Coastal acid sulfate soil processes in Barker Inlet, South Australia

Doctor of Philosophy

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Chapter Nine

9. Geochemistry and Hydrochemistry: distribution and behaviour of elements

Acid sulfate soils in both coastal and inland settings pose environmental hazards from acidification and metal mobilisation, particularly in areas, such as the Gillman study site, where the site history review indicated numerous possible contaminant sources (e.g. ammunition fired from Dean Rifle Range; refer to Chapter 3).

The aim of this chapter was to study the geochemistry of bulk soil to characterise soil contaminants and their spatial relationships within the Gillman and St Kilda study sites. Soil pore water chemistry was used at selected soil sediment profiles in order to find evidence of metal, metalloid and trace element mobilisation within the acid sulfate soil landscape. Trends in profile data were linked to pedological, hydrological and biogeochemical processes to help explain the distribution and movement of contaminants. This was in turn used to improve hazard descriptions for the acid sulfate soil map units.

Geochemistry was determined for 94 bulk soil samples from 24 soil profiles located within the St Kilda and Gillman study sites (Table 9-1), which were representative of the map units described previously. Linking contaminant issues to map units was particularly important for the Gillman study site where elevated metal concentrations were predominantly associated with topographically high areas containing non-acid sulfate soil materials, as well as former tidal creek depressions containing monosulfidic materials. The characteristics of metal contaminants within these landscapes should be considered by land managers when developing acid sulfate soil management plans.

Soil solution chemistry was hydrochemically characterised in six ‘type’ soil profiles (Table 9-1) located along two toposequences, one at Gillman and one at the St Kilda study site. The Gillman toposequence (four profiles) traversed from a disturbed, formerly intertidal landscape (profiles BG 15, BG P 5, BG 28) to a less disturbed intertidal creek depression (profile BG 24). The toposequence at St Kilda (two profiles) crossed an undisturbed intertidal landscape from a relatively elevated position within mangrove woodland (profile BSK 4) to a low lying, water filled tidal creek depression (profile BSK 5).

Table 9-1 Soil profiles from the Gillman and St Kilda study sites that were geochemically and hydrochemically characterised. In most cases the profiles selected for characterisation were ‘type’ profiles (identified by **red** text) that have been described in previous chapters. The location of profiles is shown in Figure 5-1 and Figure 6-1.

Map unit no.	**Geochemical Characterisation**		**Hydrochemical Characterisation**	
	Soil Profile ID	No. of samples analysed	Soil Profile ID	No. of samples analysed
1	**BG 30**, **BG P 5**, BG 19	5	[2]BG P 5	36
2	**BG 4**, **BG 28**, **BG 21**, BG 23	11	**BG 28**	5
3	**BG 32**	3	NA	
4	**BG 17**, **BG 22**, **GGT 5**, BG 29	12	NA	
5	**BG 15**	9	**BG 15 (drain wall)** **BG 15 (drain base)**	8 36
6	**BG 11**, **BG 5**	22	NA	
7	[1]NA		NA	
8	**GGT 2**, BG 2	13	NA	
9	**BG 24**, **BSK 5**	5	**BG 24** **BSK 5**	5 6
10	**BG 21**, **BSK 4**, **BSK 1**	9	**BSK 4**	6
11	**BG 20**	2	NA	
12	**BSK 3**	3	[2]BSK 3	4

[1] Map unit 7 is equivalent to map unit 6, but with the surface 40-50 cm removed (scalped).

[2] Hydrochemical data for these profiles is not discussed in detail.

9.1. Introduction

Metal and metalloid content in soils will depend on the composition of underlying bedrock. Any subsequent modifications to the soil profile (e.g. weathering and other pedogenic processes), or whether the soil is residual or transported will influence metal and metalloid compositions, concentrations and distributions within the soil profile and landscape. Increased concentrations of heavy metals and metalloids in a soil may also be attributed to anthropogenic sources such as dumping of wastes, dust from other contaminated sites, smelter stacks, roads and vehicle exhaust, stormwater runoff, agricultural wastes and fertilisers, to name a few. Environmental hazards derived from heavy metals are linked closely to their movement in soil profiles because even slow transport through soil and subsoil materials may eventually lead to increased content of heavy metals in the groundwaters and receiving environments. Under certain environmental conditions soils can act as a sink for contaminants, but they may be released if the conditions are changed.

Under circum-neutral to alkaline conditions heavy metals in soils predominantly occur in a sorbed state, or as insoluble compounds. This limits their movement in soils, which has generally been considered either minimal or practically nonexistent (Dowdy and Volk 1983), however it is possible for them to be mobile as oxyanions (e.g. arsenates, arsenites, molybdates). Trace elements added to a soil through different waste sources are either retained in the top soil layer or moved only a few centimetres below, and generally have a distribution pattern related to organic matter (Andersson 1977; Page and Chang 1985). Heavy metal movement with water in soils requires that the metal be in the soluble phase or associated with mobile particulates (Li and Shuman 1996; McBride 1989). The down-profile migration of trace metals can be enhanced in areas of high rainfall, irrigation, low organic matter, and where soils have coarse, sandy textures, low pH and low CEC (cation exchange capacities) (Dowdy and Volk 1983). Metals can complex with humic acids at low pH, which can carry them downward in the profile where they would be in an exchangeable organic form (McBride 1989). Therefore, movement is essentially related to the physicochemical forms of the metals in soil because these forms have different potentials for mobilization by inorganic or organic ligands in soil solution (McBride 1989).

The chemical form or oxidation state in which some elements (e.g. As, Cr, Hg) occur can determine their toxicity as well as their mobility. Therefore, for the purposes of assessing and managing the environmental hazard that contaminants pose to an area, it is important to understand the types of contaminants present, their position within a landscape and their likely chemical and physical behaviour under differing land use or development scenarios.

Mapping and characterising the contaminants within an acid sulfate soil landscape is particularly important, due to the increased potential for contaminant movement through soil acidification.

The Gillman study site, located in an industrial area of Adelaide, has been subjected to a multitude of different land uses over the past 100 years. As a result, soils in the Gillman area contain high concentrations of As, Co, Cr, Cu, Mn, Pb, V and Zn. A number of studies have been carried out in the Gillman study site that focussed on hydrology and hydrogeochemistry (Dillon *et al.* 1989; Dillon and Gerges 1993; Harbison 1986a; b; Pavelic and Dillon 1993a). These studies focussed on characterising soil, sediment and groundwater contamination, and were reviewed in Chapter 3. Harbison (1986c) found that subaqueous, reduced sediments in some former tidal creek depressions and drains contained elevated contents of metals and metalloids. Soil and sediment characterisation work carried out by Harbison (1986a) focussed on the western portion of the Gillman study site, within drains and former tidal creek depressions associated with Magazine Creek and tidal North Arm of Barker Inlet (Figure 3-2). These studies did not investigate soil in the eastern portion of the Gillman study area, where sulfuric materials occur in conjunction with low pH groundwaters.

This chapter had two main objectives: **(i)** to evaluate the extent of metal and metalloid contamination within the Gillman and St Kilda study sites and link the contamination to spatially mapped features (e.g. map units), and **(ii)** to link trends in trace element concentrations to pedological, hydrological and biogeochemical processes along toposequences at Gillman and St Kilda to help explain the distribution and movement of contaminants within this acid sulfate soil landscape. This information was later integrated into the hazard descriptions assigned to each of the map units (refer to Chapter 7 and Chapter 12) to provide a tool for the future management of the Gillman and St Kilda study sites.

9.2. Methods

9.2.1. Geochemical methods

Major and minor element analysis was carried out using X-ray fluorescence spectrometry (XRF) on 94 soil samples selected from 20 soil profiles from the Gillman study site and 4 soil profiles from the St Kilda study site (Table 9-1), representing a range of soil types at different positions in the landscape. Major elements analysed included: Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, S and Cl. Minor elements and Rare Earth

Elements (REE) analysed included: As, Ba, Br, Ce, Cd, Co, Cr, Cs, Cu, Ga, Hg, I, La, Mn, Mo, Nb, Nd, Ni, Pb, Rb, Sc, Sr, Th, U, V, Y, Zn, Zr. The location of the represented soil profiles is shown in Figure 5-1 and Figure 6-1. Total major and trace element analyses were determined on the < 2mm fraction of bulk soil samples. The soil sampling and preparation methods for XRF analysis were described in Chapter 4.

9.2.2. Hydrochemical methods

Soil pore waters were collected in-situ using peepers (Figure 9-1); which are multi-chambered (35), diffusion controlled, dialysis membrane samplers, which have semi-permeable membranes that separate receiver solution from sediment and soil solution (Teasdale *et al.* 1995; van Oploo *et al.* 2008b). Peepers were installed at five locations at the Gillman Study site in February 2003 and at three locations at the St Kilda study site in March 2004. The peepers were prepared in the laboratory by filling each dialysis chamber (6 mL) with MilliQ water and then submerging each peeper in a chamber filled with MilliQ water with nitrogen bubbling through it to exclude oxygen. The peepers were stored and transported submerged in the chamber. Peepers were inserted by pushing them vertically into relatively soft, saturated or subaqueous soil/sediments, leaving two to four cells sitting above the water/sediment boundary and left to equilibrate for at least 4 weeks. The diffusion rate through the dialysis membrane of the peepers used in this study takes two weeks to reach equilibrium. This slow equilibration rate provides for a better estimate of the longer term (seasonal) hydrogeochemical conditions, rather than responding to short term ‘events’ such as rainfall. Care was also taken to retrieve and sample the peepers following at least one week of stable (typical) climactic conditions.

Upon removing the peepers from the soil/sediment they were rinsed with deionised water, stored in clean plastic bags and packed on ice for transport back to the laboratory. The solution within each dialysis chamber was extracted to a clean centrifuge tube using a micropipette. This was done as soon as possible after removal from the field to limit oxygen diffusion into the solution chambers. All peeper chambers were analysed for pH and EC with selected chambers being analysed for major and minor cations by inductively coupled plasma optical emission spectrometry (ICP-OES) and a Cl^- auto analyser. Results are presented and discussed in Section 9.6.

Hypersaline pore water samples and surface water samples were analysed for major and minor elements by ICP-OES using a Spectroflame Modula (Spectro Analytical Instruments) optimized for high sodium solutions. In this method ions are drawn off a sample into hot (8000 – 10000K) argon plasma. Atomic and ionic emission lines are measured by viewing the appropriate region in the argon plasma tail flame and separation into individual components through a diffraction grating. Emitted light intensity is measured at specific wavelengths by photomultipliers, with elemental concentration directly proportional to intensity (Potts 1987). Elements analysed included: Al, B, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, Sr and Zn.

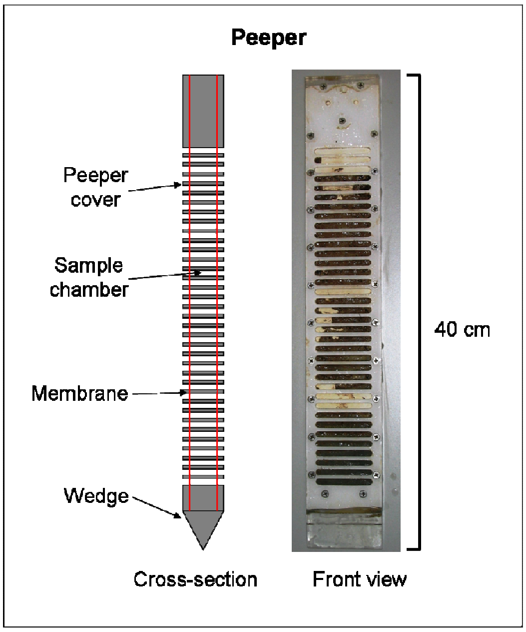

Figure 9-1 Diagram of a peeper shown from side view in cross-section and a photo of the front of a peeper that had been recently removed from sediment.

9.3. Geochemistry

Geochemical data for bulk topsoil samples (0-10 cm) from the Gillman and St Kilda study sites are summarised and compared to environmental and health investigation guidelines in Table 9-2. The topsoils were generally characterised by acidic to basic pH (3.4-9.2). The maximum concentration of elements with environmental investigation levels (EIL) measured in soils collected from the Gillman study site were; As (140 mg/kg), Cr (215 mg/kg), Cu, (638 mg/kg), Ni (40 mg/kg), Pb (377 mg/kg A), V (293 mg/kg) and Zn (1427 mg/kg). The maximum concentrations of As (17 mg/kg), Cr (39 mg/kg), Cu (27 mg/kg), Ni (3 mg/kg), Pb (31 mg/kg), V (45 mg/kg) and Zn (99 mg/kg) measured in topsoils at the St Kilda study site were considerably lower than for the Gillman site.

According to Australian and New Zealand Environment and Conservation Council guidelines (ANZECC & ARMCANZ 2000), topsoils sampled from the Gillman study site the maximum values measured for As and Pb exceeded the Health Investigation Level (HIL) A (i.e. recommended for standard residential use) (Table 9-2). The maximum values for Cu, V and Zn measured in topsoils from Gillman exceeded Ecological Investigation Levels (EIL) (ANZECC & ARMCANZ 2000). Topsoil samples from the St Kilda study site were all below EILs for As, Cr, Cu, Ni, Pb, V and Zn (Table 9-2).

Subsoil metal concentrations were generally less significant than in topsoils (Figure 9-3). Metal and metalloid values were below HIL E (i.e. parks, recreational open space and playing fields) and F (i.e. commercial/industrial use) values for all subsoils sampled from the Gillman and St Kilda study sites. Phosphate concentrations were higher at St Kilda sites than Gillman, and exceeded EIL trigger values in map units 9, 10 and 11 at St Kilda, and map unit 1 at Gillman (Table 9-2).

Geochemical results were sorted by physiographic map units, described in Chapter 7, which represent a range of soil types at different positions in the landscape. The map units presented in Table 9-2 and Figure 9-2 are portrayed as a schematic toposequence, traversing the Gillman study site, from the most topographically elevated map unit 8 (Artificially filled areas) to the lowest map unit within the non-tidal area (map unit 1 - Water), and then across the bund wall to the intertidal areas. Grouping the geochemical results according to the map units allowed comparisons to be made between the different soil types, their landscape position and hydrology (Table 9-2, Figure 9-2, Figure 9-3 and Figure 9-12). Mean geochemical results of topsoils are presented in Table 9-2 and Figure 9-2. A complete set of XRF results is displayed in Appendix E, along with ANZECC EIL trigger values (ANZECC & ARMCANZ 2000) for selected metals and metalloids from soils, groundwaters and sediments within aquatic ecosystems.

Table 9-2 Selected, mean elemental concentrations for near surface soil samples (0-10 cm) collected from the different map units (Figure 7-2). ANZECC EIL trigger levels exist for the following elements: As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, V, Zn, Bo, P and S (refer to Appendix E). Highlighted cells indicate elements for which that the mean value within the map units exceeded the [1]NEPC EIL (Interim Urban) or [2]HIL A trigger. Coloured text indicates where at least one sample (at any depth) from within the map units exceeded the [1]NEPC EIL or [2]HIL A trigger value. n = number of samples analysed in each category.

[3]Map unit no.	Gillman Non-tidal							Gillman Intertidal			St Kilda Intertidal			
	8	**6**	**5**	**4**	**3**	**2**	**1**	**9**	**10**	**11**	**9**	**10**	**12**	**LOR**
Major elements (%)														**%**
pH (1:5)	8.70	6.08	8.03	4.53	5.23	8.22	7.81	7.85	6.58	6.72	7.31	7.18	8.63	
Fe	2.41	6.76	8.79	2.84	2.35	1.76	4.31	2.77	3.06	4.26	1.11	1.50	2.16	0.01
Mg	1.79	1.70	2.82	1.01	1.26	1.66	2.23	1.78	3.24	3.83	3.53	3.00	2.52	0.01
Ca	6.46	0.67	0.52	0.40	0.58	8.56	6.28	10.15	1.38	1.90	3.86	3.74	25.54	0.01
Na	1.74	0.71	0.83	1.45	3.31	3.70	4.94	3.78	13.21	16.33	20.21	11.81	6.63	0.01
P	0.06	0.30	0.31	0.17	0.22	0.13	0.22	0.22	0.56	0.66	0.26	0.35	0.26	0.01
S	0.54	0.13	0.14	**0.82**	0.28	**0.68**	**0.82**	0.55	**0.60**	**0.95**	**0.99**	0.52	0.53	0.01
Minor elements (mg/kg)														**mg/kg**
As	**7**	**105**	**81**	**28**	**39**	**15**	**25**	13	**23**	**32**	17	14	16	1
Ba	240	**248**	242	205	166	138	216	145	71	63	**31**	41	84	10
Br	48	105	88	214	545	278	225	268	698	790	872	948	453	1
Cd	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	3
Co	**46**	**14**	17	**19**	8	11	**28**	15	2	11	4	6	**8**	4
Cr	**116**	**91**	**96**	**59**	**101**	**61**	**76**	**70**	**57**	**59**	14	19	39	2
Cu	**20**	26	25	30	21	**32**	**254**	**80**	**71**	**81**	20	24	17	1
Hg	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	6
Mn	111	**373**	347	70	77	99	241	174	47	62	38	**325**	311	6
Mo	**3**	21	**11**	**24**	**56**	**5**	**20**	6	1	1	15	1	1	1
Ni	2	12	18	13	5	8	15	5	2	2	1	1	3	2
Pb	**16**	206	112	89	18	**35**	**182**	95	184	166	10	20	31	2
Sr	249	73	77	62	63	857	337	415	138	172	244	225	1079	1
U	6	4	4	11	23	15	10	5	1	1	3	1	6	2
V	47	**235**	**223**	**83**	**120**	**63**	**93**	**56**	**52**	**54**	**36**	32	44	5
Zn	63	**209**	131	**158**	35	**88**	**677**	**276**	88	163	82	68	67	2
Zr	229	193	178	171	165	108	116	92	47	44	14	25	47	1
[4]REE (total)	108	126	143	90	97	58	92	82	38	38	22	31	60	1
n =	**3**	**2**	**1**	**4**	**1**	**4**	**3**	**1**	**1**	**1**	**1**	**2**	**1**	

[1] Interim EILs for the urban setting are based on considerations of phytotoxicity, ANZECC B levels, and soil survey data from urban residential properties in four Australian capital cities: (As, 20 mg/kg; Ba, 300 mg/kg; Cd, 3 mg/kg; Co, 50 mg/kg; Cr, 50 mg/kg; Cu, 60 mg/kg; Pb, 300 mg/kg; Mn, 500 mg/kg; Hg, 1 mg/kg; Ni, 60 mg/kg; V, 50 mg/kg; Zn, 200 mg/kg; P, 2000 mg/kg and S, 2000 mg/kg).

[2] Standard residential with garden/accessible soil (home-grown produce contributing less than 10% of vegetable and fruit intake; no poultry): this category includes children’s day-care centres, kindergartens, preschools and primary schools (ANZECC & ARMCANZ 2000): (As, 100 mg/kg; Ba, 5370 mg/kg; Cd, 20 mg/kg; Co, 100 mg/kg; Cr, 210 mg/kg; Cu, 1000 mg/kg; Pb, 300 mg/kg; Mn, 1500 mg/kg; Hg, 15 mg/kg; Ni, 600 mg/kg; Zn, 7000 mg/kg).

[3] Map units: **1**; Water (non-tidal), **2**; Benthic mat, **3**; Bare salt scald, **4**; Low dense heath, **5**; Open low scrub; **6**; Open grass plain, **8**; Artificially filled area, **9** Water (tidal), **10**; Mangrove woodland, **11**; Low growing salt marsh plants, **12**; Bare chenier ridge. [4] Total Rare Earth Elements.

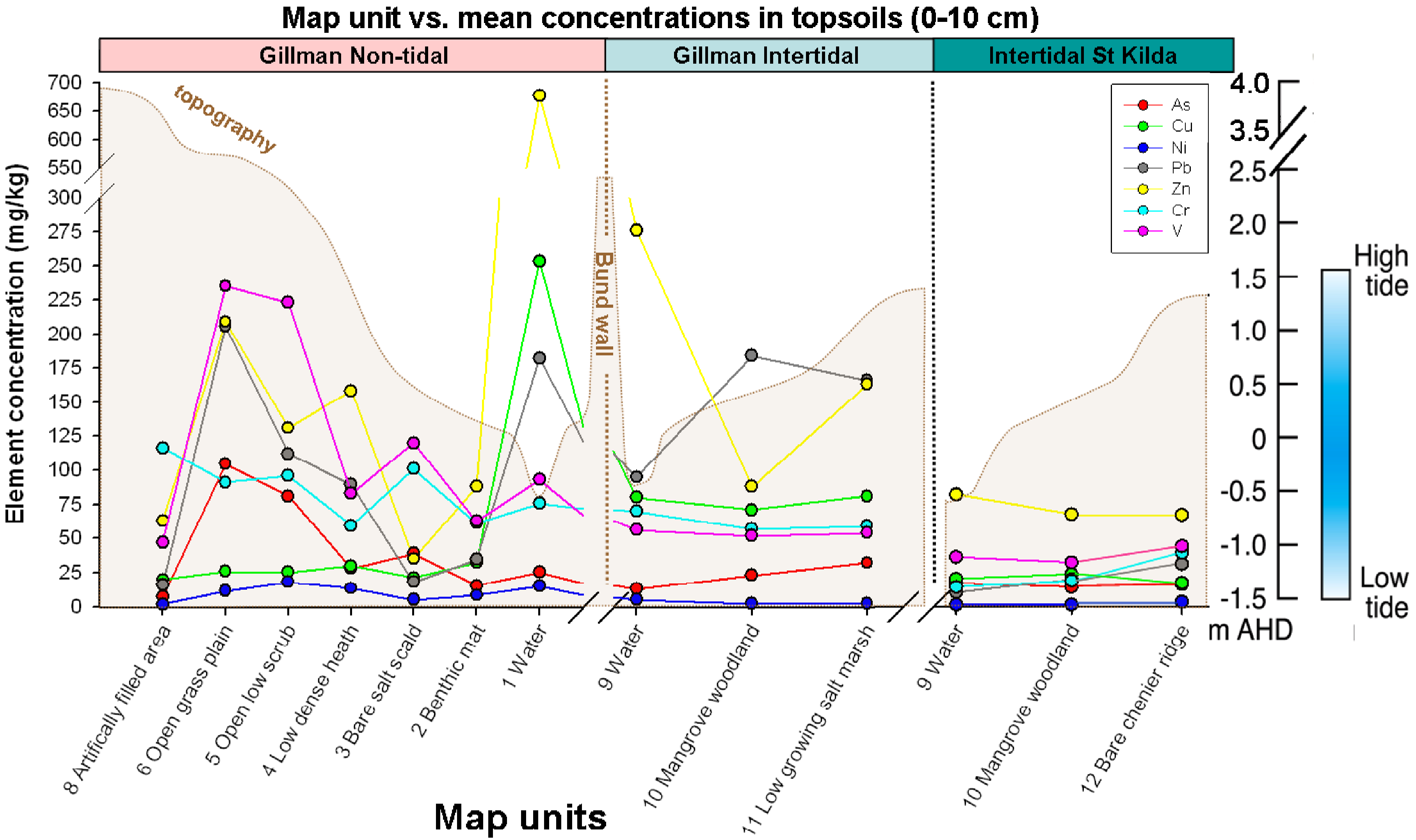

Figure 9-2 Mean metal and metalloid concentrations in topsoils (<10 cm depth) for the different map units at the Gillman and St Kilda Study sites. The map units are ordered to create a toposequence transects from non-tidal to intertidal areas at the Gillman and St Kilda study sites.

