ACID SULFATE WETLANDS IN THE NSW COAST, AUSTRALIA: CHEMICAL CHARACTERISTICS AND THEIR IMPLICATIONS FOR ENVIRONMENTAL REMEDIATION[1]

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Abstract. Acid sulfate wetlands are widespread in the New South Wales (NSW) coast, Australia. Acid sulfate soils have caused severe environmental problems in the area with land scalding, accompanied by the discharge of highly acidic drain water into estuarine waterways being the worst-case scenario in these landscapes. The investigated acid sulfate scalds are characterized by an extremely acidified topsoil layer (0–0.6 m). In general, the scalded acid sulfate soils have less organic matter and soluble phosphorus, and a greater salinity, soluble acidity, soluble Al, Mn and Zn concentrations, compared to the adjacent non-scalded acid sulfate soils. These are the most likely soil constraints for re-vegetation of the scalded lands and treatment will require acid neutralization (e.g. application of lime) and addition of P fertilizers to reduce the soluble acidity, immobilize soluble Al, Mn and Zn, and increase P availability. The evidence also shows that the higher soluble Al concentration in the scalded soils, relative to the non-scalded soils, is associated with their lower organic matter content. Hence, rehabilitation of these scalded lands should involve the addition of organic matter to reduce soluble Al concentrations; this may also help reduce Mn and Zn toxicity, and salinity. Water quality monitoring in the estuarine waterways draining the acid sulfate wetlands shows that acidic flows (pH < 4.5) of several months occurred intermittently. This may be attributed to the hydrolysis of Fe^{3+} after the oxidation of Fe^{2+} that is exported into the creek from acid sulfate soils through artificial drainage network. It is hypothesized that Fe^{2+} is being generated by biological iron reduction, which consumes H^+ and thereby drives the conversion of retained acids to soluble acids. This allows the release of retained acids and subsequently the translocation of acids from soils to the adjacent waterway. Because many acid sulfate soils in the NSW coast contain large amounts of existing acidity, flooding or liming to eliminate acidity is either ineffective or cost-prohibitive. Treatment of the acidic water appears to be a more cost-effective strategy for managing acid sulfate wetlands in the NSW coast.

Additional Key Words: sulfide minerals, land scalding, acid discharge

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Introduction

The estuarine sediments of coastal wetlands frequently contain sulfide minerals (predominantly pyrite). Oxidation of these metal sulfides following dehydration of the sulfidic sediments by artificial drainage, natural drying during drought episodes or exposure of the excavated sulfidic sediments on the land surfaces generates sulfuric acid, which acidifies the soils and elevates the levels of potentially toxic metals in soil pore water. It also reduces the bio-availability of some plant nutrients, particularly phosphorus. As a result, land degradation is common in coastal acid sulfate wetlands around the world (Dent, 1986; White et al., 1997).

It was estimated that there are over three million ha of acid sulfate lands along Australia's coastal zone. The NSW coast, located in southeastern Australia is the region that has been most affected by acid sulfate soil problems. In this area, extensive areas of acid sulfate soils have been drained, mainly for sugarcane production and cattle grazing (e.g. Smith and Smith, 1996). Artificial drainage with floodgate controls has removed much of the surface water and lowered the water table in coastal wetlands to the sulfidic layer, inducing oxidation of pyrite and acid generation. Pyrite-derived acidification can also be caused by natural drying processes during prolonged drought episodes that frequently occur along this coast (Lin, 1999). Acid sulfate soils have caused severe environmental problems in the area with land scalding, accompanied by discharges of highly acidic water draining into estuarine waterways being the worst-case scenario.

In this article, chemical characteristics of acid sulfate wetlands will be discussed based on investigations in a number of sites along the NSW coast. The implications of these data for environmental remediation of the coastal wetlands will be explored.

Study sites and research methods

Regional settings and site description

The catchments of most rivers along the New South Wales coast are fairly small due to the close proximity of the Eastern Range to the coast. This has resulted in low sedimentation rates in the estuarine embayments where the coastal floodplains have developed. The study area experiences a warm temperate climate with extremely variable rainfall regime.

Table 1 Relevant information on the investigated scalded acid sulfate soils

Study site	Depth to sulfidic layer (m)	Distance to main river (m)	Distance to foothill (m)	Distance to main drain	Area of scald (m^2)
Richmond 1	0.7	7,250	500	500	4,000
Richmond 2	0.9	9,000	120	400	2,400
Clarence	0.9	3,750	2,880	80	25,000
Nambucca	n.d.	1,380	380	550	1,000
Macleay	0.7	6,750	1,500	1,250	1,500,000
Camden	0.5	250	500	10	5,000
Manning	0.7	3,750	3,750	250	40,000
Hawkesbury	0.3	4,750	250	120	20,000
Shoalhaven	0.7	4,120	750	120	10,000

Modified from Lin et al. (2001)

Samples were collected from 11 sites along the NSW coast and relevant information on the investigated soils is given in Table 1. Detailed information about the physiography and land use history of two selected sites were described as follows:

Rocky Mouth Creek estuarine embayment. This site is located in the northern NSW coast, eastern Australia. Rocky Mouth Creek is a tributary of the Richmond River and it drains a sub-catchment of about 65 km^2. Much of the sub-catchment is a low-lying floodplain (about 24 km^2). The Rocky Mouth Creek floodplain system has been significantly modified by human activities since the early 1900s. The floodplain has been drained for cattle grazing and sugarcane growing. Main drains and smaller farm drains were constructed to accelerate the removal of surface water following heavy rainfall events. During the 1960s, the creek was straightened by a constructed cut-off at the location approximately 3.5 km upstream of its confluence with the main channel of the Richmond River. The natural channel section of the creek was blocked by a dike and a floodgate system was installed in a constructed channel section to prevent tide water from flowing into backswamps upstream of the floodgate system.

