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POSITIVE AND NEGATIVE EFFECTS OF ADDITION
OF ORGANIC CARBON AND NITROGEN FOR MANAGEMENT
OF SULFURIC SOIL MATERIAL ACIDITY UNDER GENERAL
SOIL USE CONDITIONS

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Abstract. This paper reports the findings of two studies conducted to investigate the effects on pH, Eh and sulfate content of sulfuric soil material of acid sulfate soil following the addition of organic carbon and nitrogen. The first study compared the responses to simple carbon sources (glucose, sodium acetate and molasses) with complex organic matter in the form of chopped *Phragmites*. The second experiment considered the effect of nitrogen by testing organic matter with varying nitrogen content. The results of the first study showed that the changes in Eh and sulfate contents induced by the treatments mirrored the changes in pH, the highest change being only 5.6 units induced by sodium acetate. These results showed that organic carbon alone was ineffective in treating sulfuric soil material acidity, and that nitrogen was needed. Lucerne hay which had the highest nitrogen content produced the largest increase in pH by 4.2 units and the changes of pea straw and wheat straw was 3.2 units. It was proposed that the alkalising effect of the treatments was mediated by anaerobic microbial metabolism which required sources of nitrogen as well as organic carbon. The changes in soil redox conditions by -150 mV measured indicated that sulfur-reducing bacteria induced the changes in Eh, which caused pH to increase and sulfate content to decrease in comparison with nitrate-reducing bacteria. The findings of these studies have implications for management of sulfuric soil material acidity.

Keywords: acidity management, organic carbon, organic nitrogen, organic matter

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INTRODUCTION

Acid sulfate soils (ASS) are naturally occurring soils or sediments formed under reducing and water-logged (anaerobic) conditions (e.g. Pons 1973, Simpson and Pedini 1985) that either contain sulfuric acid (H_2SO_4) or have the potential to form it, in an amount that can have serious negative impacts on the health of human and the environment (Buschmann *et al.* 2008, Ljung *et al.* 2009). The global estimation of ASS is 17–24 million ha of which 6.5 million occur in Asia, 4.5 million in Africa, 3 million in Australia, 3 million in Latin America, 235 000 in Finland, and 100 000 in North America (Simpson and Pedini 1985), respectively. When ASS materials are below the natural water table, no threat is posed unless the water table is lowered as a result of changes in land use or hydrological regimes, leading to the exposure and oxidation of sulfidic soil materials containing sulfidic minerals (e.g. pyrite, FeS_2). Oxidation of the sulfidic minerals results in production of sulfuric acid (Baldwin and Fraser 2009). Release of the sulfuric acid produced in turn leads to solubilisation of soil matrices in which potentially toxic constituents (metals and metalloids) are held (Fitzpatrick *et al.* 2008). Production of sulfuric acid, mobilisation and accumulation of toxic soil constituents, e.g. Fe and Al, coupled with deoxygenation, and production of monosulfidic black ooze are the major causes of the negative impacts of ASS on the environment (Michael 2013).

Unless the negative impacts are successfully managed, soil characteristics, water quality and biodiversity, human health, commercial and recreational fisheries, engineered and community infrastructure, scenic amenity and tourism, and agricultural productivity are seriously affected (e.g. Michael 2013). The seriousness of the impacts has made management of ASS materials an important issue, and several management strategies have been proposed, focusing on two key principles (e.g. Michael *et al.* 2015, Michael and Reid 2018). The first principle is to neutralise the actual acidity and to manage the leachate of the by-products of oxidation. The second is to curtail oxidation of sulfidic soil materials and prevent exposure (Baldwin and Fraser 2009). Among the strategies proposed and tested, application of an alkaline material, e.g. agricultural lime to neutralise sulfuric soil materials and minimise disturbance of the sulfidic soil materials are the most preferred management strategies (Ljung *et al.* 2009).

An alternative strategy that has received equal attention in managing acidified environments caused by acidic soil materials other than ASS (e.g. acid mine drainage) with varying success is the application of organic matter, preferably containing high carbon to create alkalinity using microbial processes. This strategy is beginning to be established well as the findings of more studies are beginning to become available (e.g. Michael *et al.* 2015, 2016, 2017, Jayalath *et al.* 2016, Dang *et al.* 2016). The principle is to create an anoxic environment by microbial depletion of oxygen in order to stimulate the activity of sulfur reducing microbes

to generate alkalinity to neutralise the soil (Frömmichen *et al.* 2004). This strategy has the potential to both ameliorate sulfuric soil material and to prevent the oxidation of sulfidic soil material by utilizing the biogenic alkalinity produced during microbial decomposition of organic matter (Michael *et al.* 2015).