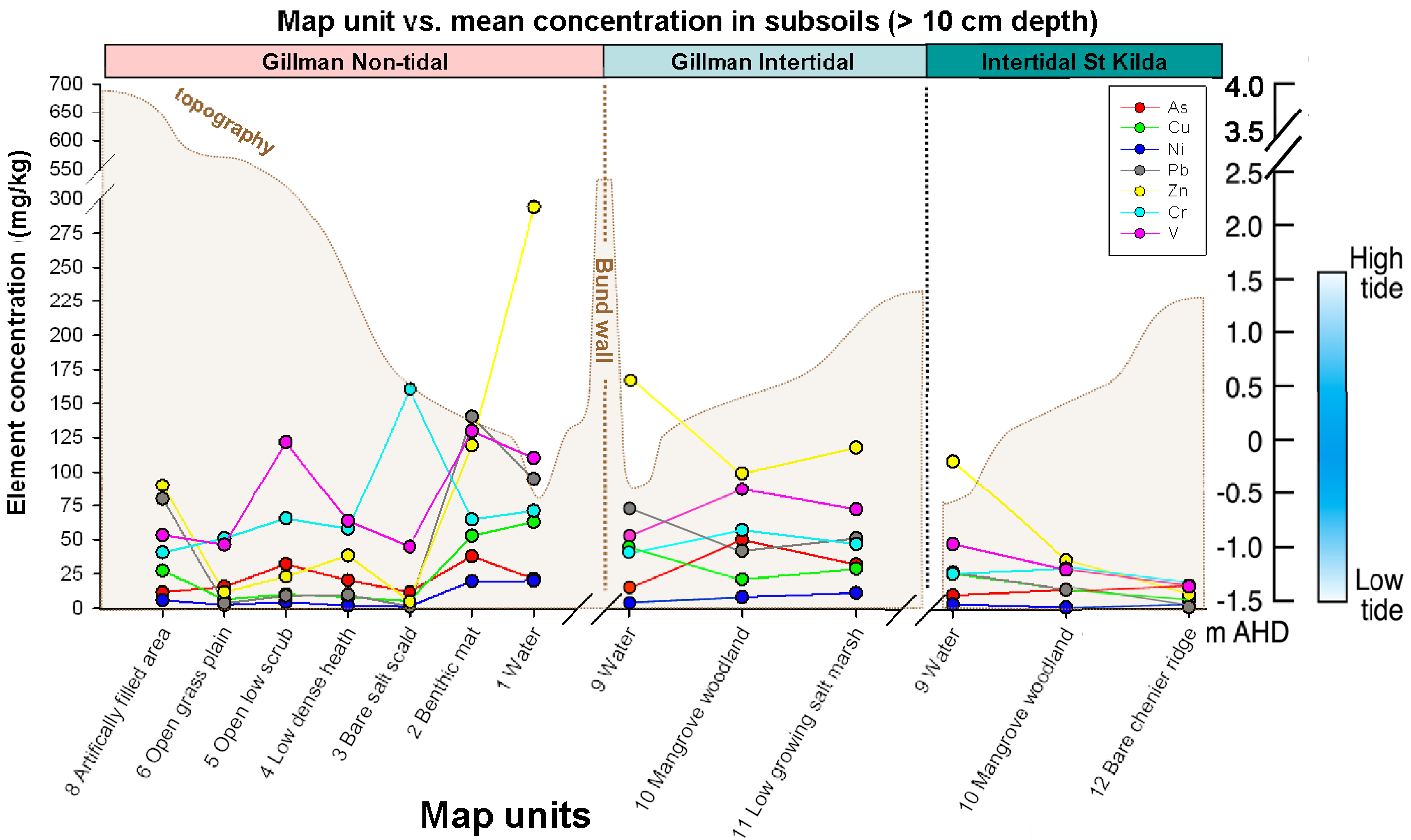

Figure 9-3 Mean metal and metalloid concentrations in subsoils (>10 cm depth) for the different map units at the Gillman and St Kilda Study sites. The map units are ordered to create a toposequence transects from non-tidal to intertidal areas at the Gillman and St Kilda study sites.

9.4. Spatial distribution of trace elements

Artificially filled areas (Map unit 8)

Artificially filled areas at Gillman (map unit 8) would inherently contain contaminants representative of the environment from which the fillings were derived. The western section of the Gillman study site was progressively filled since the late 1800s. Therefore, assessing contaminants at the surface of filled areas, as well as within the original (buried) topsoils, could provide a method for delineating the timing of wind blown contamination to the site. The rationality of this theory was realised when two soil profiles at Gillman containing artificial fill materials were assessed (profile BG 2 and profile GGT 2). Geochemical data for profile BG 2 is presented in Appendix C. Arsenic in topsoils at Gillman likely originated from the former Sulfuric Acid Plant that was located at Snowden's Beach, Largs North (about 1.7 km NW of profile GGT 2 at Gillman). Pyrite and pyrrhotite (also containing chalcopyrite, galena, and sphalerite, less arsenopyrite and rare occurrences of vanadiferous manganochromite, $(Mn,Fe)(Cr,V)_2O_4$, and a palladium diantimonide, $PdSb_2$) were mined from Brukunga in the Mt Lofty Ranges (Graham 1978). The Acid Plant, which operated between 1955 and 1972, burnt the pyrites and a particulate deposition plume spread by the wind across Torrens Island, Gillman and toward Port Adelaide and to a much lesser extent toward St Kilda (Thomas *et al.* 2001). The area containing profile BG 2 was drained in 1965 and progressively filled during the 1970s using hydraulically placed Port River dredge sediment (Thomas and Fitzpatrick 2006a). The area containing profile GGT 2 was filled in 1993 when a geotechnical mound was constructed using fill material that consisted of Port River dredge materials excavated from an area at Gillman that had previously been filled (Thomas and Fitzpatrick 2006c). Prior to fill being placed, the original topsoils at both of these profiles were mangrove peats that likely contained sulfuric materials; analogous to profiles GGT 5 and BG 29 (refer to Chapter 6 and Appendix B). The load of fill material compressed and pushed the original soils below the water table enabling sulfidic materials to re-form.

The concentrations of trace elements within fill material from profiles BG 2 and GGT 2 were characteristically low; however, Cr and V concentrations were elevated at the surface of both profiles. The Cr content of the original (buried) topsoil layers in both of these profiles was much lower than at the surface of fill materials. The V content was only elevated at the original topsoil layer within profile BG 2. However, other metals and metalloids content (As, Cu, Ni, Pb and Zn), were elevated at the original topsoil layer within both profiles, when compared to the rest of the profile (refer to Figure 9-2 and Figure 9-12). Burial and loading can re-establish reducing conditions within sulfuric materials when they are pushed below the water table and oxygen is excluded. Sulfide minerals, including monosulfides were identified within the original (buried) topsoils (refer to Chapter 6 and Appendix B). Metal contaminants are likely to be stable within the compressed mangrove peat, and scavenged by forming sulfide minerals. As well as providing a barrier to further disturbance, burial and loading of contaminated acid sulfate soil materials may be an effective amelioration method in areas where: **(i)** the sulfuric materials contain high (compressible) organic matter, **(ii)** the sulfuric materials are pushed below the permanent ground water table, **(iii)** the fill materials excludes oxygen infiltration, **(iv)** bicarbonate is present in the ground water, and **(v)** the underlying soils have high acid neutralising capacity and are able to neutralise acid expelled from the sulfuric materials during loading. These processes would be effective in other areas at Gillman where the physical and chemical conditions are suitable (e.g. within areas mapped as units 1, 2, 3, 4, 9, 10, 11 and 12), and where the addition of fill is compatible with environmental and future land-use requirements.

Areas dominated by sandy sulfuric materials (Map units 5, 6 and 7)

The most prominent, formerly supratidal, area at Gillman was mapped as units 5, 6 and 7, mainly occurs in the south eastern portion of the Gillman area, south of the bund wall (Figure 7-2). In comparison to intertidal areas at St Kilda, topsoils of map units 5 and 6 at Gillman contained elevated levels of As, Cr, Pb, V and Zn (Table 9-2 and Figure 9-2). Subsoil of map units 5 and 6 at Gillman contained elevated concentrations of Cr and V and minor elevations of As, in comparison to intertidal soils at St Kilda (Figure 9-2). The portion of the Gillman study site in which map units 5 and 6 occur was drained in 1935 and was used by the South Australian Rifle Association as a shooting range (named the Dean Rifle Range) between 1887 and June 2003. The elevated landscape position of these map units is due to their geomorphology being dominated by sandy shore face and back barrier sand units (Belperio and Rice 1989). The topsoil geochemistry soils in map units 5 and 6 are similar and reflect their drainage and contaminant histories. Concentrations of As and V measured in topsoils from map units 5 and 6 were the highest for any soil samples collected from the Gillman or St Kilda study sites and ranged between 69-140 mg/kg for As and 177-293 mg/kg for V. Lead and Zn were also elevated and measured between 27-249 mg/kg for Pb and 51-276 mg/kg for Zn (Appendix E). Chromium was slightly elevated compared to intertidal soils at Gillman and measured between 85-117 mg/kg (Figure 9-2). These metals and metalloids are likely elevated due to airborne contamination from local industries, and from ballistics (bullets and shells). Old bullets were commonly observed (at a density of about 1 shell per square metre) on the soil surface in the overshoot area in map units 2 and 3, due to the lack of vegetation cover (refer to photos in Appendix A). It could be assumed that the density of bullets was similar for the more densely vegetated map units within the overshoot area. Shot pellets contain mainly Pb (97%), Sb (2%), As (0.5%) and sometimes Ni (0.5%), whereas the metals found in jacketed bullets include Pb (90%), Cu (9%) and Zn (1%) (Tanskanen *et al.* 1991). Lead free bullets are generally composed of Cu and Cu alloys. The mineralogy of the oxide coatings of bullets collected from the Gillman site was determined by XRD. The green oxide contained paratacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), quartz and halite . The composition of the white oxide was perite ($PbBiO_2Cl$), cotunnite ($PbCl_2$) potassium lead chlorite (KPb_2Cl_5), quartz and halite plus some unidentified phases (XRD traces are shown in Appendix G).

Concentrations of Cu were very low in topsoils from map units 5 and 6, when compared to the intertidal soils at Gillman. This was surprising given the high Cu content of bullets, which were commonly observed lying on the soil surface within the Dean Rifle Range overshoot area (Figure 7-2), and covered by green and white oxides (refer to photos in Appendix G). These metals may be relatively immobile in the surface environment at Gillman due to the relatively dry conditions and the high pH of most topsoils limiting corrosion of the bullet shells. In alkaline environments Cu salts are very insoluble and diffusion is minimal. This is supported by the findings of (Fitzpatrick *et al.* 1996a) who measured very low metal contents in the Dean Rifle Range backstop (maximum metal concentrations measured: < 1.5 mg/kg Cd, 0.5 mg/kg Cr, 12 mg/kg Cu, 2.4 mg/kg Ni, 6.8 mg/kg Pb and 4.5 mg/kg Zn). Rare earth elements (REE) and Zr were also elevated in topsoils from these areas (map units 5 and 6) (Appendix E). Subsoil samples were elevated in Mo in profile BG 15 (and slightly elevated in profile BG 11) at a depth approximating the redox front (refer to Figure 9-6).

Map unit 7 represents the scalped equivalent of map units 5 and 6. During the early 1930s the topsoil from the most prominent areas at Gillman was mined (scalped) for use in constructing the backstop for the Dean Rifle Range. The trace metal content of bulk subsoil soil samples obtained from the backstop mound was investigated by (Fitzpatrick *et al.* 1996a) and found to contain much lower trace metal concentrations than topsoil sampled in this current study, for both the Gillman and St Kilda study sites. The mean concentrations of metals in backstop soil materials sampled by (Fitzpatrick *et al.* 1996a) measured: <0.1 mg/kg for Cd, 0.3 mg/kg for Cr, 7.9 mg/kg for Cu, 1.5 mg/kg for Ni, 5.4 mg/kg for Pb and 3.4 mg/kg for Zn. The low metals content of backstop samples may be due to the mound being constructed prior to the major industrial development of the Gillman area, principally by pre-dating the construction of the sulfuric acid plant at Largs North.

Areas dominated by peaty sulfuric materials (Map unit 4)

Map unit 4 (low dense heath) occurs at slightly lower landscape positions than areas mapped as unit 5, 6 and 7. The vast majority of map unit 4 occurs south of the bund wall in the western portion of the Gillman area, and was drained in 1965 (Figure 3-4 and Figure 7-2). In comparison to intertidal areas at St Kilda, topsoils of map unit 4 at Gillman contain notably elevated levels of As, Cr, Pb, V and Zn (Table 9-2 and Figure 9-2). Subsoil samples from map unit 4 at Gillman contain elevated concentrations of Cr and V and minor elevated As, in comparison to intertidal soils at St Kilda (Figure 9-3).

Low lying, bare salt scalded areas (Map unit 3)

Topsoil sampled from low lying, bare salts scalded areas (map unit 3) contained lower concentrations of Pb and Zn than all other map units within the Gillman study site (Table 9-2 and Figure 9-2). Concentrations of Zn were lower than in topsoils sampled from the St Kilda study site. However, the concentrations of Cr and V were the second and third highest measured in the map units (Figure 9-2). Subsoils from map unit 3 at Gillman contained the highest mean Cr concentration (187 mg/kg), with only one topsoil sample from profile BG 2 in map unit 8 having a higher Cr content (215 mg/kg)

(Appendix E). The apparent accumulation of As, Cr and V in topsoils from map unit 3 areas may be related to the upward wicking of groundwaters and formation of salt efflorescences the surface (these processes are explained further in Chapter 10).

Seasonally re-flooded areas covered by benthic mats (Map unit 2)

Topsoils sampled from low lying areas covered by benthic mats (map unit 2) contained low concentrations of trace metals and metalloids when compared to other map units within the Gillman study site (Figure 9-2). The relative concentration of metal and metalloids in the topsoils was very similar to the intertidal soils at St Kilda. Subsoils within map unit 2 had considerably higher concentrations of As, Cr, Cu, Ni, Pb, V and Zn than in topsoil samples (Figure 9-3). The apparent downward movement of metals and metalloids in profiles in map unit 2 is likely related to seasonal (winter) flooding that causes: **(i)** fluctuations in Eh and pH that move trace elements vertically, and **(ii)** burial of layers containing contaminated soil transported from upland areas (e.g. map units 5 and 6). During summer months the top 10 to 40 cm of the soil profile oxidises and commonly becomes acidic, promoting the downward migration of contaminants, S and Fe to the redox front where metal sulfide minerals are then able to form. Very high sulfide contents were measured at the summer redox front in profile BG 4 (measuring 3.45% AVS and 7.05% S_{CR}) and were associated with elevated concentrations of Cu (113 mg/kg), Mo (57 mg/kg), Ni (46 mg/kg), Pb (340 mg/kg), V (170 mg/kg) and Zn (259 mg/kg) (Appendix E). Concentrations of As and Cr were only slightly elevated at the summer redox front in profile BG 4. The mean concentration of As, Cu, Mo, Pb, and Zn for topsoils in map unit 2 were below the EIL trigger values (Table 9-2). The mean concentrations for these trace elements in subsoils of map unit 2 measured: 38 mg/kg As, 65 mg/kg Cr, 53 mg/kg Cu, 140 mg/kg Pb and 120 mg/kg Zn, which exceed EIL trigger values for As and Cr.

Non-tidal creek channels (Map unit 1)

The topsoil geochemistry of the non-tidal soils in creeks, creek depressions and drains (map unit 1) reflects the geochemistry of soils within the local and regional drainage systems. Soils in the Magazine Creek stormwater ponding basin (Figure 3-2) contained the highest Cu, Pb and Zn contents, measuring 638 mg/kg, 377 mg/kg and 1427 mg/kg respectively (e.g. profile BG 19, Appendix E). These elevated metal concentrations are associated with stormwater runoff containing street dusts from an industrial catchment of about 1400 ha, which has a history of pollution issues (Harbison 1986a). Topsoils collected elsewhere from within map unit 1 (i.e. not within the Magazine Creek stormwater ponding basin) also contained elevated Cu, Pb and Zn, but to a lesser extent (Figure 9-2), with concentrations ranging from 17-112 mg/kg for Cu, 26-168 mg/kg for Pb and 92-540 mg/kg for Zn. In comparison, topsoils from tidal creek channels (map unit 9) at Gillman and St Kilda contained significantly less Cu, Pb and Zn. Down profile characteristics were not obvious in soil profiles from map unit 1, primarily because sample depths were limited to the upper 30 cm.

Tidal Creek channels (Map unit 9)

The topsoil geochemistry of the tidal creeks (map unit 9) differs considerably between the Gillman and St Kilda study sites. This is likely due to St Kilda being further from water and airborne contamination sources. Topsoil sampled from a tidal stream at Gillman contained high Cr (70 mg/kg), Cu (80 mg/kg), Pb (95 mg/kg), V (56 mg/kg) and Zn (276 mg/kg) and slightly higher Ni (5 mg/kg) when compared to a similar environment at St Kilda (i.e. 14 mg/kg Cr, 20 mg/kg Cu, 10 mg/kg Pb, 36 mg/kg V, 82 mg/kg Zn and 1 mg/kg Ni). The concentration of As was slightly higher in the tidal creek at St Kilda (As 17 mg/kg) compared to Gillman (13 mg/kg) (Table 9-2 and Figure 9-2). At Gillman, metal and metalloids concentrations were significantly lower in the creek topsoils sampled from the tidal environment (map unit 9) compared to the non-tidal creeks (map unit 1). Surprisingly, however, topsoil concentration of As and Pb, were higher in the other intertidal environments (map units 10 and 11) at Gillman (Figure 9-2). The concentration of Cr, Cu, Pb, V and Zn was higher in subsoil samples than in topsoils of tidal creek depressions at St Kilda (Figure 9-2 and Figure 9-3). Both physical (e.g. sedimentation, erosion and bioturbation) and chemical (e.g. redox) processes may be responsible for the downward movement of contaminants within the tidal creek soil profile (BSK 5) at St Kilda.

Mangrove woodlands (Map unit 10)

Trace metal and metalloid concentrations were considerably higher in topsoils from intertidal mangroves woodlands (map unit 10) at Gillman compared to the same map unit at St Kilda (Table 9-2 and Figure 9-2). This was particularly evident for Cr, Cu, Pb and V. Topsoil sampled from mangrove woodlands at Gillman contained very high Pb (with a maximum value of 184 mg/kg), compared to a maximum Pb concentration of 27 mg/kg from St Kilda. Copper, Pb and Zn were generally more concentrated at the surface of soil profiles, whereas As and Mo were more concentrated in subsoil layers (Figure 9-2 and Figure 9-3). Mo and As were commonly associated with metal sulfides.

Low growing salt marsh plants (Map unit 11)

Geochemical results for map unit 11 were only obtained for the Gillman study site, from soil profile (BG 20), as the map unit covered only a small area at St Kilda (Figure 7-1). Trace metal and metalloid concentrations for topsoils in map unit 11 were very similar to topsoils from intertidal mangroves woodlands (map unit 10), although with higher Zn concentrations (Figure 9-2). Trace metals Cr, Cu, Mo, Pb and Zn were more concentrated in topsoils, but V was slightly more concentrated in subsoil layers, and As was unchanged (Figure 9-2 and Figure 9-3).

Chenier (shell grit) ridge (Map unit 12)

Geochemical results for map unit 12 were only obtained for the St Kilda study site, from soil profile (BSK 3), as this map unit was not represented at Gillman, although shell grit materials were observed in subsoil layers and were extensive in map unit 4 (Figure 7-1). At St Kilda chenier ridges are prominent features that are exposed for extended periods of time during the tidal cycle (refer to Chapter 8). The shell grit layers at Gillman generally occur within 100 cm of the surface in map unit 4; however, they are present at shallower depths (within 10 cm of the surface) in the north eastern corner of the Gillman study site, near profile BG 36 (Figure 6-1). Trace metal and metalloid concentrations for topsoils in map unit 12 were similar to topsoils from other intertidal soils at St Kilda, although with slightly higher concentrations of Cr, V and Pb (Figure 9-2). The concentrations of trace metals and metalloids were generally much lower in subsoil layers (Figure 9-2 and Figure 9-3), except for Co (110 mg/kg), which marginally exceeded the HIL A trigger value in one subsoil layer (55 to 70 cm) from profile BSK 3. Strontium has geochemical similarities with Ca and Mg and was particularly high within carbonate rich soil layers from both the Gillman and St Kilda study sites (Appendix E).

9.5. Behaviour of trace elements

In order to explain the mobility of contaminants within disturbed and undisturbed acid sulfate soil landscapes, detailed geochemical and hydrochemical data were collected along toposequences at **(i)** the Gillman study site (Figure 9-4) and **(ii)** the St Kilda study sites (Figure 9-8). Detailed, down profile geochemical data and soil pore water data, focussing on toxic elements, are described in detail here, for five soil profiles from the Gillman toposequence and two soil profiles from the St Kilda toposequence. The Gillman toposequence traverses from former supra-tidal soils (profiles BG 11 and BG 15) containing sulfuric materials, across former intertidal soils (profile BG 22) containing hypersulfidic materials to low lying soils (profiles BG 30 and BG 28) in which monosulfidic materials have developed in former tidal creek depressions. Tidal influences were cut off from this portion of the Gillman site in 1935. Undisturbed soil profile BG 24 was located in a tidal creek on the north side of the bund wall (Figure 9-4). The St Kilda toposequence transects from intertidal floodplains covered by masses of mangrove pneumatophore (profile BSK 4), to a permanently inundated tidal creek (profile BSK 5) (Figure 9-8). Full morphological descriptions of soil profiles are presented in Chapters 5 and 6 and Appendix B.

9.5.1. Gillman toposequence

The Gillman toposequence transects five soil profiles from the profile BG 11, located in an upland area (former supratidal areas in Focus area A), through a lowland area at profiles BG 28 and 30 and across the bund wall to intertidal creek sediments at profile BG 24 (in Focus area C) (Figure 9-4). Soil profiles BG 11 (map unit 6) and BG 15 (map unit 5) are dominated by sandy shore face sediments that underlie intertidal mangrove peats and supratidal samphire clays of varying thickness. Soil profile BG 11 contains a thick layer of sulfuric material between 49 and 205 cm depth, with hypersulfidic and hyposulfidic material occurring below 205 cm. Sulfuric materials also contain minor reduced inorganic sulfides. Soil profile BG 15 also contains a thick layer of sulfuric material, between 30 and 160 cm depth, with hypersulfidic material occurring below 160 cm. Sulfuric materials in profile BG 15 contained high existing acidity and extremely high reduced inorganic sulfide contents that measured S_{CR} 6.88% in lower soil layers Figure 9-6. At lower positions in the landscape at Gillman, on the southern side (non-tidal side) of the bund wall, soil profiles BG 22, BG 28 and BG 30 occur, and represent map units 4, 2 and 1 respectively. Soil profiles BG 22 and BG 28 contained hypersulfidic and hyposulfidic materials and minor monosulfidic materials, whereas soil profile BG 30 contained only hyposulfidic and monosulfidic materials (Figure 9-4). Soil profile BG 24 (map unit 9) is located in a tidal creek channel on the northern side of the bund wall and contained hyposulfidic materials and minor monosulfidic materials. The reduced inorganic sulfur contents recorded in the disturbed area of subaqueous soil profile BG 30 were considerably higher (AVS of 1.2% and S_{CR} of 1.7%) than in the tidally flushed subaqueous soil profile BG 24 (AVS of 0.32% and S_{CR} of 0.72%) (Figure 9-7).