Macleay site. A large acid sulfate scald (about 150 ha at the time when the soil samples were collected) has developed following drainage of the previously waterlogged swamp in this site. Prior to drainage, some acid and salt tolerant vegetation species grew in the swampy areas (Local farmer, personal communication). Drainage has reduced the size of the swamp and modified the previously outer zone of the swamp into scalded land. The total area of the scald is variable, depending on the weather conditions. During dry spells, the scalded area increases with the reduction in size of the ponded area in the swamp.

Methods

Field investigation. More than 150 soil cores were examined and selected soil and water samples were collected for laboratory analysis. In general, field pH was measured using a portable pH meter immediately after soil core collection. Soil samples were sealed in plastic bags and stored on ice in a container in the field and during transportation. The soil samples were oven-dried at $70^{o}C$ in the laboratory and then ground to less than 2 mm. The pH, dissolved oxygen (DO) and electrical conductivity (EC) in backswamp surface water, drain water and creek water were also measured in the field using a portable water quality meter.

Water quality monitoring. A submersible multi-parameter water quality data logger has been installed under the floodgate structure by Richmond River County Council since May 1998. Water level, temperature, pH EC, DO and turbidity at this point was monitored at 15-minute intervals.

Chemical analyses. For samples of each whole profile, pH and EC (electrical conductivity) in a 1:5 (soil:water) extract were measured using calibrated pH and EC meters, respectively. Inorganic reduced sulfur content was estimated by chromium reducible sulfur method (Sullivan et al., 2000). Total carbon was also determined using a Leco CNS Analyzer. Since inorganic C in strongly acidic soils is negligible, the total C measured can be used as a reasonable estimate of organic C. Titratable acidity in water and KCl extracts was measured by titrating an aliquot of each extract to pH 5.5 with NaOH solution. Ions in water samples, 1:5 (soil:water) extract and 1:5 (soil:1M NH_4Cl) extract were measured using an ICP-OES. The water extracts are used for

determination of the amount of an element that is present in soluble form and the NH$_4$Cl extractable concentration of an element is used as an estimate of the sum of soluble and exchangeable forms of that element. Since Cu has a strong capacity to complex with organic matter, it is assumed that the concentration of an element extracted by CuCl$_2$ may account for that in organic-complexed forms in addition to that in soluble and exchangeable forms. The acid ammonium oxalate extractable concentration of an element is considered to include soluble and highly reactive insoluble forms of that element whereas the HCl extractable concentration of an element represents a wide element pool including soluble, exchangeable and acid reactive mineral forms of that element.

In this paper, only those data that are most useful for characterizing the investigated scalded acid sulfate soils and have implications for their remediation are presented.

General Chemical Characteristics

As mentioned above, the sedimentation rate has been low in the NSW estuaries, which favors the accumulation of pyrite in the estuarine sediments(Lin and Melville, 1993; Lin, 1996). Estuarine sediments along this coast frequently contain more than 2% sulfide-S (e.g. Lin et al., 1999). Because the rainfall is highly variable annually and seasonally, extended dry spells could occur to allow the lowering of floodplain water table to sulfidic sediments and cause the oxidation of metal sulfides to produce sulfuric acid. Artificial drainage of floodplains since European settlement has further enhanced sulfide-derived soil acidification in the area (e.g. Lin et al., 1999).