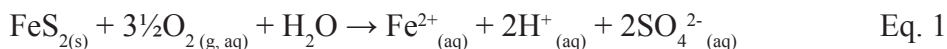
In comparison to lime, which is expensive and may not be readily accessible in poor economies (Powell and Martens 2005), organic matter is relatively cheap and readily available (Michael *et al.* 2015). This strategy, however, is currently not widely used in ASS management as well as in other land use systems, in part due to contradictory results on its efficacy and only recently studies (e.g. Michael *et al.* 2015, Jayalath *et al.* 2016) have begun to make important results available. The purpose of the current study was to examine the effects of organic nitrogen and carbon in organic matter on sulfuric soil material pH, Eh and sulfate content. This is the short-term (3 months) study of the long-term (6 months) one reported in Michael *et al.* (2016). The intention was to establish organic matter use as an alternative strategy to manage sulfuric soil material acidity under general soil use and management conditions, e.g. in farms.

MATERIALS AND METHODS

Soil

Sulfidic soil material collected from the Finnis River (35°24'28.28"S; 138°49'54.37"E) in South Australia under less than 1 m of water was oxidised to be used as sulfuric soil material. The average pH in water (pHw 1:5 w/w) of the sulfidic soil material was 6.7, with a field capacity of 49%. The average organic matter content estimated by weight loss-on-ignition (Schulte and Hopkins 1996) was 10.6%. More detailed geochemistry and metal concentrations of the collection site are given in Fitzpatrick *et al.* (2008), the sites being identified as AA26.3 and FIN 26. Soil classification using the Australian ASS Identification Key (Fitzpatrick *et al.* 2008) and Soil Taxonomy (Soil Survey Staff 2014) are given in Michael *et al.* (2016).

The soil chemical reaction that results in production of sulfuric soil material acidity (generation of H⁺) and sulfate (e.g. Michael 2020, 2013), two of the three soil factors measured is shown as Equation (eq.) 1. Soil redox is the resultant of microbial processes (Bossio and Scow 1995) and its measurements indicate the condition of the soil: an oxidised soil of low pH having positive Eh values (e.g. 800 mV) and a reduced soil of high pH having negative Eh values (e.g. – 300 mV) (e.g. Rabenhorst *et al.* 2009).



Nitrogen and carbon sources

Organic carbon was supplied either as simple compounds (glucose, sodium acetate and unsulfured molasses), or in complex form in ground (<0.5 mm) plant material. The carbon content of the plant materials can be approximated to be similar to grass (leaf) clippings from Rynk *et al.* (1992) as indicated in various studies. The nitrogen (N) content of the plant material determined by ICP-OES was: *Phragmites* shoots (3.7% N), lucerne hay (3.2% N), pea straw (1.2% N) and wheat straw (0.8% N) (Michael *et al.* 2015).

Experiments and moisture regimes

Two incubation studies were conducted under aerobic soil conditions. The aerobic soil conditions were maintained by keeping the soils at 75% field capacity on weight basis by adding water throughout the study. In the first study, effects of addition of different simple carbon sources on sulfuric soil material pH (initial pH_w 3.7), Eh and sulfate content were investigated. Glucose and sodium acetate were incorporated at the rate of 4 g per 50 g soil, and molasses and *Phragmites* mulch at 5 g per 50 g soil. In the second study, 1 g lucerne hay, pea straw and wheat straw were mixed in 80 g soil. The control treatments had no additions. All the treatments were set in 70 ml Falcon tubes, replicated 4 times ($n = 4$) and incubated under greenhouse conditions in a complete randomized design (CRD) manner for 3 months. The data presented are from only three replicates. The fourth replicate was frozen and spared in case losses of samples were encountered during measurement and analysis.

Measurements

All the measurements and sampling for analysis were made within the 0–20 mm, 20–40 mm and 40–60 mm profiles. These profiles are henceforth presented as 20 mm, 40 mm and 60 mm for the ease of presentation of the data. Redox was measured using a single Ag/AgCl reference and platinum (Pt) electrode combination using an automated data logger. To measure the Eh, a handheld electric drill, with a drill bit head the size of the Pt electrode, was used to make holes through the tubes with care taken to avoid disturbing the soil. The Pt electrode was inserted in the holes and reference electrode inserted into the soil from the surface (top open end of the Falcon tubes). This was allowed to equilibrate for 10 mins and then Eh was measured at 1 min intervals for the next 10 mins and averaged (Rabenhorst *et al.* 2009). These values were corrected for the reference offset to be relative to the potential of a standard hydrogen electrode by adding 200 mV as per Fiedler *et al.* (2007). The stability and accuracy of the electrodes were maintained according to these workers. The pH was measured using 2 g

soil (1:5 water) as per Ahern *et al.* (2004) with a pre-calibrated Orion pH meter (720SA model). To explain the changes in Eh and pH clearly, an Eh-pH diagram is shown in Fig. 1.

