

## **The Roles of Surface Soil Carbon and Nitrogen in Regulating the Surface Soil pH and Redox Potential of Sulfidic Soil Materials of Acid Sulfate Soils**

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### **ABSTRACT**

Acid sulfate soils (ASS) have been described as the “nastiest” soils on earth because of their harmful impacts on various soil and environmental systems. ASS pose no problems unless the sulfidic soil materials are disturbed or exposed and the sulfides are oxidized, leading to production of sulfuric soil materials and generation of sulfuric acidity. In sulfidic soil, unless there is disturbance or exposure in the deep soil, only the surface soil seems to be frequently exposed and disturbed, leading to oxidation as a result of oxygen penetration. We have reported recently the importance of soil carbon and nitrogen in amelioration of ASS but the roles on the surface soil was not clearly established. In this study, the roles of surface soil carbon and nitrogen in regulating the surface soil redox potential (Eh) and pH of sulfidic soil material of ASS was investigated following the addition of different sources of soil carbon and nitrogen. The results showed the mechanisms involved in curtailing of sulfidic soil material oxidation and acidification were dependent on the type of metabolic substrates and the microbial ecology the resources were capable of establishing. Addition of a single nutrient source, e.g. glucose, capable of engaging a few soil microbes, was ineffective in preventing sulfidic soil oxidation, whereas addition of complex metabolic substrates, e.g. organic matter, as a source of multiple resources for microbial metabolism effectively reduced the Eh and highly increased the pH, even under aerobic soil conditions.

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## INTRODUCTION

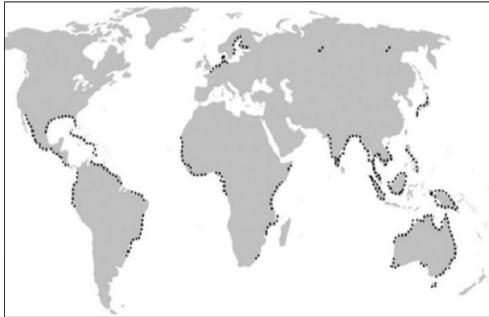
Acid sulfate soils are naturally occurring soils or sediments formed under reduced soil conditions (Dent & Pons, 1995; Fanning, 2013; Pons, 1973). The global occurrence of ASS is shown in Figure 1. These soils either contain sulfuric soil materials, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or have the potential to form them, in amounts that can have detrimental impact on soil properties (Baldwin & Fraser, 2009; Ljung, Maley, Cook, & Weinstein, 2009). In general, ASS with sulfuric soil material ( $\text{pH} < 4$ ; Isbell, 2002) and that having acidified through oxidation of pyrite are referred to as “*Sulfuric soils*” in accordance with the Australian ASS classification key (Fitzpatrick, Powell, & Marvanek, 2008). ASS with sulfidic soil material ( $\text{pH} > 4$ ; Isbell, 2002) that are oxidizable, contains pyrite and have the potential to acidify when exposed to air are referred to as “*Sulfidic soils*” (Fitzpatrick et al., 2008).

Sulfidic soil materials are formed through bacterially-induced formation of iron sulfides, mostly pyrite ( $\text{FeS}_2$ ) in coastal and inland reduced environments (Sammut, White, & Melville, 1996). In an undisturbed state below the water table, the sulfidic soil materials are benign unless exposed due to various natural processes (e.g. drought events) and anthropogenic activities (e.g. excavation) (Dent, 1986; Österholm & Åström, 2004). These processes allow the sulfides present in the sulfidic soil materials to react with oxygen and oxidize the  $\text{FeS}_2$ . The oxidation processes in turn produces  $\text{H}_2\text{SO}_4$  which acidifies the surrounding environments (Nordmyr, Åström, &

Peltola, 2008). Release of the  $\text{H}_2\text{SO}_4$  in turn solubilizes soil matrix releasing metals such as iron ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ), aluminum ( $\text{Al}^{3+}$ ) and toxic elements, making them readily available in solution to be dispersed into surrounding environments (Poch et al., 2009; Wilson, White, & Melville, 1999).