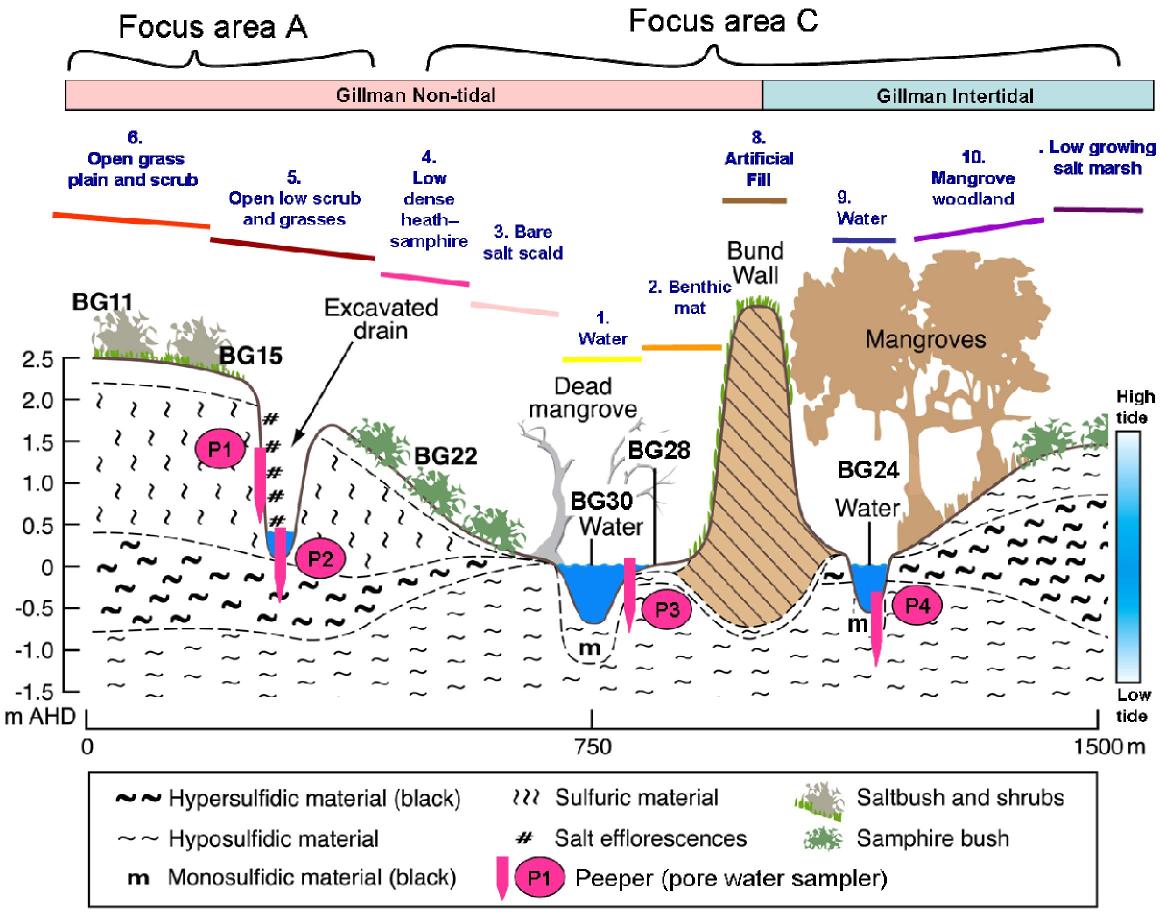

Figure 9-4 Schematic cross section of the overshoot area at the Gillman study site, transecting from the non-tidal, topographically high sandy soils (map units 5 and 6) to low lying non-tidal creek channels (map unit 1) and across the bund wall to intertidal soils. Refer to Figure 6-1 for transect location. The location is shown for four peepers (pore water samplers) at the Gillman study site (P1 to P4). The results of pore waters collected from saturated soil profiles at Gillman and St Kilda are explained in Section 9.6 of this Chapter. Refer to the soil map of Gillman study site (Figure 7-2) for the location of Focus areas A and C.

Down profile geochemical characteristics

Profile BG 11 and BG 15: Former supratidal soils (Map units 5 and 6)

Down profile variations are pronounced for most analytes in BG 11 (Figure 9-5) and BG 15 Figure 9-6). Notable variations in the vertical distribution of Zr and Ti occurred in profiles BG 11 and BG 15, which is a reflection of a diverse depositional history, and changing clay contents of soil layers. Stratification is particularly evident in the upper 100 cm of profile BG 11, where sandy layers have been transported and reworked by storms and are interbedded with clay (low energy deposits). The soil pH (1:5) of both profiles decreased with depth from circum-neutral to a minimum pH of 3.86 at 49 cm in BG 11 and 2.26 at 110 cm in BG 15. Below these depths, soil pH gradually increased again to pH 7.33 and pH 4.2 at the base of the profiles, respectively (Figure 9-5 and Figure 9-6).

Major cations Fe, Al, Mn, Ca and Mg were concentrated at the surface of profile BG 11 and in deeper, clay-rich layers (Figure 9-5). In profile BG 15, major cations Fe, Al and Ca have a relatively even down profile distribution, whereas Mg and Mn are concentrated at the surface and depleted at depth (Figure 9-6 and Appendix E). Total S was depleted at the surface of both profile BG 11 and BG 15, and concentrated at a depth approximating the redox front (Figure 9-5 and Figure 9-6).

Metal and metalloid concentrations (As, Cr, Cu, Ni, Pb, V and Zn) were elevated at the surface of soil profiles BG 11 and BG 15 (Figure 9-5 and Figure 9-6). In profile BG 11, trace elements Ba, Sr and REE (total REE) were elevated within clay rich layers, at the near surface as well as at depth (below 200 cm), whereas the distribution of Co and Mo decreased with depth (Figure 9-5). In profile BG 15, trace elements Ba, Co, Sr and REE (total REE) had a relatively uniform distribution with depth, although Ba was depleted in a subsoil layer (between 95 and 120 cm depth). This same subsoil layer was particularly enriched with Mo (238 mg/kg) and had a slightly elevated As content. This soil layer occurred (approximately) at the redox front and also contained the highest TAA (5000 mol H^+/t) and S_{CR} (6.88 %S_{CR}) contents and the lowest soil pH (pH_{field} of 1.86) measured in profile BG 15 (Figure 9-6 and Appendix E).

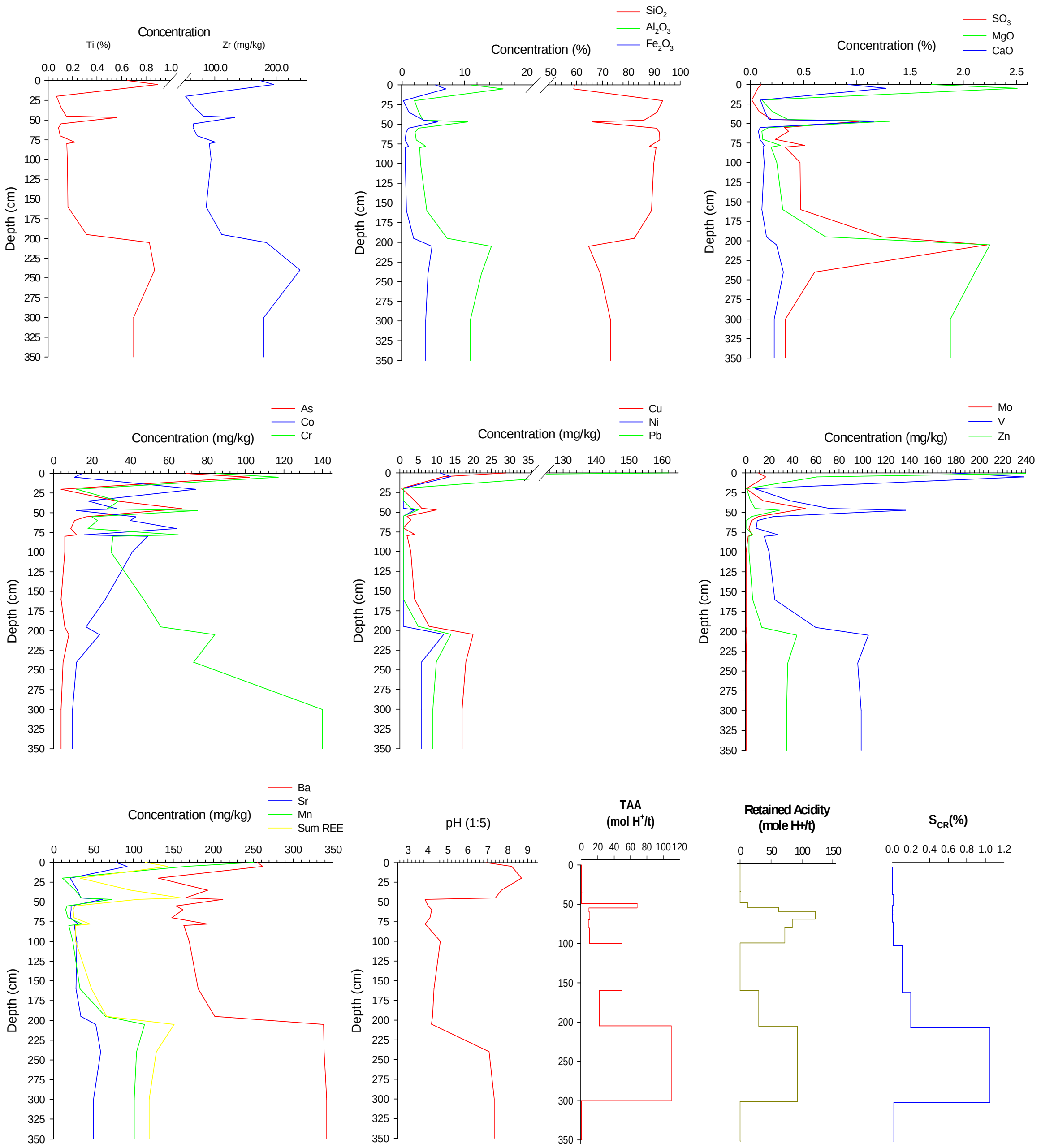

Figure 9-5 Down profile geochemistry for soil profile BG 11.

Profiles BG 22: Former intertidal soils (Map unit 4)

The vertical distribution pattern of major and trace elements in soil profile BG 22 was very similar to that of BG 15, but within a thinner profile (Figure 9-6). Variations of Zr and Ti contents were minor and decreased with depth (Appendix E). Soil pH (1:5) was circum-neutral (6.45) at the surface of the profile and decreased to a minimum pH of 5.17, and then increased with depth to a pH of 9.27, between 40 and 65 cm depth. The increase in soil pH with depth was due to a shallow groundwater table maintaining reducing conditions (at approximately 30 cm in summer months) and high carbonate content, which occurred as a shell grit layer below 25 cm (Figure 9-6).

Major elements Fe, Al, Mn and Mg were slightly more concentrated at the surface than in deeper layers (Figure 9-6). This could be due to acquisition of atmospheric dust (clay) over time. Total S content was slightly depleted at the surface and more concentrated below a depth approximating the redox front (Figure 9-6). The Ca content was low at the surface of profile BG 22 and vey high (measuring up to 24.7%) at the base of the profile due to shell grit layers. Sr and Cr contents increased dramatically in subsoil layers, where Ca contents were high.

Trace metals and metalloids As, Pb, V and Zn were considerably more concentrated in the surface layer of profile BG 22, and decreased with depth (i.e. Pb, and Zn contents were below the detection limit at the base of the profile; Figure 9-6). Trace element concentrations Ba, Co, Cu, Ni and REE (total REE) were marginally elevated at the surface of the profile and decreased with depth (Figure 9-6). Mo content was depleted at the surface and initially increased with depth (measuring 93 mg/kg at 15 cm depth) and then decreased in concentration again toward the base of the profile (Figure 9-6). The vertical distribution of Mo in profile BG 22 was similar to profile BG 15, and appears to be leached from oxidised surface layers and concentrated at a depth approximating the redox front (Figure 9-6 and Chapter 8).

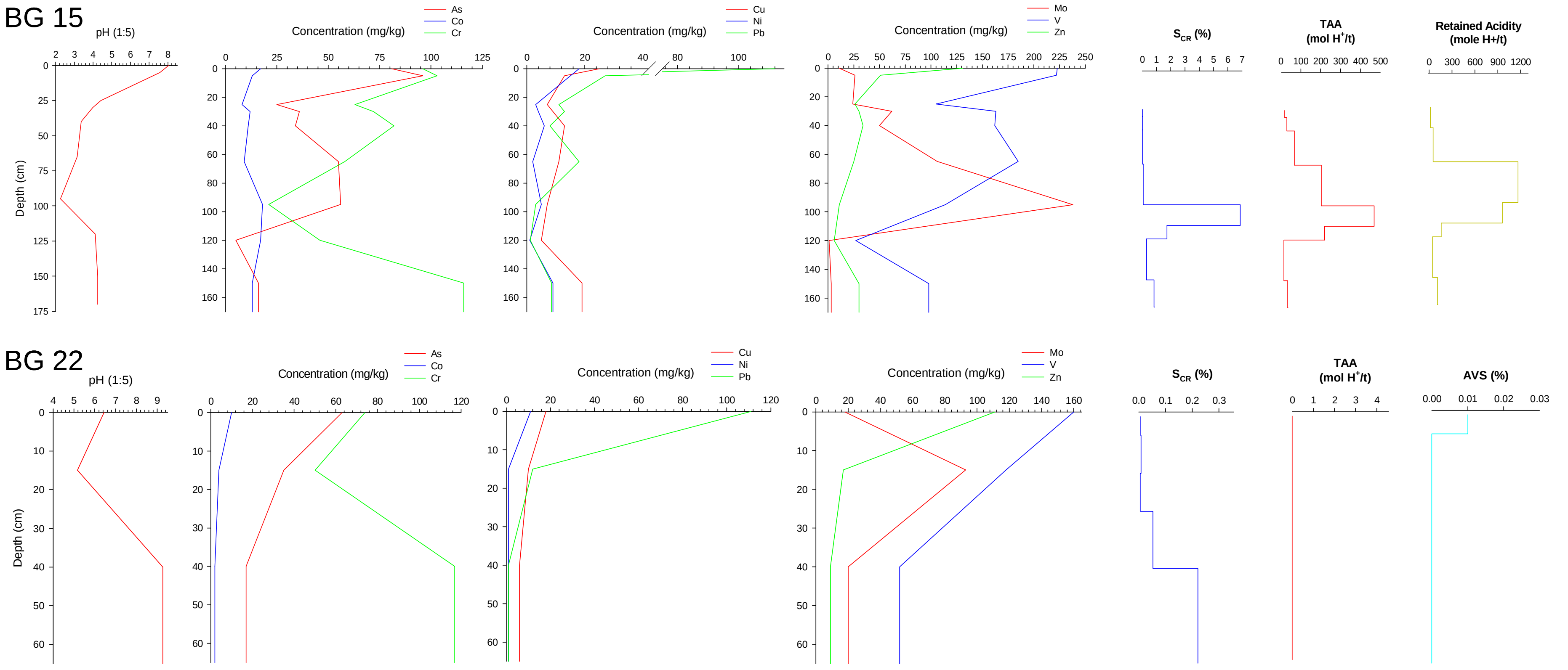

Figure 9-6 Down profile soil chemistry for Gillman soil profiles BG 15 and BG 22. These profiles occur along a toposequence that includes profile BG 11 (refer to Figure 9-5).

Profile BG 30 and BG 28: Low lying, former intertidal soils with monosulfidic materials (Map units 1 and 2)

Profile BG 30 was a subaqueous soil at the time of sampling, whereas the upper 5 cm of profile BG 28 was above the water table and oxidised (refer to Chapter 8). The vertical distribution of elements within subaqueous profile BG 30 was more uniform than in profile BG 28 and other upland soil profiles. This was in part because of the thinner profiles sampled from saturated areas, which also limited the number of soil samples per profile. The Ti and Zr content of profile BG 30 was relatively uniform with depth compared to soil profiles from higher in the landscape at Gillman (Appendix E), due to consistent clay texture. Only one sample from profile BG 28 (5 to 25 cm) was analysed for major elements; and therefore down profile variations could not be established. The pH (1:5) of surface soils for both profiles was alkaline (measuring pH 8.11 in profile BG 30 and pH 9.2 in profile BG 28; Figure 9-7). Soil pH increased slightly with depth in profile BG 30, and decreased slightly with depth in profile BG 28.

Major cations Fe, Al, Mg and Mn had relatively low concentrations at the surface of profile BG 30, whereas the Ca concentration was relatively high (Appendix E). Total S was uniform throughout profile BG 30 (measuring 0.9%). In profile BG 28, major cations Fe (1.14%), Al (2.36%) and Mn (0.01%) concentrations were about half that measured in profile BG 30, for the corresponding soil layer (0 to 25 cm), but the concentrations of Mg (2.27%) and S (1.11%) were similar for both profiles (Appendix E). Gypsum and other salt efflorescences precipitated at the oxidised surface (0-1 cm) of profile BG 28, indicating that S was likely enriched at the surface. The Ca content of the subsoil layers in profile BG 28 was 23.3%, which was considerably higher than profile BG 30, had a maximum Ca content of 12.6% at the surface layer (0 to 5 cm).

Two soil layers in profile BG 30 and three soil layers in profile BG 28 were analysed for trace elements. Trace element concentrations (As, Ba, Cr, Cu, Ni, Pb, V, Zn and REE (total REE)) were slightly depleted at the surface of soil profile BG 30, whereas Co, Mo and Sr were slightly elevated (Figure 9-7 and Appendix E). The concentrations of Cu, Cr, V and Zn were above EIL sediment quality guidelines for both soil layers in profile BG 30 (Table 9-2). The subsoil (5 to 20 cm) layer of profile BG 30 marginally exceeded the EIL for As, and the topsoil layer marginally exceeded the EIL for Mo (Table 9-2). In profile BG 28, trace elements Co, Cu, and Zn were depleted in the top 5 cm, whereas Ba, Cr, Pb and V were significantly elevated (Figure 9-7 and Appendix E); however, no analytes exceeded the EIL sediment quality guidelines (ANZECC & ARMCANZ 2000). Profile BG 28 did contain extremely high Sr contents (2836 mg/kg) in the subsoil layer and was the highest Sr content measured in any soil profile from the Gillman and St Kilda study sites by more than 1000 mg/kg (Appendix E).

Profile BG 24: Low lying, intertidal creek soils with monosulfide (Map unit 9)

Profile BG 24 was a subaqueous soil located in a permanently flooded tidal creek depression on the northern side of the bund wall, about 75 m from profile BG 28 and about 340 m from profile BG 30 (Figure 6-10 and Figure 9-7). Two soil layers (0 to 5 cm and 5 to 20 cm depth intervals) were sampled from this profile, but only the topsoil layer was analysed for major elements. Trace elements were determined for both soil layers. Soil pH (1:5) was circum-neutral (7.85) at the surface of the profile and increased with depth to a pH of 8.33 (Figure 9-7). The Zr and Ti contents of the topsoil layer were similar to the topsoil layer in subaqueous soil profile BG 30 (Appendix E). In the topsoil layer of profile BG 30, the concentration of major cations Fe (2.77 %), Al (5.43 %), Mg (1.78 %), Mn (0.02 %) and S (0.55 %) were slightly lower than in either the topsoil or subsoil layers of profile BG 30.

Trace metals and metalloids As, Ba, Co and REE were slightly depleted in the topsoil of profile BG 24, whereas Cr, Cu, Ni, Pb, V, Zn were slightly enriched (Figure 9-7 and Appendix E). When compared to the subaqueous soil profile (BG 30) located on the southern side of the bund wall, As, Co and Cr had similar concentrations, but the concentrations of Cu, Ni, Pb, V and Zn are considerably lower (about half; Figure 9-7). The concentration of Mo was 6 mg/kg in the topsoil and subsoil layers. The concentration of Cr (70 mg/kg), Cu (80 mg/kg), V (56 mg/kg) and Zn (276 mg/kg) marginally exceeded EIL sediment quality guidelines (ANZECC & ARMCANZ 2000)) for topsoils (Table 9-2).

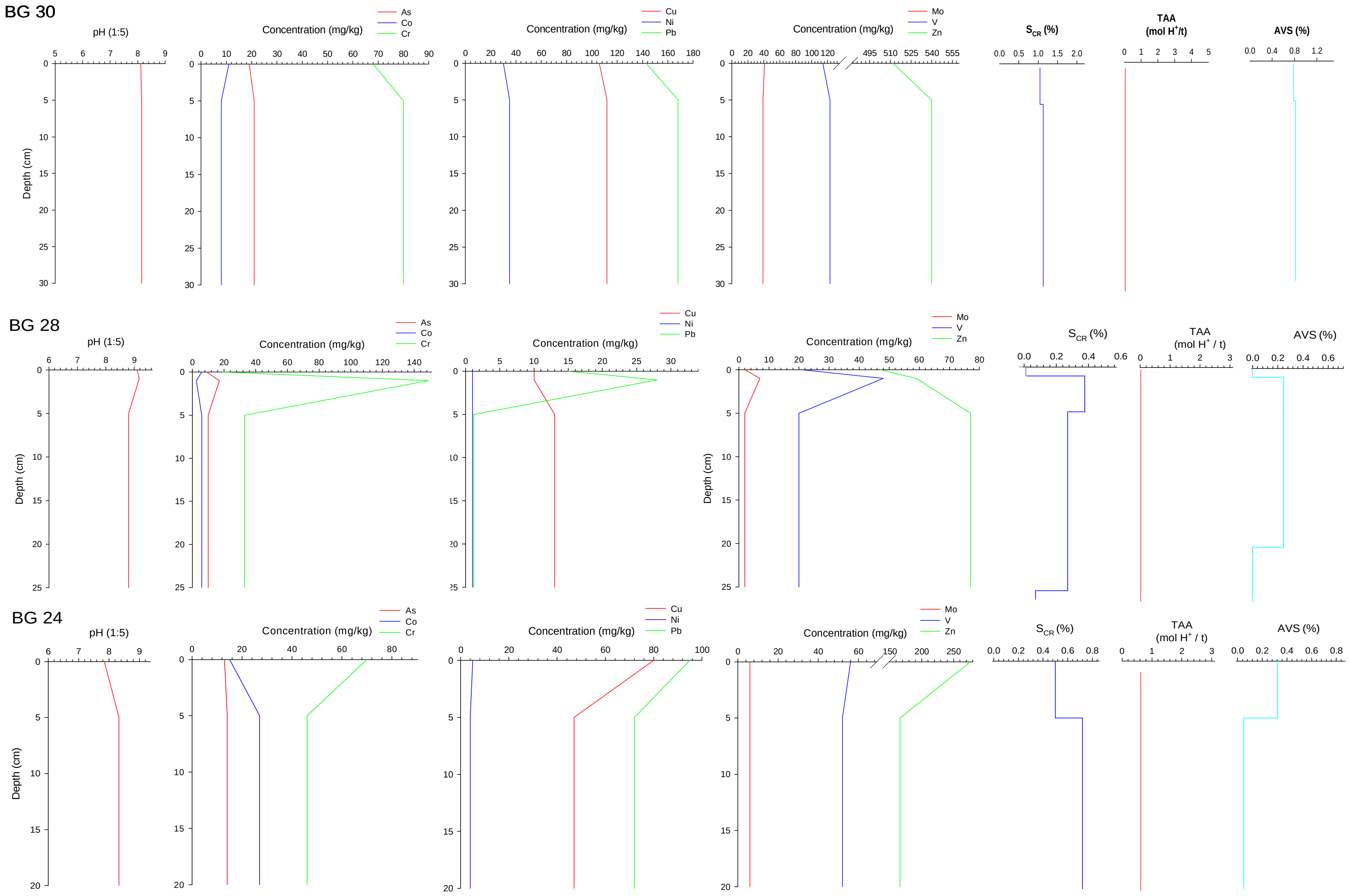

Figure 9-7 Down profile soil chemistry for Gillman soil profile BG 30 and BG 28, from former intertidal creek depressions, and profile BG 24 from a tidal creek. These profiles occur along a toposequence that includes profiles BG 11, BG 15 and BG 22 (refer to Figure 9-5 and Figure 9-6).

