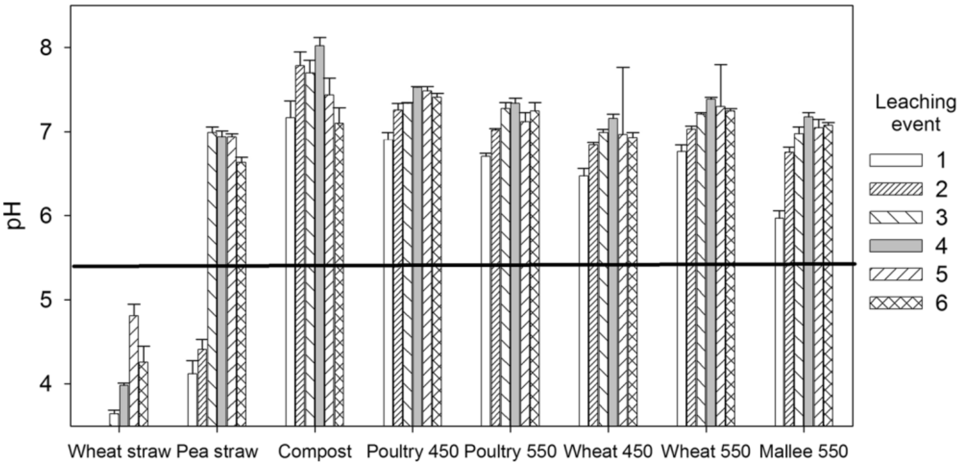


Fig. 3 pH of leachates of different organic materials that were previously leached with LMRIA water six times over six leaching events with RO water. *Thick horizontal line* is the pH of added RO water (*n* = 4, *vertical line* represents standard error)

Table 3 Fe released in micrograms per gram and as percentage of Fe retention in organic materials after the addition of RO water over six leaching events to different organic materials that were previously leached with LMRIA water six times in the first three leaching events with RO water and cumulative over six leaching events

Leaching event	1		2		3		Cumulative	
	Fe released (μg g^{-1})	%	(μg g^{-1})	%	(μg g^{-1})	%	(μg g^{-1})	%
Wheat straw	136.3 ± 11.7a	6.80	59.2 ± 13.1a	2.95	13.9 ± 2.3a	0.69	233.8 ± 13.1a	11.65
Pea straw	28.5 ± 4.9b	0.93	10.0 ± 1.3b	0.33	7.3 ± 0.9b	0.24	52.0 ± 5.2b	1.70
Compost	1.7 ± 0.4c	0.05	1.6 ± 0.5b	0.04	1.6 ± 0.3c	0.05	10.6 ± 2.3c	0.29
Poultry 450	2.1 ± 1.5c	0.06	0.7 ± 0.4b	0.02	0.2 ± 0.0c	0.00	4.5 ± 1.7c	0.12
Poultry 550	1.0 ± 0.3c	0.03	0.4 ± 0.2b	0.01	0.4 ± 0.1c	0.01	2.1 ± 0.5c	0.06
Wheat 450	1.3 ± 0.4c	0.03	0.8 ± 0.3b	0.02	1.2 ± 0.2c	0.03	7.1 ± 0.9c	0.19
Wheat 550	0.7 ± 0.2c	0.02	0.7 ± 0.4b	0.02	0.1 ± 0.0c	0.00	2.0 ± 0.6c	0.05
Mallee 550	1.3 ± 0.3c	0.04	0.4 ± 0.1b	0.01	0.2 ± 0.1c	0.01	3.3 ± 0.5c	0.09

Within columns, values followed by different letters are significantly different (Duncan test, $P \leq 0.05$)

cell walls (Ahluwalia and Goyal 2007; Shin and Rowell 2005) and humified compounds (Bailey et al. 1999; Grimes et al. 1999). Metal retention by biochar can occur via binding to oxygen-containing (carboxylic –COO^{-} and phenolic R–O^{-}) functional groups (Cao et al. 2009; Uchimiya et al. 2011) and surface adsorption and co-precipitation of Al with silicate particles (Qian and Chen 2013a; Qian and Chen 2013b; Qian et al. 2013). Trakal et al. (2014) showed that removal of metals from aqueous solution depended on feedstock and production temperature. But this was not the case in the present study except for mallee 550, which had a lower Fe retention in the first to leaching events and lower cumulative Al retention compared to other biochars.

Metal retention on organic materials is strongly pH dependent, increasing with pH (Bulut and Baysal 2006; Zhou and Haynes 2010). This can be explained by different mechanisms (e.g. Zhou and Haynes 2010). As pH increases, there is less competition for cation-binding sites with protons. Additionally, dissolved metals may precipitate as pH increases (e.g. Bigham and Nordstrom 2000). Thus, the pH increase in LMRIA drainage water by passage through biochars and compost (pH up to 7.5) can at least partly explain the greater retention compared to wheat straw which increased the pH only to 5.5 in the first leaching event. The higher pH may also explain the greater Fe and Al retention in pea straw compared to wheat straw.

In our previous study with the same organic materials (Dang et al. 2015), proton, Fe and Al retentions were also lowest in wheat straw, but there were differences among biochars whereas in the present study, retention was similar among biochars. The difference between this and our previous study could be due to the lower Fe and Al concentrations of the synthetic drainage water used in the previous study. The synthetic drainage water was based on long-term average drainage water composition in the LMRIA. The drainage water was applied at the same total volume as the present study and had a similar pH (3.0), but 10-fold lower Al concentrations (2 mg L^{-1}) and half the Fe concentration (28 mg L^{-1}) than the natural LMRIA drainage water used here. This suggests that differences among biochars and also biochars and compost in Fe and Al retention were greater when smaller total amounts of Fe and Al were applied and retained. Cumulative retention reported by Dang et al. (2015) was on average 50, 10 and 1200 μg g^{-1} for protons, Al and Fe, respectively. Thus, average proton retention was similar as in this study whereas Al retention was more than 10-fold lower and Fe retention about threefold lower in our previous study. It is possible that these were binding sites with high affinity to Fe and Al. With the large amounts of Fe and Al applied in the present study, Fe and Al may also have been bound to binding sites with lower affinity. Precipitation of Fe and Al salts within the biochars may be another reason for the lack of differences in retention among biochars. Another possible reason for the differences in results in the two studies is that in Dang et al.'s (2015), biochars were added to the cores to give the same amount of C per core (1.5 g C/core). This resulted in different amounts of material per core, ranging from 2.7 to 5.3 g. Iron and Al retention was highest in mallee 550 and wheat 450 which had the lowest amounts of material per core whereas it was low in compost, which had the greatest amount per core. Thus, the results indicated that proton, Fe and Al retentions were influenced by the amount of organic material per core. The lack of differences among biochars and compost in the present study appears to confirm this. The results of the present study also suggest that differences in properties such as ANC, CEC and surface area or proportion of C groups are not important when large amounts of Al and Fe are applied and the amount of material/core is the same.

Only a very small proportion (<1 %) of the metals that were bound on the compost and biochar following sequential acid drainage water passage was leachable with RO water (Table 3). This indicates that substantially reducing the solution ionic strength does not result in metal release from biochar and compost. This has important environmental management implications in reducing contamination via leaching from spent organic materials. For example, if organic materials that were used for treatment were left in a drain or spread on land, a pulse of low-salinity water from rain events may not result in significant metal release.

Compost had similar retention of protons, Al and Fe as the biochars and released only slightly more metals than biochars upon leaching with RO water. Release of Al and Fe was low although release of native Fe and Al (leaching with RO water without prior application of LMRIA water) was greater in compost than the biochars. However, the amounts of native Al and Fe released by compost represented less than 10 % of amounts added with LMRIA water and were also about 10-fold lower than Al and Fe concentrations in the leachate after application of LMRIA water. The repeated leaching with LMRIA water appears to have also removed mobile native Al and Fe from the organic materials because leachate Al and Fe concentrations were similar or lower than when materials were leached with RO without prior application of LMRIA water.

Retention of protons, Al and Fe was lower in the two straws than the biochars and compost and the straws released a greater proportion of the accumulated protons, Al and Fe in the subsequent leaching with RO water, e.g. Al release in percentage retained 9 % in wheat straw, 3 % in pea straw compared to 0.8 % in compost and <0.1 % in biochars. Release of native Fe and Al was also higher in the two straws than the biochars and comparable to compost. The lower retention capacity and greater release of protons, Al and Fe of the straws compared to the biochars and compost could be due to the much lower ANC (about 50-fold lower than the average of biochars and compost) and the lower specific surface area (about 10 % of the average of biochars and compost). The two straws also had higher proportions of O-alkyl and di-O-alkyl C but lower proportions of aryl and O-aryl C than the biochars and compost. Aryl and O-aryl C have been shown to be important for metal binding (Chaberek and Martell 1959; Uchimiya et al. 2012). Another possible reason is that the plant residues were decomposed during the experiment. Decomposition of compost and biochars during the experiment is unlikely because they are poorly degradable. Decomposition products such as organic acid anions may mobilise metals by chelation (Hammadi and Hanchi 2011; Park et al. 2011). Further, decomposition may reduce the capacity to adsorb protons and metals which could explain the lower percentage retention by wheat straw from the third leaching event onwards compared to the first. However, retention remained close to 100 % in all other organic materials. Longer term experiments, particularly field studies, are needed to assess if decomposition of the organic materials occurs and how this affects retention capacity for protons and metals.

This study showed that biochar and compost could be used in acid drainage treatment, particularly where conventional acid treatments such as limestone are not available or too costly. They may be considered as economical where organic materials are locally grown and acid drainage occurs on a small scale.