Fig. 1 gives an example of soil chemical characteristics in the NSW coast. The starting depth of the sulfidic layer occurs at around −0.2 m AHD (Australian Height Datum). The soil has an organic-rich surface soil. The soil has been extremely acidified with pH <3 occurred from −0.5 to −1 AHD. The topsoil also has a pH <5 and this is probably caused by upward transport of acid materials, through capillary action, from the oxidized sulfidic subsoil. The increase in pH of the soil below −1 M AHD can be attributed to weaker sulfide oxidation, relative to its upper sulfidic layer due to increasing water content. The EC (electrical conductivity) peak corresponds very well with the pH valley, probably reflecting the release of various cations from primary minerals due to acid attack. KCl extractable acidity was in excess
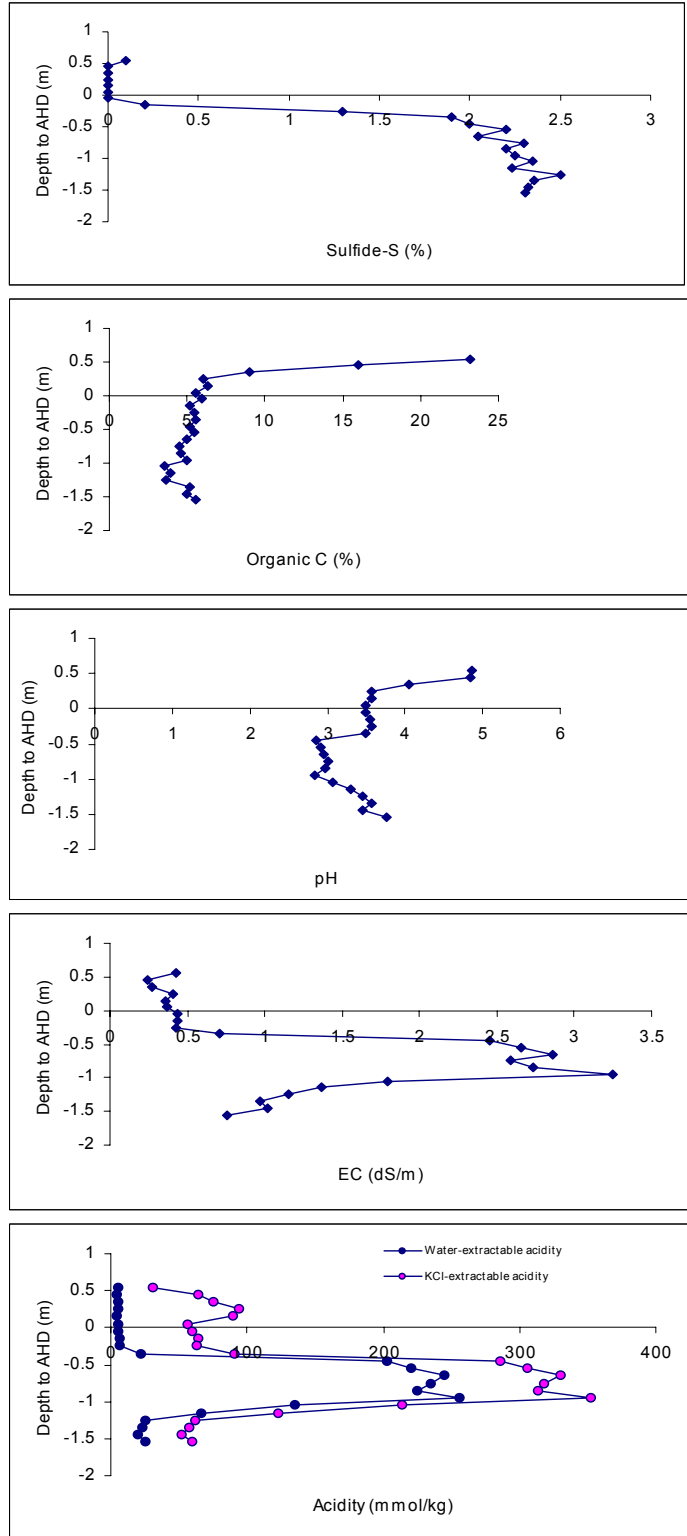
Figure 1. Vertical distribution of sulfide-S, organic C content, pH, EC and extractable acidity along a representative soil profile

of 300 mmol/kg for the extremely acidified sulfidic layer and more than 60% of the KCl extractable acidity was in water extractable forms. This suggests that the investigated soil has experienced significant sulfide oxidation, resulting in the generation of large amounts of acid that can be harmful to plants and is readily available for export to the adjacent estuarine waterways.

Acid Discharge

Figure 2 shows that there were alternating low and high pH tidal flows of several months during the period from May 1998 to July 2000. Fig. 3 shows the pH transect along the Rocky Mouth Creek upstream of the floodgate, established using data recorded on June 5, 2001. It can be seen that the entire reach had very low pH (<3.5) with little vertical variation of pH in the water column at all measured locations. It is likely that this is mainly caused by the oxidation of Fe^{2+} and the subsequent hydrolysis of Fe^{3+}, which acidifies the creek water. Fe^{2+} is produced as a result of biological iron reduction and exported to the creek with water draining from the adjacent acid sulfate soils. This process drives the conversion of retained acid to water soluble
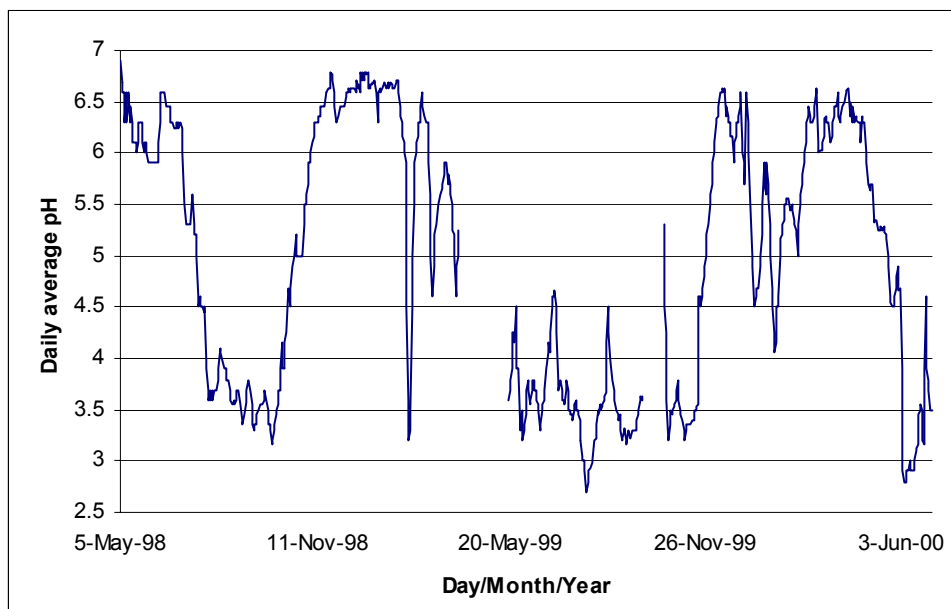