The major ecological impacts associated with oxidation of  $\text{FeS}_2$  and release of the  $\text{H}_2\text{SO}_4$ , toxic metals and metalloids are loss of natural habitats, degradation of civic infrastructure, loss of crop productivity, and deoxygenation of water bodies (Macdonald et al., 2004; Michael, 2013; Sammut et al., 1996). The major detrimental impact of  $\text{H}_2\text{SO}_4$  and release of toxic constituents of the soil matrix is on redox potential (redox) and pH. These soil properties are regulated by microbial activity, soil oxygen, organic matter and soil water status (McLean, 1982). In turn, redox and pH affect oxidation and reduction of minerals, release and mobility of metals or metalloids, and stability and availability of nutrients to crops (DeLaune & Reddy, 2005). In ASS, an oxidized soil material of high redox values (+300 mV) would mean low soil pH ( $\text{pH} < 4$ ), and a soil material of high pH ( $\text{pH} > 4$ ) would mean reduced soil conditions (-300 mV) (Fiedler, Vepraskas, & Richardson, 2007). Oxidized soil conditions of high redox values ( $\text{Eh} > 300$  mV) and low pH ( $\text{pH} < 4$ ) are characteristics of high concentrations of protons ( $\text{H}^+$ ) and acidic minerals ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  etc.), soil condition not suitable for crop production (Ljung et al., 2009; Michael, Fitzpatrick, & Reid, 2017).

In ASS, sulfuric soil material acidity is



*Figure 1.* The global distribution of ASS. Of the estimated 17-24 million ha of ASS (Ljung et al., 2009; Poch, Thomas, Fitzpatrick, & Merry, 2009), 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, respectively (Simpson & Pedini, 1985)

managed by application of mineral lime and oxidation of sulfidic soil materials by water table management (Melville & White, 2012). We have demonstrated management of soil factors responsible for producing acidity and the oxidation processes as important strategies (Michael, Fitzpatrick, & Reid, 2015, 2016). In one of these studies (Michael et al., 2016), we have reported the importance of surface soil (0–10 mm) carbon and nitrogen in amelioration of sulfuric soil materials under aerobic soil conditions. Based on the results, it became apparent that the importance of soil carbon and nitrogen in regulating the surface soil (0–10 mm) pH and redox of sulfidic soil materials needs to be investigated. Therefore, this study examined the importance of soil carbon and nitrogen on surface soil pH and redox of sulfidic soil materials when maintained under aerobic or anaerobic soil conditions.

## MATERIALS AND METHODS

### Soils

The sulfidic soil material used in this study collected from a ‘sulfuric subaqueous clayey soil’ (Fitzpatrick, 2013) at a depth of ca. 1 m in the Finniss River (Figure 2) in Adelaide, South Australia (35°24028.28”S; 138°49054.37”E) was described previously (Michael, Reid, & Fitzpatrick, 2012; Michael et al., 2015). Information on soil classification using the Australian ASS Identification key (Fitzpatrick et al., 2008) and United States Department of Agriculture Natural Resources Conservation Service (NRCS-USDA, 2014) are given in Table 1. When the sample of sulfidic soil material was freshly collected, the pH measured in water 1:5 (pH<sub>w</sub>) was 6.7; the water holding capacity was 49% and the residual organic matter content, estimated using the weight loss on ignition method (Schulte & Hopkins, 1996), was 10.6%, respectively. After peroxide treatment (pH<sub>ox</sub>) (Ahern, McElnea, & Sullivan, 2004), the pH decreased to 1.4.

### Treatments

The treatments and the compositions are shown in Table 2. In the experiments involving simple carbon and nitrogen compounds, a plant material amended treatment using lucerne hay as organic matter with high nitrogen content was included to compare the results. All the corresponding control treatments were not amended. The amendments of the three soil treatments were uniformly mixed into the soil, and placed into 70 mL Falcon tubes by

Table 1  
*Classification of acid sulfate soil materials from the Finniss River used in the study as per Michael et al. (2016)*

