Mobility and storage of metals, metalloids and trace elements in disturbed acid sulfate soils from a tidal estuary in South Australia

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Abstract

In Australia, acid sulfate soils (ASS) are widespread in both coastal and inland settings where they pose environmental hazards from acidification and metal mobilisation. In this study, three saturated soil-sediment profiles from distinct positions in a disturbed tidal ASS landscape were hydrogeochemically characterised. The soil profile geochemical data and surface water chemistry were compared in order to find evidence of metal, metalloid and trace element mobilisation. The results showed that concentrations of Cu, Ni, Pb, Zn, S, Al, Mg and Fe were elevated in the near-surface, oxidised layers of sulfuric materials of the ASS profile and were marginally elevated within nearby hyposulfidic material in circum-neutral stream sediments. Metals and metalloids, including Ni, Zn, Al and Fe, were leached to pore waters in sulfuric materials from which a range of salt efflorescences had precipitated. Acidic drain waters also contained elevated Al, Fe and other major cations and anions, but did not contain detectible concentrations of trace elements. Nearby circum-neutral stream waters only contained elevated concentrations of Fe. Leaching of trace metals was greatest at the surface of exposed sulfuric materials where salt efflorescences had formed. Covering sulfuric materials with mulch, soil or water could reduce metal mobilization by limiting salt precipitation at the surface.

Key Words

Sulfidic, sulfuric, monosulfide, pore water, metals, salt efflorescence.

Introduction

This study focussed on soil geochemical and hydrogeochemical data to find evidence of sources and pathways of metals, metalloids and trace elements in a coastal acid sulfate soil landscape located at Gillman, South Australia (Figure 1). Tidal influences were cut off from the Gillman area in 1954 when a bund wall was constructed to reclaim the area for agricultural and industrial purposes, causing sulfidic sediments to oxidise. Three soil-sediment profiles located at different positions along a toposequence were studied (Figure 2). The traverse covered former supra-tidal soils containing sulfuric materials and former tidal soils in which monosulfidic materials had developed. Vertical profiles of trace elements, focussing on toxic elements, were compared for soils, pore waters and load limits in surface waters of nearby streams and drains.