Conclusion

The organic materials retained large amounts of protons, Al and Fe when LMRIA water, which was acidic and had high Al and Fe concentrations, was applied repeatedly. Retention of protons, Al and Fe was high in biochars and compost because less than 1 % of retained amounts were released upon subsequent leaching with RO water, suggesting that they are suitable for remediation of acidic drainage water, for example in the form of permeable reactive barriers. The two straws tested had lower retention and greater release of protons, Al and Fe than compost and biochars, but would still be effective remediation materials. Further studies in the lab and the field are required to assess the maximum retention capacity of the organic materials and the influence of contaminated water through flow rate.

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References

Ahern CR, McElnea AE, Sullivan LA (2004) Acid neutralising capacity, carbonate and alkali cation methods. In: Ahern CR, McElnea AE, Sullivan LA (eds) Acid sulfate soils laboratory methods guidelines. Department of Natural Resources, Nines and Energy, Indooroopilly, Queensland, Australia

Ahluwalia SS, Goyal D (2007) Microbial and plant-derived biomass for removal of heavy metals from wastewater. Biores Technol 98:2243–2257

ANZECC (2000) Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra

APHA (2005) Standard methods for the examination of water and wastewater (21st edn). Washington, D.C: American Public Health Association, American Water Works Association and Water Environment Federation

Bailey SE, Olin TJ, Bricka RM, Adrian OA (1999) A review of potentially low-cost sorbents for heavy metals. J Water Res 33:2469–2479

Beesley L, Inneh OS, Norton GJ, Moreno-Jimenez E, Pardo T, Clemente R, Dawson JJC (2014) Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. Environ Poll 186: 195–202

Berner RA (1984) Sedimentary pyrite formation: an update. Geochim Cosmochim Acta 48:605–615

Bhatnagar A, Sillanpää M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. Chem Eng J 157:277–296

Bigham J, Nordstrom DK (2000) Iron and aluminum hydroxysulfates from acid sulfate waters. Rev Mineral Geochem 40:351–403

Bronswijk JJB, Nugroho K, Aribawa IB, Groenenberg JE, Ritsema CJ (1993) Modeling of oxygen-transport and pyrite oxidation in acid sulfate soils. J Environ Qual 22:544–554

Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Amer Chem Soc 60:309–319

Bulut Y, Baysal Z (2006) Removal of Pb(II) from wastewater using wheat bran. J Environ Manag 78:107–113

Cao X, Ma L, Gao B, Harris W (2009) Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ Sci Technol 43:3285–3291

Chaberek S, Martell AE (1959) Organic sequestering agents: a discussion of the chemical behavior and applications of metal chelate compounds in aqueous systems. Wiley, New York

Choi H-J, Lee S-M (2015) Heavy metal removal from acid mine drainage by calcined eggshell and microalgae hybrid system. Environ Sci Pollut Res 22:13404–13411

Choi S-J, Lee B-T, Kim J-Y, Kim K-W (2013) Study on adsorption/desorption of As by mine sludge depending on pH and natural organic matter. Geosys Engin 16:191–199

Dang T, Mosley L, Fitzpatrick R, Marschner P (2015) Organic materials differ in ability to remove protons, iron and aluminium from acid sulfate soil drainage water. Water Air Soil Poll 226:1–13. doi:10.1007/s11270-015-2595-z

Dang T, Mosley LM, Fitzpatrick R, Marschner P (2016) Addition of organic material to sulfuric soil can reduce leaching of protons, iron and aluminium. Geoderma 271:63–70

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

Fältmarsch RM, Aström ME, Vuori K-M (2008) Environmental risks of metals mobilised from acid sulphate soils in Finland: a literature review. Boreal Environ Res 13:444–456

Fellet G, Marchiol L, Delle Vedove G, Peressotti A (2011) Application of biochar on mine tailings: effects and perspectives for land reclamation. Chemosphere 83:1262–1267

Fitzpatrick R, Shand P, Merry R (2009) Chapter 3. Acid sulfate soils. In: Jennings J (ed) Natural history of the Riverland and Murraylands. Royal Society of South Australia (Inc.), Adelaide, pp. 65–111

Fitzpatrick R, Raven M, Self P, Shand P, Mosley L, Simpson S, Baker A (2012) Occurrence, genesis and environmental significance of schwertmannite in re-flooded acid sulfate soils in the Lower Murray Reclaimed Irrigation Area. Proceedings Combined Australian Regolith Geoscientists Association and Australian Clay Minerals Society Conference: Mildura 7–10 February, 2012; 147–152

Fraser MA, Baldwin DS, Rees GN, Silvester EJ, Whitworth KL (2012) Rehabilitation options for inland waterways impacted by sulfidic sediments—field trials in a south-eastern Australian wetland. J Environ Manag 102:71–78

Grimes SM, Taylor GH, Cooper J (1999) The availability and binding of heavy metals in compost derived from household waste. J Chem Technol Biotechnol 74:1125–1130

Hammadi MAE, Hanchi B (2011) Composition of organic and inorganic contaminants in compost produced from different organic wastes. Intern J Biol Chem 5:46–53

Hughes TA, Gray NF (2013) Co-treatment of acid mine drainage with municipal wastewater: performance evaluation. Environ Sci Pollut Res 20:7863–7877

Hughes T, Gray NF, Sánchez Guillamón O (2013) Removal of metals and acidity from acid mine drainage using liquid and dried digested sewage sludge and cattle slurry. Mine Water Environ 32:108–120

Jayalath N, Mosley LM, Fitzpatrick RW, Marschner P (2016) Addition of organic matter influences pH changes in reduced and oxidised acid sulfate soils. Geoderma 262:125–132

Kirby CS, Cravotta CA III (2005) Net alkalinity and net acidity 1: theoretical considerations. Appl Geochem 20:1920–1940

Liang Y, Cao XD, Zhao L, Arellano E (2014) Biochar- and phosphate-induced immobilization of heavy metals in contaminated soil and water: implication on simultaneous remediation of contaminated soil and groundwater. Environ Sci Pollut Res 21:4665–4674

Liu P, Ptacek CJ, Blowes DW, Berti WR, Landis RC (2015) Aqueous leaching of organic acids and dissolved organic carbon from various biochars prepared at different temperatures. J Environ Qual 44:684–695

Ljung K, Maley F, Cook A, Weinstein P (2009) Acid sulfate soils and human health—a millennium ecosystem assessment. Environ Intern 35:1234–1242

Macdonald BCT, White I, Åström ME, Keene AF, Melville MD, Reynolds JK (2007) Discharge of weathering products from acid sulfate soils after a rainfall event, Tweed River, eastern Australia. Appl Geochem 22:2695–2705

McBeath AV, Smernik RJ, Krull ES, Lehmann J (2014) The influence of feedstock and production temperature on biochar carbon chemistry: a solid-state 13C NMR study. Biom Bioen 60:121–129

McCartney D, Wichuk KM (2010) Compost stability and maturity evaluation—a literature review. Can J Civ Engin 37:1505–1550

Michael PS, Fitzpatrick R, Reid R (2015) The role of organic matter in ameliorating acid sulfate soils with sulfuric horizons. Geoderma 255–256:42–49

Mosley L, Fitzpatrick R, Palmer D, Leyden E, Shand P (2014a) Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. Sci Tot Environ 485–486:281–291

Mosley LM, Shand P, Self P, Fitzpatrick R (2014b) The geochemistry during management of lake acidification caused by the rewetting of sulfuric (pH < 4) acid sulfate soils. Appl Geochem 41:49–61

Mosley L, Willson P, Hamilton B, Butler G, Seaman R (2015) The capacity of biochar made from common reeds to neutralise pH and remove dissolved metals in acid drainage. Environ Sci Pollut Res:1–10

Park JH, Lamb D, Paneerselvam P, Choppala G, Bolan N, Chung J-W (2011) Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. J Haz Mat 185:549–574

Pedra F, Plaza C, García-Gil JC, Polo A (2008) Effects of municipal waste compost and sewage sludge on proton binding behavior of humic acids from Portuguese sandy and clay loam soils. Biores Technol 99: 2141–2147

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. Mar Poll Bull 51:149–164

Qian L, Chen B (2013a) Dual role of biochars as adsorbents for aluminum: the effects of oxygen-containing organic components and the scattering of silicate particles. Environ Sci Technol 47:8759–8768

Qian L, Chen B (2013b) Interactions of aluminum with biochars and oxidized biochars: implications for the biochar aging process. J Agric Food Chem 62:373–380

Qian L, Chen B, Hu D (2013) Effective alleviation of aluminum phytotoxicity by manure-derived biochar. Environ Sci Technol 47:2737–2745

Rayment GE, Lyons DJ (2011) Soil chemical methods. Australia, vol 3. CSIRO publishing, Victoria

Shamshuddin J, Elisa Azura A, Shazana MARS, Fauziah CI, Panhwar QA, Naher UA (2014) Chapter three—properties and management of acid sulfate soils in Southeast Asia for sustainable cultivation of rice, oil palm, and cocoa. In: Donald LS (ed) Advances in agronomy, Volume 124. Academic Press, pp 91–142

Shin EW, Rowell RM (2005) Cadmium ion sorption onto lignocellulosic biosorbent modified by sulfonation: the origin of sorption capacity improvement. Chemosphere 60:1054–1061

Simpson S, Fitzpatrick R, Shand P, Angel B, Spadaro D, Merry R, Thomas M (2008) Chapter 3: acid and metal mobilisation following rewetting of acid sulfate soils from the River Murray, South Australia: a rapid laboratory method. In: R. F, P. S (eds) Inland acid sulfate soil systems across Australia. vol CRC LEME Open File Report No. 249 (Thematic Volume). CRC LEME, Perth, pp 90–97