Figure 2. Variation of daily average water pH in Rocky Mouth Creek at the water quality monitoring station during the period from May 1998 to May 2000

acid in the soils, which provides the H^+ that enhances iron reduction. The acid sulfate soils in the study area contain considerable amounts of retained acid that has been accumulated in the soils due to sulfide oxidation following the construction of flood mitigation works.
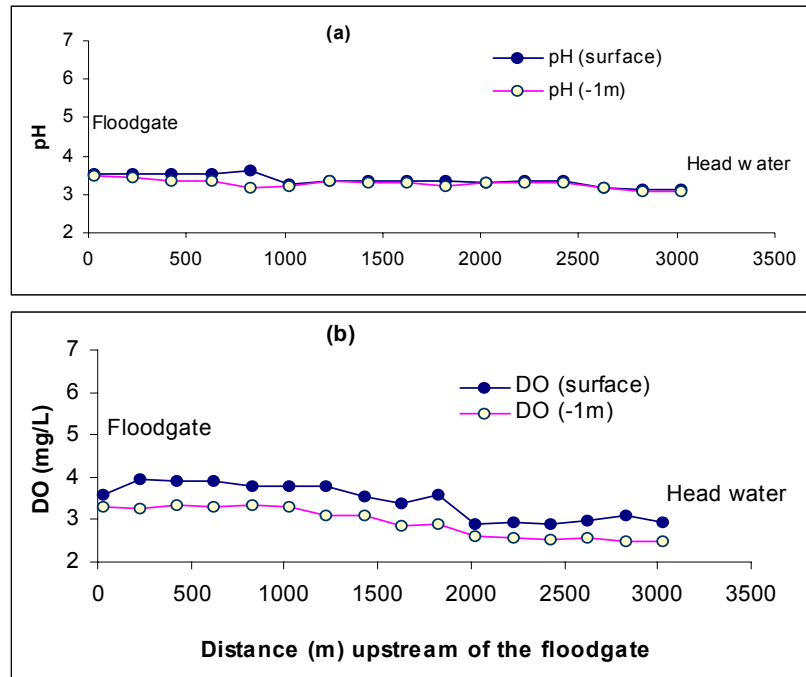

Figure 3. pH and DO transects along the Rocky Mouth Creek upstream of the floodgate, established using data collected on 05/06/2001

In addition to continuous acidic flows of several months, a significant drop in the creek water pH also occurs following heavy rainfall events during high pH (> 6)-dominated flow periods (Fig. 4). This is frequently accompanied by a drop in DO in the creek water. Although the acidification and de-oxygenation in the creek water may be related to the oxidation of Fe^{2+} contained in the discharging water from the inundated acid sulfate floodplain, it appears that other DO-consuming substances play more important roles in the process.
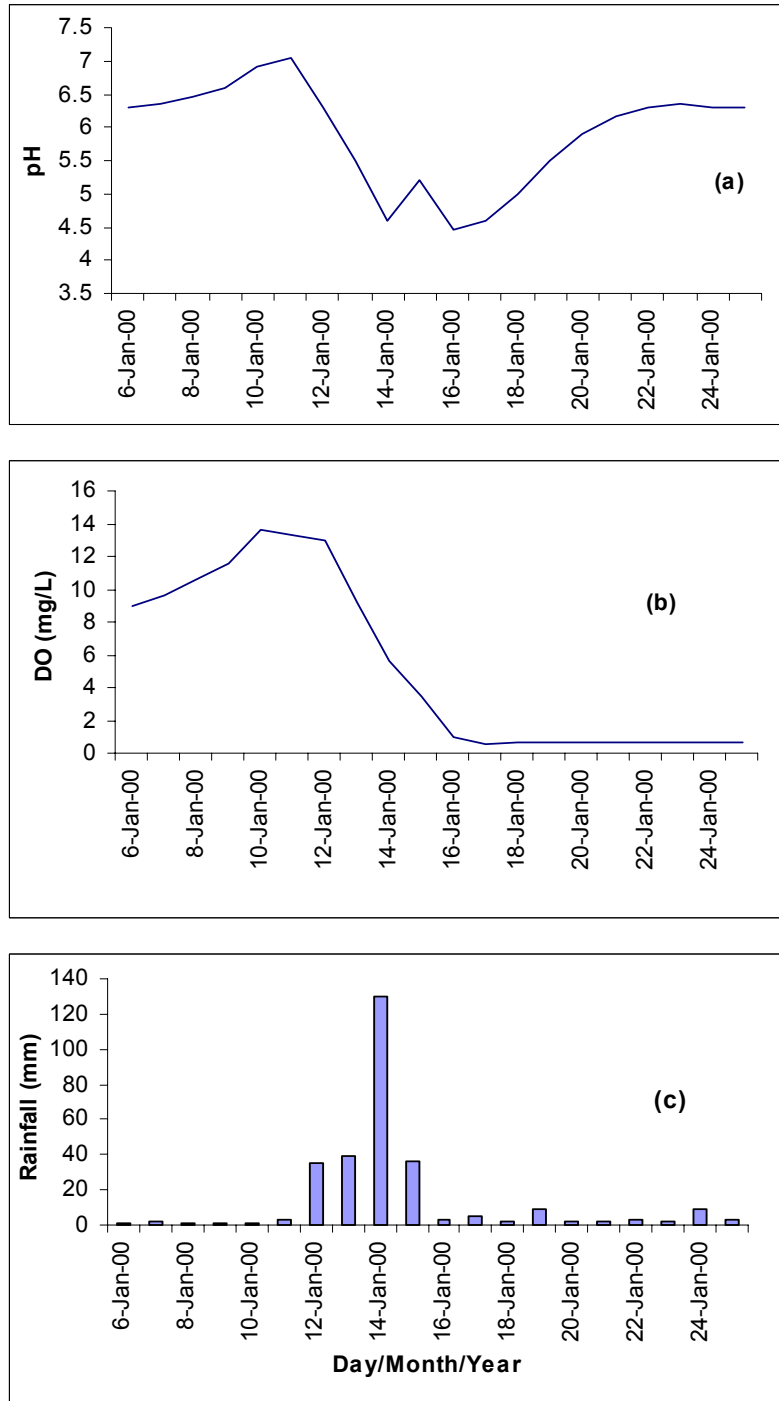
Figure 4. Changes in (a) pH and (b) DO of creek water at the water quality monitoring station, during and following (c) a heavy rainfall event

