The effects of increasing salinity on exchange processes in coastal lowland acid sulfate soils

Vanessa NL Wong[A], Scott G Johnston[A], Richard T Bush[A], Leigh A Sullivan[A], Edward D Burton[A], Peter G Slavich[B]

[A]Southern Cross GeoScience, Southern Cross University; PO Box 157, Lismore NSW 2480, Australia
[B]Wollongbar Primary Industries Institute; New South Wales Department of Industry and Investment; 1243 Bruxner Highway, Wollongbar NSW 2477, Australia

Abstract
10 coastal lowland acid sulfate soils (CLASS) from floodplains in eastern Australia were subjected to increasing seawater concentrations to determine the effects of exchange processes on metal desorption due to increasing ionic strength. Soils were subjected to one of six treatments; 0%, 10%, 20%, 50%, 80% or 100% seawater diluted in deionised water. pH decreased with increasing seawater concentration. In general, concentrations of Al, Cd, Fe^{2+} and Mn increased in soils sampled from levees, organic and mineral sulfuric horizons with increasing salinity. Increasing trace metal concentrations with increasing seawater concentration is attributed to both exchange processes and pH effects. The increasing ionic strength of the seawater treatments displaced trace metals and protons adsorbed on sediments. These processes have implications for rapid water quality changes in CLASS environments when subjected to seawater inundation.

Key Words
Climate change, sea level rise, desorption

Introduction
Coastal lowland acid sulfate soils (CLASS) frequently contain high concentrations of acidity and trace metals. These soils commonly occur in large, low elevation (0-1 m Australian Height Datum; AHD) backswamp basins on coastal floodplains in eastern Australia. In these backswamp locations, the mineral sulfuric horizon is frequently close to the surface (< 1 m) capped by a thin layer of fluvial sediments and hence, can be an important contributor to surface water quality due to upward capillary and advection processes. Increasing ionic strength as a result of seawater inundation will alter decomposition and geochemical processes in sediments, surface- and groundwaters. In particular, the addition of seawater can increase the concentrations of aqueous Fe^{2+}, Al and Si (Mkadam *et al.* 2006; Portnoy and Giblin 1997) and decrease pH (Wright *et al.* 1988). Previous studies have shown that reflooding of CLASS can result in reductive mobilisation of a number of trace metals, which has implications for water quality in these areas (Burton *et al.* 2008).

Due to the low elevation and location of these backswamp basins, which are at, or below sea level, there is a high susceptibility to pulses of saline water caused by saltwater intrusion, storm surge, king tides and rising sea levels. This risk will increase in the future with predicted increases in sea level and extreme events due to climate change. This study aims to determine the effects of increasing ionic strength on exchange processes and trace metal desorption caused by increasing salinity in CLASS sediments.

Materials and Methods

Site Description and Field Sampling
Soils were sampled from three CLASS backswamp located on estuarine Holocene sediments; Tuckean (Tuck), Rocky Mouth Creek (RMC) and Shark Creek (SC), in the sub-tropical region of eastern Australia. The Tuckean and Rocky Mouth Creek backswamps are located in the mid-estuary of the Richmond River. The Shark Creek backswamp is located in the lower Clarence River estuary.

Bulk soils were sampled from three horizons at each site; levee, organic and mineral sulfuric horizons. Each levee horizon was sampled from the 0 – 0.1 m depth and was located on a natural levee of the CLASS backswamp. The organic horizon was sampled from the 0 – 0.1 m depth and located in the CLASS backswamp. An additional organic horizon was sampled in a forest dominated by tea tree (*Melaleuca quinquenervia*) at the SC site (termed SC Melaleuca). The mineral sulfuric horizon was sampled from the same location as the organic horizon, and characterised by the presence of jarosite. This horizon occurred at

a depth of 0.6-0.8 m at the Tuck and SC sites, and 0.7-0.9 m at the RMC site. Samples were placed into polyethylene bags and stored at 4°C until analysis.

Sample Preparation and Laboratory Analysis
Bulk soils were oven-dried at 40°C for 48 hours and lightly crushed to pass through a 2 mm sieve. Soil pH, EC and soluble cations were determined on 1:5 soil: water extracts (Rayment and Higginson 1992). Exchangeable cations were extracted with 1:5 soil:2M $BaCl_2$/NH_4Cl (Rayment and Higginson 1992). Where the $EC_{1:5} \geq 0.3$ dS/m, soluble salts were removed by washing three times with an ethanol/glycerol solution. Soluble and exchangeable cations were determined by inductively coupled plasma-mass spectrometry (ICP-MS).