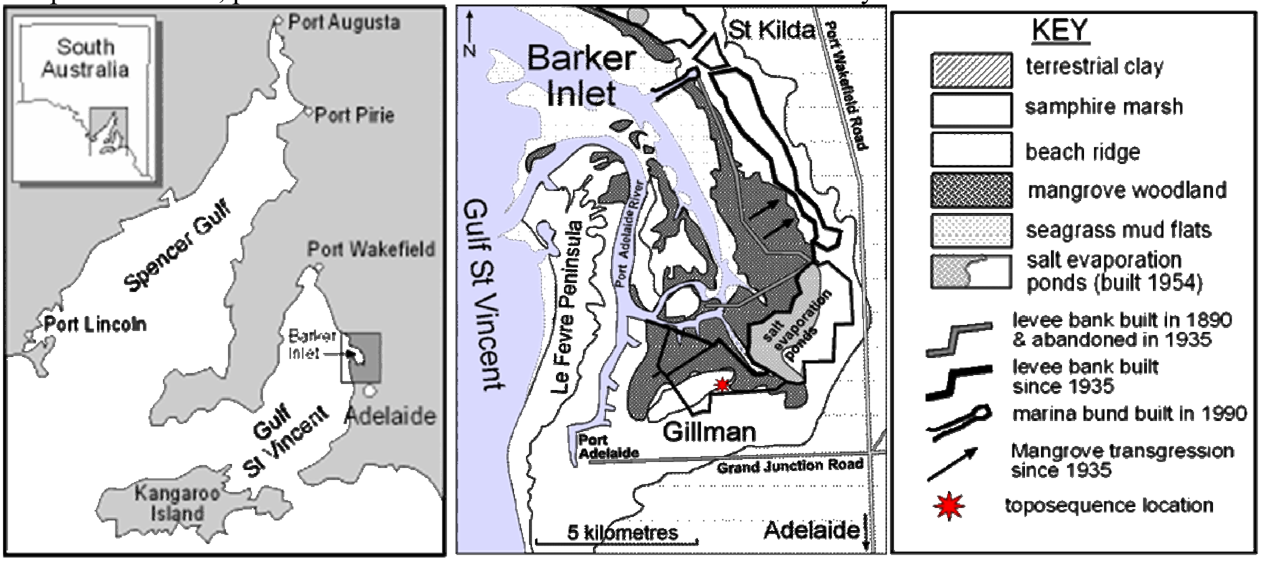

Figure 1. Barker Inlet, originally a tidal estuary, is located 20 km north of Adelaide, South Australia. This figure depicts the pre-European environment, overlain by a network of tidal barriers that were since installed. Toposequence 'A' (Figure 2) is located at Gillman where inter-tidal mangrove woodlands and supra-tidal samphire salt marsh were reclaimed for agriculture and industry in the 1950s. The land was soon abandoned due to severe acidification, salinity and storm-water ponding (from Fitzpatrick *et al*. 2008, Thomas 2010).

Methods

Soil chemistry was determined from selected layers in soil-sediment profiles BG 15 and BG P 5 (Figure 2). Total major and trace element analyses were determined on the < 2mm fraction of 11 bulk soil samples using X-ray fluorescence spectroscopy (XRF). Soil pore waters were collected using peepers; multi (35) chambered dialysis samplers, which have semi-permeable membranes that separate receiver solution from sediment and soil solution (e.g. van Oploo *et al.* 2008). Peepers were installed in saturated soil-sediments in February 2003 and left to equilibrate for 8 weeks. Water samples were analysed for major anions and cations and selected trace elements by ICP-OES. Mineralogy was determined by powder x-ray diffraction (XRD).

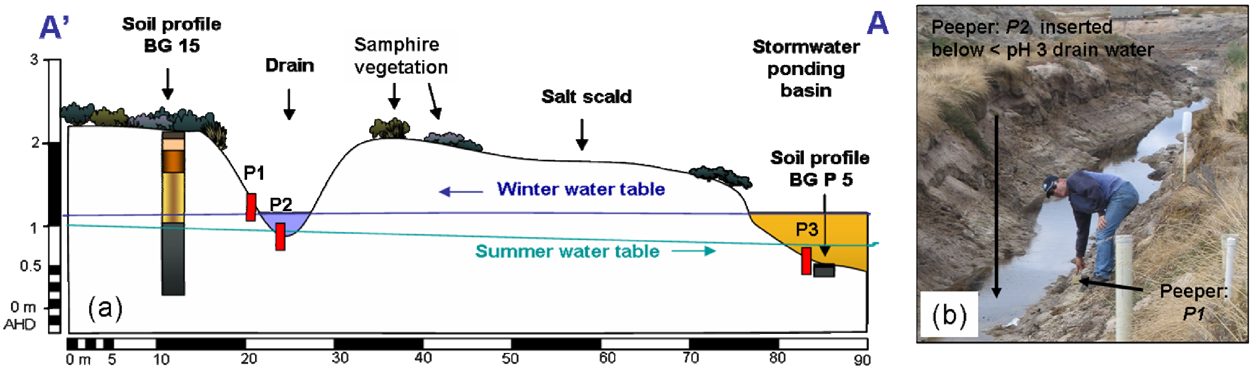

Figure 2. Schematic cross-section showing localities of soil-sediment profiles and peepers (P1, P2 and P3) along toposequence A'-A. The drain was excavated in August 2002 and was not open to the stormwater ponding basin.