9.5.2. St Kilda toposequence

The St Kilda toposequence traversed St Kilda Focus area A, which was described in Chapter 5. The toposequence extends from relatively high intertidal floodplain covered by thick mangrove pneumatophore root masses (profile BSK 4 in map unit 10) to a permanently inundated tidal creek (profile BSK 5 in map unit 9) (Figure 9-8). Profile BSK 4 contained hyper- and hyposulfidic materials; whereas, profile BSK 5 only contained hyposulfidic materials. Minor monosulfidic materials were detected in both profiles (< 0.02% AVS; Figure 9-8).

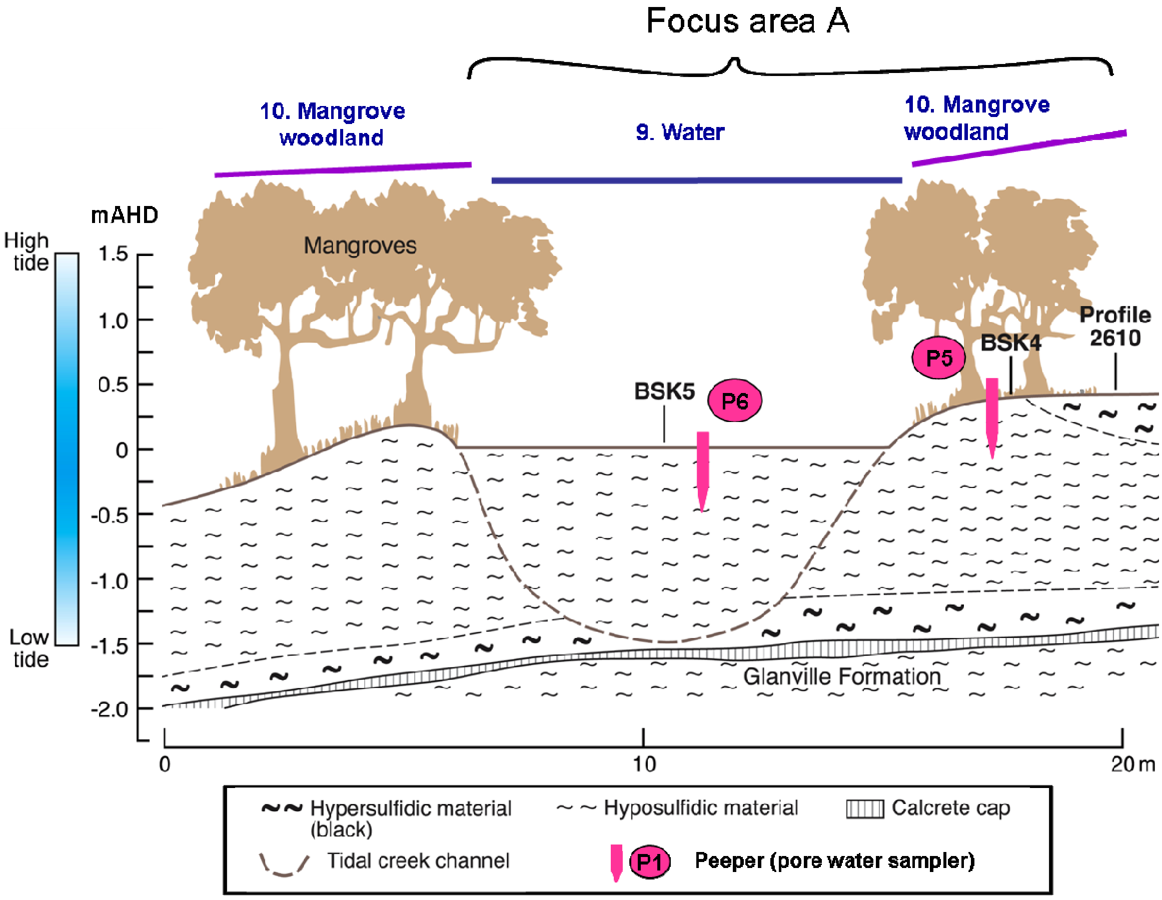

Figure 9-8 Schematic toposequence of the St Kilda study site showing the map units within an undisturbed intertidal area. The location of peepers (pore water samplers) is shown for soil profiles BSK 4 and BSK 5. The results of pore waters collected from saturated soil profiles at Gillman and St Kilda are explained in Section 9.6 of this Chapter. Refer to the soil map of the St Kilda study site (Figure 7-1) for the location of Focus area A.

Down profile geochemical characteristics

Profile BSK 4 and BSK 5: Intertidal soils (Map units 10 and 9)

The Zr and Ti content of surface soils from profiles BSK 4 and BSK 5 were similar; however, their contents increased dramatically just below the surface layer (below 5 cm) in profile BSK 4, but remained similar in subsoil layers of BSK 5, reflective of the Si mineral content of the soil layers (Appendix E). The soil pH (1:5) of both profiles was circum-neutral at the surface, measuring 7.24 in BSK 4 and 7.31 in BSK 5 (Figure 9-9 and Figure 9-10). Soil pH remained similar with depth down profile BSK 5, but decreased with depth in profile BSK 4 to a minimum pH (1:5) of 5.81 at 110 cm, and then gradually increased again to a pH (1:5) of 8.37 at the base of the profile (200 cm). The surprisingly low pH (1:5) at 110 cm depth in profile BSK 4 was likely due to partial oxidation of sulfides during sample preparation.

Major cations Fe, Al and Mg had similar, relative concentrations within surface soils from both profiles BSK 4 and BSK 5. The vertical distribution of Fe, Al and Mg was also similar, being slightly less at the surface and only varied slightly with depth (Figure 9-9 and Figure 9-10). The Ca content of surface soil layers in both profiles was also similar (5.4% in BSK 4 and 3.9% in BSK5); however, it increased dramatically at the base of profile BSK 4 (Ca of 25.6%) but only marginally at the base of profile BSK 5 (Ca of 5.8%; Figure 9-9 and Figure 9-10). The Mn concentration was high (531 mg/kg) at the surface of profile BSK 4, but was much lower in subsoil layers (ranging from 48 to 125 mg/kg; Figure 9-9). The Mn content at the surface of profile BSK 5 measured 38 mg/kg, and increased gradually with depth (to a maximum of 99 mg/kg at 110 cm; Figure 9-10).

Metal and metalloid concentrations within profile BSK 4 generally decreased with depth; however, As, Co, Cr, Cu, Pb and V concentrations were minor at the surface, although Zn was elevated (Figure 9-9). Trace elements Ba, Mo, Ni, and REE were only slightly lower in the surface soil layer of profile BSK 4 than at depth. In profile BSK 5, the concentration and distribution of trace elements was similar to profile BSK 4; however, the lower content at surface showed less contrast (Figure 9-10). The trace metal concentrations of Ba, Cr, Cu, Mo, Ni, Pb, V and REE (total REE) in profile BSK 5 generally increased with depth; however, below 110 cm depth the concentration of Pb and Zn decreased (Figure 9-10). The concentration of As decreased slightly with depth in profile BSK 5. In both profiles, Sr contents increased with depth and followed the Ca distribution pattern.

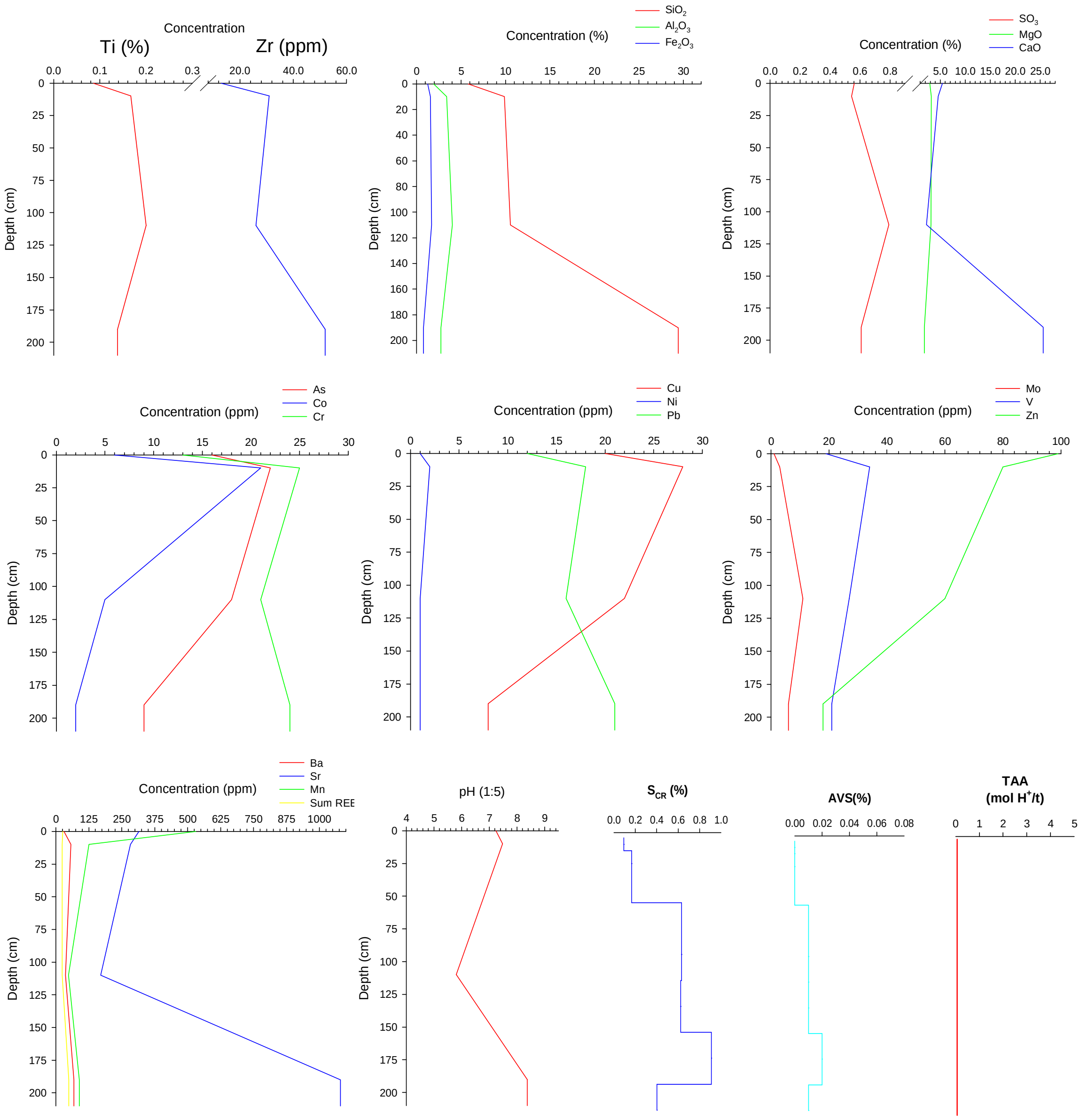

Figure 9-9 Down profile soil chemistry for St Kilda soil profiles BSK 4. This profile occurs along toposequence A'-A that transects from intertidal mangrove woodlands (BSK 4) to a tidal creek depression filled with organic wrack (BSK 5) in Focus area A (refer to Figure 9-8).

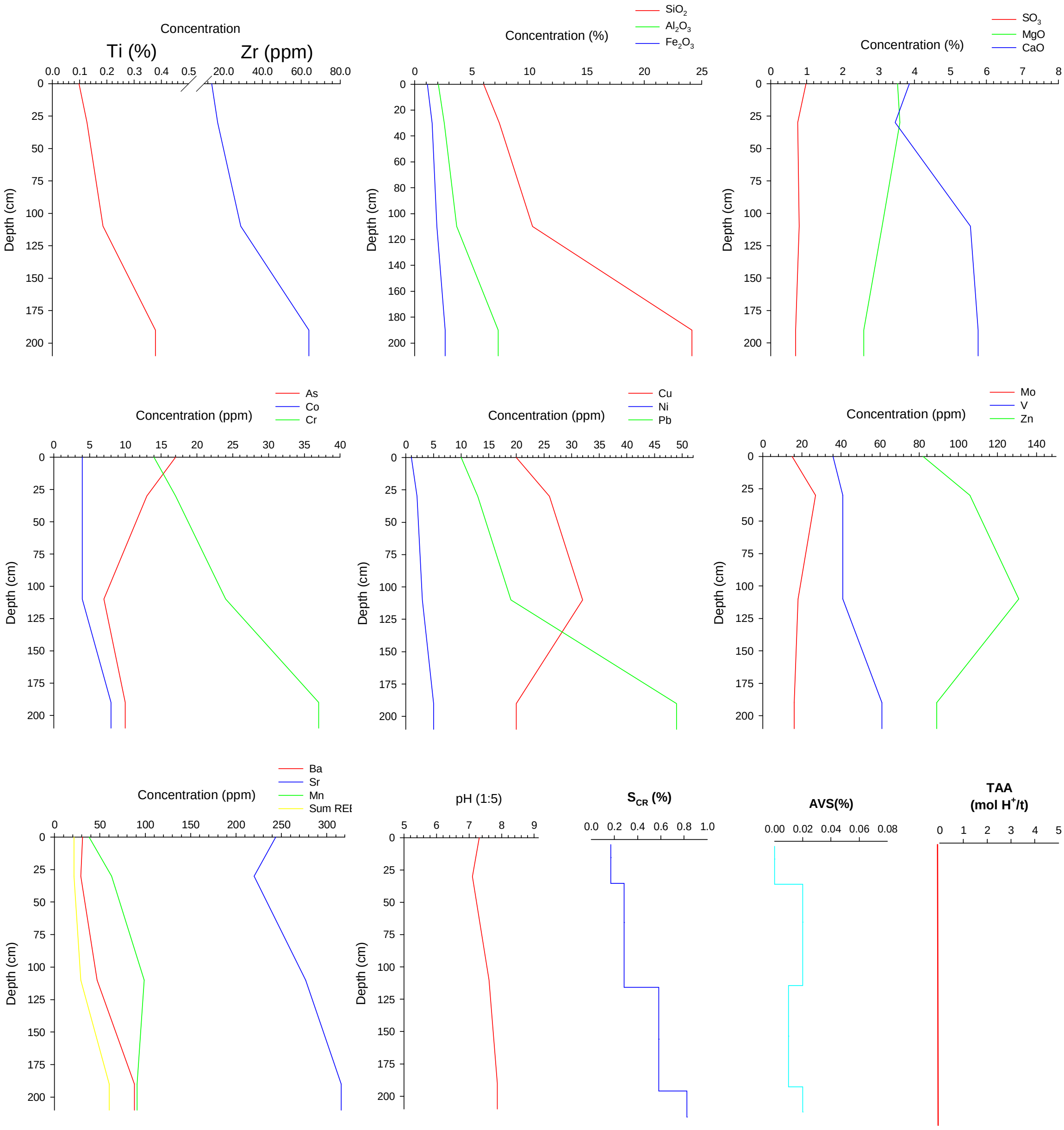

Figure 9-10 Down profile soil chemistry for St Kilda soil profiles BSK 5. This profile occurs along toposequence A'-A that transects from intertidal mangrove woodlands (BSK 4) to a tidal creek depression filled with organic wrack (BSK 5) in Focus area A (refer to Figure 9-8).

9.5.3. Discussion

The XRF data provides an overview of the total elemental composition of the soils (Appendix E). Variations in the composition of quartz (Si) and heavy minerals, such as rutile (Ti) and zircon (Zr), and changing clay contents and compositions (Si, Al and K) provide an insight to the depositional environment in which soil layers formed.

The Ti/Zr ratios for St Kilda profiles BSK 4 and BSK 5 were smaller and less variable than soil profiles from Gillman and are indicative of the low rutile and zircon contents and uniform depositional environment of the St Kilda profiles. Non-tidal soils at Gillman contained considerably higher amounts of monosulfide than intertidal soils at Gillman and St Kilda. Soil layers containing monosulfides generally had low silicate mineral contents (i.e. aluminosilicates and quartz), partially due to dilution from the increased organic matter and carbonate contents of these layers (Appendix E).

Quartz (Si) is a major component in sulfuric materials and its distribution is concomitant with a corresponding decrease in Al, K, Mg, Mn and Ca (Appendix E). The geomorphic history of the Gillman area has controlled soil clay and carbonate contents, resulting in sulfuric materials being coarser grained and having low acid buffering capacities. Some of these components, particularly Ca, would be removed by leaching following the acidification process.

All soil profiles from upland areas at Gillman (map units 4, 5 and 6) had a characteristic pH pattern, measuring circum-neutral pH conditions near the surface and becoming more acidic down the profile to a specific depth, which approximated the depth of the redox front. The lowest pH values were recorded in sandy soil profiles (e.g. BG 11 and BG 15), with the minimum pH (1:5) of 2.26 recorded in profile BG 15 at 95 cm depth (Figure 9-6). The surface of soil profiles at low positions in the landscape (e.g. map units 2 and 3) were approximately at the water table (e.g. profile BG 28), and generally had a pH that remained circum-neutral from the surface (Figure 9-7). Subaqueous soil profiles from non-tidal (excluding profiles containing sulfuric materials) and tidally influenced areas (map units 1 and 9) had a down-profile pH pattern that remained circum-neutral from the surface (Figure 9-9 and Figure 9-10). Clay within sandy sulfuric materials is likely decomposing and being removed; however, due to the large textural contrast of soils within the study sites, it is not apparent, from soils data alone, whether Al is being leached during pyrite oxidation and subsequent acidification (Figure 9-11). The pH control over the removal of Fe, Mn, Mg and P from acidic soil layers is more obvious (Appendix E). In monosulfidic materials there is a positive linear relationship between Al and AVS contents (Appendix E). This could be due to precipitation of Al oxyhydroxides which were sometimes visible in surface water draining areas containing sulfuric materials.

At the surface of upland, freely draining soil profiles, the S concentration (occurring largely in the form of SO_4^{2-}) is leached from topsoils ($S < 0.2\%$ in topsoil of profiles BG 11 and BG 15). At the surface of soil profiles at lower positions in the landscape the concentration of S is elevated (measuring > 1% in BG 28) due to capillary action and evapo-concentration from S rich ground waters, and precipitation as gypsum and other sulfate salts. Sulfate salts also precipitate on the surface of profile pit walls and drains during summer. In subaqueous and tidally influenced soils, the concentration of S is relatively constant with depth and measures between 0.5 and 1%. Below the redox front, S is in the form of metal sulfides (Figure 9-4). Because sulfate is soluble, it is leached from the upland topsoils (Figure 9-11) and becomes concentrated in local groundwaters, creeks and drains that receive drainage from acid sulfate soils. This process may also explain the enrichment of S (as sulfides) at depth (approximately at the redox front) in some acid sulfate soil profiles (e.g. BG 15).

The soils contain a large pool of organic C that was generally higher in topsoils than at depth (Appendix E). Buried organic C rich layers were present in some soil profiles (e.g. BG 15). Organic C content were very high in topsoils from tidally influenced soil profiles (ranging from 16% to 23%) and is unlikely to limit Fe and SO_4 reduction.

Iron is relatively abundant in the soils at both study sites, but was particularly elevated at Gillman, where Fe contents of up to 12.3% were measured in sulfuric material at 95 to 110 cm depth in profile BG 15. This soil layer had an S_{CR} content of 6.88%. In comparison, the highest Fe content measured at St Kilda was 2.8% (in profile BSK 5). After release from sulfides, Fe largely precipitates as insoluble Fe oxyhydroxides and is not leached from topsoil layers of map units 5 and 6, which have remained as oxidising and circum-neutral pH since tidal influences were excluded in 1935. This is evident in the bimodal distribution shown by the plot of total Fe and total S for the different acid sulfate soil types that separates topsoils from sulfuric and sulfidic soil materials (Figure 9-11). A similar distribution pattern is shown in the plot of total Fe and EC for the different acid sulfate soil types (Figure 9-11). Iron contents are lower in the profiles at Gillman and Fe is leached from sulfuric materials (Figure 9-11) to pore waters and surface waters and moves to lower positions in the landscape. Iron may be reduced to form Fe sulfides where favourable conditions occur (e.g. map units 1 and 2). There is a linear relationship between Fe and Al content of soils (Figure 9-11). The outliers containing excess Fe are organic C rich samples.

The carbonate contents of intertidal soil profiles at St Kilda were very high and generally increased with depth. This trend was reversed for intertidal soil profiles at the Gillman study site which had considerably lower carbonate contents that decreased with depth. Carbonate contents were depleted in sulfuric materials, whereas depletion of organic C was less apparent (Appendix E).

Within the Gillman study site, metal and metalloid contaminants were characteristically concentrated at the surface of soil sediment profiles, and have been leached from sulfuric materials to lower positions in the soil profile and the landscape. At St Kilda, surface concentrations were less evident. This is likely a characteristic of the two sites having different contamination histories, rather than drainage and geomorphological histories, as intertidal soils at Gillman had similar metal concentration to the reclaimed area at Gillman (Figure 9-2 and Figure 9-3).