Soil Type <sup>1</sup>	Previous sampling location reference	Depth (cm bgl)	Sulfuric horizon <sup>2</sup> / Sulfidic material <sup>6</sup>	Soil Class <sup>7</sup>	Australian ASS classification key <sup>8</sup>	Sulfuric horizon <sup>5</sup> / Sulfidic material <sup>6</sup>	Soil Class <sup>7</sup>	Australian ASS identification key <sup>8</sup>
Finniss River: Prior to rewetting (2009)								
Sulfidic soil	FIN26	0-5	Sulfuric	Hydaquentic	<b>Sulfuric</b>	<i>Sulfidic</i>	<b>Typic</b>	Sulfuric subaqueous clay soil
	M3-4 <sup>2</sup>	5-17	Sulfuric	Salfaquent	<b>cracking clay soil</b>	<b>Sulfidic</b>	<b>Sulfowassept</b>	
	FC10740 <sup>3</sup>	17-40	<b>Sulfuric</b>			Sulfuric		clay soil
	LF01-B <sup>4</sup>	40-60	<b>Sulfuric</b>			Sulfuric		
		60-150	<b>Sulfidic</b>			Sulfidic		
Finniss River: Post rewetting (post 2010)								

<sup>1</sup> Soil type label used in this paper when this layer of sulfidic material is used to conduct soil organic matter experiments in 70 ml Falcon tubes.  
<sup>2</sup> Sampling location label used in (Fitzpatrick et al., 2009).  
<sup>3</sup> Sampling location label used in (Fitzpatrick, Shand, & Hicks, 2011).  
<sup>4</sup> Sampling location label used in (Bake, Shand, & Fitzpatrick, 2013).  
<sup>5</sup> Acid sulfate soil horizon (NRCS-USDA, 2014).  
<sup>6</sup> Acid sulfate soil material (NRCS-USDA, 2014).  
<sup>7</sup> Currently no subgroup exists in Soil Taxonomy (NRCS-USDA, 2014) that adequately describes these Finniss River soils following their rewetting. They are best described as subaqueous soils with sulfuric horizons or "Sulfuric subaqueous clayey soils" in accordance with the Australian ASS classification key (Fitzpatrick et al., 2008). Consequently, the following new proposal is currently being submitted by Fitzpatrick and Grealish (personal communication) to USDA-NRCS to consider for inclusion in revised versions of the Keys to Soil Taxonomy is: (i) a new suborder, which would be Wassepts, (ii) with the existence of Wassepts suborder, a great group of Sulfowassepts will need to be proposed within the suborder and (iii) with the existence of Sulfowassepts great group, a subgroup of Typic Sulfowassepts will need to be proposed within the great group.  
<sup>8</sup> Australian acid sulfate soil classification (Fitzpatrick et al., 2008).

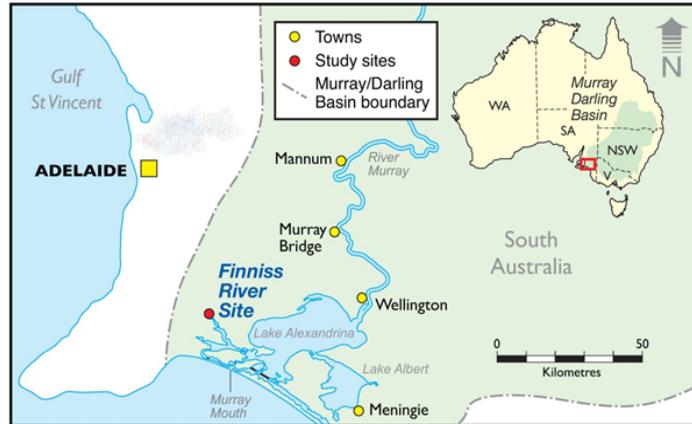


Figure 2. Locality of samples from the Finnis River site at Wally's Landing (Michael et al., 2015)

Table 2

Details of soil treatments with slight modification from Michael et al. (2016)

Amendments	Composition of treatments	
	g/80 g soil	Total N (mg)
<b>Organic matter</b>		
Lucerne hay	1	32
Pea straw	1	12
Wheat straw	1	8
<b>Simple carbon sources</b>		
Glucose	4	
	0.1	
Sodium acetate	4	
Molassess	5	<sup>b</sup>
<b>Simple nitrogen sources</b>		
Sodium nitrate	0.30	50
Ammonium chloride	0.19	50
Urea	0.24	50

<sup>b</sup>Molasses may contain a small amount of nitrogen in the syrup.

weighing. The dried plant materials (hereafter referred to as organic matter) were chopped in an electric blender to pass through a sieve size of 0.5 mm before use. The sulfidic soil material used in the treatments is hereafter referred to as “sulfidic soil” to be consistent with our recent publications (e.g. Michael, 2014, 2017).