Sulfate was extracted according to the method of Hoefl *et al.* (1973) for soluble soil sulfate. Replicate samples (0.5 g each) were placed in tubes with 1.5 ml of an extraction solution (0.2 g CaH_2PO_4 , 12 g glacial acetic acid and 88.5 g deionized water). After 30 min, soil was sedimented by centrifugation for 5 min, and duplicate aliquots from the three replicates were transferred into 4 mL cuvettes and diluted with 1.5 ml of the extraction solution. The samples were mixed with 0.7 ml of 0.5 M HCl, and 0.7 ml of 0.1 M barium chloride-polyethylene glycol reagent and mixed again. After 10 min, the samples were mixed again and the absorbance read at 600 nm using a spectrophotometer. The readings were compared with a standard solution of 0–2 mM Na_2SO_4 . The initial sulfate content of the sulfuric soil material prior to use ranged from between 21–32 $\mu\text{mol g}^{-1}$ soil. The detection limit based on an absorbance reading of 0.1 of this method is 0.6 $\mu\text{mol g}^{-1}$ soil.

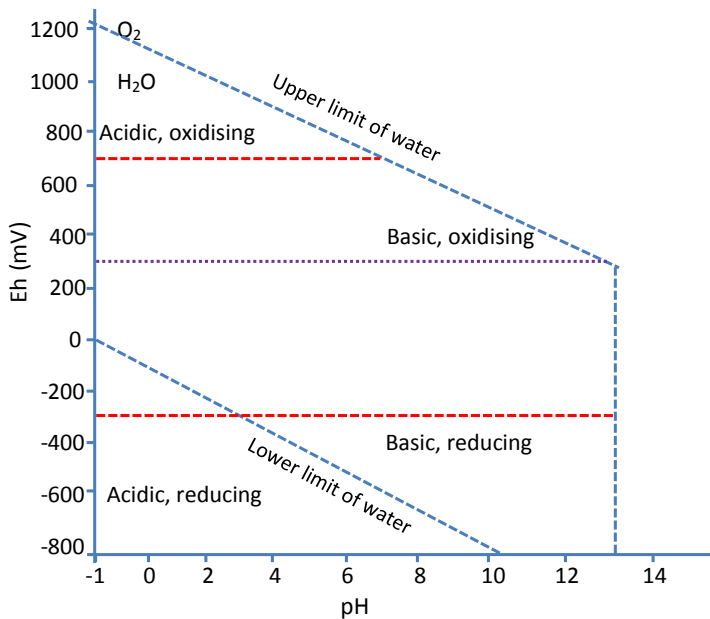


Fig. 1. The Eh-pH range in surface environments showing four redox classes: (i) acidic-oxidising, (ii) basic-oxidising, (iii) acidic-reducing and, (iv) basic-reducing, with slight modifications after Krauskopf (1967), Delaune and Reddy (2005) and Poch *et al.* (2009). The lower and upper Eh limits are shown by the red dotted lines. The purple dotted line shows the break between an aerobic and anaerobic condition (Fiedler *et al.* 2007)

Statistical analyses

The Eh values obtained over a 10 min period were averaged and a treatment average obtained by taking the mean of the three replicates. Similarly, treatment average pH was obtained by taking the mean of the three replicates. To compare the treatment means, significant differences ($p < 0.05$) between treatments means of a profile were determined by two-way ANOVA using statistical software JMPIN, AS Institute Inc., SAS Campus Drive, Cary, NC, USA 27513. If an interaction between the treatments and profile depths was found, one-way ANOVA with all combination was performed using Tukey's HSD (honest significant difference) and pairwise comparisons. In all the data tables and figures, the values are mean \pm standard error of three replicate ($n = 3$) measurements. The broken line is the initial pH of 3.8 units and the sulfate content of the sulfuric soil material used ranged from between 16–32 $\mu\text{mol g}^{-1}$ soil. An asterisk indicates a significant difference ($p \leq 0.05$) between the controls and the treatments at the same depth.