Simpson S, Vardanega CR, Jarolimek C, Jolley DF, Angel BM, Mosley LM (2014) Metal speciation and potential bioavailability changes during discharge and neutralisation of acidic drainage water. Chemosphere 103:172–180

Smernik RJ, Oades JM (2000) The use of spin counting for determining quantitation in solid state 13C NMR spectra of natural organic matter: 1. Model systems and the effects of paramagnetic impurities Geoderma 96:101–129

Trakal L, Bingöl D, Pohořelý M, Hruška M, Komárek M (2014) Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: engineering implications. Biores Technol 171:442–451

Uchimiya M, Chang S, Klasson KT (2011) Screening biochars for heavy metal retention in soil: role of oxygen functional groups. J Haz Mat 190:432–441

Uchimiya M, Bannon DI, Wartelle LH (2012) Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. J Agric Food Chem 60:1798–1809

Vahedian A, Aghdaei SA, Mahini S (2014) Acid sulphate soil interaction with groundwater: a remediation case study in east trinity. APCBEE Proceed 9:274–279

Westholm LJ, Repo E, Sillanpää M (2014) Filter materials for metal removal from mine drainage—a review. Environ Sci Pollut Res 21:9109–9128

Yang J-S, Kim Y-S, Park S-M, Baek K (2014) Removal of As (III) and As (V) using iron-rich sludge produced from coal mine drainage treatment plant. Environ Sci Pollut Res 21:10878–10889

Yuan C, Fitzpatrick R, Mosley LM, Marschner P (2015a) Sulfate reduction in sulfuric material after re-flooding: effectiveness of organic carbon addition and pH increase depends on soil properties. J Haz Mat 298:138–145

Yuan C, Mosley LM, Fitzpatrick R, Marschner P (2015b) 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 BA, Mclaughlin MJ, Smart MK (1996) The effect of acid digestion technique on the performance of nebulization systems used in inductively coupled plasma spectrometry. Comm Soil Sci Plant Anal 27:1331–1354

Zhang J, Lü F, Luo C, Shao L, He P (2014) Humification characterization of biochar and its potential as a composting amendment. J Environ Sci 26:390–397

Zhou Y-F, Haynes RJ (2010) Sorption of heavy metals by inorganic and organic components of solid wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents. Crit Rev Environ Sci Technol 40:909–977

Supplementary data

Figure. S1. Acidic (pH <4) iron rich drain water in Lower Murray Reclaimed Irrigation Area (LMRIA) near Murray Bridge, with reddish-yellow (orange) coloured precipitate of schwertmannite, which commonly forms in surface acid drainage waters with pH values between 3 and 4.5 (modified from Fitzpatrick et al. 2012).

Table S1. Properties of organic materials (from Dang *et al*. 2015)

	pH_w	C	N	C/N	ANC	CEC	Surface area	Acid extractable	
								Al	Fe
		(mg g^{-1})			(% $CaCO_3$)	cmol(+) kg^{-1}	(m^2 g^{-1})	(mg g^{-1})	
Wheat straw	5.5	427.3	4.3	100	0.03	15.6	0.8	0.2	0.2
Pea Straw	6.3	439.9	8.8	50	0.4	43.4	0.9	0.4	0.3
Compost	8.2	282.6	20.2	14	7.5	53.9	4.0	9.4	8.9
Poultry 450	7.7	475.0	16.8	28	4.8	44.9	1.2	2.1	2.9
Poultry 550	9.6	372.0	16.6	22	7.1	50.9	7.9	2.9	3.7
Wheat 450	8.4	529.2	23.4	23	2.5	54.8	1.1	1.7	2.6
Wheat 550	9.0	385.2	14.2	27	6.7	51.0	6.1	1.8	2.2
Mallee 550	7.5	551.6	5.6	98	3.8	39.3	2.5	3.8	19.8

Table S2. Carbon groups of organic materials based on NMR spectroscopy (from Dang *et al*. 2015)

	Alkyl	N-Alkyl/ Methoxyl	O-Alkyl	Di-O-Alkyl	Aryl	O-Aryl	Amide/ Carboxyl	Ketone
				% of organic C detected				
Wheat straw	4.8	4.3	61.3	14.1	7.4	3.2	4.1	0.7
Pea Straw	6.8	5.6	59.4	12.8	7.2	2.8	4.7	0.6
Compost	20.3	8.9	31.2	7.7	16.1	6.1	8.2	1.5
Poultry 450	9.2	5.5	26.6	8.2	34.3	9.9	4.1	2.2
Poultry 550	10.4	2.8	5.1	4.1	61.7	10.4	3.3	2.1
Wheat 450	15.3	5.2	14.9	5.2	39.2	10.9	6.2	3.1
Wheat 550	13.2	3.9	5.6	3.7	52.9	12.9	4.5	3.3
Mallee 550	10.3	3.1	4.5	3.6	57.5	13.6	4.3	3.2

Table S3. Leachate volume in six leaching events after addition of 45 ml LMRIA drainage water to different organic materials.

Leaching event	1	2	3	4	5	6
	leachate volume (ml core^{-1})					
Wheat straw	20	30	30	30	30	30
Pea Straw	20	30	25	30	25	25
Compost	30	35	30	30	35	30
Poultry 450	25	40	30	30	35	30
Poultry 550	30	40	30	30	35	30
Wheat 450	25	30	30	35	35	30
Wheat 550	20	35	30	30	35	30
Mallee 550	35	35	30	30	35	30

Table S4. Retention of protons, Al and Fe in percentage of added LMRIA drainage water for first 3 leaching events and cumulative retention

	% Proton retained			% Al retained			% Fe retained		
Leaching event	1	2	3	1	2	3	1	2	3
Wheat straw	100	99	90	87	86	58	78	74	46
Pea Straw	100	100	100	84	99	97	77	88	96
Compost	100	100	100	99	98	97	95	97	99
Poultry 450	100	100	100	98	97	98	98	100	100
Poultry 550	100	100	100	98	97	98	100	100	100
Wheat 450	100	100	100	98	98	98	99	99	100
Wheat 550	100	100	100	99	98	98	100	99	99
Mallee 550	90	99	99	81	84	86	92	96	98

Table S5. Cumulative proton, Fe and Al retention (positive values) or release (negative values) in different organic materials after leaching six times with RO water (n=1).

	Proton (µg g^{-1})*	Al (µg g^{-1})	Fe (µg g^{-1})
Wheat straw	0.2	-0.4	-19.8
Pea Straw	0.2	-1.4	-15.7
Compost	0.2	-2.6	-46.0
Poultry 450	0.2	-0.5	-14.7
Poultry 550	0.2	-2.9	-14.7
Wheat 450	0.2	-2.8	-28.5
Wheat 550	0.2	-2.0	-10.6
Mallee 550	0.2	-1.4	-14.1

* 1 µMol H^+ = 1 µg

Table S6. Al concentration (mg L⁻¹) of leachate after addition of LMRIA drainage water (21. 8 mg L⁻¹) to different organic materials over 6 leaching events. Within columns, values followed by different letters are significantly different (Duncan test, P≤ 0.05).

Leaching event	1	2	3	4	5	6
	Al concentration (mg L⁻¹)					
Wheat straw	6.3 ± 0.9 bc	4.6 ± 0.6 b	13.7 ± 0.6 c	14.2 ± 0.5 b	17.9 ± 1.1 b	15.4 ± 0.3 c
Pea Straw	7.8 ± 0.8 c	0.4 ± 0.1 a	1.1 ± 0.0 a	1.1 ± 0.1 a	0.3 ± 0.1 a	1.6 ± 0.5 ab
Compost	0.3 ± 0.2 a	0.6 ± 0.1 a	1.1 ± 0.0 a	1.2 ± 0.1 a	0.8 ± 0.2 a	1.1 ± 0.1 ab
Poultry 450	0.7 ± 0.2 a	0.8 ± 0.1 a	0.8 ± 0.1 a	1.1 ± 0.1 a	0.7 ± 0.1 a	1.0 ± 0.2 ab
Poultry 550	0.6 ± 0.1 a	0.7 ± 0.0 a	0.8 ± 0.2 a	0.8 ± 0.1 a	0.9 ± 0.1 a	1.1 ± 0.1 ab
Wheat 450	0.8 ± 0.4 a	0.5 ± 0.0 a	0.7 ± 0.2 a	0.8 ± 0.2 a	0.9 ± 0.1 a	0.9 ± 0.2 ab
Wheat 550	0.4 ± 0.1 a	0.6 ± 0.1 a	0.6 ± 0.1 a	0.9 ± 0.1 a	1.0 ± 0.1 a	0.9 ± 0.1 ab
Mallee 550	5.2 ± 1.0 b	4.6 ± 0.4 b	4.5 ± 0.3 b	0.6 ± 0.1 a	0.7 ± 0.1 a	0.7 ± 0.2 b

Table S7. Fe concentration (mg L^{-1}) of leachate after addition of LMRIA drainage water (47.9 mg L^{-1}) to different organic materials over 6 leaching events. Within columns, values followed by different letters are significantly different (Duncan test, $P \leq 0.05$).