Results

Soils

Metal concentrations (Cu, Ni, Pb and Zn) were elevated at the surface of soil-sediment profile BG 15 and marginally elevated at the surface of profile BG P 5 (Table 1). The source of metals was likely anthropogenic (e.g. Fitzpatrick *et al.* 2008, Thomas 2010). The soil pH (1:5) of profile BG 15 decreased with depth to a minimum pH of 2.3 at 110 cm, just above the summer water table. Below this depth soil pH gradually increased to pH 4.2 at the base of the profile. Soil EC was highest just above the water table, between 65 and 110 cm depth, at the level where salt efflorescences had accumulated on the drain wall (Figure 3). The soil pH and EC of subaqueous profile BG P 5 were relatively consistent with increasing depth (Table 1). Profile BG 15 comprised sulfuric materials and hypersulfidic materials (Fitzpatrick *et al.* 2008; Sullivan *et al.* 2009; Thomas, 2010). Sulfuric materials occurring between 30 cm and 120 cm depth contained significant acidity, in the form of titratable actual acidity (TAA) and retained acidity. Potential sulfidic acidity was highest between 95 cm and 120 cm, with chromium reducible sulfur (S_{CR}) concentrations up to 6.88 %, adding to a positive net acidity of 5000 mol H^+/t (Figure 3).

Subaqueous profile BG P 5 did not contain sulfuric materials. However, it did contain hyposulfidic materials (Sullivan *et al.* 2009): it did not experience a drop in pH by at least 0.5 unit to 4 or less after incubation, and monosulfidic materials. Occurrence of sulfidic materials was greatest between 0 cm and 5 cm with an acid volatile sulfur content of 1.15 % (AVS) and a reduced inorganic sulfur content of 0.95 % S_{CR}. The acid neutralising capacity (ANC) of most soil layers was not sufficient to neutralise the potential acidity, resulting in a positive net acidity (Figure 4).

Table 1. Selected soil chemical properties for soil-sediment samples from profiles BG 15 and BG P 5.

Profile	Layer	Depth (cm)		SiO_2	Al_2O_3	Fe_2O_3	MnO	SO_3	MgO	CaO	K_2O	P_2O_5	Sr	Cd	Cr	Cu	Ni	Pb	Zn	pH	EC
		from	to	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(1:5)	dS/m
BG 15	0A	0	5	55.63	14.93	8.79	0.05	0.14	2.82	0.52	2.95	0.31	77	1.5	96	25	18	112	131	8.03	0.75
	A	5	15	58.71	16.73	7.35	0.04	0.12	2.33	0.39	2.91	0.18	69	1.5	103	13	15	27	51	7.57	1.05
	2Ey1	25	30	76.43	9.54	4.00	0.01	0.37	0.92	0.27	1.82	0.06	45	1.5	63	7	3	11	26	4.42	3.04
	2Ey2	30	40	72.55	11.02	4.94	0.01	0.47	1.09	0.25	2.11	0.06	51	1.5	72	9	4	13	30	3.98	5.20
	3Bg	40	65	63.05	14.83	4.30	0.01	0.59	1.53	0.24	2.69	0.09	58	1.5	82	13	6	8	34	3.37	8.83
	4Bgj	65	95	37.80	9.60	10.70	0.01	1.90	1.28	0.33	3.16	0.09	67	1.5	58	11	2	18	25	3.15	23.90
	5Bigj	95	110	26.24	3.14	12.29	0.00	2.63	1.25	1.02	1.61	0.04	61	1.5	21	7	5	3	11	2.26	45.15
	6Bg2	120	150	89.58	3.66	0.76	0.00	0.76	0.29	0.13	1.02	0.01	30	1.5	46	5	1	1	6	4.12	3.89
	7Bg1	150	170	74.66	10.17	3.81	0.01	2.61	1.15	0.18	1.78	0.03	42	1.5	116	19	9	9	30	4.24	4.87
BG P5	Oge1	0	5	73.53	7.72	5.73	0.01	0.76	1.08	0.47	1.67	0.08	79	1.5	64	17	3	26	92	7.01	5.06
	Oge2	15	20	77.68	8.29	2.82	0.01	0.74	0.99	0.22	1.76	0.07	77	1.5	62	14	5	22	48	7.49	4.46
		LLD (ppm)		29	24	10	5	8	36	20	16	5	1	3	2	1	2	2	2		