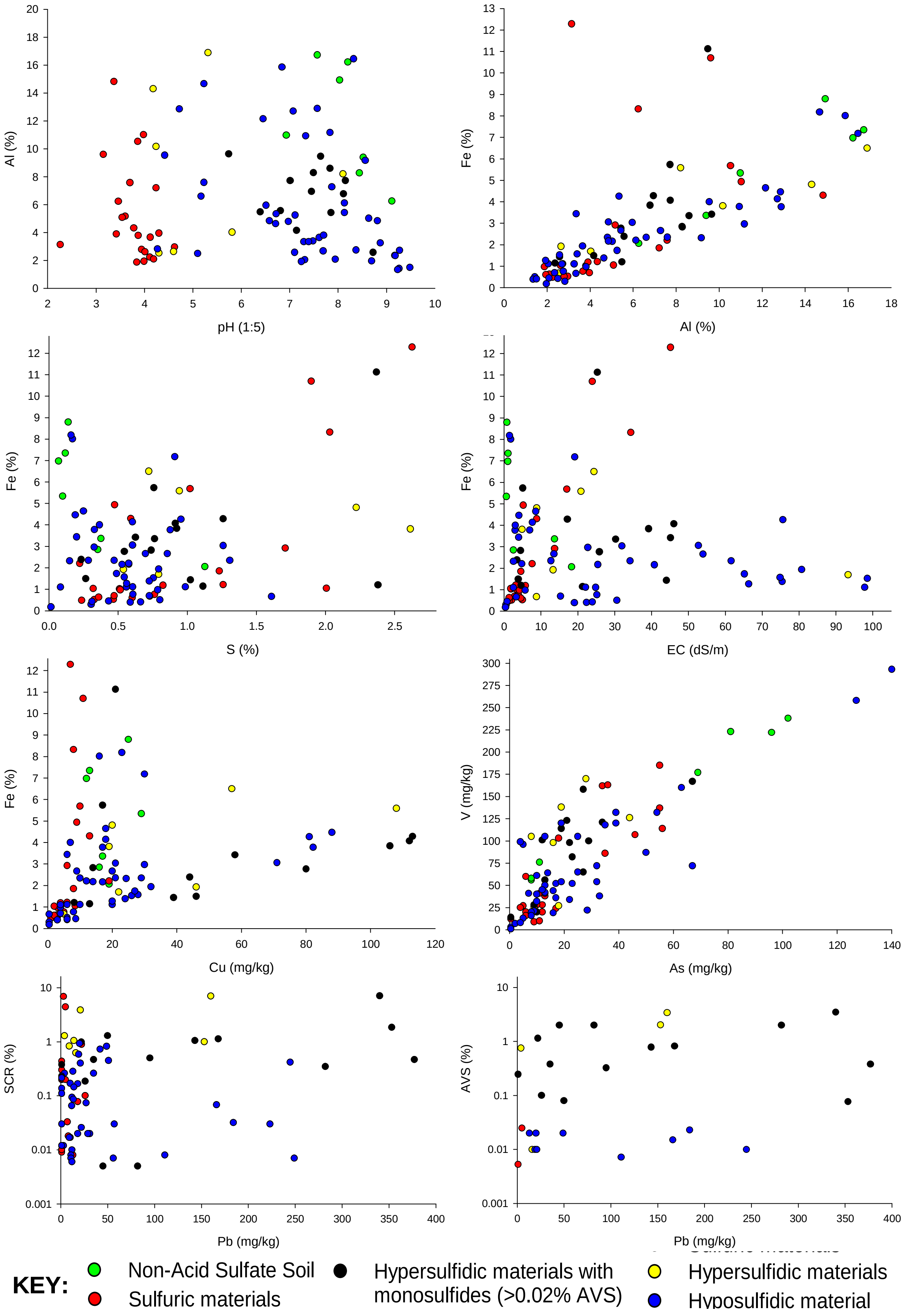

Figure 9-11 Selected plots showing relationships between major components, trace metals and metalloids for the various acid sulfate soil materials. Remaining plots are included in Appendix E.

In the majority of sub-aerial soil profiles at the Gillman study site (i.e. map units 3, 4, 5 and 6), the concentrations of As, Pb, V and Zn were particularly elevated in topsoils, and depleted in acidic subsoil layers (sulfuric materials; Figure 9-13). The concentrations of Cr, Cu and Ni were slightly elevated in topsoils from these areas. There was a strong linear relationship between As and V distributed across all acid sulfate soil types (Figure 9-11). Soil profiles from upland areas showed elevated concentrations of trace elements at the redox front (Mo and Cr were considerably elevated, and Co, Cu, Ni, Pb, V and Zn were slightly elevated; Figure 9-6 and Figure 9-7). These relationships are shown in Figure 9-12, but are more obvious in the individual pH versus trace element graphs presented in Figure 9-11 and Appendix E. The metal contaminants appear to be relatively immobile at the surface of oxidised soil profiles in which soil pH remained near neutral (i.e. non-acid sulfate soil materials and post active hyposulfidic materials; refer to Figure 9-12), which is likely due to sorption to Fe and Mn oxides. The contrasting distribution of Fe and metals Cu, Mo, Ni, Pb and Zn largely distinguishes oxidised soils (non-acid sulfate soil and sulfuric materials) from reduced soils (sulfidic materials). This relationship is shown in the plot of Fe *v.* Cu (Figure 9-11) where Cu is associated with reduced (sulfidic) soils. The remaining plots are shown in Appendix E.

Due to the efficient fixation of trace metals (Cd, Cu, Fe, Mn, Ni, Pb and Zn), sulfides are considered the dominant solid phase controlling their concentrations in sulfidic soils (Emerson *et al.* 1983). In reduced environments these metals can exchange for Fe in monosulfides and pyrite to form insoluble metal sulfides, and are therefore not considered bioavailable (Simpson *et al.* 1998). Subaqueous soil profiles containing monosulfidic materials (e.g. BG 30) that receive runoff from map units 4, 5, 6 and 7, appear to be acting as a sink for trace metals Cu, Mn, Ni, Pb and Zn. However the concentration of trace elements As, Mo and V are relatively low in subaqueous soils when compared to topographically higher soil profiles that contain non-acid sulfate soils and sulfuric materials (Figure 9-2 and Figure 9-3). Trace elements As, Mo and V exist as anions in oxidised environments and have a high affinity for Fe oxide surfaces (McBride 1989). The plots of metals S_{CR} and AVS show that concentrations of As, Cr, Cu, Mn, Ni, Pb, Mo, V and Zn correlate better with increasing AVS content than increasing S_{CR} content in sulfidic soils (Figure 9-11 and Appendix E). These relationships indicate that anthropogenic influences have impacted the Gillman study site by increasing trace metal and metalloid concentrations for As, Cu, Cr, Pb, V and Zn in topsoils of both intertidal and non-tidal (drained) soil profiles in upland areas at Gillman. Therefore, they probably originated from airborne sources. These relationships also indicate that contaminants are moving to lower positions in the landscape where they are being sequestered by sulfides. However, the exposure to O_2 through resuspension, excavation, draining or bioturbation could lead to the liberation of trace elements to the water column (Burton *et al.* 2006b; Gagnon *et al.* 1993). The distribution patterns showing concentrations of Cu, Pb, Ni, and Zn within the different acid sulfate soils types distinguishes the high metal loads in soils within the Magazine Creek ponding basin (Figure 9-11, Figure 9-12 and Appendix E).

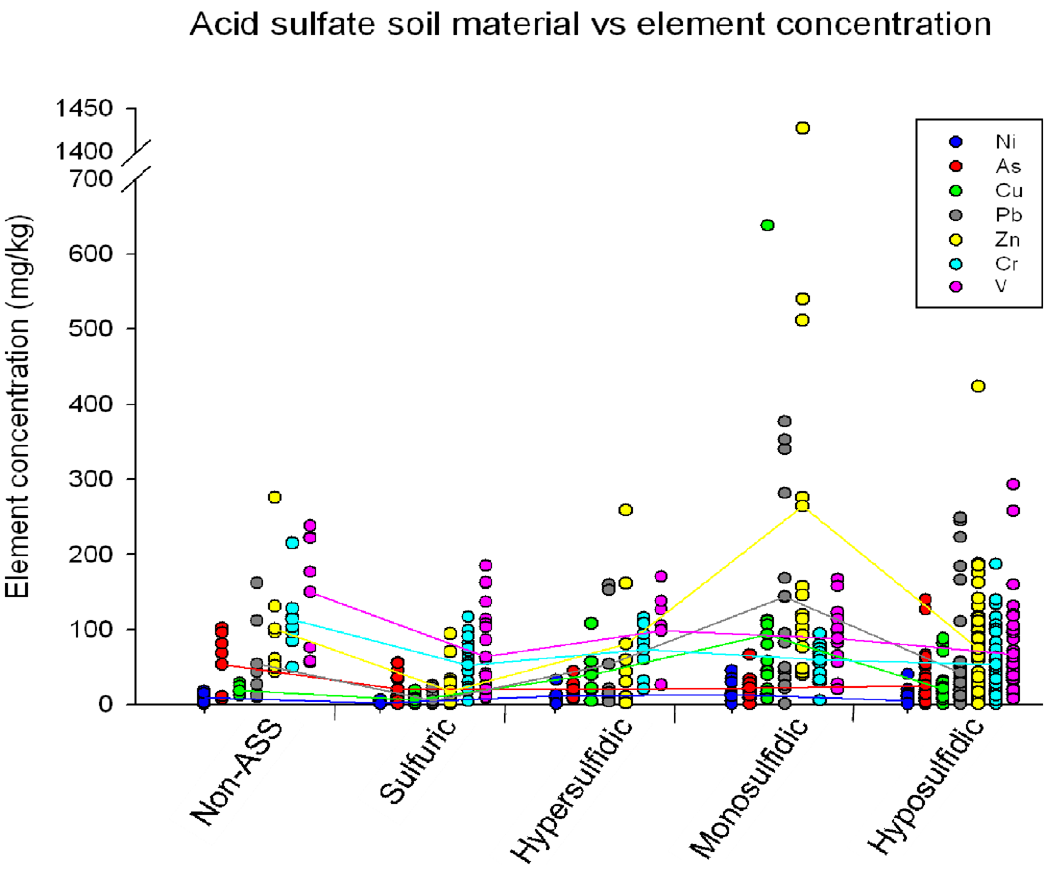

Figure 9-12 Metal and metalloid distribution within the various acid sulfate soil materials identified at the Gillman and St Kilda study sites. The concentration of metals and metalloids are relatively elevated in non-acid sulfate soils and are depleted in sulfuric materials. In non-tidal drains and creeks that drain the areas containing sulfuric materials, Cu, Ni, Pb and Zn have accumulated in subaqueous soils that contain high inorganic reduced sulfur contents in the form of monosulfides and pyrite.

9.6. Hydrochemistry

Many of the processes occurring in soil and sediments are mediated by water. Water is one of the main agents for physical and chemical weathering of soil constituents, transport of solutes, biological activity and surface erosion. Water flow paths and contents control salt movement in the landscape that strongly influences types and density of vegetation. Map units are; therefore, related to the hydrochemical processes occurring in the soils.

In order to identify the processes by which acidity and trace elements are released from soils and ultimately to surface waters in acid sulfate soil landscapes, peepers (Figure 9-1) were installed within four soil profiles to sample soil pore waters. Peepers were installed at three non-tidal locations (profiles BG 15, BG 28, BG P 5) and one tidally influenced location (profile BG 24) along the Gillman toposequence (i.e. traversing from Gillman Focus area A to Gillman Focus area C; refer to Figure 9-4). For comparison to a less disturbed environment, two peepers were installed in tidally influenced soil profiles (BSK 4 and BSK 5) along a toposequence at St Kilda in Focus area A (refer to Figure 9-8). Surface waters were sampled from a number of creeks and drains at the Gillman study site to trace the movement of trace elements across the landscape. Results are summarised in Table 9-3.

9.6.1. Results

Analysis of peeper samples provided down profile chemical data of pore waters within two sulfuric, and four sulfidic soil profiles. Water samples were also collected from seven water bodies within the Gillman study site for comparison to the pore water samples. Selected samples were analysed for pH, EC, major anions and cations (Al, Ca, Cl, Fe, K, Mg, Mn, Na, S and Si) and trace elements (B, Cd, Cr, Cu, Ni, P, Pb, Sr and Zn). Results are compared to ANZECC trigger values using protection levels for Marine environments: 80% protection for the Gilman study site (value used for highly disturbed systems) and 95% protection for the St Kilda study site (ANZECC & ARMCANZ 2000). Results are summarised in Table 9-3. A complete data set is provided in Appendix F.

Table 9-3 Summary of pore water chemistry obtained from peepers installed in saturated and subaqueous soils at the Gillman and St Kilda study sites. Samples were analysed major anions and cations (Al, Ca, Cl, Fe, K, Mg, Mn, Na, S and S) and for minor elements (B, Cd, Cr, Cu, Ni, P, Pb, Sr and Zn). Red values are those elements that exceed trigger levels for: ground water investigations in aquatic ecosystems, marine waters and fresh waters (ANZECC & ARMCANZ 2000), where they exist. Note: ANZECC groundwater investigation levels for Al is a low reliability marine trigger value and should only be used as an indicative interim working level (Al >0.005 mg/L at all pH values or >0.002 mg/L at pH<6.5). *Interim value used for Fe (no marine values exist in the ANZECC guidelines). n = number of water samples analysed. Where results were below the detection limit half the detection value was for statistical calculations.

Peeper samples		**Parameter**																		
		pH	**EC**	**Si**	**Al**	**Fe**	**Mn**	**S**	**Mg**	**Ca**	**K**	**P**	**B**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Sr**	**Zn**
Gillman P1 (n=8)	min	1.94	94.0	13.7	880	690	22.0	7870	6800	150	1500	1	39	0.1	0.1	0.1	2.0	0.1	19.2	1.5
	max	3.21	133.0	57.1	3100	2200	97.0	25800	25000	780	3600	10	130	0.1	11.4	2.0	14.9	2.0	35.4	9.6
	mean	2.88	111.3	27.5	1609	1133	45.7	13141	12178	504	2233	3	62	0.1	2.9	0.6	5.7	0.6	30.2	3.9
Gillman P2 (n=36)	min	2.01	79.7	0.1	28	330	2.5	3800	4100	550	1200	1	14	0.1	0.1	0.1	0.2	0.1	na	0.1
	max	3.88	112.6	36.8	900	840	29	8800	8200	1100	1800	1	37	0.1	0.1	0.1	0.2	0.1	na	0.1
	mean	2.55	94.1	21.8	648	707	21	7325	6950	679	1606	1	30	0.1	0.1	0.1	0.2	0.1	na	0.1
Gillman P3 (n=5)	min	7.55	66.0	1.0	1	2	0.1	1800	2500	920	850	1	8	0.1	0.1	0.1	0.2	0.1	14.1	0.1
	max	7.74	115.0	2.3	1	5	0.1	2450	3500	1200	1200	1	11	0.1	0.1	0.1	0.2	0.1	18.3	0.1
	mean	7.66	81.2	2.0	1	3	0.1	1970	2760	1008	940	1	9	0.1	0.1	0.1	0.2	0.1	15.4	0.1
Gillman P4 (n=5)	min	6.35	45.0	1.0	1	1	0.1	1120	1800	740	640	1	6	0.1	0.1	0.1	0.2	0.1	10.7	0.1
	max	8.38	66.0	14.2	1	6	0.1	1430	2200	880	750	1	8	0.1	0.1	0.1	0.2	0.1	12.8	0.1
	mean	7.70	54.2	9.0	1	2	0.1	1290	1900	794	666	1	7	0.1	0.1	0.1	0.2	0.1	11.4	0.1
St Kilda P5 (n=6)	min	7.46	49.0	1.0	1	1	0.1	820	1200	450	390	1	4	0.1	0.1	0.1	0.2	0.1	0.1	0.1
	max	8.14	58.0	4.8	1	1	0.7	1090	1500	550	460	1	7	0.1	0.1	0.1	0.2	0.1	0.1	0.1
	mean	7.90	54.3	3.4	1	1	0.3	977	1350	507	437	1	5	0.1	0.1	0.1	0.2	0.1	0.1	0.1
St Kilda P6 (n=6)	min	7.90	50.0	6.2	1	1	0.1	600	1200	440	380	1	5	0.1	0.1	0.1	0.2	0.1	0.1	0.1
	max	8.40	61.0	12.9	1	1	0.1	1070	1600	560	530	1	7	0.1	0.1	0.1	0.6	0.1	0.1	0.5
	mean	8.22	57.0	9.9	1	1	0.1	818	1417	510	447	1	6	0.1	0.1	0.1	0.3	0.1	0.1	0.2
	LLD	0.01	0.1	0.2	2	2	0.2	10	10	10	10	2	1	0.2	0.2	0.2	0.4	0.2	0.2	0.2
	Unit	pH	dS/m	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	mg/L
Level of Protection		**ANZECC 2000 guidelines**																		
Fresh Water 95%					55	300	1900							0.2	1	1.4	11	3.4		8.0
Fresh Water 80%					150		3600							0.8	40	2.5	17	9.4		31
Marine 95%					0.5	300*	80							5.5	4.4	1.3	70	4.4		15
Marine 80%						300*								36	85	0.33	560	12		43
	Unit				ug/L	ug/L	ug/L							ug/L	ug/L	ug/L	ug/L	ug/L		ug/L

Hydrochemistry of sulfuric materials at Gillman

Peeper P1 was installed into the exposed profile face of soil profile BG 15, which had remained open for one year prior. The top of the peeper was contacting with salt efflorescence that had precipitated on the soil surface (Figure 9-13). The base of the peeper was about level to the surface water in the adjacent drain, where peeper P2 was installed (Figure 9-14). The schematic cross section displayed in Figure 9-15 (a) shows the relative positions of the peepers: P1 within the very acidic soil profile BG 15 and P2 in the base of the drain containing acidic surface water. Figure 9-15 (b) shows the acid sulfate soil characteristics of soil profile BG 15. Both peepers were installed in February 2003 and removed during May 2003.

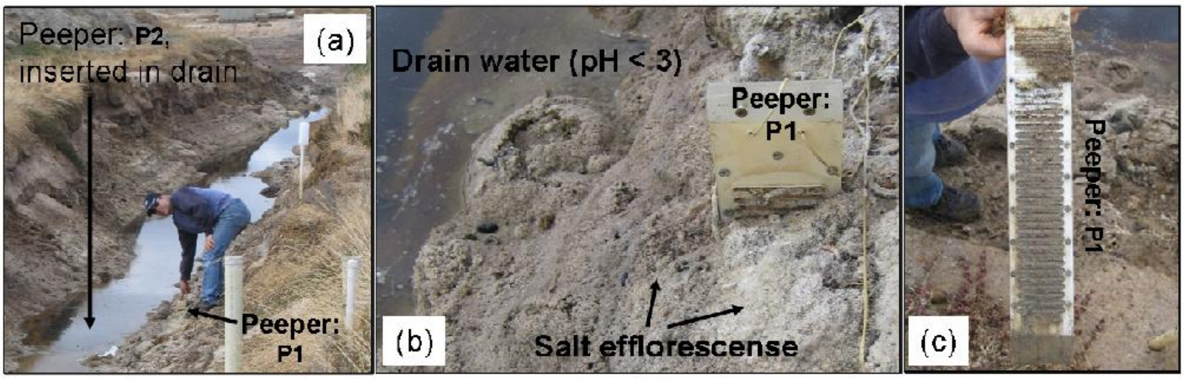

Figure 9-13 (a) peepers were installed at the edge of the drain (P1) and into the bottom of the drain (P2). (b) salt efflorescences precipitated on the drain wall and around the top of peeper P1. (c) peeper P1 was removed 4 weeks after installation to reveal salt effloresces covering the upper 5 peeper chambers.

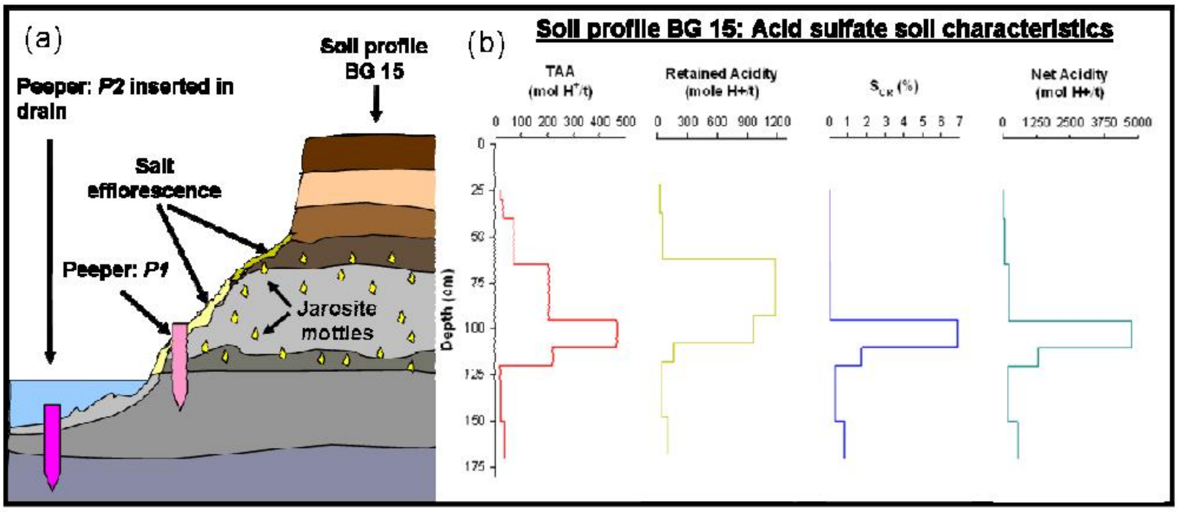

Figure 9-14 (a) schematic diagram showing a cross section of the western wall of the drain, showing the location of soil profile BG 15 and relative positions of peepers P1 and P2. Peeper P1 was located within sulfuric material at the drain wall. Peeper P2 was located within sulfuric and sulfidic materials in the bottom of the drain. The drain water had a pH < 3. (b) acid sulfate soil characteristics determined for soil profile BG 15.

Peeper P1 (sulfuric sub aerial)

Soil pore water chemistry collected by peeper P1, located in the oxic-acidic wall of 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 9-15). The upper six chambers of the peeper were in contact with salt efflorescences that had precipitated on the surface of the pit face. The lower portion of the peeper was pushed into clayey sand.

The EC of pore water from peeper P1 was very high, and decreased gradually from 102.2 dS/m at the surface to 94.4 dS/m at a depth of 14 cm, before increasing again to a maximum of 132.5 dS/m at 32 cm depth. Pore water pH measured 2.31 at the surface and decreased to a minimum of 1.94 at 4 cm depth, and then gradually increased again to a pH of 3.17 at the base of the peeper profile (Figure 9-15). Concentrations of major elements K, Mg, Mn, Al, Fe, B and Si, and trace element concentrations were highest in the top 5 cm, where salt efflorescence occurred, and decreased with depth, whereas pH, Ca and Sr showed the opposite trend (Figure 9-15).

The maximum concentrations of Al (3100 mg/L), Fe (2200 mg/L), S (25800 mg/L) and Mg (25000 mg/L) were an order of magnitude higher than pore waters sampled from within the adjacent drain (peeper P2). Metal concentrations were also very high in the top 5 cm and exceeded ANZECC trigger values (80% protection) for ground water investigations in marine ecosystems (ANZECC & ARMCANZ 2000) for Cr, Cu, Ni, Pb and Zn (Table 9-3). Metals Cr, Cu and Pb dropped to below detection limits below 9 cm depth, even though the water remained acidic. The concentrations of Ni and Zn also dropped significantly at about 9 cm depth (Figure 9-16), but still remained above the ANZECC guidelines.