Leaching event	1	2	3	4	5	6
	Fe concentration (mg L^{-1})					
Wheat straw	23.3 ± 2.5 d	18.8 ± 1.6 c	38.6 ± 1.9 c	53.5 ± 5.6 b	36.9 ± 3.6 c	33.3 ± 3.8 b
Pea Straw	24.3 ± 0.6 d	8.3 ± 0.6 b	3.6 ± 0.1 b	3.5 ± 0.1 a	16.6 ± 2.6 b	34.6 ± 5.3 b
Compost	3.7 ± 1.0 bc	1.9 ± 0.4 a	0.8 ± 0.2 a	0.5 ± 0.1 a	0.4 ± 0.1 a	0.9 ± 0.4 a
Poultry 450	1.5 ± 0.5 abc	0.2 ± 0.1 a	0.3 ± 0.1 a	0.5 ± 0.2 a	0.5 ± 0.1 a	0.4 ± 0.2 a
Poultry 550	0.4 ± 0.0 ab	0.2 ± 0.2 a	0.4 ± 0.1 a	0.3 ± 0.2 a	0.3 ± 0.1 a	0.3 ± 0.1 a
Wheat 450	0.5 ± 0.1 ab	0.9 ± 0.1 a	0.3 ± 0.1 a	0.4 ± 0.3 a	0.3 ± 0.0 a	0.2 ± 0.1 a
Wheat 550	0.1 ± 0.0 a	0.6 ± 0.1 a	0.4 ± 0.2 a	0.1 ± 0.0 a	0.2 ± 0.0 a	0.2 ± 0.1 a
Mallee 550	4.7 ± 1.2 c	2.2 ± 0.3 a	1.1 ± 0.3 a	0.9 ± 0.3 a	2.6 ± 0.3 a	1.9 ± 0.1 a

Table S8. Al and Fe concentrations (mg L^{-1}) of leachate after addition of RO water to different organic materials over 6 leaching events

Leaching event	1	2	3	4	5	6
	Al concentration (mg L^{-1})					
Wheat straw	0.02	0.01	nd	0.02	nd	nd
Pea Straw	0.16	0.02	0.01	0.01	0.02	nd
Compost	0.04	0.13	0.06	0.01	0.02	0.02
Poultry 450	nd	0.02	0.01	nd	0.01	0.01
Poultry 550	0.01	0.05	0.04	0.08	0.08	0.07
Wheat 450	0.05	0.09	0.08	0.04	0.02	0.05
Wheat 550	0.05	0.02	0.07	0.04	0.03	0.03
Mallee 550	0.03	0.01	0.05	0.02	0.02	0.03
	Fe concentration (mg L^{-1})					
Wheat straw	0.21	0.71	0.53	0.17	0.76	nd
Pea Straw	0.26	0.96	0.11	0.31	0.36	nd
Compost	0.46	0.92	0.42	3.17	0.05	0.20
Poultry 450	0.21	0.25	0.48	0.23	0.40	0.03
Poultry 550	0.42	0.04	0.01	0.63	0.46	0.06
Wheat 450	1.19	0.79	0.41	0.40	0.32	0.28
Wheat 550	0.15	0.09	0.27	0.10	0.31	0.30
Mallee 550	0.13	0.18	0.09	0.37	0.26	0.52

nd = not detectable

Table S9. Al concentration (mg L⁻¹) of leachate after addition of RO water to different organic materials previously treated with LMRIA water over 6 leaching events. Within columns, values followed by different letters are significantly different (Duncan test, P≤ 0.05).

Leaching event	1	2	3	4	5	6
			Al concentration (mg L⁻¹)			
Wheat straw	10.26 ± 0.58 c	0.33 ± 0.08 b	0.15 ± 0.05 b	0.11 ± 0.02 c	0.06 ± 0.02 a	0.08 ± 0.02 a
Pea Straw	4.21 ± 0.68 b	0.36 ± 0.05 b	0.23 ± 0.04 c	0.18 ± 0.02 d	0.14 ± 0.03 b	0.96 ± 0.60 b
Compost	nd a	0.01 ± 0.01 a	0.04 ± 0.1 a	0.07 ± 0.02 b	0.04 ± 0.02 a	0.07 ± 0.01 a
Poultry 450	nd a	nd a	nd a	nd a	0.02 ± 0.01 a	0.02 ± 0.00 a
Poultry 550	nd a	nd a	0.01 ± 0.01 a	nd a	nd a	0.03 ± 0.01 a
Wheat 450	nd a	nd a	0.04 ± 0.01 a	0.02 ± 0.00 a	0.03 ± 0.00 a	0.06 ± 0.02 a
Wheat 550	nd a	nd a	0.02 ± 0.00 a	nd a	nd a	0.07 ± 0.03 a
Mallee 550	nd a	nd a	0.02 ± 0.01 a	0.01 ± 0.00 a	0.03 ± 0.00 a	0.03 ± 0.00 a

nd = not detectable

Table S10. Fe concentration (mg L^{-1}) of leachate after addition of RO water to different organic materials previously treated with LMRIA water over 6 leaching events. Within columns, values followed by different letters are significantly different (Duncan test, $P \leq 0.05$).

Leaching event	1	2	3	4	5	6
	Fe concentration (mg L^{-1})					
Wheat straw	15.91 ± 1.37 c	6.91 ± 1.52 b	1.94 ± 0.32 c	1.80 ± 0.32 c	1.23 ± 0.17 c	1.23 ± 0.31 b
Pea Straw	3.32 ± 0.57 b	1.40 ± 0.18 a	1.02 ± 0.12 b	0.53 ± 0.12 b	0.42 ± 0.03 b	0.13 ± 0.01 a
Compost	0.19 ± 0.04 a	0.22 ± 0.06 a	0.19 ± 0.04 a	0.24 ± 0.04 ab	0.20 ± 0.10 a	0.16 ± 0.06 a
Poultry 450	0.24 ± 0.17 a	0.08 ± 0.05 a	0.02 ± 0.00 a	0.03 ± 0.00 a	0.06 ± 0.03 a	0.10 ± 0.04 a
Poultry 550	0.11 ± 0.03 a	0.04 ± 0.02 a	0.04 ± 0.01 a	nd a	0.02 ± 0.00 a	0.02 ± 0.01 a
Wheat 450	0.15 ± 0.05 a	0.08 ± 0.03 a	0.15 ± 0.03 a	0.13 ± 0.01 a	0.17 ± 0.05 a	0.16 ± 0.04 a
Wheat 550	0.10 ± 0.03 a	0.07 ± 0.04 a	0.01 ± 0.00 a	0.01 ± 0.00 a	0.01 ± 0.00 a	0.05 ± 0.01 a
Mallee 550	0.15 ± 0.04 a	0.04 ± 0.01 a	0.03 ± 0.02 a	0.02 ± 0.01 a	0.03 ± 0.01 a	0.10 ± 0.04 a

nd = not detectable

CHAPTER 5

ASSESSMENT OF BINDING OF PROTONS, Al AND Fe TO BIOCHAR AT DIFFERENT pH VALUES AND SOLUBLE METAL CONCENTRATIONS

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Contribution to the Paper	Performed experiment, analyses of leachate, data analysis and interpretation, wrote 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.		
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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.

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Assessment of the binding of protons, Al and Fe to biochar at different pH values and soluble metal concentrations

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Abstract

Previous studies have shown that biochar can retain large amounts of protons and metals in the drainage water from oxidised hypersulfidic material in acid sulfate soils and mine sites. Metal sorption can, however, be influenced by many factors, such as pH and metal composition. The aim of this study was to investigate proton, Al and Fe retention capacity of eucalypt biochar (at concentration of 1% w/v) at different pH and metal concentrations. The pH buffering capacity of the biochar in the absence of metals was tested by titration and showed that the biochar had a high proton binding capacity, (up to 0.035 mmol of H^+), whereas its capacity to retain hydroxide ions was limited. A batch experiment was carried out at pH 4 and pH 7 with 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} M of added Fe or Al. A large proportion of added Al and Fe precipitated prior to addition of the biochar except that Al remained highly soluble at pH 4. Thus the concentration of soluble Al and Fe only ranged from 10^{-6} to 6×10^{-3} – 10^{-6} M and 4.9×10^{-4} – 10^{-6} M, respectively. The biochar had a high retention capacity for Al and Fe, at high (> 1 mM) concentrations over 80% of soluble metals were retained. To study metal competition for

binding sites, both Al and Fe were added at different ratios, but increasing concentrations of one metal did not reduce retention of the other. The results confirm that biochar has a high metal binding capacity under both acidic and neutral conditions.

5.1 Introduction

Upon rewetting due to rainfall or flood irrigation, oxidised hypersulfidic material in acid sulfate soils (ASS) release large amounts of acidity and soluble metals (particularly Al and Fe) to ground and drainage water (Cook et al. 2000; Simpson et al. 2008). Some ASS have been drained for over hundred years and are still discharging acidity into streams or waterways (Sammut and Lines-Kelly 2000). White et al. (1997) predicted that ASS in floodplains containing rich iron sulfide materials may be continuously oxidised for thousands of years. It is estimated that one tonne of sulfide produces approximately one and a half tonnes of sulfuric acid (Sammut and Lines-Kelly 2000). ASS in floodplains of the Tweed river discharged proximately 110 kg of sulfuric acid per hectare in a few days of rain (Macdonald et al. 2007). Drainage water seeping from sulfuric material (pH <4) in ASS also contains high amounts of metals that are released due to the low pH. Concentrations of Al, As, Cd, Co, Cr, Cu, Ni, Pb, V and Zn in pore and drainage water have been shown to exceed Australian Water Quality Guidelines (ANZECC 2000) up to 100 fold (Hicks et al. 2003; Simpson et al. 2008).

We showed previously that organic materials such as plant residues, composts and biochar retained large amounts of protons and Al and Fe from ASS drainage water and released less than 1 % of that retained when subsequently leached with pure water (Dang et al. 2016a, b). Among the materials tested, retention was greater in biochars and composts than in plant residues. Biochar has received considerable interest as a low cost and sustainable biosorbent to remove metal contamination such as As, Cd, Pb, Zn from waste water or acid mine drainage water (Beesley et al. 2014; Elaigwu et al. 2014; Houben et al. 2013; Lu et al. 2012; Mohan et al. 2014; Trakal et al. 2014). Metal adsorption efficiency varied however, and is affected by factors such as functional groups, surface area and environmental conditions (Kołodyńska et al. 2012; Lu et al. 2012; Uchimiya et al. 2012). Metal retention on organic materials is strongly pH dependent (Bulut and Baysal 2006; Zhou and Haynes 2010). As pH increases, there is less competition for cation binding sites with protons (Zhou and Haynes 2010). Additionally, dissolved metals may precipitate as pH increases (e.g. Bigham and Nordstrom 2000).