RESULTS AND DISCUSSION

Roles of organic carbon in pH

Assessment of soil pH under various land use conditions, particularly involving establishment of vegetation or growing of crops is important because it affects nutrient availability and mobility (Michael and Reid 2018). The pH measurement is in fact the negative log of the hydrogen ion (H^+) concentration and is the basis of determining whether a soil is acidic ($\text{pH} < 4$) or alkaline ($\text{pH} > 4$) so a choice of vegetation is made. The process that generates sulfuric acidity (protons) in ASS was shown in Eqn. 1. Typical of sulfuric soil material, the initial pH was 3.7, a highly acidic soil in which vegetation including crops cannot be established under general soil use systems, e.g. in a farmland. When this soil was incubated for three months without amendment, the pH increased to 5.6 within the 20 mm depth and 6.3 at the 60 mm depth, respectively. The probable cause of these increases in pH occurred as a result of the aerobic microbial oxidation of the residual organic matter content (10.6%) that acted on it (Lambers *et al.* 2009) and reduced the soil to Eh to near 0 mV. We have asserted this phenomenon in similar studies using soils collected from the same site (e.g. Michael *et al.* 2016, 2017). Primavesi (1984) made a similar assertion that strongly acidic or highly alkaline soils affect the growing conditions of microbes (Hinsinger *et al.* 2009), resulting in low levels of biological oxidation of organic matter.

The changes in pH measured in the first study are shown in Fig. 2. The pH of the soil to which glucose was added did not change much from the initial pH,

while molasses increased the pH by approximately 1 unit. Glucose is a simple sugar and readily converted to CO_2 by soil microbes (Essington 2004) and could be CO_2 that lowered the pH. Rukshana *et al.* (2010) observed that addition of glucose in an acidic soil of pH 4.3 units and incubated over 60 days had no effect on pH even if the cumulative respiration was four-fold. The increase in pH caused by addition of molasses compared to the glucose suggests the changes could just be physiochemical than microbial in nature (Rukshana *et al.* 2010). In contrast, the soil mixed with *Phragmites* mulch had increased to near 7 units throughout, increasing the pH by 3.3 units (Fig. 2). The effects of all the amendments on pH were near or closer to the results of the study lasting 6 months reported in Michael *et al.* (2016), a strong indication that the changes measured are long-term.

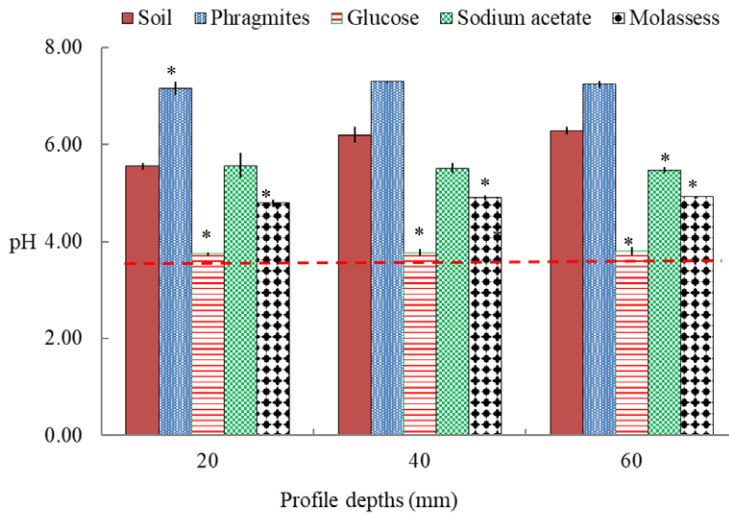


Fig. 2. Changes in pH of a sulfuric soil material with and without added organic carbon under aerobic conditions

Roles of organic carbon in reduction oxidation potential

The pH changes corresponded to the Eh changes as per Fig. 1. For example, when the Eh of the glucose amended soil at the 20 mm depth was 376 mV (Fig. 3), pH was 3.7 units (Fig. 2), an indication of an acidic, oxidising soil condition. The control soil Eh remained close to 0 mV down the depth (Fig. 3). In the amended soils, sodium acetate or glucose remained in the range of 240–412 mV, while the molasses treatment declined from 247 mV in the 20 mm to 77 mV at the 60 mm depth. The greatest change was seen in the soil mixed with *Phragmites* mulch, where the Eh declined to between -153 mV at the 10 mm depth to -172 mV at the 60 mm depth (Fig. 3), respectively. The overall changes in the

control soil ranged from between 15 mV at the 20 mm depth and -29 mV at the 60 mm depth (Fig. 3), an indication of basic, reducing soil conditions ($\text{pH} > 6$). This reducing soil condition was caused by microbial oxidation of the native organic matter content (10.6%) which was observed to be more efficient under aerobic soil conditions (e.g. Michael *et al.* 2016, 2016, Jayalath *et al.* 2016).