Samples were subjected to one of six treatments; 0, 10, 20, 50, 80 or 100 % synthetic seawater. The synthetic seawater consisted of the major cations and anions found in natural seawater (Cavanaugh 1975). 5 g of soil was extracted with synthetic seawater at a ratio of 1:10. Samples were shaken on an orbital shaker for four hours, centrifuged and filtered through a 0.45 µm filter. The extracts were analysed for pH and EC. Major cations and trace metals were determined on the extracts by ICP-MS. Aqueous Fe speciation was determined using 1, 10-phenanthroline (APHA 2005). Fe^{3+} was determined from the difference between total Fe and Fe^{2+} following reduction with hydroxylammonium chloride.

Results and Discussion

The bulk soil characteristics are shown in Table 1. The levee soils had higher pH and lower EC compared to the organic and mineral sulfuric soils from the same site. The organic and mineral sulfuric soils were saline and acidic with high concentrations of soluble and exchangeable Al.

Table 1. Soil characteristics prior to treatment.

Horizon	Site	pH$_{1:5}$	EC$_{1:5}$ (dS/m)	Soluble Al	Cd	Fe	Mn	Exchangeable Al	Cd	Fe	Mn
				(mmol/kg)				(cmol$_c$/kg)			
Levee	RMC	5.68	0.06	7.07	nd	3.49	0.25	22.0	0.01	0.00	283.06
	Tuck	4.96	0.08	1.81	nd	0.68	0.31	370.8	0.00	0.00	46.68
	SC	5.57	0.08	3.00	nd	1.71	0.19	20.4	0.09	0.00	51.15
Organic	RMC	3.68	1.26	122.76	nd	0.53	2.23	2045.7	0.00	0.00	4.07
	Tuck	3.99	0.98	28.94	nd	1.47	3.68	990.2	0.01	0.00	11.10
	SC	4.43	0.53	2.49	nd	0.21	0.78	541.8	0.01	0.00	11.74
	SC Melaleuca	3.61	1.85	44.61	nd	1.86	6.85	1150.3	0.01	13.83	18.85
Mineral sulfuric	RMC	3.31	1.58	95.08	nd	1.79	2.26	1791.4	0.00	0.61	4.13
	Tuck	3.26	1.56	58.47	nd	5.12	5.10	1309.9	0.00	19.57	9.39
	SC	3.96	0.33	0.69	nd	0.09	0.53	852.4	0.00	0.00	7.74