Acidity of ASS drainage water varies over time (Creeper et al. 2015a; Creeper et al. 2015b; Mosley et al. 2014b; Santos and Eyre 2011; Simpson et al. 2014). It is well-known that pH plays an important role in metal speciation, solubility and complexation. For example, ferrous ions are often dominant in acidic reducing environments (Johnston et al. 2011; Mosley et al. 2014a). Under acidic oxidising conditions, ferric species in the form of iron oxyhydrosulfate (e.g. Schwertmannite, Jarosite minerals) are precipitated (Mosley et al. 2014a). The effect of pH on aluminium speciation is quite complex (Hicks et al. 2009; Krstic et al. 2012). At pH above 4, aluminium is present as mononuclear species $AlOH_2^+$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^+$, or forms soluble complexes with e.g., sulfate or fluoride (Krstic et al. 2012). Between pH 3 and 5 such as commonly found in areas impacted by oxidised hypersulfidic material in ASS, Al^{3+} species are dominant (Hicks et al. 2009). At pH 7, insoluble $Al(OH)_3$ or polynuclear aluminium species are formed (Krstic et al. 2012). pH is likely to influence metal binding to biochar through its effect on cation exchange capacity, surface complexation, metal solubilisation and precipitation. More systematic studies are needed to better understand proton, Al and Fe binding to biochar to optimise its use in semipermeable barriers for ASS drainage water.

The main objective of this study was to evaluate the proton and Al and Fe retention capacity of a eucalypt biochar that had high Al and Fe retention in our earlier studies (Dang et al. 2016). Proton sorption to biochar was tested firstly by acid-base titration in the absence of metals. A series of batch experiments was conducted at either pH 4 or 7 to investigate individual binding of Al and Fe to biochar. Further a competition experiment with Al and Fe was conducted at pH 7.

5.2 Materials and Methods

5.2.1 Experimental design

Mallee biochar used in this study was produced by pyrolysis of eucalyptus wood in a low-oxygen environment at 550 ˚C and ground and sieved to less than 0.5 mm. The biochar then was washed four times with reverse osmosis (RO) water at a 1:10 ratio (w/v) to remove salts until the conductivity of the leachate was low and stable. The washing protocol was amended from a pre-treatment method for measuring exchangeable cations (Rayment and Lysons 2011). The biochar was then dried at 40 ˚C.

For the experiment of proton binding to biochar, titration procedures were amended from the pH buffer capacity measurement protocol developed by Aitken and Moody (1994). The biochar (0.25 g) was added to 20 ml of 0.1 M KNO_3 background pH electrolyte solution. The solutions were titrated to pH 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 9 and 10 with standardized 0.04 M HNO_3/KOH. There were 3 replicates of each pH solution. Then, 0.1 M KNO_3 solution was added to reach a final volume of 25 ml. The suspensions were equilibrated for 24 h on an end-over shaker at room temperature followed by further addition of standardized 0.04 M HNO_3/KOH until the desired pH was reached. The volume of standardized 0.04 M HNO_3/KOH added was recorded.

For the experiments of single metal binding to biochar, Al and Fe adsorption isotherms were determined at constant pH 4 or pH 7 in a batch approach in accordance with Weber et al. (2006). Biochar (0.25 g) was added to a 50ml tube containing 20 ml of 0.1 M KNO_3 background pH electrolyte solution. Different amounts of $Al(NO_3)_3$ and $Fe(NO_3)_3$ stock solutions were added to the tubes to give metal concentrations of 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} M. The control was 0.25 g biochar in 25 ml of 0.1 M KNO_3 solution. The pH of the suspensions was adjusted to 4 or 7 by standardised 0.04 M HNO_3 or KOH. The suspensions were equilibrated for 24 hours on a horizontal shaker after which the pH was again adjusted to either 4 or 7. After another 24 hours on the shaker, the pH was again re-adjusted to the desired pH if necessary. Then 0.1 M KNO_3 solution was added to reach the final volume of 25 ml. Concentrations of soluble Fe and Al were measured as described below. There were 3 replicates per metal and pH combination.

For the Al/Fe competition experiment the pH was adjusted to 7 as described above. Iron concentrations (added as $Fe(NO_3)_3$) of 10 x 10^{-3}, 5 x 10^{-3}, and 1 x 10^{-3} M) were combined with Al concentrations (added as $Al(NO_3)_3$) of 10 x 10^{-3}, 5 x 10^{-3}, and 1 x 10^{-3} M). There were 3 replicates per combination.

In addition, to test the influence of metal precipitation on the concentration of soluble Al and Fe at pH 4 and 7, soluble metal concentrations in the absence of biochar were measured using the same metal concentrations and procedures described above.

5.2.2 Analyses

The pH of the biochar was measured in water at a 1:1 ratio (w/w). Total organic C and total N were measured by dry combustion using a LECO Trumac CN analyser.

Acid neutralising capacity (ANC) expressed as $CaCO_3$ equivalent was determined by the rapid titration method as described in Ahern et al. (2004). Briefly, 1 g of finely ground biochar was placed into a 250 ml flask with 50 ml of deionised water and 25 ml of standardised 0.1 M HCl. The suspensions were boiled on a hotplate for 2 min and then allowed to cool to room temperature. The unreacted acid in the flask was titrated with standardised 0.1 M NaOH to pH 7.

Surface area was analysed by a nitrogen gas adsorption method and calculated as described by Brunauer et al. (1938). The biochar was degassed overnight at a vacuum of 10^{-5} kPa prior to measuring nitrogen adsorption. Biochar was degassed at 200 °C. Nitrogen gas adsorption was measured at 77K using a Belsorp-max gas adsorption apparatus. Ultra high purity (>99.999 %) helium and nitrogen were used for dead space measurements and adsorption experiments, respectively.

Cation exchange capacity (CEC) was determined after Rayment and Lysons (2011). The biochar was extracted with 0.1 M NH_4Cl at a 1:30 w/w ratio in an end-over-end shaker for 1 h. The extracts were centrifuged at 3000 rpm for 10 min, the supernatant filtered through Whatman #42 filter paper. The solution was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Acid extractable Al and Fe in the biochar were determined after aqua regia (1:3 concentrated HNO_3:HCl) acid dissolution (Zarcinas et al. 1996). The extracts were filtered through Whatman #42 filter paper and analysed for Al and Fe by ICP-OES.

Chemical groups of biochar were measured by solid-sate ^{13}C nuclear magnetic resonance (NMR) spectroscopy as described in McBeath et al. (2014).

The amount of standardised HNO_3 and KOH added to the solution containing 1% (w/v) of eucalypt biochar were expressed as mmol of acid and base to obtain the titration curve.

The solutions from the precipitation experiment were filtered onto 0.025 µm nitrocellulose membrane filters, the soluble Al and Fe in the filtrates were then measured by ICP-MS. The soluble metal concentrations were expressed as µg per tube.

The solutions of single metal binding or metal binding competition experiments were centrifuged for 30 minutes at 4000 rpm. The supernatants were then removed and filtered through 0.025 µm nitrocellulose membrane filters before measuring metal concentrations by

ICP-MS. Binding of Al and Fe to biochar (µg metal/g biochar) was calculated as follows: [added soluble metal concentration per tube – (concentration of metal in filtrate (µg/l) * volume (l) of filtrate solution per tube)]/ amount of biochar (g) per tube.

Data was analysed by one way ANOVA. Differences between means were compared by Duncan analysis ($P \leq 0.05$) using GenStat 15th edition (GenStat 2013).

5.3 Results

The properties of mallee biochar produced at 550 °C was presented in Table 1. The biochar had pH 7.5, high organic C concentration, low total N concentration (551 mg g^{-1}) therefore high C/N ratio. The ANC (3.8 % $CaCO_3$), CEC (39 cmolc kg^{-1}) and surface area of (2.5 m^2 g^{-1}) contents of the biochar were moderate, whilst the extractable metal concentrations, Al and Fe, were high. The dominant functional groups were Aryl and O-Aryl C.

The biochar had a high proton binding capacity whereas its capacity to bind OH^- was limited (Figure 1).

At pH 4, all of the added Al remained soluble up to an Al concentration of 0.1 mM. At higher concentrations, about two-thirds of the added Al remained soluble (Table 2). At pH 7 on the other hand, only about one third of the added Al was soluble up to Al concentrations of 0.1 mM. At higher concentrations, less than 10% of the added Al was soluble. Less than 1% of added Fe remained soluble at pH 4 and pH 7 except at the lowest addition rate (Table 3). Soluble Fe concentrations were lower at pH 7 than pH 4.

Because of release of native Al from the biochar, no binding could be detected at the lowest Al addition rate (3 µg Al/g biochar) (Table 4). At pH 4 and 7 and the three highest Al addition rates (270–17210 µg Al/g biochar), more than 90% of added soluble Al was bound to the biochar.