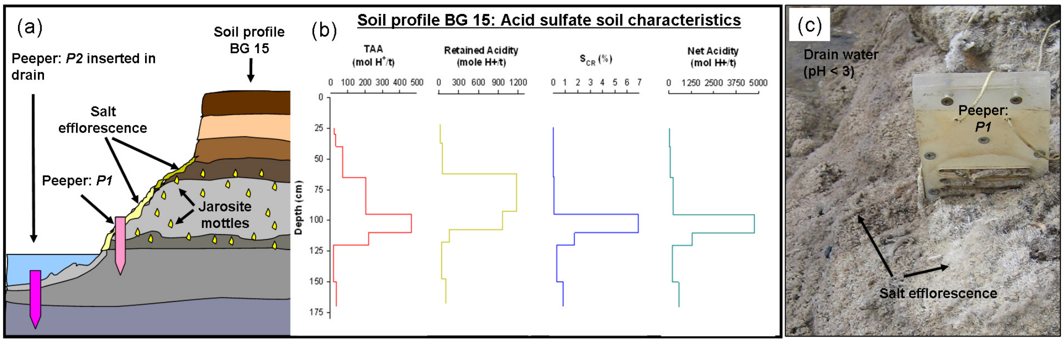

Figure 3. (a) – schematic cross section of the drain showing position of peeper P1 within the drain wall and peeper P2 in the bottom of the drain. (b) – down profile (to scaled with (a)) ASS characteristics (TAA, retained acidity, S_{CR}% and net acidity) for profile BG 15. (c) – salt efflorescences on the surface around peeper P1.

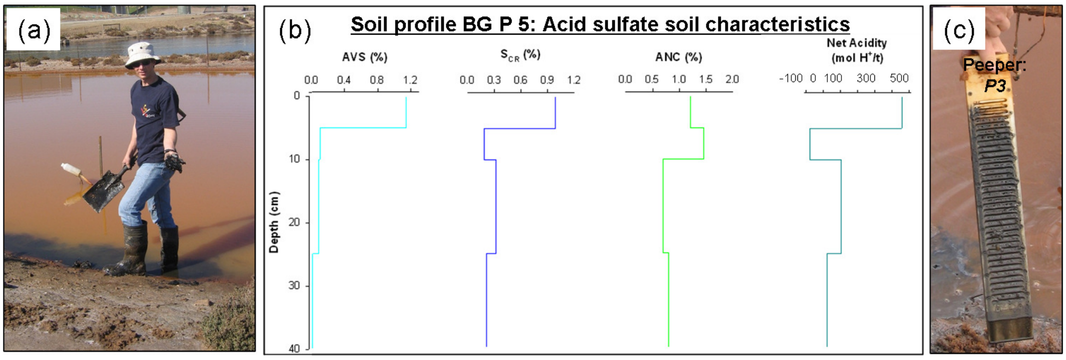

Figure 4. (a) – photo showing iron floc in surface water of the storm water ponding basin and disturbed monosulfidic material that formed at the sediment surface. (b) – acid sulfate soil characteristics (AVS, S_{CR}%, ANC and net acidity) of profile BG P 5. (c) – peeper P3 removed from the pond (profile BG P 5).

Pore waters and surface waters

Soil pore water chemistry collected by peeper P1, located in the oxic-acidic drain wall at profile BG 15 showed considerable variation in pH and EC as well as anions, cations and trace element concentrations from the surface to a depth of 35 cm (Figure 5). Most anion, cation and trace element concentrations were highest near the surface and decreased with depth, with Ca and Sr showing the opposite trend. Metals (Zn, Ni, Fe, and Al) were particularly elevated near the surface, where salt efflorescence occurred.