Acid Scalds

Figure 5 shows the distribution of pH, EC and Cl/SO$_4$ along the various investigated soil profiles. EC and Cl/SO$_4$ are highly variable among the investigated soils collected from different sites. However, all of the investigated scalded soils have an extremely acidic topsoil (0–0.6 m) although the pH in the subsoil layer varies from strongly acidic to neutral. The strong variation in EC (whole profiles) and pH (sulfidic subsoil layers) among the various sites reflects that the investigated scalded acid sulfate soils originate from sediments with different salinity conditions and that the sulfides in the soils have oxidized to differing degrees. The acidified topsoil layers are sulfide free, except at the Hawkesbury site (refer to Table 1). Detailed research on acid sulfate soils at some sites on the NSW coast has suggested that the topsoil layer of most acid sulfate soils might originate from non-sulfidic sediments deposited during freshwater flooding (e.g. Lin and Melville, 1993; Lin et al., 1998). It is therefore likely that acidification of the topsoil layer in the investigated soils was not caused by *in situ* sulfide oxidation. Upward translocation of acid materials, through capillary action, from the underlying oxidized sulfidic layer is possible. However, at several sites the pH in the oxidized sulfidic layers is higher than that in the overlying non-sulfidic topsoil layers. This suggests that there may also be lateral inputs of acid into the scalds. In our experience, acid sulfate scalds almost always occur at locations with low surface elevations, relative to their surrounding areas. Such hollows may act as sinks to receive acid runoff from the surrounding areas. Therefore, lateral inputs of acid materials could contribute to the acidification of the topsoil layers in the acid sulfate scalds.