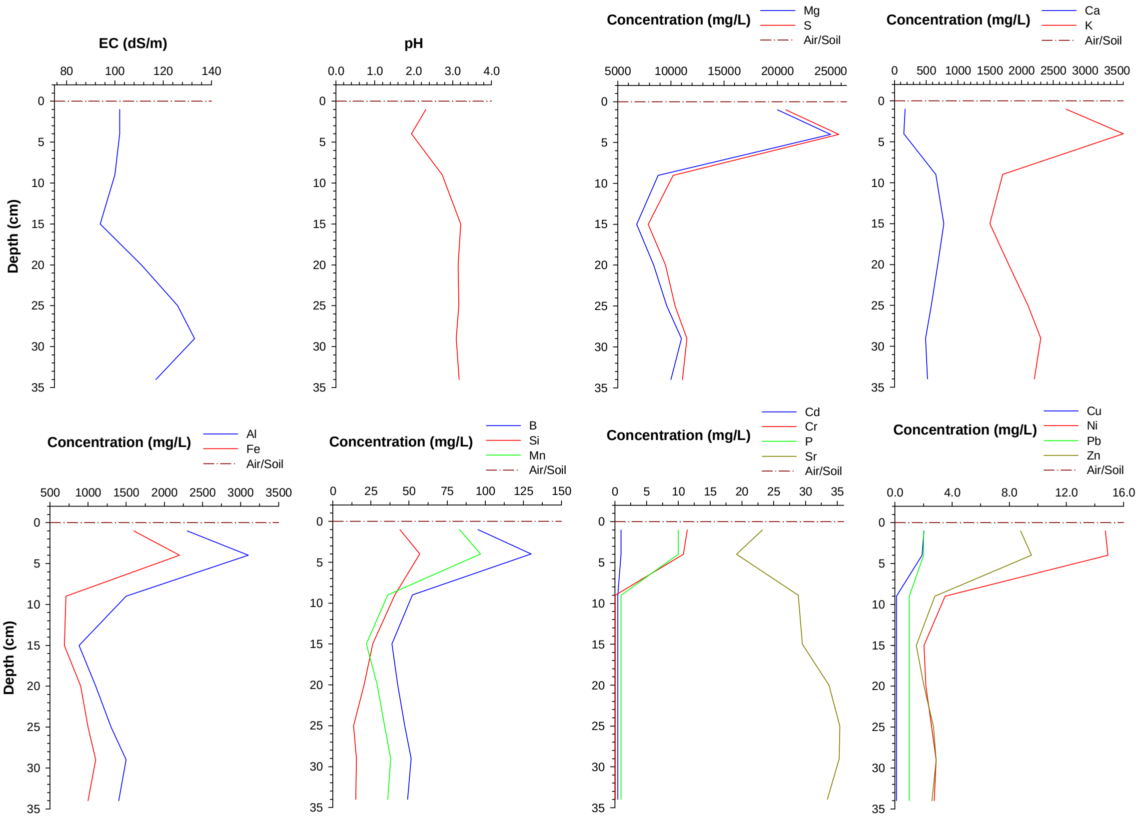

Figure 9-15 Down profile soil pore water data collected from peeper P1, located at the toe of the drain excavation, adjacent to soil profile BG 15. Depth intervals indicate the distance that each peeper chamber was above (negative values) or below (positive values) the soil surface. Each (selected) peeper chamber was analysed separately.

Peeper P2 (sulfuric subaqueous)

Soil pore water chemistry collected by peeper P2, located in the oxic-acidic drain sediment, showed a trend for pH and EC, anions, cations and metal concentrations similar to peeper P1; however, element concentrations were generally lower (Table 9-3). The top four chambers of the peeper were within the surface water. The top 20 cm of sediment consisted of clayey sand that had washed into the drain from the drain walls. The lower peeper chambers, below 20 cm, were pushed into light bluish grey, gleyed heavy clay. The pore water chemistry from the drain bottom sediment had an EC that increased from 99.7 dS/m at the sediment/water interface to 112.6 dS/m at 5 cm below it. The EC then decreased with depth to 80.7 dS/m at 32 cm below the sediment surface. Pore water pH increased from 2.01 at the water/sediment interface to 3.88 at 32 cm depth. Element concentrations for K, Mg, Mn, Al, Fe, B and Si decreased with increasing depth, with a sharp decrease at 22 cm depth, just below the contact between the transported clayey sand and the underlying heavy clay (Figure 9-16). Concentrations of Ca increased with increasing depth. Trace metals and metalloids Cd, Cr, P, Cu, Ni, Pb and Zn were all below detection limits for surface water and soil pore waters (Table 9-3). Surface water sampled by P2 in the drain (in cells above the sediment/water interface) generally had higher concentrations of elements than in pore waters, but lower EC and slightly lower pH and Ca content (Figure 9-16). The acidity of surface water in the drain (in which peeper P2 was installed) varied between 3000 mg/L $CaCO_3$ equivalent during winter months to 12500 mg/L $CaCO_3$ equivalent during summer months when water levels in the drain are low (refer to Chapter 10). Possible explanations for the surface waters having slightly higher major ion concentrations than pore waters may be due to the pH gradient, sulfides forming in the clays, or salt efflorescences having been washed into the drain and evapo-concentration. The down profile trend for EC is in contrast to the trend for cation concentrations. This suggests that Na^+ ions may control EC, however Na^+ concentrations in the soil were slightly lower in the soil than in the surface water (Appendix F).

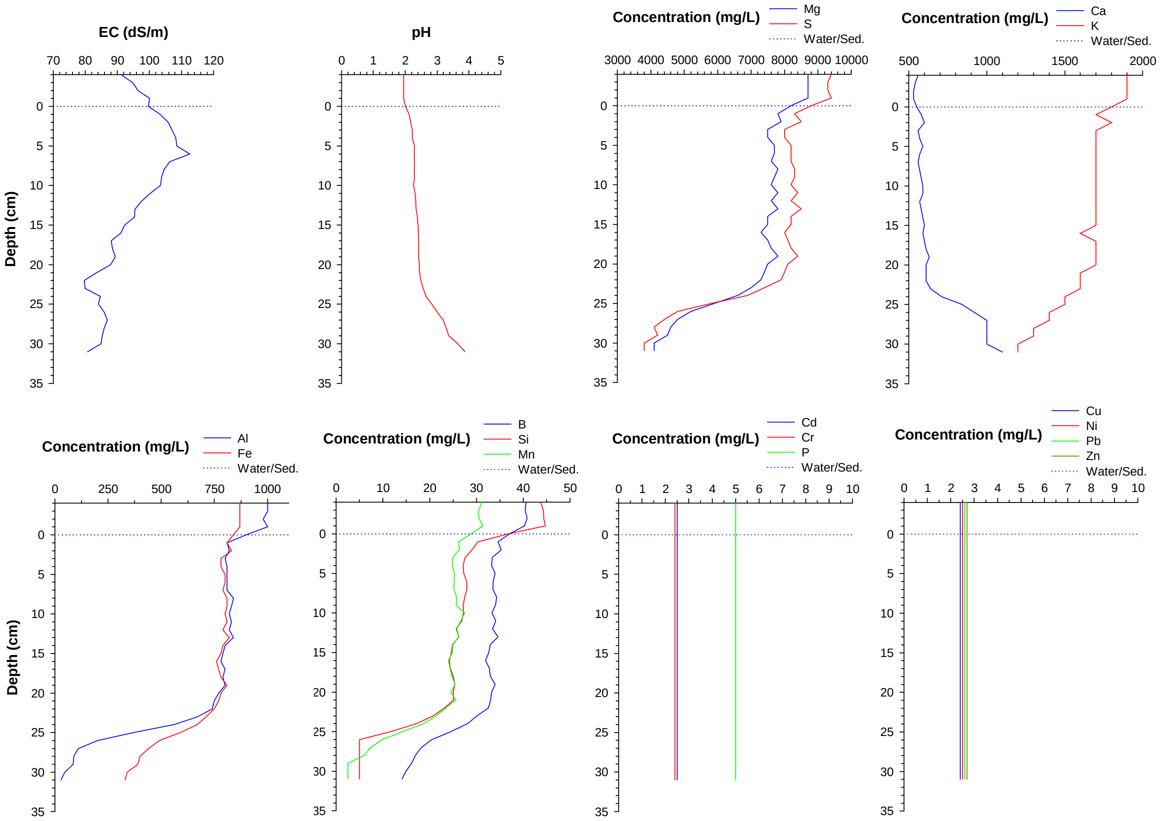

Figure 9-16 Down profile soil pore water data collected from peeper P2, located in the base of the drain adjacent to soil profile BG 15 and peeper P1. Depth intervals indicate the distance that each peeper chamber was above (negative values) or below (positive values) the sediment / water interface. Each (selected) peeper chamber was analysed separately. Plots showing concentrations for Cd, Cr, Cu, Ni, P, Pb and Zn are half the detection limit.

Hydrochemistry of sulfidic material at Gillman

Two peepers were installed at Gillman focus area C into water-filled depressions: P3 was inserted into a channel on the drained side of the bund wall and P4 was inserted into a small tidal creek on the northern side of the bund wall (Figure 9-17). Peeper P3 was positioned adjacent to soil profile BG 28. Peeper P4 was positioned next to soil profile BG 24. Both peepers were installed during December 2003 and removed in March 2004. Peeper P3 was removed to reveal the top three peeper chambers were located within the water column and the lower chambers were contacting dark grey, carbonate rich hyposulfidic material. Peeper P4 was removed to reveal the top three peeper chambers were located within the water column and the lower chambers were contacting very dark grey, clayey hyposulfidic material (Figure 9-17).

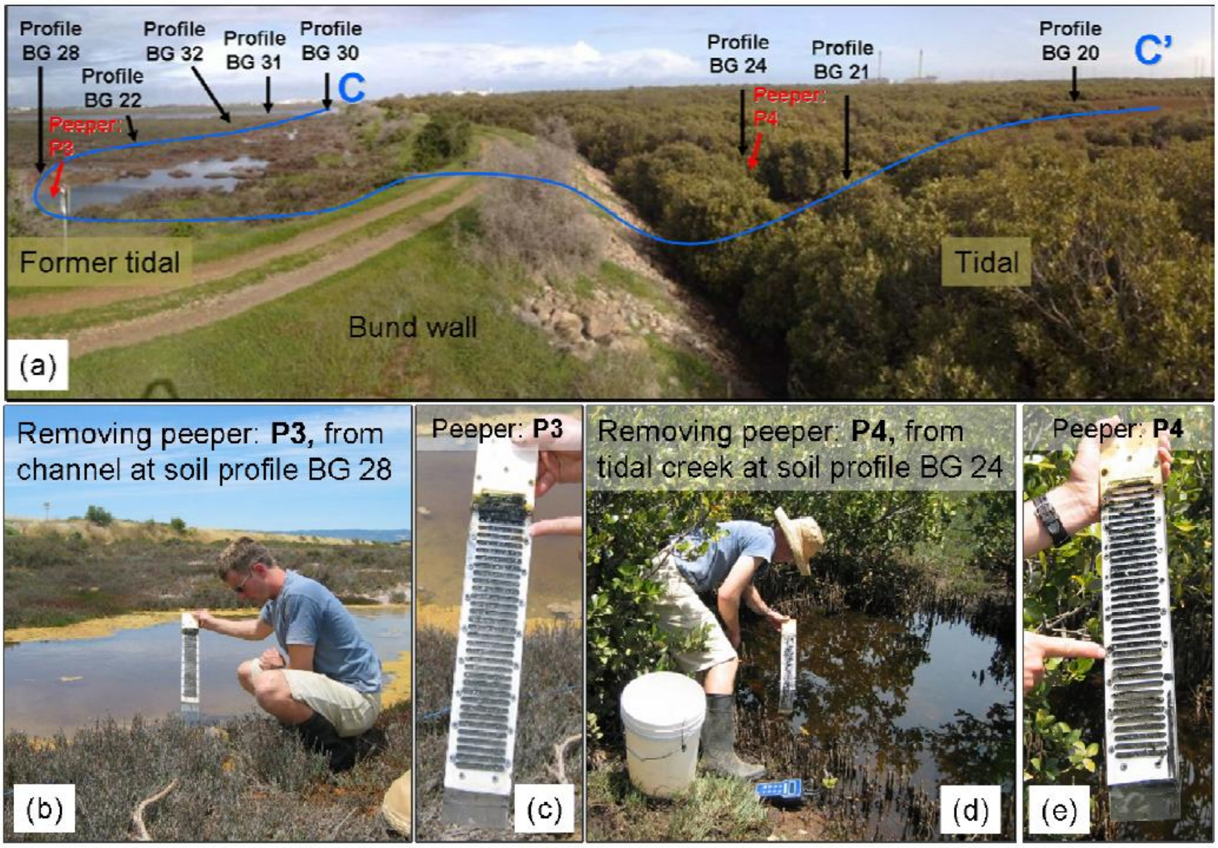

Figure 9-17 (a) photograph showing the location of two peepers installed at Gillman focus area C, along toposequence C-C'. (b) Peeper P3 was located on the drained (south) side of the bund wall and installed into a drainage channel, adjacent to soil profile BG 28. (c) peeper P3 was removed to reveal the top three peeper chambers were located within the water column and the lower chambers were contacting dark grey, carbonate rich hyposulfidic material. (d) Peeper P4 was located on the intertidal (northern) side of the bund wall among mangroves and installed into the bottom of a tidal creek channel, adjacent to soil profile BG 24. (e) peeper P4 was removed to reveal the top three peeper chambers were located within the water column and the lower chambers were contacting very dark grey, clayey hyposulfidic material.

Peepers P3 (non-tidal)

Soil pore water chemistry collected by peeper P3, located in strongly reducing subaqueous soil, showed considerably lower concentrations and less down-profile variation of analytes than for the two peepers located in sulfuric soils (P1 and P2). The soil material in which peeper P3 was placed was likely to have high sulfide and monosulfide contents, similar to soil profile BG 28 in which an AVS of 0.25% and a S_{CR} of 0.38% were measured in the top 20 cm of the profile. The pH of pore water in P3 was circum-neutral and remained constant down the profile and across the sediment/water interface and ranged from 7.56 in the surface waters to 7.72 at the base of the peeper profile. The EC of surface water was very high measuring 115 dS/m. The EC dropped substantially across the sediment/water interface to a minimum of 66.0 dS/m at 20 cm depth, and remained constant to the base of the profile (Figure 9-18).

The decrease in concentration across the sediment/water interface was similarly evident for major elements Mg, S, Ca and K, which respectively measured maximums of 3500 mg/L, 2450 mg/L, 1200 mg/L and 1200 mg/L in the surface water peeper cells (Figure 9-18). Boron and Sr concentrations were also highest in the surface water, measuring 11 mg/L and 18.3 mg/L respectively, and dropped slightly across the sediment/water interface (Figure 9-18). The concentration of Fe and Si increased slightly with depth, but were still very low when compared to their concentrations in pore waters of sulfuric materials. The concentration of Fe ranged from 3 mg/L in the surface water to 5.0 mg/L at the base of the profile, 32 cm below the sediment/water interface (Figure 9-18). The concentration of Si rose from 1.0 mg/L in the surface water to 2.3 mg/L at 20 cm below the soil surface (Figure 9-18). The concentration of Al and Mn, and trace metals Cd, Cr, Cu, Ni, P, Pb and Zn were below detection limits for all peeper cells sampled (Figure 9-18).

The lowest points in the drainage network that receives drainage waters from sulfuric materials within the eastern portion of the Gillman study site are represented by peeper profile BG P 5 (Focus area A, Figure 6-3) and surface water sampling site BG 23 (Focus area C, Figure 6-11). The pH of surface waters at these two locations (BG P 5 and BG 23) measured 6.49 and 5.86 respectively. The ECs of surface waters measured 73.3 dS/m at BG P 5 and 71.4 dS/m at BG 23. Surface waters from BG P 5 contained 12 mg/L of Al, and up to 490 mg/L of Fe, which both decreased to less than detection limits (<1 mg/L) below the sediment/water interface. In surface water samples from BG 23, Al contents measured 54 mg/L and Fe measured 11 mg/L. These Fe and Al contents are high for near neutral water and was probably due to the deposition of colloids within the peeper cells in an alternating oxidising/reducing environment, rather than Fe(III) oxide Al hydroxides passing through the dialysis membrane of the peepers and 0.45μm filters.

The concentration of major elements (Mg, S, Ca and K) were slightly higher in surface water from BG P 5 compared to BG 23, which measured 2800 mg/L, 2200 mg/L, 870 mg/L and 860 mg/L respectively for BG P 5, and measured 2500 mg/L, 1700 mg/L, 640 mg/L and 760 mg/L respectively for BG 23 (Appendix F). Trace elements (B, Cd, Cr, Cu, Mn, Ni, P, Pb and Zn) were below detection limits for surface waters at BG 23 and pore waters and surface waters at BG P 5 (Appendix F). The $Cl^-:SO_4$ mass-ratio measured 6.6 in surface water from BG P 5 and 6.9 in surface water at BG 23, which approaches seawater $Cl^-:SO_4$ mass-ratio of 7.2, suggesting seawater may be leaking through the bund wall, or spraying over the wall. Sulfate reduction was occurring in soils at both locations (BG P 5 and BG 23), but probably varied in intensity. Alkalinity of surface water measured 340 mg/L (mg $CaCO_3$/L equivalent) at BG P 5, and 150 mg/L (mg/L $CaCO_3$ equivalent) at BG 23.

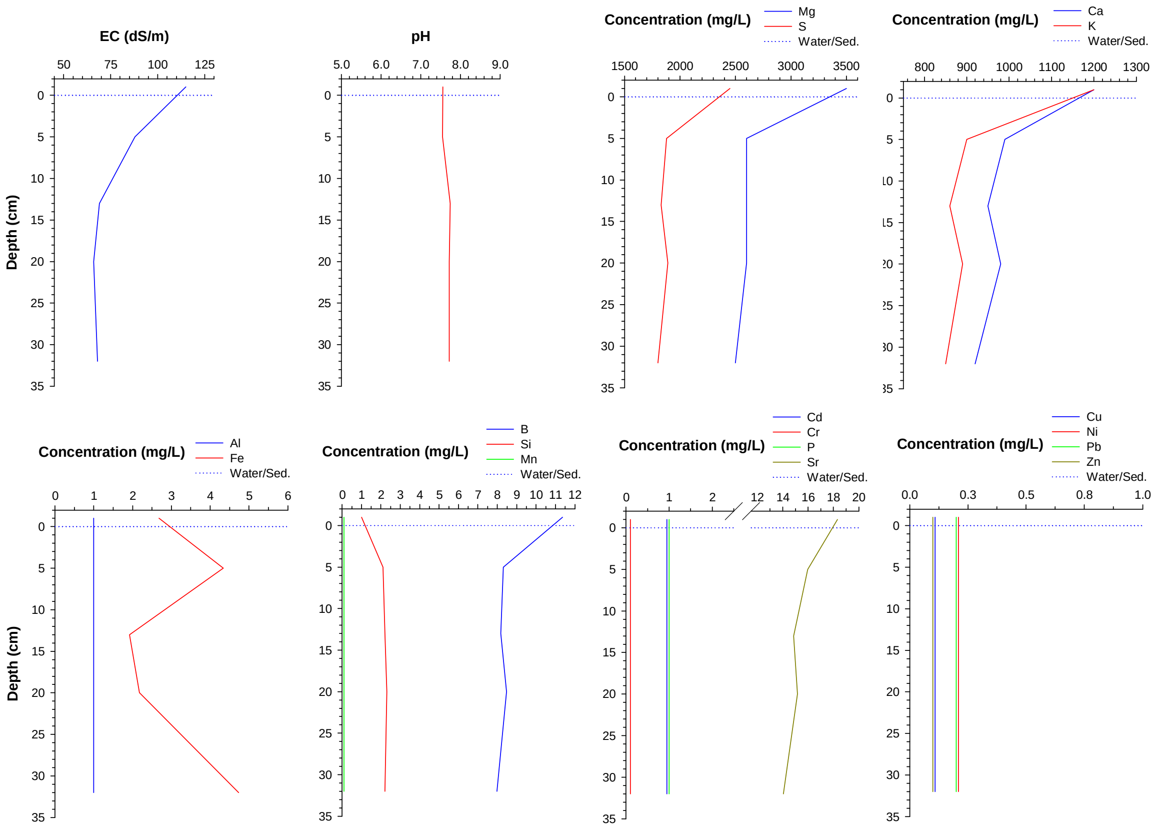

Figure 9-18 Down-profile soil pore water data collected from peeper P3, located adjacent to soils-sediment profile BG 28. Each (selected) peeper chamber was analysed separately.

Peeper P4 (intertidal)

Soil pore water chemistry collected by peeper P4, located in strongly reducing subaqueous soil of a tidal stream, showed similar concentrations of analytes as for the peeper located in the non-tidal channel (i.e. peeper P3), but with more variability in the near surface. The soil material in which peeper P4 was installed probably contained high sulfide and monosulfides contents, similar to soil profile BG 24 in which an AVS of 0.32% and a S_{CR} of 0.72% was measured in the top 20 cm of the profile. The pH of surface water collected in peeper P4 was circum-neutral (7.26) and dropped sharply across the sediment/water interface to a minimum pH of 6.35 at 1 cm below the soil surface (Figure 9-19). The soil pore water pH then rose quickly again to measure 8.16 at 4 cm depth, and remained relatively constant to the base of the soil profile at a depth of 33 cm.

The down-profile pattern for EC had a similar inflection across the sediment/water interface, but in the opposite direction (Figure 9-19). The highest EC value occurred just below the sediment/water interface and measured 66.0 dS/m, which was about half the value measured in surface water at peeper P3. The EC then decreased gradually with increasing depth to the base of the peeper, measuring a minimum of 48 dS/m. The concentration of major elements (Mg, S, Ca and K) in the surface water in the tidal creek were about half the value measured in the non-tidal channel. The concentrations of the surface water for Mg, S, Ca and K measured 1900 mg/L, 1420 mg/L, 810 mg/L and 660 mg/L, respectively. Their concentrations decreased slightly across the sediment/water interface to a minimum value at about 12 cm depth, before increasing again with depth (Figure 9-19). Boron and Sr concentrations were slightly lower than in the non-tidal soil profile, and followed a similar down profile trend as Mg.

The maximum concentration was 8 mg/L for B and was 12.7 mg/L for Sr (Figure 9-19). The concentration of Si measured 1.0 mg/L in the surface water and increased significantly across the sediment/water interface to a maximum of 14.2 mg/L at 4 cm depth, then decreased slightly with increasing depth (Figure 9-19). The Fe concentration of surface water measured 6 mg/L but was below the detection limit of 2 mg/L in the soil pore waters (Figure 9-19). The concentration of Al and Mn, and trace metals Cd, Cr, Cu, Ni, P, Pb and Zn were all below detection limits for all surface water and soil pore water samples in peeper P4 (Figure 9-19). The hydrochemical conditions of profile BG 24, particularly in the top 5 cm of soil, are likely to change between tidal extremes.