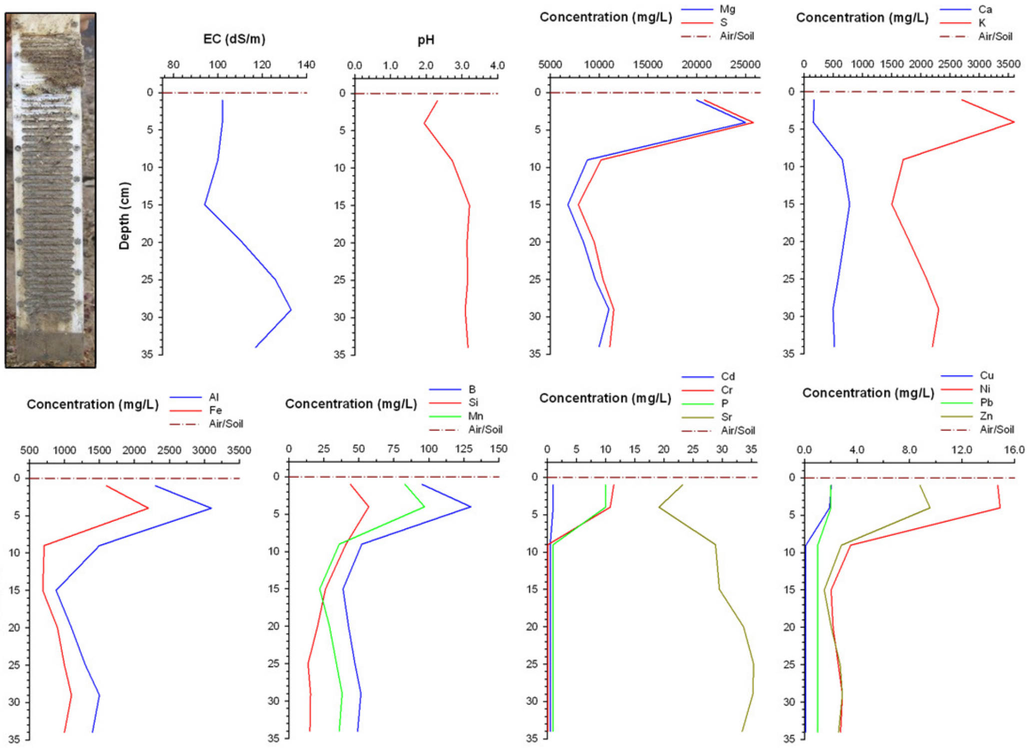

Figure 5. Down profile pore water chemistry collected by peeper P1, located within the drain wall.

Soil pore water chemistry collected by peeper P2, located in the oxic-acidic drain sediment, showed a trend for pH and EC similar to peeper P1, however the concentration of most trace elements fell below detection limits (Table 2). Calcium increased with depth below the water/sediment interface in P2. Drain surface water concentrations were generally higher than in P2 pore waters (Table 2). Soil pore water chemistry collected by peeper P3, located in the reducing-circum-neutral bottom sediment of the stormwater pond showed an increasing trend for pH and EC and major cations and anions with depth. Concentrations were considerably lower than in the oxic-acidic environments, with most trace elements being below detection limits (Table 2). Surface water concentrations were generally higher than in P3 pore waters, particularly Fe (Table 2).

Table 2. Maximum, minimum and mean values for selected pore water and surface water chemistry.

Peeper sample data		**Si**	**Al**	**Fe**	**Mn**	**S**	**Mg**	**Ca**	**K**	**P**	**B**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**pH**	**EC**
Porewater		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		dS/m
P1	max	57.1	3100	2200	97.0	25800	25000	780	3600	10	130.0	1.0	11.4	2.0	14.9	2.0	9.6	3.21	133.0
(n=9)	min	13.7	880	690	22.0	7870	6800	150	1500	1	38.7	0.5	0.1	0.1	2.0	1.0	1.5	1.94	94.0
	mean	27.5	1609	1133	45.7	13141	12178	504	2233	3	61.7	0.6	0.1	0.5	5.4	1.2	3.9	2.88	111.3
P2	max	36.8	900	840	29	8800	8200	1100	1800	1	37	0.1	0.1	0.1	0.2	0.1	0.1	3.88	112.6
(n=31)	min	0.1	28	330	2.5	3800	4100	550	1200	1	14	0.1	0.1	0.1	0.2	0.1	0.1	2.01	79.7
	mean	21.8	648	707	21	7325	6950	679	1606	1	30	0.1	0.1	0.1	0.2	0.1	0.1	2.55	94.1
P3	max	0.1	1	47	0.1	1200	1400	410	340	1	1.0	0.1	0.1	0.1	0.2	0.1	0.1	8.19	55.2
(n=33)	min	0.1	1	1	0.1	690	940	260	230	1	1.0	0.1	0.1	0.1	0.2	0.1	0.1	6.62	39.1
	mean	0.1	1	7	0.1	879	1085	328	276	1	1.0	0.1	0.1	0.1	0.2	0.1	0.1	7.36	44.9
Surface water																			
P2 (n=4)	mean	44.3	995	870	30.9	9350	8700	540	1900	1	40.5	0.1	0.1	0.1	0.2	0.1	0.1	1.95	95.7
P3 (n=2)	mean	9.4	10	260	2.5	735	915	300	233	1	1.0	0.1	0.1	0.1	0.2	0.1	0.1	6.50	53.1
	LLD	0.2	2	2	0.2	10	10	10	10	2	2	0.2	0.2	0.2	0.4	0.2	0.2	0.01	0.1