On a field-scale, the organic matter applied as amendment (estimated for acre-furrow-slice weighing 1000 tonnes) is between 29.8 (80:1, soil: organic matter) and 149 (16:1) tonnes per ha (Michael et al., 2016). Each treatment was set in triplicates and the tubes arranged in complete randomized design (CRD). Three experiments (Table 2) lasting 6 months were conducted to investigate the changes in soil pH and redox when:

1. Sulfidic soil was mixed with plant materials containing different nitrogen contents and incubated under aerobic and anaerobic conditions.

2. Sulfidic soil was mixed with simple carbon compounds or chopped of lucerne hay and incubated under anaerobic conditions only. The aerobic treatment component was reported as Figure 3 in Michael et al. (2016).

3. Sulfidic soil was mixed with simple nitrogen compounds or chopped lucerne hay and incubated under aerobic and anaerobic soil conditions.

The aerobic and anaerobic treatment conditions were maintained as we described in earlier studies (e.g. Michael, 2015; Michael et al., 2015). The aerobic treatments were maintained under 75% field capacity

by adding water on weight basis. The anaerobic treatments were kept flooded (100% field capacity based on initial weight) throughout the study period by adding 50 -100 ml of tap water twice (once in the morning and once in the afternoon) daily as where necessary.

### Measurements

Soil pH and Eh were measured within the surface (0–10 mm). Redox was measured using a single Ag/AgCl reference and platinum (Pt) electrode combination using an automated data logger (Michael et al., 2015). The Pt and reference electrodes were inserted into the soil and allowed to equilibrate for 10 min and then Eh measured at 1 min intervals for the next 10 min and averaged (Rabehorst, Hively, & James, 2009). These values were corrected for the reference offset to be relative to the potential of a standard hydrogen electrode by adding 200 mV, and the stability and accuracy of the electrodes were maintained as per Fiedler et al. (2007). Redox conditions of the experimental soils are categorized as: (i) oxidized ( $\geq +300$  mV), (ii) moderately reduced (+300 to 0 mV), (iii) reduced (0 - -100 mV) and (iv) highly reduced (-100 - -400 mV) in reference to the change in surface environments shown in Figure 3.

The pH was measured using a 2 g soil (1:5, soil: water w/w) with a pre-calibrated Orion pH meter (720SA model) as described (Michael et al., 2015). The results were compared to the Eh-pH range of surface environment shown in Figure 3. The mechanisms responsible for the changes

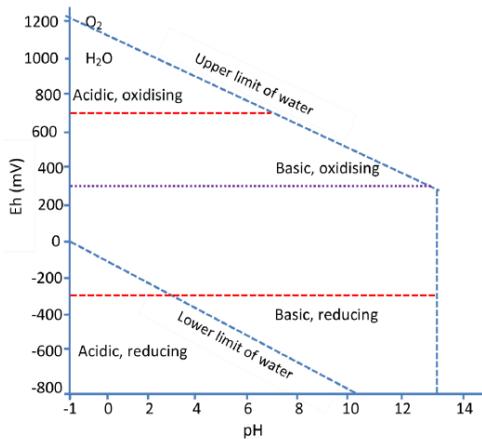


Figure 3. The Eh-pH range in surface environments showing four redox classes: (i) acidic-oxidizing, (ii) basic-oxidizing, (iii) basic-reducing and, (iv) acidic-reducing (adapted with slight modifications from Krauskopf (1967) as per (Delaune & Reddy, 2005; Poch et al., 2009). The lower and upper Eh limits are shown by the red dotted lines. The purple dotted line shows the break between an aerobic and anaerobic condition (Fiedler et al., 2007)

in pH or redox measured are discussed in the last section, based on the observation that the mechanisms involved in inducing the changes in the two soil properties seem to be the same under the two soil moisture regimes. Under aerobic soil conditions, the changes in pH and redox of studies shown in Figures 4 and 6 are inconsistent. This is thought to be caused by the type of microbial ecology that was present in the soil prior to or was established during the study that was capable of utilizing the residual organic matter content (10.6%).