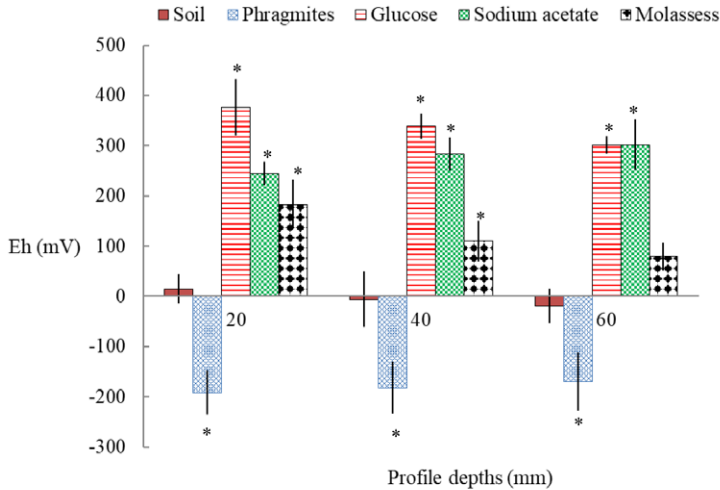


Fig. 3. Changes in Eh of a sulfuric soil material with and without added organic carbon under aerobic conditions

Microbial-mediated reduction of soil leads to Eh values as low as -300 mV (Fielder *et al.* 2007). When the different carbon sources were added, varying effects on Eh were measured and in almost all cases, rendered the soil to basic, oxidising conditions. Under general soil use and management condition, soil of $\text{Eh} > 200$ mV, iron has high phosphorus sorption capacity, and at reduced redox, iron is reduced and phosphorus is released, making the nutrient available to plants. Under highly oxidised conditions, a sulfuric soil material is a potent source of acidic minerals and metalloids, e.g. Fe^{2+} , Al^{3+} and H^+ , therefore, these results strongly indicated that application of sole carbon sources for management of soil acidity is not an option, compared to organic compounds such as molasses that would contain other resources (Pyakurel *et al.* 2009) in addition to carbon for microbial metabolism.

Roles of organic carbon in sulfate content

Redox, as discussed above, regulates biogeochemical processes in a surface environment. A soil gets reduced when its inorganic oxidants like oxygen, nitrate, nitrite, manganese (Mn^{4+}), iron (Fe^{3+}), sulfate and CO_2 are reduced.

Nitrate, manganese and iron are used as electron acceptors in microbial metabolism within an Eh range of 300–100 mV (Delaune and Reddy 2005). For sulfate reduction, the soil needs to be significantly reduced to -100 – -150 mV (e.g. Michael *et al.* 2015, 2016, Delaune and Reddy 2005). Compared to this, addition of the carbon sources did not reduce the soil to the Eh range conducive for sulfur-reducing bacteria (SRB) to function, as shown by the sulfate content measured (Fig. 4). For simple carbon sources without nitrogen, the sulfate content remained constant, whereas quite large reductions were observed following addition of plant material, more so at the depth.

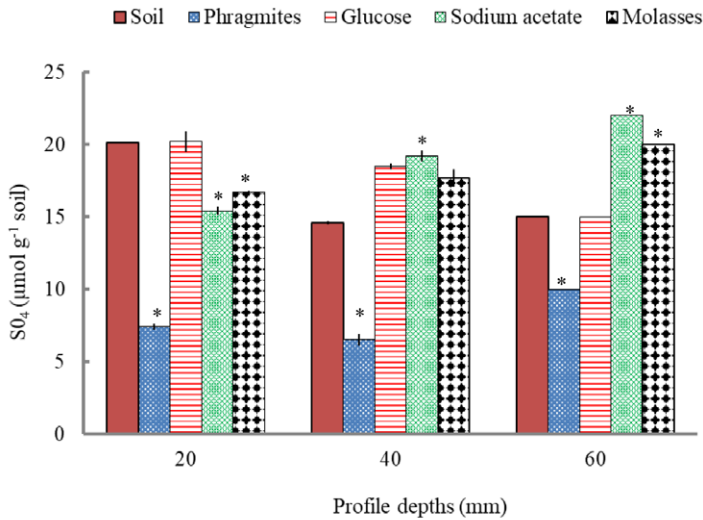


Fig. 4. Changes in sulfate content of a sulfuric soil material with and without added organic carbon under aerobic conditions

It is a common knowledge that increases in pH in soils high in sulfate content are mediated by microbial activity. It was expected that aerobic microbial activity would increase oxygen demand and cause the Eh of the soil to decrease to a level at which nitrate and SRB would be advantaged. The lack of effect of glucose on pH (Fig. 2) and the relatively small reduction in Eh (Fig. 3) was therefore surprising, resulting in no effect on sulfate content (Fig. 4). Sodium acetate and molasses did produce moderate changes in pH but less than those of the control soil, except at the surface (Fig. 2). These have resulted in very small changes in the sulfate contents, consistently agreeing to the changes in pH and Eh measured. The overall result of the changes in sulfate content except in the plant material amended soil occurred as a result of physiochemical processes induced that microbial. It is probable that a microbial ecology other than SRB was established by the carbon sources that were present in the soil.