Salt efflorescences and iron oxyhydroxide minerals

Salt crusts formed on the exposed pit face by the wicking and evaporation of soil solution containing Na^+, Cl^- and SO_4^{2-}. White “fluffy” salt crust consisting of halite, gypsum and pentahydrite ($MgSO_4.5H_2O$) occurred where soil pH, clay and carbonate content was higher, in the upper 30 cm of drain wall. Some goethite (FeOOH), occurred between 5 and 30 cm as yellowish orange mottles. Lower in the profile (between 30-75cm) a thicker (5-10 mm thick) creamy white to yellow crust formed on acidic quartz sands and was dominated by halite, gypsum and starkeyite ($MgSO_4.4H_2O$). Thick agglomerations (5-30 mm thick) of yellowish green salts comprising tamarugite [$NaAl(SO_4)_2.6H_2O$], sideronatrite [$Na_2Fe(SO_4)_2(OH).3H_2O$], jarosite and pentahydrite ($MgSO_4.5H_2O$) formed where TAA, retained acidity and potential sulfidic acidity was greatest (Figure 3). These largely soluble salts dissolve during rain events and contribute to acidity and metal content in drainage waters. The salt minerals are indicators of subsurface biogeochemical soil-water processes (e.g. pH, Eh, EC and parent mineralogy) operating in this landscape (e.g. Fitzpatrick *et al.* 1997).

Conclusion

Sulfuric acid that has been produced in profile BG 15 should remain in the soil profile due to the low hydraulic gradient of the area, unless this is altered by drains or pumping. Open drains allow soluble sulfate-containing minerals that are a store of Na, Ca, Mg, Cl, Sr and SO_4 and metals (e.g., Al, Fe, Zn, Ni) to precipitate in oxic-acidic conditions and may present an environmental hazard to connected water bodies following rainfall. The salts (containing Fe and S) may also contribute to the formation of the monosulfidic materials in water bodies lower in the landscape where soil conditions are reducing and circumneutral.

References

Fitzpatrick RW, Self PG (1997) Iron oxyhydroxides, sulfides and oxyhydroxysulfates as indicators of acid sulphate surface weathering environment. In ‘Soils and Environment: Soil Processes from Mineral to Landscape Scale. Advances in GeoEcology 30’. (Eds K Auerswald, H Stanjek , JM Bigham) pp. 227-240. (Catena Verlag: Reiskirchen, Germany).

Fitzpatrick RW, Thomas BP, Merry RH (2008) Acid Sulfate Soils in Gulf St Vincent. In ‘Natural History of Gulf St Vincent’. (Eds SA Shepherd, S Bryars, IR Kirkegaard, P Harbison, JT Jennings) pp. 106-120. (Royal Society of South Australia Inc., Adelaide, South Australia).

Sullivan LA, Fitzpatrick RW, Bush RT, Burton ED, Shand P, Ward NJ (2009) Modifications to the classification of acid sulfate soil materials. Southern Cross GeoScience Tech Report 309.

Thomas BP (2010) Coastal acid sulfate soil-landscape relationships in temperate climates: Linking soil processes to hazard management in the Barker Inlet, Gillman area, South Australia. PhD Thesis, Adelaide University, Earth and Environmental Science Dept.

van Oploo P, White I, Ford P, Melville MD, Macdonald BCT (2008) The use of peepers to sample pore-water in acid sulfate soils. *Eur. J. Soil Sci.* **59,** 762-770.