### Statistical Analyses

Data from the surface soil (0–10 mm) are presented in this paper. The Eh values obtained over a 10 mins-period were

averaged and a treatment average obtained by taking the mean of the three replicates. These values were corrected for the reference offset to be relative to the potential of a standard hydrogen electrode by adding 200 mV (Fiedler et al., 2007). 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 profile was determined by two-way ANOVA (Michael et al., 2017) using statistical software JMPIN, AS Institute Inc., SAS Campus Drive, Cary, NC, USA 27513.

## RESULTS AND DISCUSSION

### Roles of Organic Matter Derived Soil Nitrogen on Sulfidic Soil pH and Redox

The long-term (6 months) effects on sulfidic soil pH and redox measured following the addition of organic matter with varying nitrogen content are shown in Figures 4 and 5. Under aerobic conditions, the unamended sulfidic soil strongly acidified, the pH declining to near 4 (Figure 4). In the amended treatments, lucerne hay and pea straw significantly ( $p < 0.05$ ) prevented the soil from acidifying and increased the pH to well over 8, whereas with wheat straw, the pH fell but not as much as in the control. The pH changes were correlated with changes in Eh. Lucerne hay addition significantly reduced the redox to near 100 mV and the other two amended soils were higher but lower than 300 mV. The overall increase in pH caused by addition of organic matter was 1.5, and changes in Eh ranged from between 100 – 300 mV (Figure 4).

Under anaerobic soil conditions, the pH of all the amended soils were increased compared to the initial pH but the increase was lower than 8, similar to the control soil which decreased to near 6 (Figure 5). The effects of the varying nitrogen content of the organic matter on pH were quite similar among the treatments, and not distinct as observed under aerobic conditions. The only dominant effect was the low Eh produced by the amendments (Figure 5). Eh of the control soil under the anaerobic conditions was near 40 mV, compared to the 475 mV under aerobic condition (Figure 4). The overall changes in pH in all the organic matter amended treatments was 0.5, the change in lucerne hay treatment being slightly higher. The reduction in redox caused by organic matter amendment was insignificant except in the lucerne hay amended treatment, ranging from between -29 – -14 mV (lucerne hay > pea straw > wheat straw). These results point out that organic matter plays an important role in reducing the redox, thereby buffering sulfidic soil material oxidation.

### **Roles of Surface Soil Nitrogen in Regulating pH and Redox of Sulfidic Soil**

The studies presented in Figures 4 and 5 assessed the role of nitrogen derived from organic matter. Organic matter of plant material origin is complex and is a source of multiple metabolic substrates for soil microbes. The organic matter being a source of multiple nutrients including carbon made the roles of the organic matter derived nitrogen inconclusive.

This inconclusiveness was addressed by the studies presented in Figures 6 and 7 following the addition of simple nitrogen sources that contain nitrogen alone, nitrogen and carbon, or nitrogen and other ions. Lucerne hay as organic matter of high nitrogen content was included to compare the results.

The control soil did not strongly acidify under the aerobic condition and the decrease in pH was by 0.7 (Figure 6), contrasting the change in pH of the control soil shown in Figure 4. In the amended soils, urea addition strongly increased the pH to nearly 8, and nitrate and ammonium lowered it to near 6. The changes in pH were correlated with the changes in redox. The control soil was moderately reduced to near 100 mV, agreeing to the circumneutral pH of 6, and the amended soils were reduced to below -50 mV (Figure 6).

The highest reduction in redox was caused by lucerne hay amendment, significantly reducing the Eh to -160 mV. The changes in pH and Eh measured under anaerobic conditions are shown in Figure 7. The control soil pH was stable compared to the initial pH, similar to the small increase of the study shown in Figure 8. In the amended soils, urea increased the pH to 7.8, and nitrate and ammonium moderately lowered the pH to below 6, compared to the changes in the control soil (Figure 7). The changes in pH measured were in agreement with the changes in Eh, which were mainly reduced, ranging from between -50 – 50 mV. These changes are, again, within the range measured in the other studies like

that shown in Figure 5 under the same soil conditions. The overall results show the treatment conditions employed were capable of inducing similar type of changes in the soil properties measured.