Tables 2 and 3 provide a comparison of a range of soil chemical properties between the scalded and the non-scalded acid sulfate soils at the Macleay site. There is a clear trend where the scalded soils have lower total carbon and soluble phosphorus, and greater titratable soluble acidity, EC, soluble Al, Mn and Zn concentrations, compared to the adjacent non-scalded acid sulfate soils. The lower organic carbon contents of the scalded soils are a direct consequence of land scalding. The greater soil acidity and EC value in the scalded hollows, relative to their adjacent non-scalded soils may be attributed to inputs of acid runoff from the surrounding areas, as well as upward movement of soluble salts and acid sulfate materials, through capillary action, from the underlying sulfidic sediments.
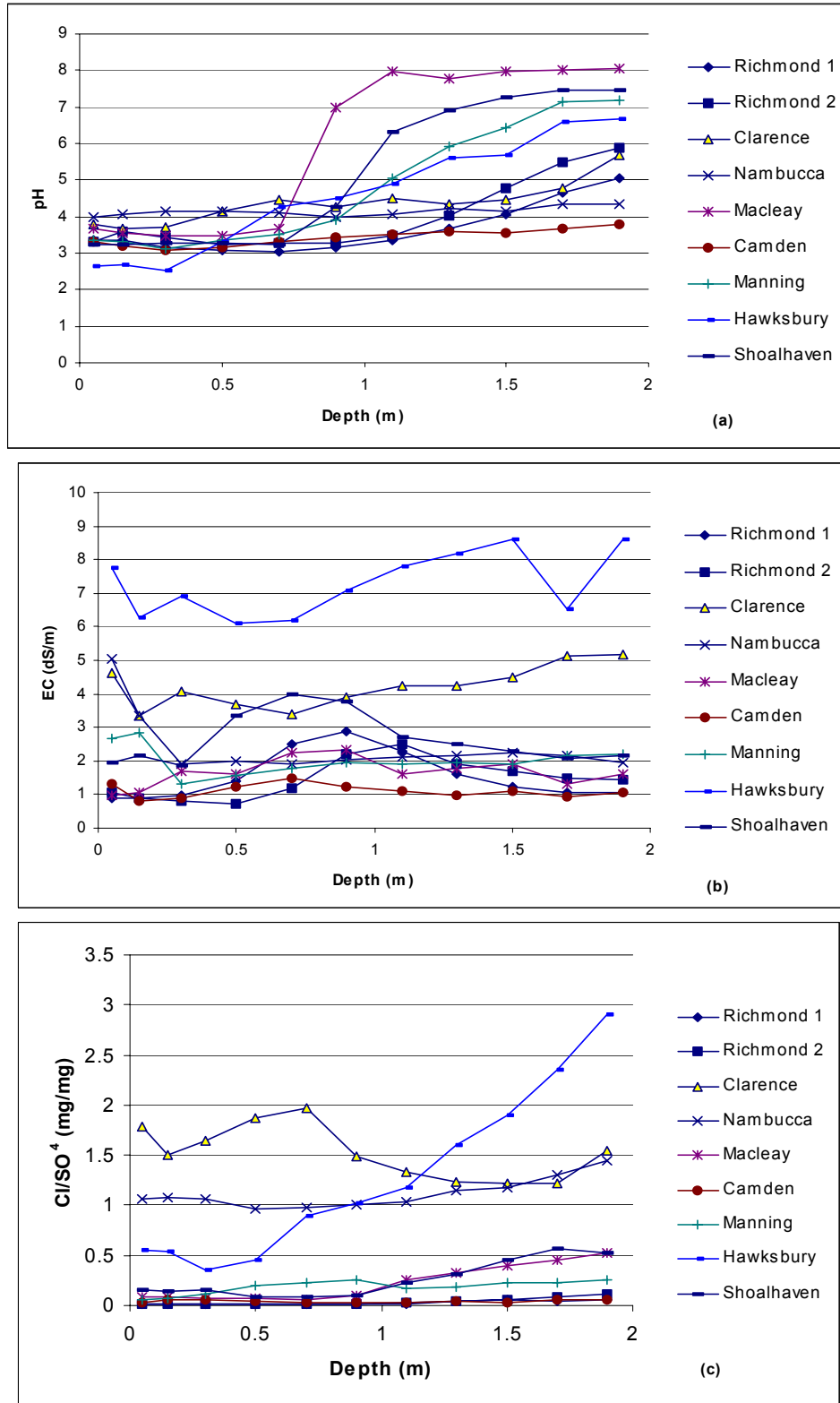
Fig. 5 Vertical distributions of (a) pH, (b) EC, and (c) Cl/SO_4 along various soil profiles of the investigated acid sulfate scalds
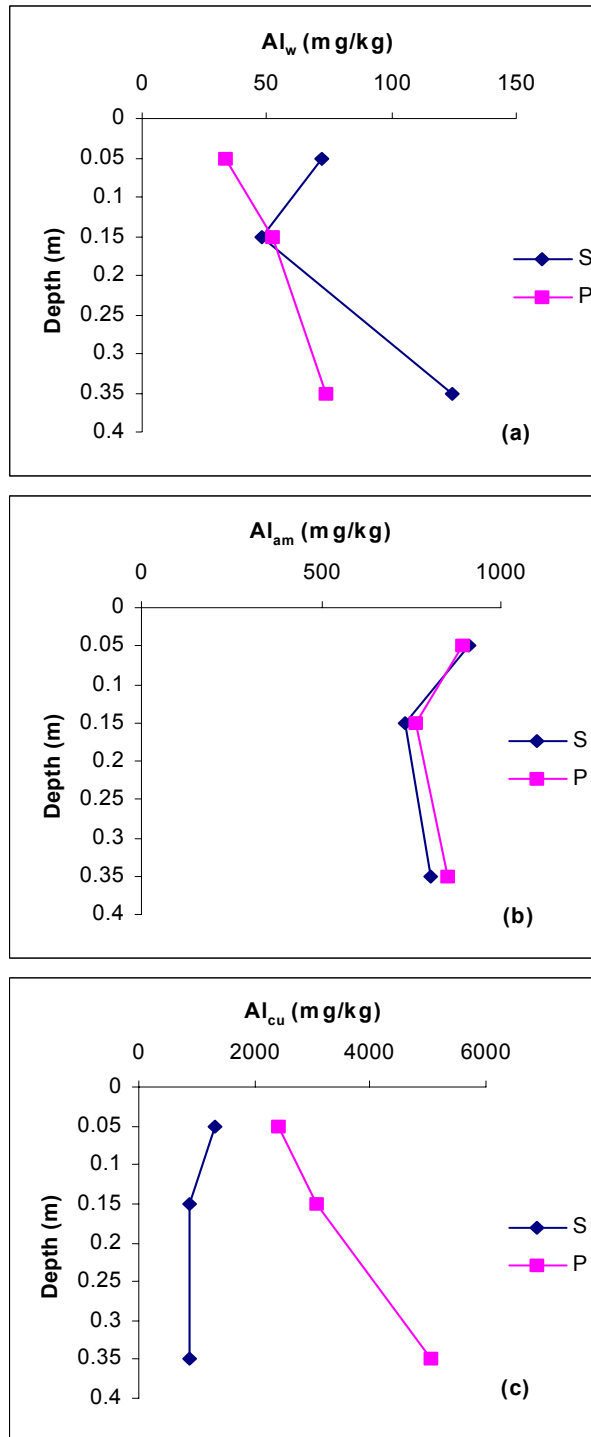
Figure 6. Comparison of (a) Water extractable Al, (b) NH_4Cl extractable Al, and (c) $CuCl_2$ extractable Al between the scalded soil and the adjacent non-scalded paddock soil at the Macleay site