Roles of organic nitrogen in pH

The second study employed smaller additions of plant matter, but included a range of nitrogen contents. As in the first study, the pH of the control soil was largely unchanged at the surface but increased by approximately 1.4 units at 80 mm depth (Fig. 5). All treatments with added plant material showed significant pH increases over the control with only slight variations. Lucerne hay, which had the highest nitrogen content (3.2%, similar to that of *Phragmites*, 3.7%) was much more effective at increasing pH than pea straw (1.2% N) and wheat straw (0.8% N) (Fig. 2). pH of the control soil changed at the surface by 1.6 units and 2.5 units compared to the initial pH (3.8 units). Compared to the changes in the control soil, changes induced by lucerne hay > pea straw > wheat straw from within the surface was well as at depth (Fig. 4).

Under aerobic soil conditions (75% water holding capacity), the pH of the control soil was expected to remain closer to the initial pH of 3.7 units. The control soil pH, however, increased by 1.7 at the 20 mm profile and much higher at depth by 2.3 units. These changes are consistent with the first study and the mechanism responsible seems to be the same, as discussed in other studies (e.g. Michael *et al.* 2015, 2016). In an incubation study lasting 12 months under anoxic conditions, Kölbl *et al.* (2018) reported an unamended sulfuric soil of pH 3.5 units losing 10% of native organic carbon content, raising the pH to >5.0 units. This supports the changes in pH of the control measured in the first (Fig. 2) and the second study (Fig. 5) that the increase in pH was caused by microbial depletion of the organic carbon content of the native organic matter. In oxidised sulfuric soil material, a large amount of protons and metals are expected to be present, which are potential sources of threat to the environment as leachates and high concentration of protons of extremely low pH (pH < 4). The increase in pH in the control soil indicates the protons were consumed as microbial processes acted on the native carbon supply. Reduction in proton concentration further paved the conditions favourable for other microbial ecology, e.g. the facultative ones, to establish and function.

When organic matter was added in such sulfuric soil material, changes in pH measured were as high as 8 units, quite similar to the results shown in Fig. 5 and was concluded that aerobic bacteria depleted oxygen during decomposition and creates reducing soil conditions (Michael *et al.* 2015). This microenvironment of reduced condition resulted in consumption of protons and reduction of the oxidised forms of the acidic metals (Michael *et al.* 2016). Organic matter can further form organo-complexes, increasing the pH to as high as 6.5 and decreasing the metal concentration (Opala *et al.* 2012), a strong indication of the probable cause of the increase in pH measured (Fig. 5). The ameliorative effects have implications even when climate is projected to change, affecting local conditions, particularly temperature increases and soil moisture loss, resulting in exposure and oxidation of sulfidic soil material, offsetting acidity that would be generated.

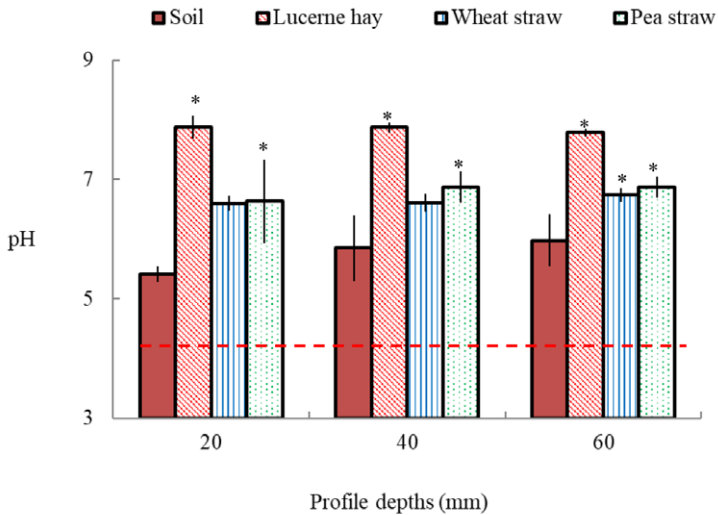


Fig. 5. Changes in pH of a sulfuric soil material with and without added organic matter with varying nitrogen content under aerobic conditions

Roles of organic nitrogen in reduction oxidation potential

Soil redox in all treatments essentially mirrored the changes in pH (Fig. 6). The control soil remained relatively aerobic at the surface but declined to -29 mV at 60 mm depth. Lucerne hay reduced the Eh to -200 mV. Pea straw and wheat straw also produced large shifts in Eh, but not as great as lucerne hay, although much greater than the control treatment, especially near the surface (Fig. 6). Wheat straw, the plant matter containing the lowest nitrogen content (0.8%), had the least effect on the Eh. Comparatively, the tendency for the soil to reduce increased as depth increased, with nearly all soils at the 60 mm depth being highly reduced to Eh conducive for SRB to function, reducing the sulfate content (Fig. 7).