### **The Roles of Surface Soil Carbon in Regulating pH and Redox of Sulfidic Soil**

The studies presented in Figures 4 and 5 show the roles of organic matter derived nitrogen in regulating the pH and redox of sulfidic soil. These results were compared to the studies shown in Figures 6 and 7. The results obtained following the addition of the simple nitrogen sources pointed out the roles of nitrogen in regulating soil chemistry but significant changes were induced by the compounds containing both nitrogen and carbon, e.g. urea (Figure 6). So the roles of carbon of the organic matter of plant materials or the simple nitrogen compounds, e.g. urea, were not clear. Therefore, the study shown in Figure 8 was conducted to investigate the roles of soil carbon in regulating pH and redox of sulfidic soil under anaerobic soil conditions. The aerobic component was presented as Figure 3 in Michael et al. (2016).

Under the anaerobic conditions, the control soil pH was raised just above the initial pH (Figure 8). Among the simple carbon compounds, acetate increased the pH above 7 and glucose and molasses strongly lowered it, well below 5. The increase in pH induced by organic matter amendment was high as in the other experiments. Under the anaerobic conditions, all the treatments soils

were reduced in agreement with the changes in pH, with glucose and molasses recording the highest Eh values (Figure 8).

### **The Mechanisms Regulating The Changes in pH and Redox in Sulfidic Soil**

As initially pointed out, the changes measured in the two soil properties seem to be regulated by the same mechanism. Under aerobic soil conditions, the control sulfidic soil strongly acidified as a result of sulfidic soil oxidation (Figure 4). This did not happen in the study shown in Figure 6. The explanation for this seems to come from the microbial ecology present that was capable of oxidizing the residual organic carbon content (10.6%) and generate alkalinity. Studies elsewhere show these types of variations in changes in soil chemistry are caused by the type of microbial ecology present capable of generating microbial alkalinity prior to or established following the addition of metabolic substrates (Condon, Stark, O'Callaghan, Clinton, & Huang, 2010; Kuzyakov, Friedel, & Stahr, 2000). The increase in pH caused by organic matter addition was closely correlated with reduction in Eh, consistent with the involvement of sulfur-reducing bacteria (Michael et al., 2016). These bacteria are unable to function under aerobic conditions (Hamilton, 1998), so the reduction in Eh to below 0 mV (e.g. Figure 6) was caused by depletion of oxygen by aerobic bacteria capable of using the organic matter as metabolic substrate (Michael et al., 2015; 2016). Addition of refined carbon sources,

e.g. glucose, did not generate these reducing conditions, even under the anaerobic soil conditions (Figure 8), implying this carbon source was 'recalcitrant' to microbial breakdown (Marschner et al., 2008). When refined nitrogen sources were added, the Eh was reduced but the level of reduction was smaller than the organic matter, both under aerobic (Figure 6) and anaerobic (Figure 7) soil conditions. Some bacteria are able to use acetate and nitrate as the energy sources with the net consumption of protons (Thauer, Zinkhan, & Spormann, 1989). This seems to be the reason nitrate reduced the soil and sustained the pH around circumneutral level under aerobic soil condition (Figure 6).

Under anaerobic conditions, the surface soil often experiences frequent fluctuation in the amount of water that ponds on the surface. In this study, this was prevented from happening by ensuring a sufficient amount of water (5–10 cm) was ponding on the surface by adding 50-100 ml of tap water daily. Consequently, the soil was expected to remain moderately reduced (300–0 mV) to reduced (0 – -100 mV) (Fiedler et al., 2007; Ponnampereuma, 1972). In the presence of a suitable metabolic substrate, a certain degree of reduction (-100 – -400 mV) is expected because of microbial oxidation of the resources (e.g. carbon and nitrogen) and reduction reaction of the anaerobic soil condition caused by flooding, sufficient to sustain the alkalinity (Michael, 2014; 2015; Sarwani, Shamshuddin, Ishak, & Husni, 2006). In almost all cases, the control soils remained

moderately reduced because of the reducing conditions of flooding (Figures 5, 7 and 8). In the amended soils, glucose and molasses moderately reduced the soil and caused the pH to drop to nearly 3 and 4, respectively (Figure 8). The reduction in pH caused by glucose seemed to have resulted from microbial breakdown of the glucose into fatty acid as observed in an alkaline sodic soil (Chorom, 1996). In the other treatments, the additions reduced the soils (Figure 6), causing the pH to remain near the circumneutral levels (pH 5 – 6).