Table 1: Properties of mallee biochar 550 °C

pH_w		7.5
C	mg g^{-1}	551.6
N	mg g^{-1}	5.6
C/N		98
ANC	% $CaCO_3$	3.8
CEC	cmol(+) kg^{-1}	39.3
Surface area	m^2 g^{-1}	2.5
Acid extractable Al	mg g^{-1}	3.8
Acid extractable Fe	mg g^{-1}	19.8
Chemical functional groups	*% C detected*	
Alkyl		10.3
N-Alkyl/Methoxyl		3.1
O-Alkyl		4.5
Di-O-Alkyl		3.6
Aryl		57.5
O-Aryl		13.6
Amide/Carboxyl		4.3
Ketone		3.2

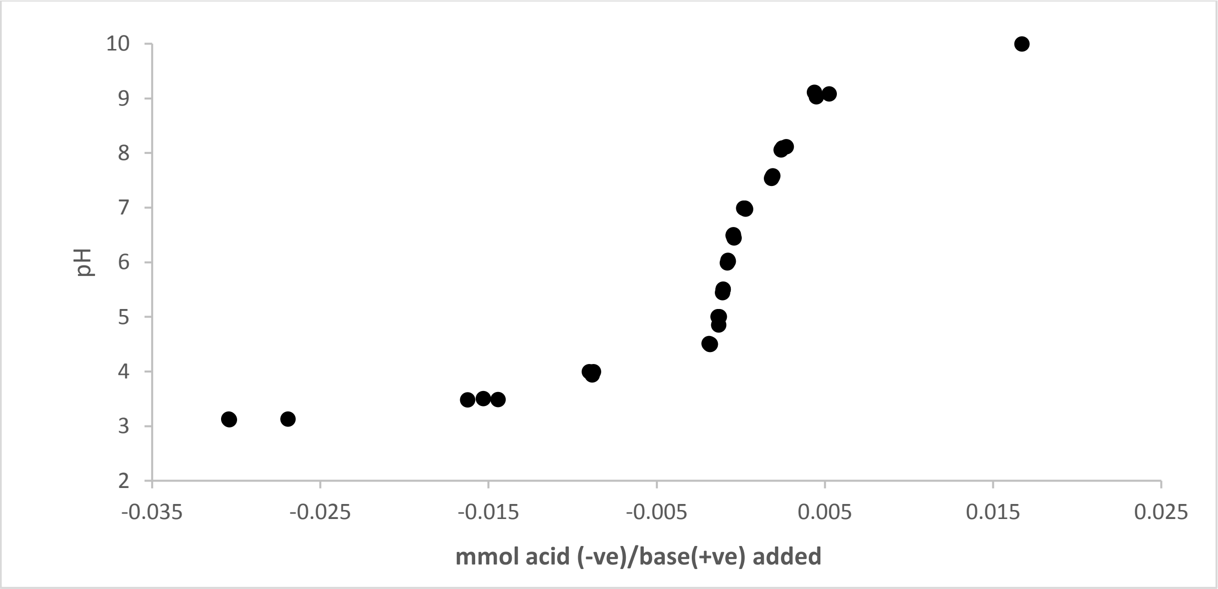

Figure 1: The effect of addition of acidic (-ve)/base (+ve) on 1% (w/v) mallee biochar

Table 2: Soluble Al in solution (no biochar present) at different concentrations after adjusted to pH 4 and pH 7

Added Al		Amount of soluble Al after adjusted pH (µg per tube)	
(mM)	(µg per tube)	pH 4	pH 7
0.001	0.7	0.7	0.7
0.01	6.7	6.7	2.3
0.1	67.5	67.5	15.9
1	674.5	562.6	21.3
5	3372.5	2177.8	29.8
10	6745.0	4302.5	36.7

Table 3: Soluble Fe in solution (no biochar present) at different concentrations after adjusted to pH 4 and pH 7

Added Fe		Amount of soluble Fe after adjusted pH (µg per tube)	
(mM)	(µg per tube)	pH 4	pH 7
0.001	1.4	1.3	1.3
0.01	14.0	2.1	1.6
0.1	139.6	9.1	6.7
1	1396.3	43.5	47.7
5	6981.3	229.0	339.9
10	13962.5	685.2	415.8

At pH 7 and lower Al addition rates (3–27 µg Al/g biochar), between 60 and 75% of added soluble Al was bound to the biochar. At pH 4, 50% of the 27 µg Al/g biochar was bound, whereas no binding was measured in the 3 µg Al/g biochar treatment.

No Fe binding was detected at pH 4 at the three lower addition rates due to release of native Fe (Table 5). At higher Fe addition rates, 83-91% of added soluble Fe was bound to the biochar.

At pH 7 and 5−6 µg Fe/g biochar addition, about 70% of added soluble Fe was bound to biochar. At higher Fe addition rates (27−1663 µg Fe/g biochar), 87-99% of added soluble Fe was bound.

Table 4: Al binding to biochar at pH 4 and pH 7

pH 4			pH 7		
Soluble added (µg/g)	binding (µg/g)	binding (%)	Soluble added (µg/g)	binding (µg/g)	binding (%)
0	-20	0	0	-1	0
3	-9	0	3	2	60.5
27	14	51.0	9	7	74.7
270	243	90.1	64	61	95.9
2250	2096	93.1	85	80	93.9
17210	16990	98.7	147	140	95.4

Table 5: Fe binding to biochar at pH 4 and pH 7

pH 4			pH 7		
Soluble added (µg/g)	binding (µg/g)	binding (%)	Soluble added (µg/g)	binding (µg/g)	binding (%)
0	-18	0	0	-1	0
5	-13	0	5	4	74.6
8	-13	0	6	4	64.2
37	31	83.7	27	25	93.3
174	153	88.0	191	189	98.8
2741	2489	90.8	1663	1438	86.5

Table 6: Al and Fe binding to biochar at pH 7 in mixtures of different metal concentrations

Soluble Added		Al binding		Fe binding	
Fe (µg/g)	Al (µg/g)	Al (µg/g)	%	Fe (µg/g)	%
191	85	82.5	89.5	190.3	99.7
	119	113.1	96.7	188.3	98.7
	147	140.7	99.5	188.4	98.7
1360	85	83.2	97.8	1358.2	99.9
	119	113.4	95.3	1356.2	99.8
	147	120.6	97.5	1355.5	99.7

1663	85	84.9	95.7	1662.6	100
	119	115.4	94.8	1660.7	99.9
	147	131.5	96.8	1658.8	99.7

In the Fe/Al competition experiment, 99% of the added soluble Fe was bound to the biochar (Table 6). Iron reduced the percentage of bound Al only at the lowest Al addition rate (85 µg soluble Al g^{-1}) combined with the lowest Fe addition rate (191 µg soluble Fe g^{-1}). At the higher Al addition rates more than 95% of added soluble Al was bound to the biochar.

5.4 Discussion

This study showed that the mallee biochar had a high proton, Al and Fe binding capacity. Biochar can contain humification products (fulvic acid- and humic acid-like materials), which contribute to their proton binding capacity (Milne et al. 1995; Zhang et al. 2014). The mallee biochar had 4% $CaCO_3$ (Table 1). Therefore protons may also be neutralised by carbonates (Mosley et al. 2015; Qian and Chen 2013b). Humic acids are important components of decomposed organic matter which have high proton affinity and metal binding (Milne et al. 1995). Non-Ideal Competitive Adsorption (NICA) model as well as NICA-Donnan or NICA-EPN models can predict proton and metal binding to humic acids (Milne et al. 1995; Montenegro et al. 2014). However, the data of this study could not be expressed with these models suggesting that several properties contributed to proton and metal binding.

Speciation of Al and Fe is complex and controlled by pH (Hicks et al. 2009; Krstic et al. 2012). In this study a large proportion of added Al and Fe precipitated prior to adding biochar, even at pH 4, possibly due to hydrolysing and oxidizing conditions during shaking of the suspension. However, at low pH (pH 4) and highest addition rate (10 mM) concentrations of remaining soluble Al (172 mg $L^{-}1$) and Fe (28 mg L^{-1}) rate were higher than in drainage water from oxidised ASS (Al: 2 mg L^{-1}; Fe: 28 mg L^{-1}) (Mosley et al. 2014a). As 90% or more of the dissolved Al and Fe were bound, even at high concentrations, the maximum binding capacity of biochar is greater than 17,000 µg Al and 2700 µg Fe per g of biochar. The lack of competition between Fe and Al when both metals were added may also be due to their being sufficient binding sites for both metals at the concentrations used.

We had expected binding to be lower at pH 4 than at pH 7 because of the lack of negatively charged binding sites at pH 4 (Bulut and Baysal 2006; Zhou and Haynes 2010). However, the reverse was true; more Al and Fe were bound at pH 4 than at pH 7 which can be explained by the higher soluble metal concentration at the lower pH. The release of native Al and Fe from the biochar resulted in no apparent binding at low Al and Fe addition rates. Al and Fe may be bound to biochar via oxygen-containing (carboxylic -COO− and phenolic R-O−) functional groups (Cao et al. 2009; Uchimiya et al. 2011), surface adsorption and co-precipitation of Al with silicate particles (Qian and Chen 2013a, b; Qian et al. 2013). Further, carbonates may have induced precipitation within the biochar. This suggests that biochar has a potential to be used for metal removal in drainage channels of sulfuric ASS which is in agreement with our previous studies (Dang et al. 2016a, b). Pilot scale field trials are required to confirm this.

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References

Ahern, C.R., McElnea, A.E., Sullivan, L.A., 2004. Acid neutralising capacity, carbonate and alkali cation methods. In: C.R. Ahern, A.E. McElnea, L.A. Sullivan (Eds.), Acid Sulfate Soils Laboratory Methods Guidelines. Department of Natural Resources, Nines and Energy, Indooroopilly, Queensland, Australia.

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

ANZECC, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.

Beesley, L., Inneh, O.S., Norton, G.J., Moreno-Jimenez, E., Pardo, T., Clemente, R., Dawson, J.J.C., 2014. Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. Environmental Pollution 186(0), 195-202.