When organic matter is added in soil, it influences Eh and its bioavailability acts as an electron reservoir for reduction reactions (Chadwick and Chorover 2001). Depending on the type, decomposable organic matter makes oxidation processes to consume oxygen, leading to formation of organic compounds with reducing properties (Lovley *et al.* 1998). These organic compounds with reducing properties in turn establish microbial ecology capable of inducing changes in Eh. The type of microbial ecology established following organic matter addition is largely dependent on the resources; nitrogen, phosphorus, potassium as well as carbon that serve as substrates for microbial biomass. Presumably, the energy requirement of the microbes is met by utilisation of the components

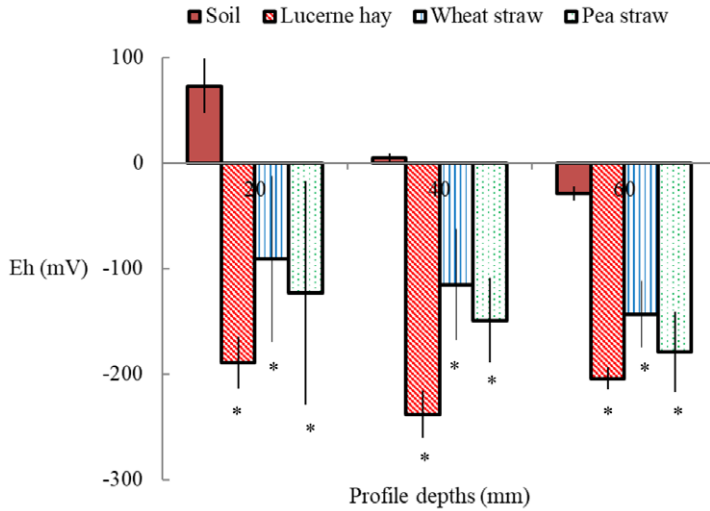


Fig. 6. Changes in Eh of a sulfuric soil material with and without added organic matter with varying nitrogen content under aerobic conditions

of hemicellulose or some products of the decomposition processes (e.g. Halsall and Gibson 1985, Ladha *et al.* 1986). The nitrogen content, e.g. from the lucerne hay, is utilized by the microorganisms for their own biomass, whereas a major component of it is released to the soil (microbial nitrogen) as plant nutrition (e.g. Irisarri *et al.* 2001, Michael *et al.* 2016). Organic matter decomposition and ultimate effect on Eh is influenced by the C:N ratio, with plant material containing more carbon, e.g. wheat straw having lesser reducing effect (Fig. 6). Plant materials such as lucerne hay and pea straw have low C:N ratio, therefore, decompose quickly, resulting in increased microbial ecology and much effective reduction processes (e.g. Delgado *et al.* 1996). Although most crop plants prefer an Eh range of 300–500 mV (Husson 2013), addition of organic matter of low C:N seems to be important to significantly reduce the soil and increase the pH (Figs. 5 and 6).

Roles of organic nitrogen in sulfate content

By far the greatest change in sulfate content was seen with additions of plant material containing a range of potential nutrients for soil microbes, in addition to carbon (Fig. 7). The magnitude of the changes in both pH and Eh were correlated with the nitrogen content, which may suggest the involvement of SRB, but equally this may simply reflect a nitrogen requirement for growth of bacterial biomass in general, including nitrate reducing bacteria. Overall, the results seem to suggest that addition of organic carbon alone is not an effec-

tive strategy for ameliorating sulfuric soil material acidity. The control soil sulfate content in all the profiles was within the initial range, indicating not much change (Fig. 7). Among the additions, sulfate was completely depleted in the 20 mm depth lucerne hay was added. In the lower profiles, from 40–60 mm depths, addition of pea straw, plant material containing similar amount of nitrogen, significantly reduced the sulfate content (Fig. 7). This may have been enhanced by CO₂ reduction as the soil got more reducing, lowering Eh to near -150 mV (Fig. 6) and even much lower (Fielder *et al.* 2007).

Sulfate reducing bacteria operate under highly reduced soil conditions with Eh ranging from between 0–150 mV and addition of different plant matter induced the soils to fall within this range. This probably indicates that the changes in pH measured resulted from the reduction in sulfate by SRB. Reduction of nitrate by facultative bacteria occurs in moderately reduced soil of 300 mV, compared to reduction of CO₂ in highly reduced soil of -200 – -300 mV by anaerobic bacteria (Fielder *et al.* 2007). The overall changes in Eh induced by addition of plant material (Fig. 6) ranged from between -100 mV at the 20 mm depth to -200 mV at the 60 mm depth. These point out that the changes in soil chemistry measured were not induced by nitrate reducing bacteria but SRB followed by anaerobic bacteria which reduced CO₂ when the soil got highly reduced.