EC was lowest in the 0% seawater treatment in all horizons at all sites, and increased following treatment with increasing seawater concentration due to the addition of soluble salts (Figures 1a, 1b and 1c). In the levee sediments, pH decreased with increasing seawater concentration, reaching a minimum with the 20% treatment (Figure 1). In the mineral sulfuric sediments, samples from Shark Creek showed a similar trend, decreasing with increasing seawater concentration to a minimum in the 20% treatment. Conversely, pH in sediments from RMC and Tuck showed little change between treatments. Similarly, in the organic horizon, the pH of sediments from RMC and Tuck showed little change between treatments, while those from RMC and SCM decreased with increasing seawater concentration to a minimum with the 20% seawater treatment.
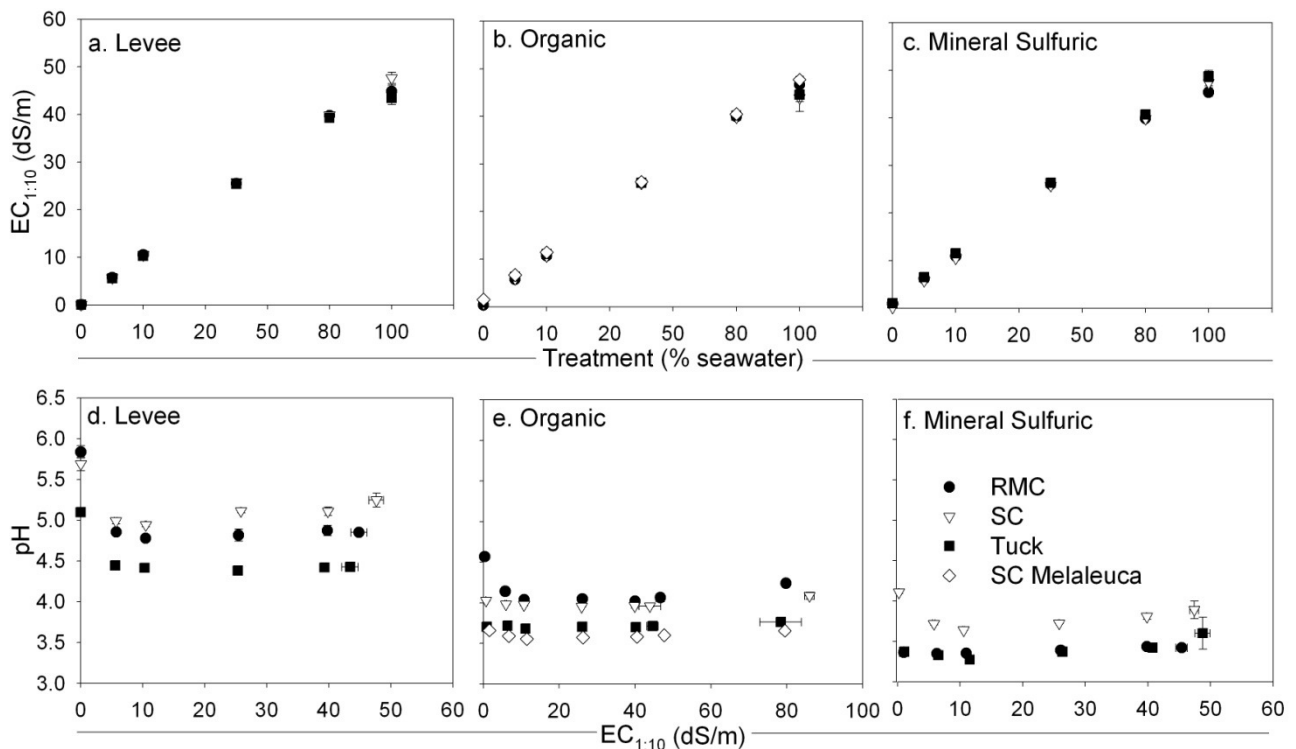
Figure 1. EC$_{1:10}$ of soil extracts following treatment with seawater in sediments from a) levee; b) organic, and c) mineral sulfuric horizons; and pH$_{1:10}$ of soil extracts following treatment with seawater in sediments from d) levee; e) organic, and f) mineral sulfuric horizons. Error bars indicate standard deviation.
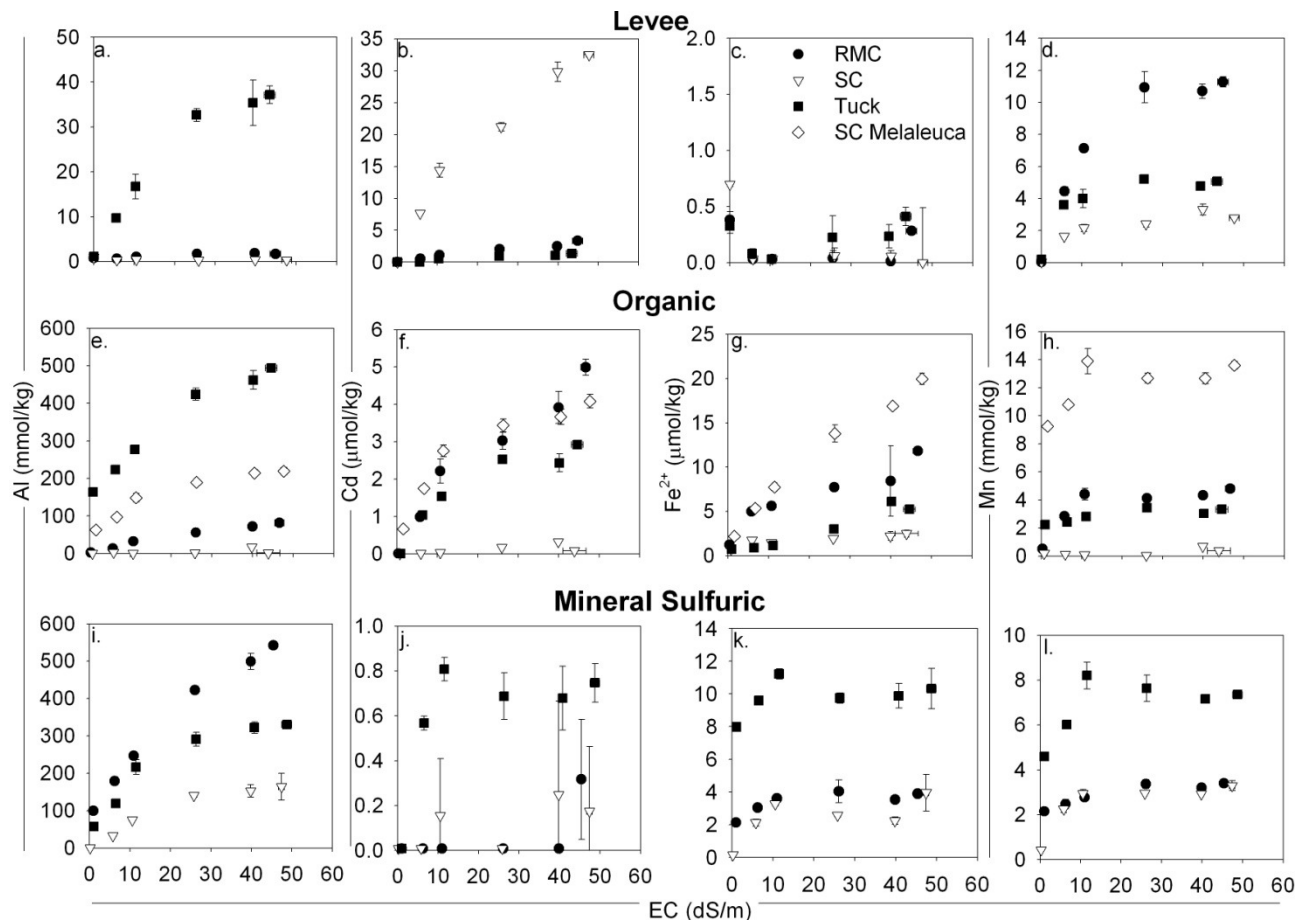