Bigham, J., Nordstrom, D.K., 2000. Iron and aluminum hydroxysulfates from acid sulfate waters. Reviews in mineralogy and geochemistry 40(1), 351-403.

Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society 60(2), 309-319.

Bulut, Y., Baysal, Z., 2006. Removal of Pb(II) from wastewater using wheat bran, . Journal of Environment Management 78, 107-113.

Cao, X., Ma, L., Gao, B., Harris, W., 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environmental Science & Technology 43(9), 3285-3291.

Cook, F.J., Hicks, W., Gardner, E.A., Carlin, G.D., Froggatt, D.W., 2000. Export of Acidity in Drainage Water from Acid Sulphate Soils. Marine Pollution Bulletin 41(7–12), 319-326.

Creeper, N.L., Hicks, W.S., Shand, P., Fitzpatrick, R.W., 2015a. Geochemical processes following freshwater reflooding of acidified inland acid sulfate soils: An in situ mesocosm experiment. Chemical Geology 411, 200-214.

Creeper, N.L., Shand, P., Hicks, W., Fitzpatrick, R.W., 2015b. Porewater Geochemistry of Inland Acid Sulfate Soils with Sulfuric Horizons Following Postdrought Reflooding with Freshwater. Journal of environmental quality 44(3).

Dang, T., Mosley, L.M., Fitzpatrick, R., Marschner, P., 2016a. Addition of organic material to sulfuric soil can reduce leaching of protons, iron and aluminium. Geoderma 271, 63-70.

Dang, T., Mosley, L.M., Fitzpatrick, R., Marschner, P., 2016b. Organic materials retain high proportion of protons, iron and aluminium from acid sulphate soil drainage water with little subsequent release. Environ Sci Pollut Res 23, 23582-23592.

Elaigwu, S.E., Rocher, V., Kyriakou, G., Greenway, G.M., 2014. Removal of Pb2+ and Cd2+ from aqueous solution using chars from pyrolysis and microwave-assisted hydrothermal carbonization of Prosopis africana shell. Journal of Industrial and Engineering Chemistry (0).

Hicks, W., Fitzpatrick, R., Bowman, G., 2003. Managing coatal acid sulfate soils: The East Trinity example. In: I.C. Roach (Ed.), Advances in Regolith. CRC LEME Regional, Bentley, W.A, pp. 174-177.

Hicks, W.S., Bowman, G.M., Fitzpatrick, R.W., 2009. Effect of season and landscape position on the aluminium geochemistry of tropical acid sulfate soil leachate. Soil Research 47(2), 137-153.

Houben, D., Evrard, L., Sonnet, P., 2013. Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. Chemosphere 92(11), 1450-1457.

Johnston, S.G., Keene, A.F., Bush, R.T., Burton, E.D., Sullivan, L.A., Isaacson, L., McElnea, A.E., Ahern, C.R., Smith, C.D., Powell, B., 2011. Iron geochemical zonation in a tidally inundated acid sulfate soil wetland. Chemical Geology 280(3–4), 257-270.

Kołodyńska, D., Wnętrzak, R., Leahy, J.J., Hayes, M.H.B., Kwapiński, W., Hubicki, Z., 2012. Kinetic and adsorptive characterization of biochar in metal ions removal. Chemical Engineering Journal 197(0), 295-305.

Krstic, D., Djalovic, I., Nikezic, D., Bjelic, D., 2012. Aluminium in Acid Soils: Chemistry, Toxicity and Impact on Maize Plants. In: A. Aladjadjiyan (Ed.), Plants, Food Production - Approaches, Challenges and Tasks. InTech, Rijeka, Croatia.

Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R., 2012. Relative distribution of Pb2+ sorption mechanisms by sludge-derived biochar. Water Research 46(3), 854-862.

Macdonald, B.C.T., White, I., Åström, M.E., Keene, A.F., Melville, M.D., Reynolds, J.K., 2007. Discharge of weathering products from acid sulfate soils after a rainfall event, Tweed River, eastern Australia. Applied Geochemistry 22(12), 2695-2705.

McBeath, A.V., Smernik, R.J., Krull, E.S., Lehmann, J., 2014. The influence of feedstock and production temperature on biochar carbon chemistry: A solid-state 13C NMR study. Biomass and Bioenergy 60(0), 121-129.

Milne, C.J., Kinniburgh, D.G., de Wit, J.C.M., van Riemsdijk, W.H., Koopal, L.K., 1995. Analysis of proton binding by a peat humic acid using a simple electrostatic model. Geochimica et Cosmochimica Acta 59(6), 1101-1112.

Mohan, D., Sarswat, A., Ok, Y.S., Pittman Jr, C.U., 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. Bioresource Technology 160, 191-202.

Montenegro, A.C., Orsetti, S., Molina, F.V., 2014. Modelling proton and metal binding to humic substances with the NICA–EPN model. Environmental Chemistry 11(3), 318-332.

Mosley, L., Fitzpatrick, R., Palmer, D., Leyden, E., Shand, P., 2014a. Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. Science of The Total Environment 485–486(0), 281-291.

Mosley, L., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., Baker, A., W. Fitzpatrick, R., 2014b. Acidification of floodplains due to river level decline during drought. Journal of Contaminant Hydrology 161(0), 10-23.

Mosley, L., Willson, P., Hamilton, B., Butler, G., Seaman, R., 2015. The capacity of biochar made from common reeds to neutralise pH and remove dissolved metals in acid drainage. Environ Sci Pollut Res, 1-10.

Qian, L., Chen, B., 2013a. Dual Role of Biochars as Adsorbents for Aluminum: The Effects of Oxygen-Containing Organic Components and the Scattering of Silicate Particles. Environmental Science & Technology 47(15), 8759-8768.

Qian, L., Chen, B., 2013b. Interactions of Aluminum with Biochars and Oxidized Biochars: Implications for the Biochar Aging Process. Journal of Agricultural and Food Chemistry 62(2), 373-380.

Qian, L., Chen, B., Hu, D., 2013. Effective alleviation of aluminum phytotoxicity by manure-derived biochar. Environmental science & technology 47(6), 2737-2745.

Rayment, G.E., Lysons, D.J., 2011. Soil chemical methods-Australia, Vol 3. CSIRO publishing, Victoria.

Sammut, J., Lines-Kelly, R., 2000. An introduction to acid sulphate soils. Natural Heritage Trust, Sydney.

Santos, I.R., Eyre, B.D., 2011. Radon tracing of groundwater discharge into an Australian estuary surrounded by coastal acid sulphate soils. Journal of Hydrology 396(3–4), 246-257.

Simpson, S., Fitzpatrick, R., Shand, P., Angel, B., Spadaro, D., Merry, R., Thomas, M., 2008. Chapter 3: Acid and Metal Mobilisation Following Rewetting of Acid Sulfate Soils from the River Murray, South Australia: A Rapid Laboratory Method. In: F. R., S. P. (Eds.), Inland acid sulfate soil systems across Australia. CRC LEME, Perth, pp. 90-97.

Simpson, S., Vardanega, C.R., Jarolimek, C., Jolley, D.F., Angel, B.M., Mosley, L.M., 2014. Metal speciation and potential bioavailability changes during discharge and neutralisation of acidic drainage water. Chemosphere 103(0), 172-180.

Trakal, L., Bingöl, D., Pohořelý, M., Hruška, M., Komárek, M., 2014. Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: Engineering implications. Bioresource Technology 171(0), 442-451.

Uchimiya, M., Bannon, D.I., Wartelle, L.H., 2012. Retention of Heavy Metals by Carboxyl Functional Groups of Biochars in Small Arms Range Soil. Journal of Agricultural and Food Chemistry 60(7), 1798-1809.

Uchimiya, M., Chang, S., Klasson, K.T., 2011. Screening biochars for heavy metal retention in soil: Role of oxygen functional groups. Journal of Hazardous Materials 190(1–3), 432-441.

Weber, T., Allard, T., Tipping, E., Benedetti, M.F., 2006. Modeling Iron Binding to Organic Matter†. Environmental Science & Technology 40(24), 7488-7493.

White, I., Melville, M.D., Wilson, B.P., Sammut, J., 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. Wetlands Ecology and Management 5(1), 55-72.

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. Communications in Soil Science and Plant Analysis 27 (5-8), 1331-1354.

Zhang, J., Lü, F., Luo, C., Shao, L., He, P., 2014. Humification characterization of biochar and its potential as a composting amendment. Journal of Environmental Sciences 26(2), 390-397.

Zhou, Y.-F., Haynes, R.J., 2010. Sorption of Heavy Metals by Inorganic and Organic Components of Solid Wastes: Significance to Use of Wastes as Low-Cost Adsorbents and Immobilizing Agents. Critical Reviews in Environmental Science and Technology 40(11), 909-977.

CHAPTER 6

CONCLUSIONS AND FUTURE RESEARCH

1 Conclusions

Oxidized hypersulfidic material in ASS can release large amounts of protons and metals into surrounding environments (e.g. Fältmarsch et al. 2008). Remediation, for example by liming, may be ineffective and/or too costly. To minimize the impact of oxidized ASS on the environment, the released protons and metals have to be retained *in situ* and/or within drainage channels. Organic materials have been shown to bind protons and metals (Pedra et al. 2008; Rees et al. 2014) and have the added benefit of promoting sulfate reduction in flooded ASS (Jayalath et al. 2015; Yuan et al. 2015). However, the composition of organic materials can vary, which may influence their ability to bind protons and metals. In this project, the remediation potential of a range of organic materials was tested using two approaches: (i) addition to soil and (ii) as a permeable reactive barrier for drainage water.