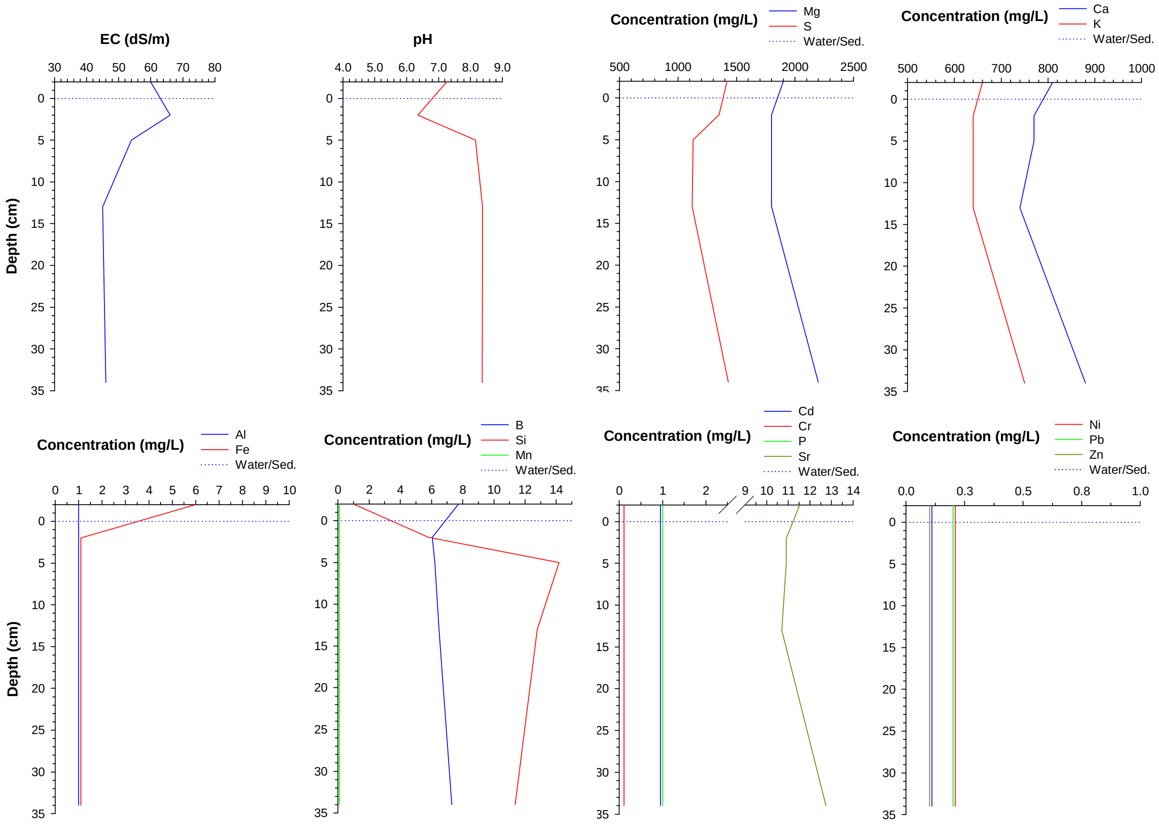

Figure 9-19 Down-profile soil pore water data collected from peeper P4, located adjacent to soils-sediment profile BG 24. Each (selected) peeper chamber was analysed separately. Plots showing concentrations for Al, Cd, Cr, Cu, Mn, Ni, P, Pb and Zn are half the detection limit.

Surface water samples

Surface water sample BG 40 was collected from Magazine Creek during a winter storm that had created a significant flow. The EC of the water was 3.9 dS/m, and had a pH of 6.12. Surface water sample BG 41 was collected at the same time but from North Arm Creek, adjacent to the tidal gates that regulate water levels in the Magazine Creek ponding basin (Figure 6-1). These two water samples represent the drainage outlet for the Magazine Creek ponding basin, constituting the western portion of the Gillman study site. A significant flow of water was coming out of the tidal gates at the time of sampling, indicated by the relatively low EC (13.9 dS/m) for a marine setting. The pH of the water from North Arm Creek was 6.47. Trace metal concentrations were below detection limits for both water samples (Appendix F). The Cl^{-}:SO_4 mass-ratios measured 6.3 and 7.1 for sites BG 40 and BG 41, respectively. Alkalinity of surface water measured 100 mg/L (mg/L $CaCO_3$ equivalent) at BG 40, and 150 mg/L (mg/L $CaCO_3$ equivalent) at BG 41.

Surface water that had collected at the base of soil profile BG 3 had a pH of 1.63, and contained very similar concentrations of Ni (10.0 mg/L) and Zn (13.5 mg/L) as those measured in near surface cells of peeper P1; however, the concentrations of other metals (Cr, Cu and Pb) were below detection limits (Appendix F). Profile BG 3 was located within map units 6 and about 700 m to the south west of profile BG 15 (Figure 6-1). The pit walls of soil profile BG 3 were extensively covered by salt efflorescences.

Hydrochemistry of sulfidic material at St Kilda

At St Kilda focus area A, two peepers were installed into sulfidic soil profiles BSK 4 and BSK 5, which were subject to strong tidal influences (Figure 9-20). Peeper P5 was inserted into peaty mangrove soils that had abundant mangrove pneumatophores and was submerged on the high tide only. Peeper P6 was inserted into a permanently inundated tidal creek channel that was filled with organic wrack (Figure 9-20).

Both peepers were installed during December 2003 and removed in March 2004. Peeper P5 was removed to reveal the top two peeper chambers were located within the water column during high tide, and the lower chambers were contacting dark brown, sapric material and hyposulfidic material. Peeper P6 was removed to reveal the top two peeper chambers were located within the water column and the lower chambers were contacting dark brown sapric to fibric material and hyposulfidic material (Figure 9-20). In dynamic hydrochemical conditions such as a tidal zone, the water sample in peeper chambers provides an average of the chemical conditions it experienced over the preceeding one to two week period. This is due to the slow diffusion rate through the dialysis membrane of the peepers used in this study. It is estimated that about two weeks would be required for the peeper chambers to reach equilibrium, under stable environmental conditions (Teasdale *et al.* 1995; van Oploo *et al.* 2008b).

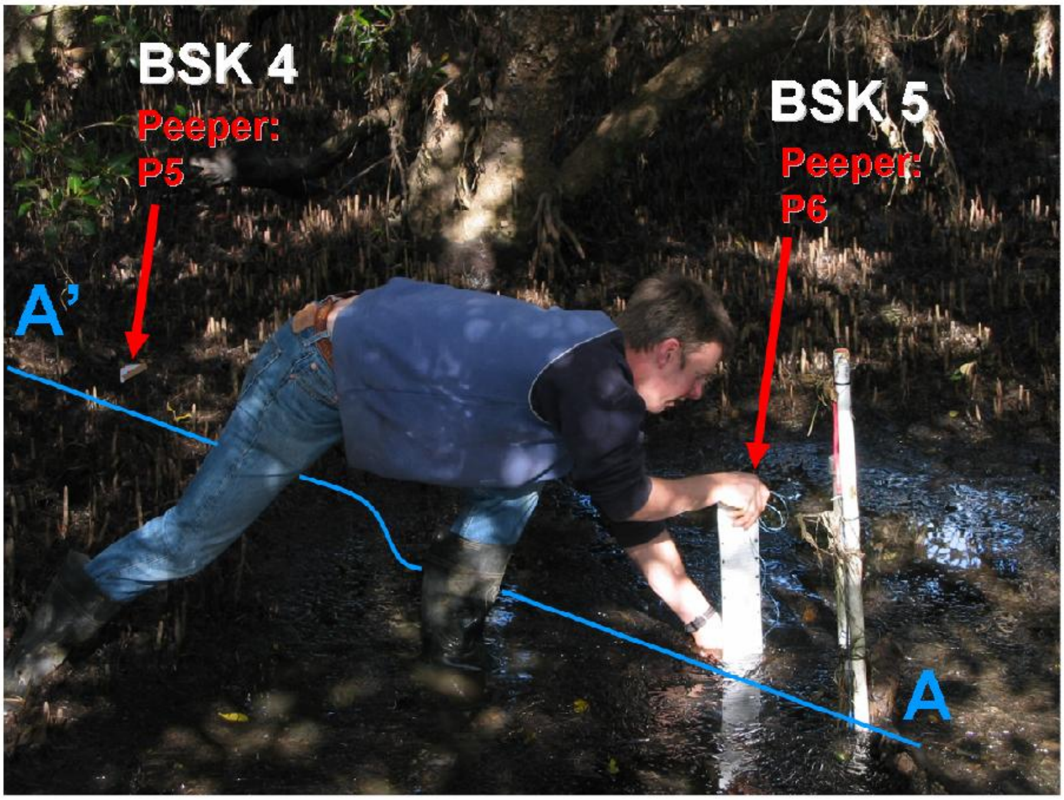

Figure 9-20 Inserting a peeper into subaqueous soil profile BSK 5, where a tidal creek depression was filled with organic wrack (predominantly consisting of debris from seagrass, mangroves and Ulva).

Peeper P5 (intertidal)

Peeper P5 was probably in contact with sulfidic materials of similar concentration as those measured in soil profile BSK 4 that contained between 0.09 and 0.17% S_{CR}, but no measurable AVS content in the top 40 cm of the profile (Chapter 5). The pH of water in P5 was circum-neutral (7.46) in peeper cells that were in contact with tidal waters at the surface. Water pH increased slightly across the sediment/water interface and down the soil profile, measuring a maximum of 8.14 at 26 cm below the soil surface (Figure 9-21). The EC of surface water (54.0 dS/m) was, as expected, close to that of seawater and increased across the sediment/water interface to measure a maximum of 58.0 dS/m at 12 cm below the surface, and then dropped with depth to a minimum EC of 49.0 dS/m at 26 cm below the surface (Figure 9-21). The EC of near-surface pore waters in peeper P5 was about half the value measured in peepers installed in the drained areas at Gillman (e.g. peepers P1, P2 and P3) and slightly lower than the EC of intertidal soil profiles BG 24 (peeper P4) and BSK 3 (refer to Appendix F). The down-profile EC pattern was reflected by the concentration of elements Mg, S, Ca and K, B and Si (Figure 9-21). The concentration of Mg, S, Ca and K measured 1300 mg/L, 1000 mg/L, 510 mg/L and 440 mg/L, respectively, in the upper most peeper cell that contacted tidal water during high tides. The concentration of these elements increased with depth to a maximum at 12 cm below the surface of 1500 mg Mg/L, 1090 mg S/L, 550 mg Ca/L and 460 mg K/L (Figure 9-21). The concentration of B and Si increased from 4 mg/L and 1.0 mg/L respectively in the surface water, to a maximum of 7 mg/L for B and 4.8 mg/L for Si at 18 cm below the surface (Figure 9-21). The concentration of Mn was low (ranging from 0.4 to 0.7 mg/L), and which may be due to changes in pH and or redox conditions (Figure 9-21). The concentration of Al and trace metals Cd, Cr, Cu, Ni, P, Pb and Zn were below detection limits for all peeper P5 cells sampled (Figure 9-21). Soil pore water chemistry collected by peeper P5, located in strongly reducing intertidal soils, showed slightly lower concentrations of analytes than peepers located in similar intertidal soils, but which experienced less extensive tidal flushing (e.g. peepers P3 and BSK 3). Peeper BSK 3 was located in the shell grits of the chenier ridge at St Kilda focus area B (Appendix F).

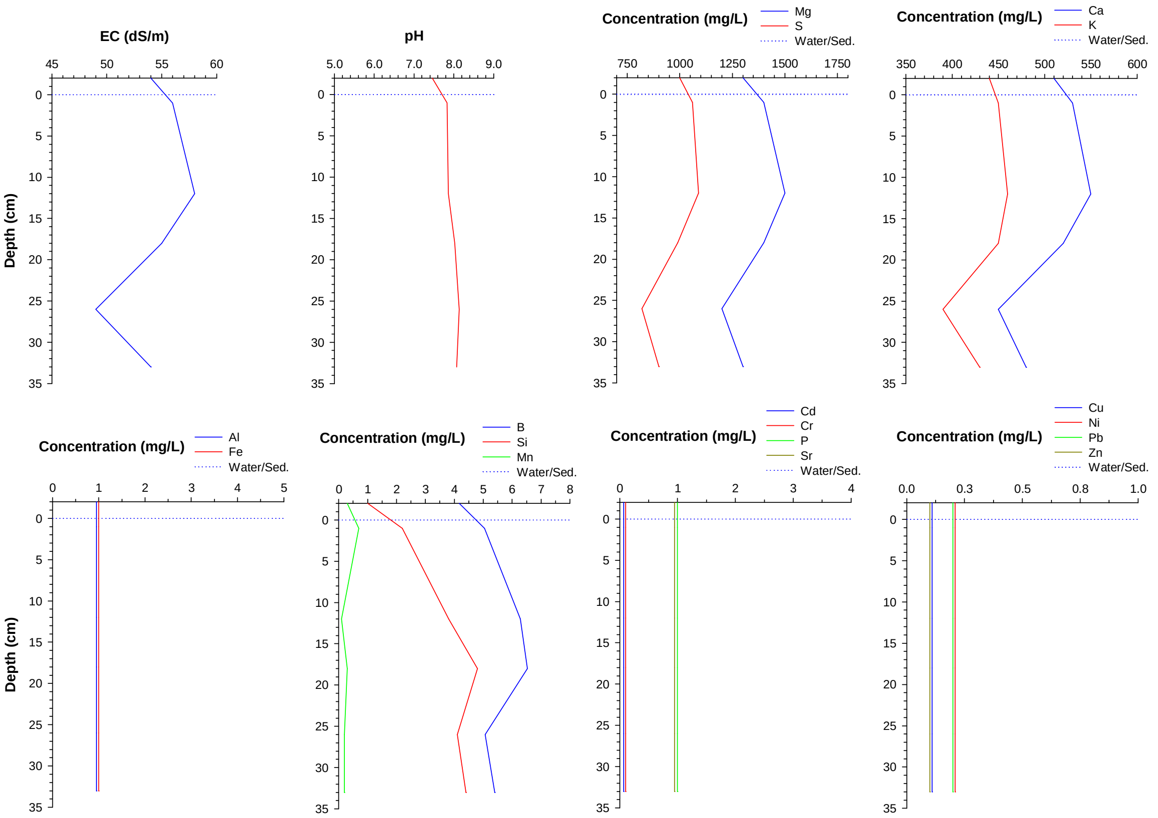

Figure 9-21 Down-profile soil pore water data collected from peeper P5, located adjacent to soil profile BSK 4. Each (selected) peeper chamber was analysed separately. Plots showing concentrations for Al, Cd, Cr, Cu, Fe, Ni, P, Pb, Sr and Zn are half the detection limit.

Peeper P6 (intertidal)

Peeper P6 was probably in contact with sulfidic materials of similar concentration to those measured in the top 40 cm of soil profile BSK 5, which contained between 0.17 and 0.28% S_{CR} and 0.02% AVS (Chapter 5). The pH of surface water in peeper P6 was slightly alkaline (7.95) and was stable across the sediment/water interface, then increased slightly down the soil profile, measuring a maximum of 8.40 at 33 cm below the soil surface (Figure 9-22). The EC of surface water (57.0 dS/m) was similar to that of seawater and slightly increased across the sediment/water interface to 58.0 dS/m at 2 cm below the surface, and then decreased with depth to a minimum EC of 50.0 dS/m at 14 cm below the surface (Figure 9-22). The EC increased again with depth below 14 cm to reach a maximum of 61.0 dS/m at the base of the peeper.

The down-profile concentrations of Mg, S, Ca and K and B crudely reflected the EC profile (Figure 9-22). The concentration of Mg, S, Ca and K measured 1500 mg/L, 1070 mg/L, 560 mg/L and 470 mg/L, respectively, in the surface waters, collected in the uppermost peeper cells. The concentrations of these elements decreased with depth across the sediment/water interface to a minimum at 14 cm below the surface of 1200 mg Mg/L, 600 mg S/L, 440 mg Ca/L and 380 mg K/L (Figure 9-22). The concentration of B was relatively stable with increasing depth and ranged between 6 mg/L in the surface water to a minimum of 5 mg/L at 14 cm depth and increasing to 7 mg/L at 33 cm depth (Figure 9-22). The concentrations of Si was lowest in the surface water (measuring 6.2 mg/L) and increased with depth to a maximum of 12.9 mg/L at 33 cm below the surface (Figure 9-22).

The concentrations of Al, Fe and trace metals Cd, Cr, Cu, P and Pb were below detection limits for all peeper P6 cells sampled (Figure 9-22). However, concentrations for Ni (0.6 mg/L) and Zn 0.5 mg/L) were slightly above detection limits in the peeper cell sampled from 14 cm depth (Figure 9-22). Soil pore water composition collected by peeper P6, located in strongly reducing subaqueous soils in a tidal creek depression showed slightly lower concentrations of analytes than peeper P4, which was also located in a tidal creek at Gillman, but was subject to less extensive tidal flushing.

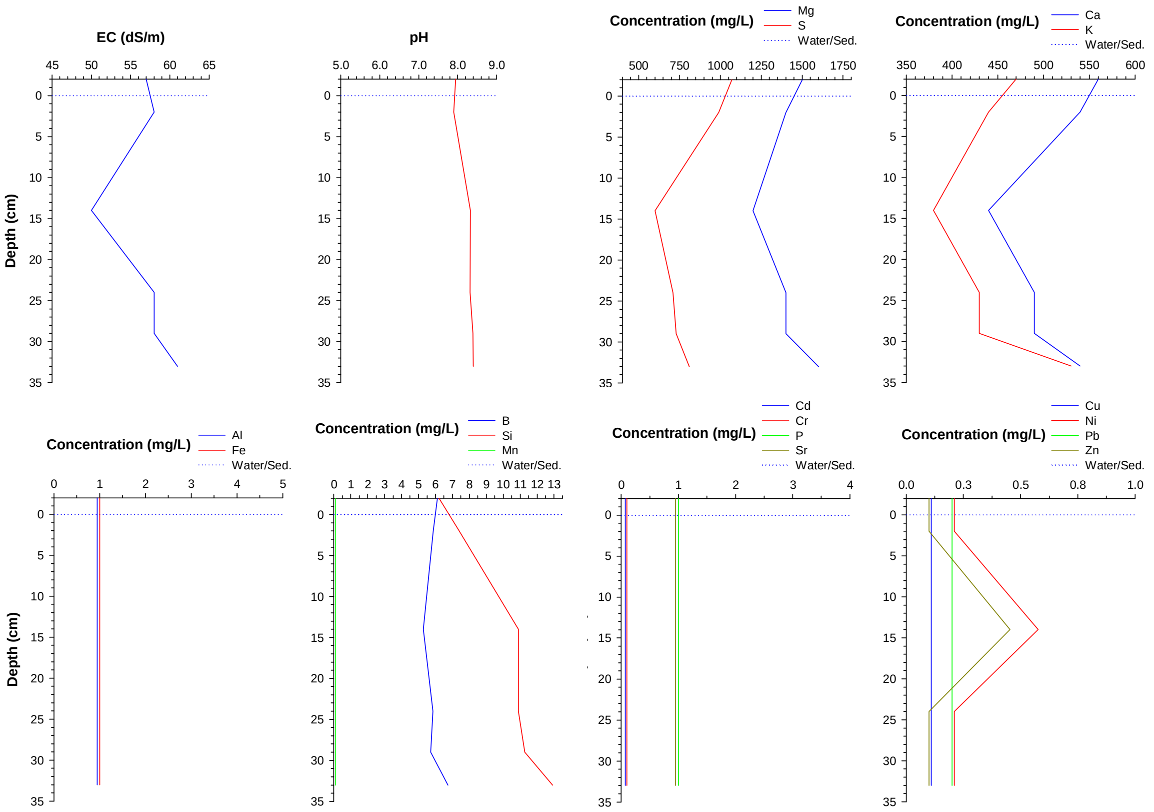

Figure 9-22 Down profile soil pore water data collected from peeper P6, located adjacent to soil profile BSK 5. Each (selected) peeper chamber was analysed separately. Plots showing concentrations for Al, Cd, Cr, Cu, Fe, Ni, P, Pb, Sr and Zn are half the detection limit.

9.6.2. Discussion

The pH of solution collected in peepers generally increased with depth below the sediment/water interface. The increase in pH was most significant in profile peeper P4 (at profile BG 24) which contained the highest concentration of AVS (0.32%) in the surface soil layers, demonstrating that the formation of monosulfides consumes acidity present in pore waters (Figure 9-19). The pH of peepers inserted in sulfuric materials (peepers P1 and P2) also increased with depth, although these soils did not contain monosulfides (Figure 9-23). The increase in pH in this case was probably due to the dissolution of clay minerals (e.g. gibbsite, kaolinite, and montmorillonite) and Al-hydroxides, which consumes 3 moles of acidity (H^+) for every 1 mole of Al^{3+} dissolved, and provides some buffering (van Breemen 1973; Wolt 1994). The Al concentration in pore waters of up to 3100 mg/L were observed in peeper profile P1 and up to 5600 mg/L in surface water from the pit of soil profile BG 3, which equates to 208 mmol/L. As expected, the Al concentration of surface waters and pore waters was below detection limits at non-tidal sites, where pH values were circum-neutral to basic (e.g. peepers P3 and BG P 5), as well as at tidally influenced sites. There is a strong correlation between pH and Al concentrations (Figure 9-23) that shows a clear distinction between peepers P1 and P2, due to their locations in different soil materials. As a result of weathering of aluminosilicates in sulfuric materials, Al is one of the most elevated elements in acidic pore waters and surface waters at Gillman, and was several orders of magnitude higher than the ANZECC guidelines for fresh and marine water trigger level of 0.0005 mmol/L. Aluminium hydrolysis increases acidification which further promotes the release of cations and anions (e.g. Na, Mg, Ca, Ba, Cl, SO_4^{2-}, SiO_4^{4-} etc.) and trace elements to pore waters and surface waters (Hicks *et al.* 2009).

The relationships between Al activity and the solubility of Al hydroxy species is illustrated in Figure 9-24 (pAl(OH)3 activity (commonly referred to as gibbsite activity) v. SAP (sulfuric acid potential; 2pH+pSO4) solubility diagram). The solubility lines for minerals typically associated with acid sulfate soil drainage were sourced from the literature. Extended Debye–Huckel theory was applied to calculate activity coefficients (Lindsay 1979). Most surface water and pore water samples collected from the Gillman and St Kilda study sites were supersaturated with respect to alunite when the solubility constant derived by (Adams and Rawajfih 1977; Nordstrom *et al.* 1990) was used (Figure 9-24). The water samples that had a SAP <4 correspond to water samples containing metals Cr, Cu, Ni, Pb and Zn. The precipitation of sulfate salts may contribute to the low activities of sulfate in these samples and the release of metals to solution. Acid sulfate waters are complex with several aluminium and iron hydroxy sulfate phases potentially present. The method used here to calculate activities does not account for high ionic strengths and therefore provides indicative trends only. Further geochemical modelling that corrects for high ionic strengths (e.g. The Geochemist's Workbench®) would be required.

Iron was abundant in soils from the Gillman and St Kilda study sites. In surface waters draining sulfuric materials, Fe contents were very high, measuring 870 mg/L in profile P2 and 1300 mg/L in profile BG 3, which had pH values of 1.95 and 1.63 respectively. The pore water profile for Fe in P2 showed a slight drop across the sediment/water interface to a depth of about 25 cm and then declined sharply to 330 mg/L at the base of the profile (Figure 9-16). In peeper P2, the decrease in Fe with depth follows the same pattern as Al, Mg, K, Si, B and Mn. The sharp drop in Fe concentration at about 25 cm depth corresponds to the transition from sandy clay to heavy clay and an increase in pH. The S_{CR} content of the heavy clay layer at the base of the drain was originally 0.81% when the drain was first excavated. It is unlikely that sulfide formation was occurring in soil layers at the base of the drain since its excavation, as soils remained oxic for the duration of the study, with Eh measurements >600 mV (Chapter 8). In acidic environments, Fe had a similar relationship with pH as Mg, Mn and Al (Figure 9-23).