The differences in the changes in the soil properties measured are significant to deduce that the changes were dependent on the type of microbial ecology the metabolic substrates as resources were capable of establishing. The refined carbon and nitrogen sources, for instance, are simple nutrient sources and are only capable of engaging a simplified microbial ecology capable of causing a smaller change in soil properties. For instance, glucose ( $C_6H_{12}O_6$ ) as a sole carbon source moderately reduced the redox and lowered the pH even under anaerobic soil condition whereas addition of acetate ( $C_2H_3NaO_2$ ) containing carbon and sodium reduced the soil and increased the pH (Figure 8). It was clear too that simple nitrogen compound such as urea ( $CH_4N_2O$ ) containing both carbon and nitrogen increased the pH under the two soil moisture conditions to 8. These are strong indications that multiple nutrient sources are needed by the soil microbes to generate alkalinity sufficient to induce observable changes in soil chemistry (Michael, 2017).

The organic matter being complex plant materials and source of multiple nutrient employed complex microbial community which highly reduced the soils and increased the pH, even under aerobic soil conditions where sulfides were expected to oxidize and strongly acidify the sulfidic soil materials (Figure 4).

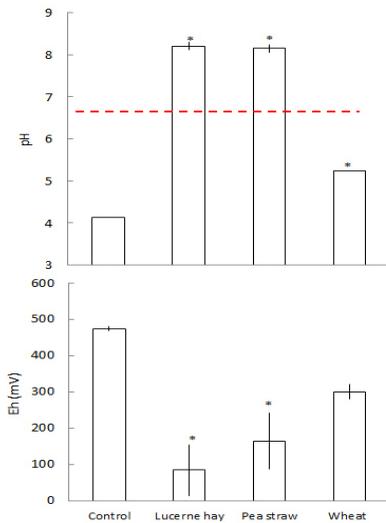


Figure 4. Changes in pH and Eh of sulfidic soil mixed with plant material containing different nitrogen contents. The treatments were incubated under aerobic soil conditions (75% field capacity) for 6 months. Each value is the mean ± s.e. of three measurements. The dotted line is the initial pH. Asterisks indicate significant differences ( $p < 0.05$ ) between treatment and control at each depth

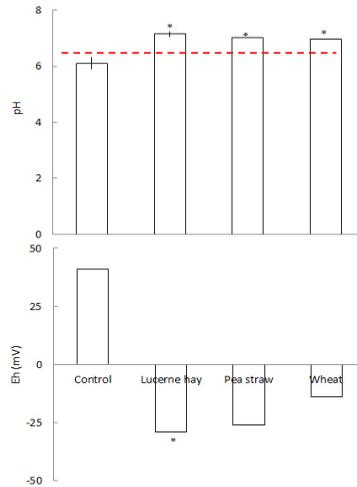


Figure 5. Changes in pH and Eh of sulfidic soil mixed with plant material containing different nitrogen contents. The treatments were incubated under anaerobic (flooded) soil conditions for 6 months. Each value is the mean ± s.e. of three measurements. The dotted line is the initial pH. Asterisks indicate significant differences ( $p < 0.05$ ) between treatment and control at each depth

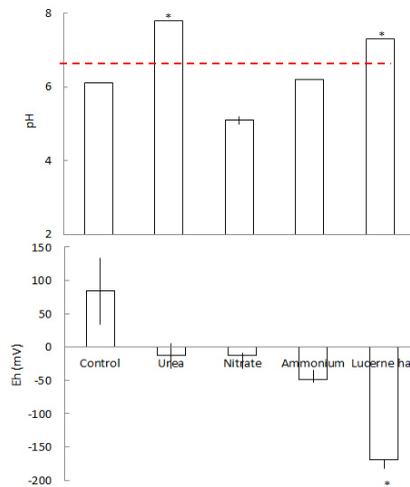


Figure 6. Changes in pH and Eh of sulfidic soil mixed with simple nitrogen compounds or chopped of lucerne hay. The treatments were maintained under aerobic soil conditions (75% field capacity) for 6 months. Each value is the mean ± s.e. of three measurements ( $n=3$ ). The dotted line is the initial pH. An asterisk indicates significant difference ( $p < 0.05$ ) between treatment and control at the same depth

