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

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II. ABSTRACT

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

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

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

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

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

The hypotheses to be tested were:

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

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

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

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

The second experiment was carried out to assess the effect of OM addition on pH in a wet-dry cycle followed by a second wet period. A further aim was to investigate the influence of water content during the dry period on acidification. Three ASS (sulfuric, hypersulfidic and hyposulfidic) were collected from one profile and unamended or amended with 10 g C kg^{-1} as finely ground wheat straw. The soils were exposed to a submerged (wet) period, a dry period, followed by another wet period. In the first wet period (10 weeks), the pH increased only in the amended soils, which was accompanied by a strong decrease in Eh. To investigate the effect of water content during the dry period on pH, the soils were rapidly dried to 40, 60, 80 or 100% of WHC at the start of the dry period. This water content was maintained during the dry period. The pH decrease during the 10-week dry period was greater in amended than in unamended soils and greater at 60, 80 or 100% than at 40% of WHC. At the end of the dry period, the pH was higher in amended than in unamended soils and higher at 40% of WHC than at the higher water contents. In the second wet period (16 weeks), the pH increased only in the amended soils. The pH increase was accompanied by a decrease in Eh in the amended soils. The water content in the previous dry period did not influence pH in the second wet period in the unamended soils, but in the amended soils, the pH was higher in soils previously maintained at 40% of WHC than that maintained at higher water contents. At the end of the second wet period, the pH was higher in amended than in unamended soils. This study shows the ameliorative effect of OM addition in ASS. OM addition can improve energy supply for sulfate reducers which results in an increase in pH during the wet period and lead to a higher pH in the oxidation period. The smaller pH increase and Eh decrease in amended soils in the second compared to the first wet period suggests that OM decomposition was lower in the second wet period likely because rapidly decomposable compounds had been utilised in the previous wet and dry periods and only recalcitrant OM remained. Therefore OM may have to be added repeatedly for sustained amelioration of ASS.

The aim of the third experiment was to investigate the effect of addition of hyposulfidic clay soils to a sufuric sandy soil on pH changes in reduced and oxidised conditions. A sulfuric sandy soil (pH 4.1) was mixed with three hyposulfidic clay soils (with clay contents ranging between 38 and 72%) to give clay soil proportions of 0, 25, 50, 75 and 100 (% dry soil). According to their net negative acidity, the three clay soils are referred to as: NA-334, NA-54 and NA-8 (values in moles H^+ tonne$^-$). The soils were amended with wheat straw at 10 g of C kg $^{-1}$ and then incubated for 14 weeks under reducing conditions (wet period) followed by 11 weeks incubation under oxidising conditions (dry period) during which they were maintained at 100% of maximum WHC. The pH of the sulfuric soil alone increased during the wet period

by about two pH units (to pH 6) and decreased by more than two pH units (to pH <4) during the dry period. In the clay soils alone and treatments with sulfuric soil, the pH during the wet period decreased by 0.5 to 1 unit with NA-334 and NA-54 and increased by one unit with NA-8. The pH was >6 in all clay treatments at the end of the wet period. During the dry period, the pH remained above pH 7 with NA-334 and decreased by about one unit (to pH 5.5) with NA-8. In treatments with NA-54, the pH decrease during the dry period depended on the proportion of clay soil, ranging from 0.5 pH unit with 75% clay soil to two pH units with 25% clay soil. The capacity of the clay soil treatments to maintain stable pH during wet and dry periods depended mainly on the negative net acidity of the added clay soils, but was not related to their concentration of reduced inorganic sulfur or clay content. It can be concluded that addition of clay soils with high negative net acidity could be used to ameliorate acidity in ASS.

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

III. DECLARATION

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

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V. LIST OF ABBREVIATIONS

Aluminium (Al)

Acid Neutralising Capacity (ANC)

Analysis of Variance (ANOVA)

Arsenic (As)

Acid Sulfate Soils (ASS)

Acid Volatile Sulfur (AVS)

Carbon (C)

Calcium (Ca)

Chromium (Cr)

Carbon: Nitrogen ratio (C/N ratio)

Cobalt (Co)

Copper (Cu)

Redox Potential (Eh)

Inductively Coupled Plasma (ICP)

Iron (Fe)

Monosulfidic black ooze (MBO)

Manganese (Mn)

Murray Darling Basin (MDB)

Murray Darling Basin Authority (MDBA)

Nickel (Ni)

Nitrogen (N)

N concentration (Nitrogen concentration)

N demand (Nitrogen demand)

N Transformations (Nitrogen transformations)

Millivolts (mV)

Organic Carbon (Organic C)

Organic Matter (OM)

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

Phosphorous (P)

Revolutions per minute (rpm)

Reduced Inorganic Sulfur (RIS)

Chromium Reducible Sulfur (Scr)

4M HCl extractable sulfur (S_{HCl})

1M KCl extractable sulfur (S_{KCl})

Soil Organic Matter (SOM)

Sulfate Reducing Bacteria (SRB)

Total C (Total carbon)

Total N (Total nitrogen)

Zn (Zinc)

VI. LIST OF FIGURES