In the experiment reported on in Chapter 2 the *in situ* remediation potential was tested by amending a sulfuric sandy soil with organic materials either placed as a layer under the soil or mixed within the soil. The soil was leached several times to induce release of protons and metals. In the first leachate, 67, 71 and 90% of the total leached protons, Fe and Al respectively were released in the unamended soil. Amendment with organic materials reduced proton and metal leaching by 50-90%, particularly in the first leaching event. We had assumed that organic materials placed as a layer under the soil would be more effective in retaining protons and metals than mixing them in the soil. However, amendment forms differed little in retention. In the field, placing organic materials as a layer under the soil would be too expensive and disruptive whereas mixing them in the soil is a more practical approach. However, mixing could also increase oxidation and thus promote acidification. The type of organic material had a strong effect on retention because eucalypt biochar and wheat biochar had the highest cumulative retention, wheat straw and compost the lowest. Differences in retention were related to chemical composition as proton retention positively correlated with C concentration of organic material, while Fe and Al retention was positively correlated with percentage of Aryl and O-Aryl groups and negatively correlated with percentage of O-Alkyl and Di-O-Alkyl groups.

Sulfuric ASS release large amounts of protons and metals into drainage water which can be a hazard for the surrounding areas. Therefore, proton and metal retention in drainage water from sulfuric materials in ASS by addition of organic materials was investigated in Chapters 3 and 4. In the study in Chapter 3, synthetic drainage water based on the long term average of acid drainage in the LMRIA was used. In the long term average, metal concentrations were lower than those that may occur after a period with little rain and thus leaching. To study retention capacity at high concentrations, drainage water collected in autumn was used in the experiment in Chapter 4, which also investigated if retained metals and protons could be released when leached with RO water. The experiment with the synthetic drainage water (Chapter 3) confirmed the high retention capacity for protons, Fe and Al of eucalypt biochar and wheat biochar. The correlations between retention of protons, Fe and Al with organic material properties was also similar as in the experiment with the sulfuric sandy soil. Additionally, the organic materials were leached with RO water to determine release of native Fe and Al which also influenced apparent Fe and Al retention when synthetic drainage water was applied.

In the experiment described in Chapter 4, the organic materials were leached six times with LMRIA drainage water followed by 6 leaching events with RO water to assess if retained protons, Fe and Al could be released. Compost and biochars increased the leachate pH by up to 4.5 units and had a high retention capacity for metals whereas pH increase and metal retention were low with wheat straw. The metal and proton release during subsequent leaching with RO water was very small, cumulatively less than 1% of retained metals and protons. These results suggest that permeable reactive barriers comprising compost and biochars could be used in ASS drainage channels and would retain protons and metals even if leached with water. This is particularly important after removal of the organic materials from the barriers, which may be necessary when the organic materials are strongly decomposed or have reached their sorption capacity. The results indicate that the risk of proton and metal leaching upon exposure to rain (e.g. if used organic materials were subsequently spread on or mixed into soils) is likely to be low.

The capacity to retain metals by biochar may be limited which would in turn influence how effective biochar can be used as barrier in ASS drainage channels. In Chapter 5, eucalypt biochar produced at 550 ˚C was tested for its capacity to retain protons Al and Fe. In the absence of metals, biochar had a high proton retention capacity whereas its capacity to retain hydroxide ions was limited. The single metal binding experiment showed that the biochar had a high retention capacity for Al and Fe, at high concentrations > 80% of soluble metals was retained. In the competition experiment, increasing concentrations of one metal did not reduce retention of the other. Metal retention mechanisms could include binding to organic matter functional groups and/or surface precipitation.

The experiments showed that organic materials, particularly biochars have great potential to be used in ASS drainage water to minimize the impact of oxidized ASS on the surrounding environment. However, further pilot-scale field research is needed before they can be used on a large scale in the field.

2 Future research

2.1. Sorption capacity of other metals to organic materials

In this thesis, the experiments focused on the binding of Al and Fe to organic materials because these metals are dominant in ASS drainage water and are a risk for aquatic environments (Hicks et al. 2009; Johnston et al. 2010), including in our study area (Mosley et al. 2014a). However, oxidised hypersulfidic material in ASS may also release other toxic soluble metals. For example, Zn concentrations in soil, discharge and receiving water at East Trinity were up to 40 fold higher than water quality guidelines (WQG). Sulfuric material in ASS can also release high concentrations of dissolved metals such as As, Cd, Co, Cr, Cu, Ni, Pb and Zn, which exceeded WQG up to 100 fold (Simpson et al. 2008). Therefore, further studies are needed to assess the capacity of organic materials to retain other dissolved metals. Similar to this study, retention could be studied with synthetic drainage water as well as drainage water from the field.

2.2 Binding mechanisms

The organic materials used in the experiments had high proton and metal retention. The retention was strongly correlated with organic material properties and certain chemical functional groups. However, an understanding of the mechanisms underlying retention is limited. Adsorption to organic materials may involve exchange of metals cations or anions with surface ligands, covalent bonds, ion exchange or chelation with surface functional groups (Zhou and Haynes 2010). Retention could also be due to surface precipitation as oxides, hydroxides, sulfides (Apak 2002). Metal retention mechanisms could be studied by examination of functional groups of the treated organic materials with FTIR spectroscopy, while scanning electron microscopy (SEM) coupled with electron dispersive X-ray analyser (EDX) analyses could be used for the precipitated phases (Trakal et al. 2014).

2.3 Flow rate

In the experiments in this thesis, the flow rate of the drainage water was quite low and only a small amount of drainage water was applied at a given time. In the field, flow rates may be quite variable and reach high rates after strong rainfall. Flow rate will influence the time of contact between metals and protons in the drainage water and the organic materials and thus retention. Experiments could be conducted to study metal and proton retention at flow rates in the range found in the field.

2.4 Using organic materials as permeable reactive barriers for drainage water treatment in the field

Eucalypt biochar and wheat biochar produced at 550 ˚C and 450 ˚C respectively, had high proton and metal retention capacity of which very little was released by leaching with water. These organic materials could therefore by used in permeable reactive barriers (PRB). The barriers are passive, in situ water treatment constructions that are considered to be an economical remediation approach, with little maintenance and suitable for small areas (Waite et al. 2003). For acid mine drainage environments permeable reactive barriers are commonly filled with limestones or crushed recycle concrete. However precipitation of iron and aluminium oxides may limit their reactivity and longevity (Regmi et al. 2009; Waite et al. 2003). Maximum metal retention and longevity of barriers with organic materials would also have to be studied before they can be used on a larger scale.

References

Apak, R., 2002. Adsorption of heavy metal ions on soil surfaces and similar substances. In: A.T. Hubbard (Ed.), Encyclopedia of surface and colloid science, Marcel Dekker, New York, pp. 385-417.

Hicks, W.S., Bowman, G.M., Fitzpatrick, R.W., 2009. Effect of season and landscape position on the aluminium geochemistry of tropical acid sulfate soil leachate. Soil Research 47(2), 137-153.

Jayalath, N., Mosley, L.M., Fitzpatrick, R.W., Marschner, P., 2015. Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions. Journal of Soils and Sediments (in press).

Johnston, S.G., Burton, E.D., Bush, R.T., Keene, A.F., Sullivan, L.A., Smith, D., McElnea, A.E., Ahern, C.R., Powell, B., 2010. Abundance and fractionation of Al, Fe and trace metals following tidal inundation of a tropical acid sulfate soil. Applied Geochemistry 25(3), 323-335.

Pedra, F., Plaza, C., García-Gil, J.C., Polo, A., 2008. Effects of municipal waste compost and sewage sludge on proton binding behavior of humic acids from Portuguese sandy and clay loam soils. Bioresource Technology 99(7), 2141-2147.

Rees, F., Simonnot, M.O., Morel, J.L., 2014. Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. European Journal of Soil Science 65(1), 149-161.

Regmi, G., Indraratna, B., Nghiem, L.D., 2009. Long-term Performance of a Permeable Reactive Barrier in Acid Sulphate Soil Terrain. Water, Air, & Soil Pollution: Focus 9(5), 409-419.

Simpson, S., Fitzpatrick, R., Shand, P., Angel, B., Spadaro, D., Merry, R., Thomas, M., 2008. Chapter 3: Acid and Metal Mobilisation Following Rewetting of Acid Sulfate Soils from the River Murray, South Australia: A Rapid Laboratory Method. In: F. R., S. P. (Eds.), Inland acid sulfate soil systems across Australia. CRC LEME, Perth, pp. 90-97.

Trakal, L., Bingöl, D., Pohořelý, M., Hruška, M., Komárek, M., 2014. Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: Engineering implications. Bioresource Technology 171(0), 442-451.

Waite, T.D., Desmier, R., Melville, M., Macdonald, B., 2003. Chapter 3 - Preliminary Investigation into the Suitability of Permeable Reactive Barriers for the Treatment of Acid Sulfate Soils Discharge. In: L.N. David, J.M. Stan, C.F. Christopher, S.J.M.C.C.F. James A. DavisA2 - David L. Naftz, A.D. James (Eds.), Handbook of Groundwater Remediation using Permeable Reactive Barriers. Academic Press, San Diego, pp. 67-104.

Yuan, C., Fitzpatrick, R., Mosley, L.M., Marschner, P., 2015. Sulfate reduction in sulfuric material after re-flooding: Effectiveness of organic carbon addition and pH increase depends on soil properties. Journal of Hazardous Materials 298(0), 138-145.

Zhou, Y.-F., Haynes, R.J., 2010. Sorption of Heavy Metals by Inorganic and Organic Components of Solid Wastes: Significance to Use of Wastes as Low-Cost Adsorbents and Immobilizing Agents. Critical Reviews in Environmental Science and Technology 40(11), 909-977.