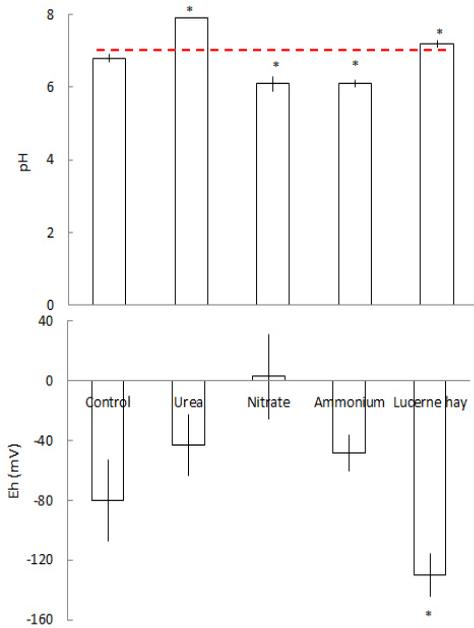


Figure 7. Changes in pH and Eh of sulfidic soil mixed with simple nitrogen compounds or chopped of lucerne hay. The treatments were maintained under anaerobic (flooded) soil conditions for 6 months. Each value is the mean  $\pm$  s.e. of three measurements (n=3). The dotted line is the initial pH. An asterisk indicates significant difference ( $p < 0.05$ ) between treatment and control at the same depth

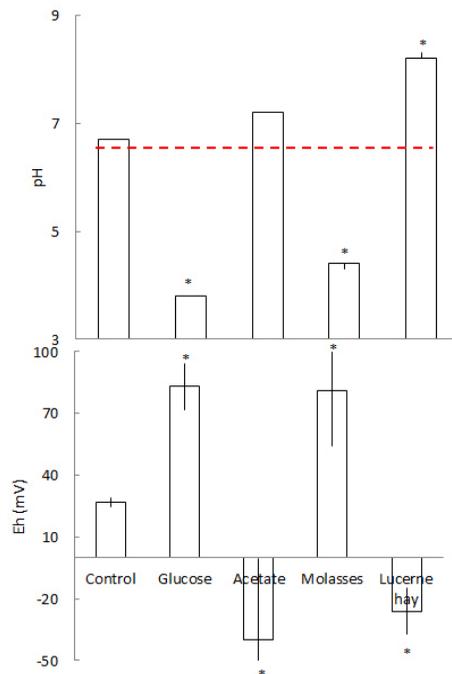


Figure 8. Changes in pH and Eh of sulfidic soil mixed with simple carbon compounds or chopped of lucerne hay. The treatments were maintained under anaerobic (flooded) soil conditions for 6 months. Each value is the mean  $\pm$  s.e. of three measurements (n=3). The dotted line is the initial pH. An asterisk indicates significant difference ( $p < 0.05$ ) between treatment and control at the same depth

## CONCLUSIONS

Organic matter as a source of multiple metabolic substrates for soil microbes significantly prevented sulfidic soil oxidation under aerobic condition and sustained the sulfidic soil material alkalinity ( $pH > 4$ ) under anaerobic condition, respectively. Addition of glucose as a source of carbon alone resulted in oxidization of the sulfidic soil even under anaerobic conditions and led to strong acidification ( $pH < 4$ ). Metabolic compounds like acetate and urea containing

both carbon and nitrogen had the opposite effects on soil redox and pH. The mechanisms responsible for the changes in soil chemistry measured appear to be dependent on the type of microbial ecology engaged by the metabolic substrates. Organic matter being a source of multiple metabolic substrates effectively established a complex microbial ecology that was capable of generating significant soil alkalinity, reducing the

redox and increasing the sulfidic soil pH. The single metabolic substrate sources had no significant effect on redox and pH, dependent on the types of microbial ecology establishment by these resources being limited to the single nutrients. The findings of this study have implications for management and general use of the surface soils of sulfidic soils under a range of soil moisture regimes.

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