Figure 2. Concentrations in the levee sediments of a) Al; b) Cd; c)Fe^{2+}; d) Mn; in the organic sediments of e) Al; f) Cd; g)Fe^{2+}; h) Mn; and mineral sulfuric sediments of i) Al; j) Cd; k)Fe^{2+}; l) Mn following treatment with seawater . Error bars indicate the standard deviation.

In the levee sediments, Al concentrations increased with increasing EC at RMC and Tuck sites (Figure 2a). The Tuck site had the highest exchangeable Al concentrations in the levee sediments compared to RMC and SC sites. Cd concentration increased with increasing salinity, and was at least six times higher compared to other horizons at the same site. Similarly, in the levee sediments at the RMC and Tuck sites, Cd concentrations increased with increasing salinity but were substantially lower than that found at the SC site (Figure 2b). Concentrations of Mn increased with increasing seawater concentration to 50% seawater at all sites in the levee sediments (Figure 2d).

In the organic horizon sediments, Al concentrations increased with increasing salinity and were substantially higher than the concentrations found in the levee soils at the same site (Figure 2e). Cd concentrations increased with increasing salinity at the SC and SC Melaleuca sites (Figure 2f). At the RMC and Tuck sites, Cd concentrations increased with salinity to the 50% seawater treatment. Similarly, Fe^{2+} concentrations increased with increasing salinity (Figure 2g). The organic soils have the potential to release much more iron into solution compared to the other horizons. These soils released the highest concentrations of Fe^{2+} to solution, despite having generally lower soluble Fe^{2+} concentrations (Table 1). Mn concentrations generally increased with increasing salinity to the 20% seawater treatment in the organic horizon sediments (Figure 2h).

In the mineral sulfuric sediments, Al concentrations increased with increasing salinity and were an order of magnitude higher than the levee sediments from the same site (Figure 2i). Fe^{2+} concentrations increased with increasing salinity to 20% seawater at all sites (Figure 2k). Cd concentrations were generally lower in the mineral sulfuric sediments than the organic sediments at the same site (Figure 2j). Mn concentrations in this horizon showed a similar pattern to that found in the organic horizon sediments, increasing with salinity to 20% seawater treatment.

Increasing seawater concentration resulted in decreases in pH in all sediments. This is attributed to the displacement of adsorbed protons on the exchange surface. The higher ionic strength solution displaces those ions adsorbed on the surface of the soil particles. We suggest that the desorption of some pH dependent species such as Al and Fe are also partially driven by the decline in pH in addition to increasing ionic strength of the treatment solution. Similarly, the specific adsorption of Cd is also strongly pH dependent.

These exchange processes have implications for water quality in these environments. CLASS are highly susceptible to seawater inundation as a result of climate change induced sea level rise, while seawater intrusion at depth will impact on the mineral sulfuric sediments. The experimental results show that the initial addition of marine derived salts will result in a decrease in pH and increase in trace metals, even at low salt concentrations such as that found in brackish waters in estuarine environments.

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