Table 2 pH, titratable acidity, soluble phosphorus, total nitrogen and total carbon in scalded and non-scalded soils at Macleay site

Parameter		Depth (m)		
		0 - 0.1	0.1 –0.2	0.2 – 0.4
pH	S[1]	3.89	3.53	3.46
	P[2]	4.07	4.19	3.93
Soluble acidity (mmol/kg)	S	15	11	15
	P	2.0	5.5	6.0
KCl extractable acidity	S	69	25	25
(mmol/kg)	P	67	29	63
Soluble phosphorus	S	0.56	0.46	0.33
(mg/kg)	P	1.30	2.05	0.35
Total nitrogen (%)	S	0.59	0.76	0.79
	P	1.25	1.15	0.90
Total carbon (%)	S	10.9	2.16	1.3
	P	24.9	24.7	22.5

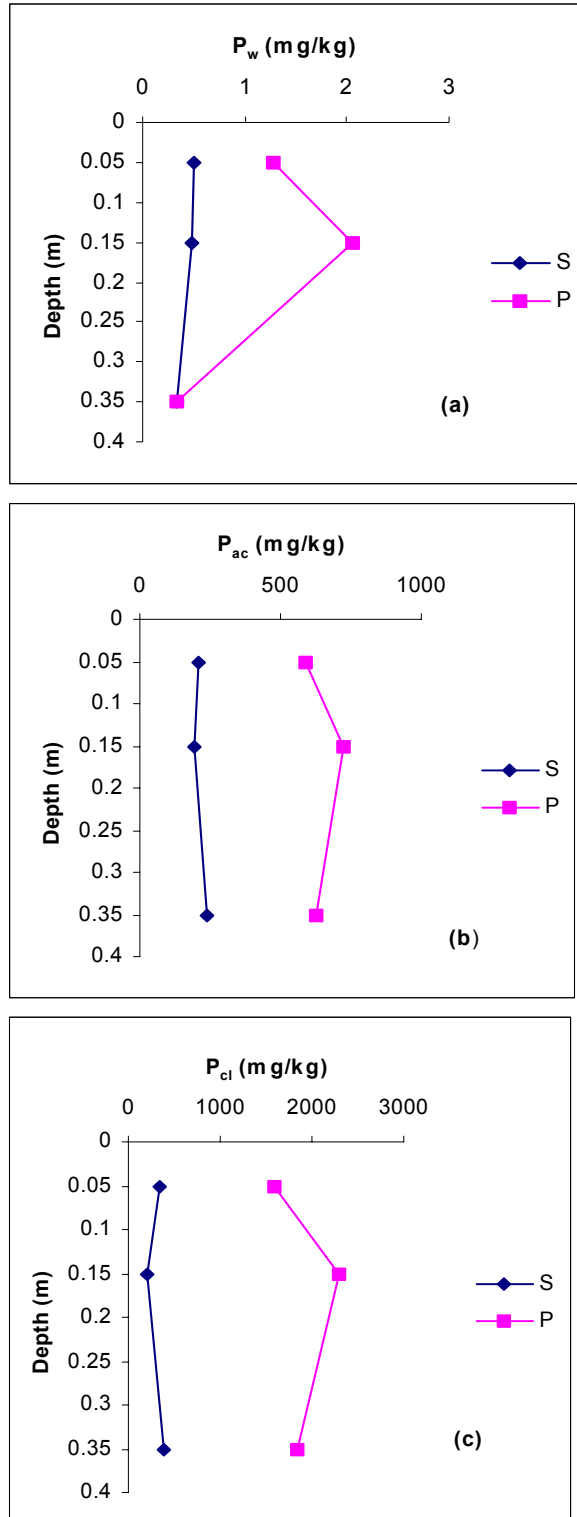S[1]: scalded soils

P[2]: non-scalded paddock soils

Figure 7. Comparison of (a) water extractable P (P_w), (b) acid ammonium oxalate extractable P (P_{ac}), and HCl extractable P (P_{cl}) between the scalded soil and the adjacent non-scalded paddock soil at the Macleay site