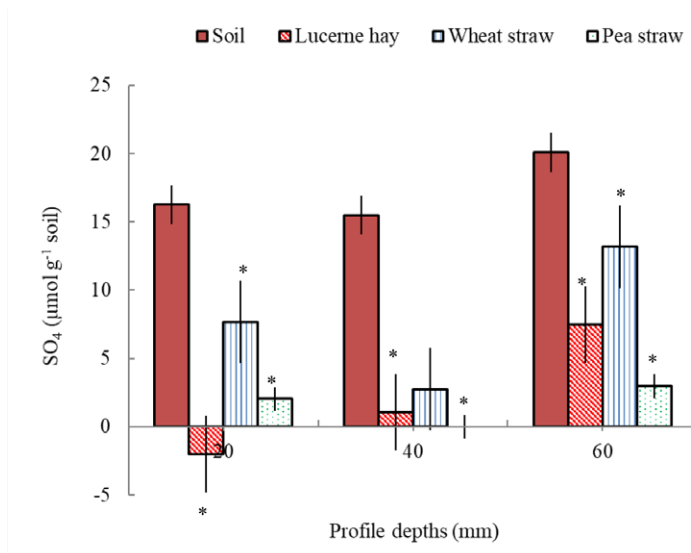


Fig. 7. Changes in sulfate content of a sulfuric soil material with and without added organic matter with varying nitrogen content under aerobic conditions

In an oxidised sulfuric soil material, reduction of oxygen and nitrate is expected at 0 mV and fair amounts of bio-reducible Mn⁴⁺ and Fe³⁺ under aerobic soil redox conditions, moderately reduced to anaerobic, reduced conditions, Eh

ranging from between 300–100 mV (Delaune and Reddy 2005). These could mean that aerobic bacteria initially depleted the available oxygen whilst acting on the plant material which was then taken over by facultative microbes that reduced manganese and iron, significantly reducing the soil to redox condition sufficient for SRB to function and act on sulfate. In addition to amelioration of sulfuric soil material acidity (reduction of proton concentration), Fe^{3+} and Al^{3+} leachates are major environmental and ecological concerns (Jayalath *et al.* 2016), and their reductions following addition of plant materials is a bonus for bioremediation. As widely established, decomposition of the plant materials is expected to add other benefits for general soil use and management (e.g. revegetation, which would have been otherwise impossible because of severe acidity).

In all, most plants grow within a close Eh range of 400–450 mV and at a pH range of 6.5–7 units (Husson 2013). These Eh-pH ranges were only evident in the first study following addition of sodium acetate and molasses (see Figs. 3 and 4) than the second, demonstrating that addition of these carbon sources are important for general sulfuric soil material use. Some possible risks at these Eh-pH ranges are that nutrient (P, Mn, Fe) deficiency and heavy metal (e.g. Pb, Cd) toxicity may develop and limitation at alkaline pH (>8) under reduced soil conditions (Eh < -200 mV) (Husson 2013). Mineralisation of important minerals is even high under highly oxidised soils. In the second study, organic matter addition resulted in Eh (< -150 mV) unfavourable for the plant rhizosphere, however, conducive to cultivation of adaptive ones, e.g. rice (*Oryza* sp.). Plants adapted to reduced soil conditions modify the rhizosphere Eh by supplying oxygen through modified anatomical structures (Michael and Reid 2018), thereby oxygenating the roots. The results of the second study showed plants with such adaptive mechanisms may be used in revegetation of the sulfuric soil material acidity scalded land. Limitation in organic matter in soil leads to low poise and rise in Eh, so organic matter addition and vegetation establishment have benefits in sulfuric soil material acidity management.

CONCLUSIONS

Under general soil use and management conditions, highly oxidised sulfuric soil material of extremely low pH (<4) and high sulfate content is an environmental as well as land use concern, and is often managed by addition of an alkaline material, such as an agricultural lime. The affordability of lime, however, continues to be an issue world-wide, especially in the low-income countries. The findings of this study showed that addition of plant materials capable of establishing microbial ecology would highly reduce the oxidised sulfuric soil material, lower the sulfate contents and increase the pH. Complex plant matter and simple organic compounds containing both carbon and nitrogen were more

effective in inducing the changes in soil chemistry measured. Since plant matter are readily available and relatively cheap compared to fine agricultural lime, the findings of these studies have implications for management of sulfuric soil material acidity.

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