Table 3 EC and various metal concentrations in the water extracts

Parameter		Depth (m)		
		0 - 0.1	0.1 –0.2	0.2 – 0.4
EC (dS/m)	S[1]	0.79	0.89	1.98
	P[2]	0.03	0.06	0.49
Soluble Al (mgkg)	S	71	50	122
	P	33	53	76
Soluble Mn (mg/kg)	S	11.5	10.2	20.9
	P	2.30	5.06	4.79
Soluble Na (mg/kg)	S	200	190	346
	P	60	113	135
Soluble K (mg/kg)	S	17.0	16.1	12.2
	P	2.52	8.89	15.1
Soluble Fe (mg/kg)	S	13.2	10.6	14.5
	P	5.93	45.5	2.99
Soluble Zn (mg/kg)	S	1.90	1.60	3.05
	P	0.57	3.35	1.12

S[1]: scalded soils

P[2]: non-scalded paddock soils

The organic matter content (as indicated by total C % and field observation) is much lower in the scalded acid sulfate soil than in the acid sulfate soil of the adjacent grazing paddock. Although the water titratable acidity is much greater in the scalded acid sulfate soil than in the non-scalded acid sulfate soil, the KCl titratable acidity is similar in both soils (refer to Table 2). This is actually a reflection of the difference between water and KCl extractable Al in both soils (Figs. 6a and 6b). The above result suggests that larger amounts of Al are adsorbed on the negatively charged surfaces of organic-mineral complexes in the non-scalded soil than in the scalded soil. Possibly, the much higher organic matter content is responsible for the stronger Al adsorption in the non-scalded soil. The effect of organic matter on the retention of Al is even clearer from the comparison of $CuCl_2$ extractable Al between the scalded soil and the non-scalded soil. In addition to soluble and exchangeable Al, $CuCl_2$ extractable Al includes Al

species that are tightly complexed with organic matter and thus are not extractable using 1 M KCl. From Fig. 6c, it can be seen that $CuCl_2$ extractable Al is much greater in the non-scalded soil than in the scalded soil. This suggests that retention of Al by organic matter is likely to contribute to the reduction of Al toxicity in the non-scalded soils.

Figure 7 shows a comparison of various P fractions between the scalded soil and non-scalded soils at the Macleay site. Although the scalded soil has a lower concentration of soluble P (P_w) than the non-scalded soil, the corresponding lower acid oxalate and HCl extractable phosphorus concentrations (P_{ox} and P_{cl}) in the scalded soil do not suggest that phosphate retention is stronger in the scalded soil than in the non-scalded soil. This trend is also clear for the soils at the Shoalhaven site (data not shown). However, at the Manning site where the organic matter content is relatively high in the scalded soils, the HCl extractable P is also high (data not shown). The relationship between organic matter and insoluble P observed in this study suggests that the accumulation of P in the topsoil may be mainly through biological processes that are associated with plant growth. No matter what the cause is, the low reserve of P in the scalded soils suggests that the availability of P may be insufficient in the scalded soils even after liming to raise pH.

Implications for remediation

The findings of this study have important implications for the rehabilitation of these acid sulfate wetlands. It is likely that the major soil constraints for re-vegetation of the scalded acid sulfate soils include high acidity, Al, Mn and Zn toxicity and low P availability. Forced leaching by tidewater could assist in the removal of acid materials from the scalds, but this would cause off-site environmental problems by exporting acidic and toxic materials to the adjacent waterways. From the viewpoint of on-site treatment, to enable the establishment of appropriate vegetation species in the scalds, application of liming materials and P fertilizers will be necessary to reduce the soluble acidity, immobilize soluble Al, Mn and Zn, and increase P availability. However, soil salinity remains a problem. Therefore, where possible, salts and acid materials should be partially leached out of the scalds by drainage with appropriate measures for drain water treatment (e.g. drain liming). Because the higher soluble Al level is related to the lower organic matter content in the scalded soils, which have weaker capacity to retain soluble Al, compared to the adjacent non-scalded soils, rehabilitation of these scalded lands should

therefore involve addition of organic matter. Increases in the organic matter content could also reduce Mn and Zn toxicity (Sumner et al., 1991) and the salinity by increasing cation exchange sites of the soils, which adsorb more soluble salts.

The acid discharge from acid sulfate wetlands represents a severe environmental threat to the estuarine ecosystems (e.g. Callinan et al., 1993; Corfield, 2000). This is further complicated by the concurrent de-oxygenation in estuarine waters. Inundating acid sulfate soils is a widely adopted practice to reduce soil acidity in many Southeast Asian countries where the focus is placed on the improvement of soil conditions for paddy rice cultivation. However, in Australia, the major concerns have been the off-site environmental impacts of acid sulfate soils. Given the fact that most acid sulfate soils on the NSW coast contain large amount of existing acidity, either in soluble or retained forms, maintenance of water saturation in acid sulfate soils may minimize further sulfide oxidation and temporarily raise soil pH, but will not prevent estuarine waterways from acidification because although hydrogen ion is consumed during iron reduction, the export of ferrous Fe and subsequent oxidation will regenerate equal amount of acidity in the estuarine waterways. Addition of equivalent amounts of acid neutralizing agents, such as lime to eliminate soil acidity is effective but may be cost-prohibitive for environmental remediation of broadacre agricultural lands. Where the environmental goal is to reduce acid drainage, treatment of drain water appears to be a more cost-effective management strategy.

Acknowledgments

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