In sulfidic soil profiles, the concentration of Fe was much lower than in acidic environments (Figure 9-23). At the sediment/water interface of peeper profiles P4, BG P 5 and BSK 3, Fe was more elevated than at depth. At the near surface of these circum-neutral, reducing soil profiles, Fe was likely to be in the form of Fe^{2+} and sourced from the reduction of Fe oxides (Huerta-Diaz *et al.* 1998). Deeper in the profiles, the concentration of Fe decreased due to the formation of Fe sulfides, and corresponds to the occurrence of monosulfides (AVS) in the profiles. A thin film of Fe oxyhydroxide precipitate was observed on peeper chambers at the sediment surface interface of profiles P3, P4 and BG P 5 (Figure 9-17) and was probably due to the deposition of Fe(III) oxide colloids in an alternating oxidising/reducing environment. This could explain the peak Fe concentrations measured at the sediment/water interface at these three sites. In sulfidic environments, S concentrations were much higher than Fe. This is particularly notable at the St Kilda study site where Fe concentrations were below detection limits throughout peeper profiles P5 and P6, suggesting that pyrite and monosulfide formation in these environments is limited by a lack of soluble Fe.

Sulfides are considered the main solid phase controlling the concentration of trace metals in sulfidic soils, either by co-precipitation, adsorption, or formation of discrete metal sulfides (Simpson *et al.* 1998). This explains the negligible concentrations of trace metals detected in pore waters from most sulfidic soil profiles. Minor amounts of Ni (0.6 mg/L) and Zn (0.5 mg/L) were measured at 14 cm below the soil surface in peeper P6, but were below detection limits for the remainder of the profile (Figure 9-22). These peaks coincided with the lowest concentrations of S, Mg, Ca, K and EC for the profile, and may; therefore, be related to reductive dissolution of ferric-bearing secondary minerals (Ribeta *et al.* 1995) under redox conditions, which fluctuate from oxidising to strong reducing over a tidal cycle (refer to Chapter 8).

Significant amounts of metals can be released during sulfide oxidation when pH decreases below 4.5 (Blake and Goulding 2004; Song and Müller 1995). Leaching from Finnish (Boreal) acid sulfate soils has resulted in metals including Cd, Co, Cr, Cu Ni, Y and Zn being significantly enriched in recipient streams (Aström 2001; Aström and Aström 1997; Aström and Deng 2003). In pore waters of sulfuric materials (peeper profile P1) at Gillman, concentrations of trace metals Cr, Cu, Ni, Pb and Zn were measured that exceed ANZECC trigger levels for ground water investigations in aquatic ecosystems and, marine waters (Table 9-3). The maximum concentrations of these trace metals occurred as peaks (indicating metal release) near the soil surface and therefore present a hazard to surface water quality (Figure 9-15). Trace metals Cu and Pb were only measured in the top 5 cm of the peeper profile, whereas Ni and Zn concentrations were measured throughout the profile. In surface water from profile BG 3, trace metals Ni (10 mg/L) and Zn (13.5 mg/L) were also detectable. In peeper P2, trace metals were below detection limits in pore waters or surface waters with a pH < 1.95. The release of metals to solution may therefore be related to the precipitation of salt efflorescences that formed thick accumulations on the surface of soil pit profiles BG 3 and BG 15 (refer to Chapter 10). The release of Pb and other trace metals may also be related to the decomposition of organic matter (Song and Müller 1995) which was high in the corresponding soil layers of profile BG 15 (in which organic C measured between 7.3% and 14.8%). Organic matter was associated with Pb bearing secondary sulfides identified by SEM in tidally influenced soils at Garden Island, located about 1 km north of the

Gillman study site (refer to Chapter 10). Trace metals may also be bound to solid phases unaffected by redox conditions, such as the exchangeable or heavy mineral fractions (Smith and Melville 2004), but are greatly affected by pH.

Manganese (likely as insoluble Mn oxyhydroxides) rich layers occured at the top of drained soil profiles (e.g. profiles BG 11 and BG 11). The Mn concentration in pore water of sulfuric material was an order of magnitude higher than in pore water of sulfidic materials. Soluble Mn decreased with depth in both acidic and circum-neutral soils indicating the solubility of Mn is influenced by redox conditions, and may be being removed as MnS in reducing environments.

Nickel and Zn are quite mobile metals at Gillman, entering solution at slightly higher pH of 3.2, than Cr, Cu and Pb, which entered solution at a pH of 2.3 (Figure 9-23). Ranking the mobility of metals is not possible here, as these results were obtained from different soil layers. At St Kilda, low concentrations of Ni and Zn were measured and may have entered solution through reductive dissolution processes. Trace metals Cr, Cu, Ni, Pb, and to a lesser extent Cd and Zn, have a high affinity for organic matter, especially at alkaline pH values.

Figure 9-23 shows that Na concentrations have a control over the release of metals to solution, namely Cr, Cu and Pb. According to its formula sideronatrite [$Na_2Fe(SO_4)_2.OH.3H_2O$] may be one salt efflorescence influencing the concentration of metals in solution. Sideronatrite was identified by XRD in salt efflorescence blooms sampled from the drain wall at the location of peeper P1, and contained elevated concentrations of Cr, Cu, Ni and Zn (determined by XRF). The concentration of Pb in salt efflorescences sampled from the drain was below detection limits. The increased concentration of metals Cr, Cu, Ni, Pb and Zn at the near surface of peeper P1 may also be due to evapo-concentration. These relationships are discussed further in Chapter 10.

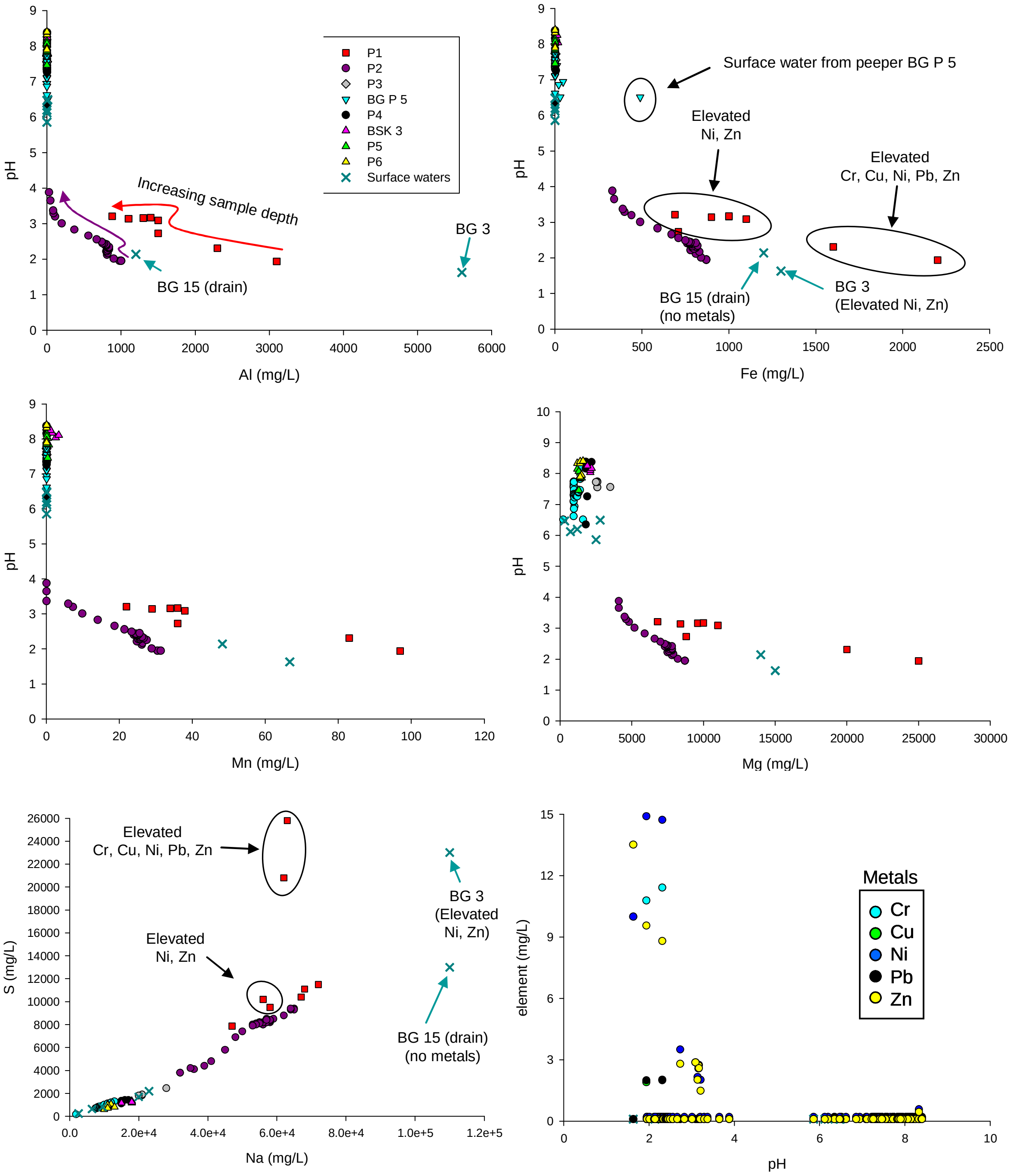

Figure 9-23 Plots showing surface water and pore water profile (peeper) characteristics.

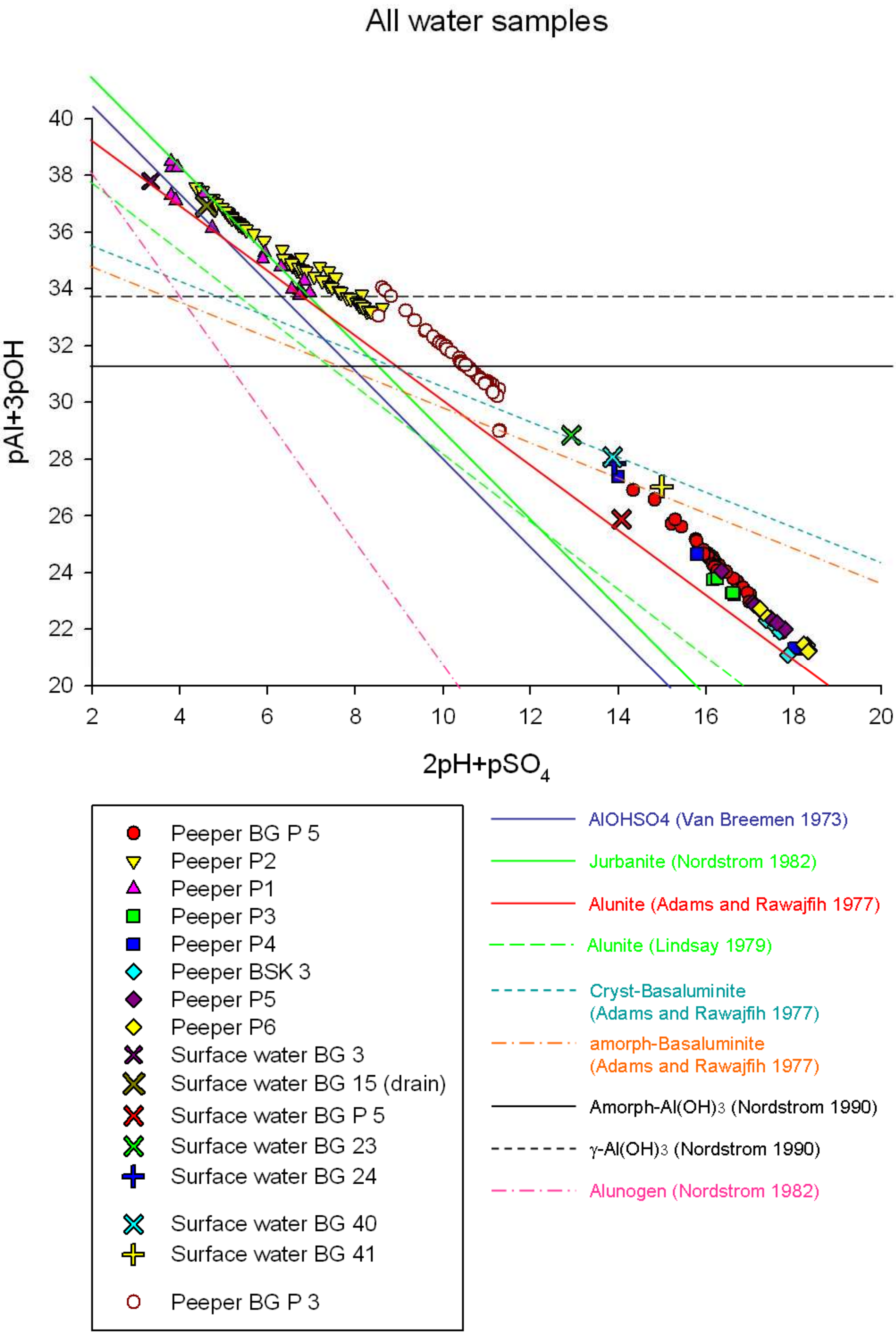

Figure 9-24 Plot of $Al(OH)_3$ activity (pAl^{3+} + $3pOH^-$) against sulfuric acid potential (pSO_4^{2-} + 2pH). Data plotted for Peeper BG P 3 was sourced from (Thomas 2004).

9.7. Summary

Published work (Dillon *et al.* 1989; Harbison 1986a) has indicated that the Gillman study site has been contaminated. In upland areas contamination was most probably by aerial accession from local (industrial) sources and dispersed urban sources such as Pb from motor vehicle exhausts (Gulson *et al.* 1981; Tiller *et al.* 1987). In low land areas subject to flooding, contamination was most probably from stormwater entering the site. The likely aerial sources might be identified by investigating and comparing contaminants in exposed areas with those covered by fill materials, especially where the date of filling is known. This technique would work best where the original topsoil has been compressed and maintained in a moist environment that promoted the formation of sulfides within the buried topsoil layers.

The soil geochemical and hydrochemical data provide evidence of the behaviour of trace elements in acid sulfate soil materials at Gillman and St Kilda. Metals and metalloids (As, Pb, and Zn) were elevated in topsoils of both intertidal and non-tidal (drained) soil profiles at Gillman, and are likely contaminants due to windblown material from industrial sources. In non-tidal areas, Cu and V, and to a lesser extent Ni, were also elevated in topsoils. Integration of geochemical, hydrochemical and pedological characteristics along toposequences has allowed a 3D soil-regolith model to be developed, which depicts the spatial distribution and movement of elements and acidity within the landscape at Gillman (Figure 9-25). In non-tidal areas, As, Cr, Pb, V and Zn are relatively stable in topsoils due to their high pH, and high Mn and Fe contents. The topsoils from relatively elevated positions in the landscape that are dominated by post active hypersulfidic materials (refer to Chapter 11) occur in map units 4, 5 and 6 (Figure 9-25). At lower positions in the landscape at Gillman (map units 2, and 3), the water table fluctuates seasonally causing acidic oxidising conditions during summer and circum-neutral, strongly reducing conditions during winter. These dynamic conditions promote the down-profile migration of trace elements, which are leached from the surface and concentrated at the redox front.

Rain water that soaks into the surface of upland areas becomes acidic as it percolates through sulfuric materials. However, acidic runoff waters that enter creeks at the Gillman study site have not acidified the creek waters (Figure 9-25). This is because discharge to the creeks is minimal as the groundwater movement within this environment is very slow (0.3 to 0.6 m/yr) and dominated by vertical migration rather than lateral flow (Pavelic and Dillon 1993a). The high pH of creek waters and water in historic drainage networks is also due to: **(i)** geomorphology, as creeks and drains generally intersect carbonate rich soil layers, and **(ii)** acidity consumed during monosulfide formation in drain sediments.

Zinc, Cu, Pb, V and other trace metals have accumulated in subaqueous soils, which contain high concentrations of pyrite and monosulfide in the drains and creeks that fringe areas containing sulfuric materials (Figure 9-25). This contrasts with intertidal areas where subaqueous, sulfidic soils occur in permanently flooded tidal creeks that have not accumulated contaminants from more elevated positions in the intertidal landscape. This indicates that the vertical and lateral mobility of contaminants at Gillman has been greatly enhanced by the loss of tidal flooding, and consequent acidification of soils.

The hydrochemical data presented in Table 9-3 shows that trace elements Cd, Cu, Cr, P, Ni, Pb and Zn are not significantly enriched in pore waters or surface waters draining these acid sulfate soils. Trace elements Cu, Cr, Ni, Pb and Zn were only elevated in extremely acidic (pH < 3.2) surface or soil pore waters in the side walls of soil pits or drains where salt efflorescences occurred. These conditions are only likely to occur in areas mapped as units 5 and 6, and only if the subsoils are exposed. Hydrochemical data suggest that the lateral mobility of contaminants is predominantly by erosion of topsoils, which also promotes the movement of nano-particulate Fe and Al oxyhydroxides into drains and creeks. These oxidation products are then reduced and metal contaminants sequestered by sulfides at the lowest positions in the landscape at Gillman (i.e. map unit 1). Iron, S and organic C are not limiting in the subaqueous soils, so the formation of monosulfides and their subsequent transformation to pyrite is expected to continue. The bioavailability of these metals has not been investigated in this study; however, it is assumed that metals (Cu, Ni, Pb and Zn) within strongly reduced soils are associated with metal sulfides and are unlikely to be bioavailable in environments with neutral to alkaline pH (Cooper and Morse 1998). Metals are more likely to be bioavailable in acidic environments. However, As can be mobile over a wide pH range. This work has implications for assessing contaminant dispersion for coastal or inland landscapes, particularly in areas where the known contamination sources are airborne, such as at

Port Pirie (smelting), Mt Isa and Port Augusta (dust) (e.g. Cartwright *et al.* 1977; Thomas and Fitzpatrick 2006b).

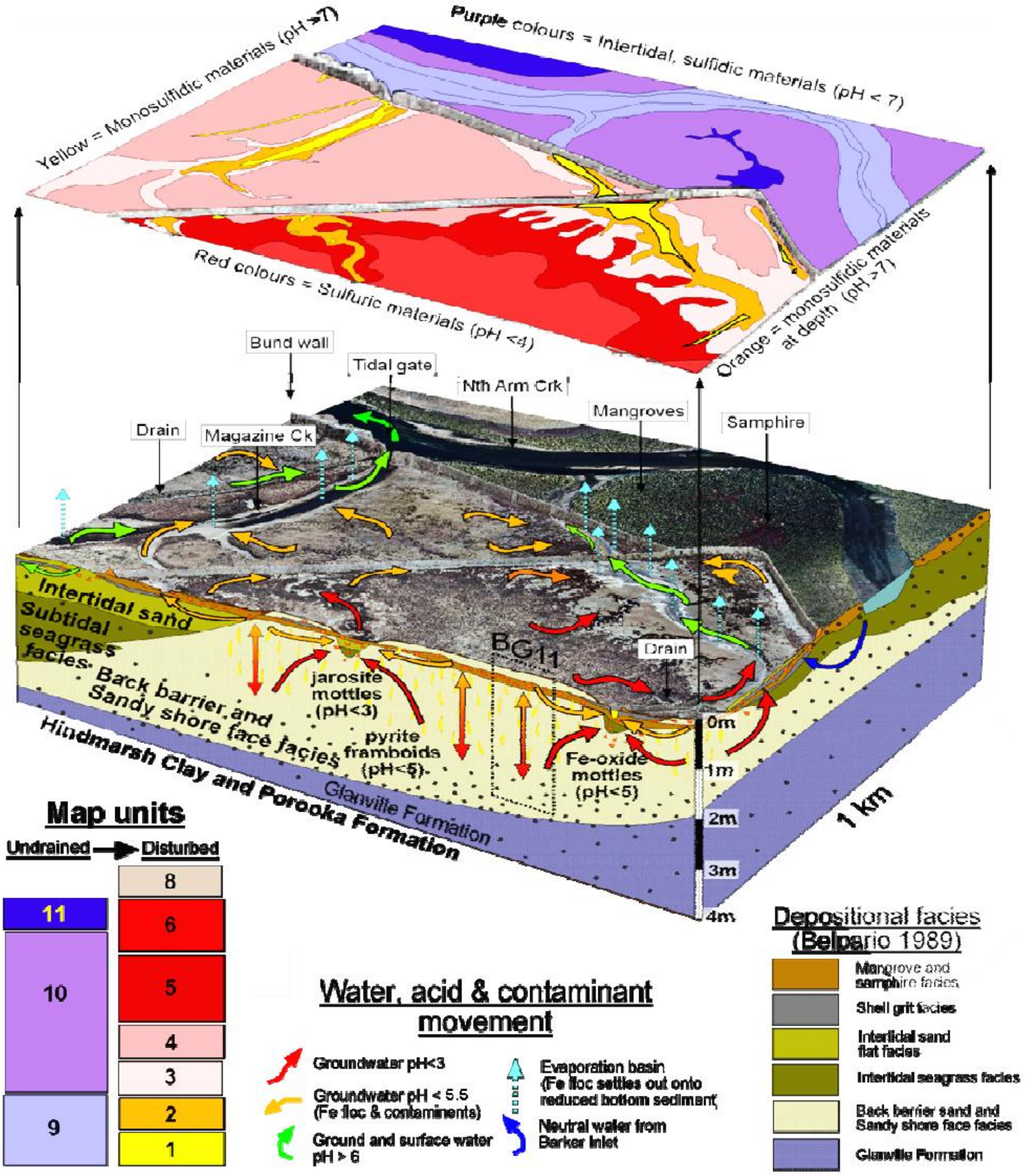

Figure 9-25 Soil-regolith explanatory model of the northern portion of the Gillman study site, showing hydrogeochemical processes in relation to sulfuric materials (e.g. profiles BG 11 and BG 15) sulfidic materials which occur at low lying areas in the landscape (e.g. profile BG 30) and areas flooded by ponding stormwater during winter months.

Note on soil taxonomy and classification:

Sulfuric material that occurs below a layer of water is not accounted for in the Australian Soil Classification (Isbell 2002) and Keys to Soil Taxonomy (Soil Survey Staff 2010). These soil conditions were identified in areas where acidic groundwater permanently occurred above the surface of acidic soil profiles (e.g. as in the open drains located at Gillman where peeper P2 was located, which has continually contained surface water of < pH 3 since 2002; refer to Figure 9-16).

Consequently, these soil profiles should be described as being subaqueous and containing a sulfuric horizon (Soil Survey Staff 2010) or sulfuric material (Isbell 2002).

At present, sulfuric subaqueous soil profiles are not effectively classified in Keys to Soil Taxonomy (Soil Survey Staff 2010) because unlike Entisols (i.e. Wassents) and Histosols (i.e. Wassists), Inceptisols do not have a Suborder for “subaqueous conditions”. It is suggested that some consideration should be given to introduce a new Suborder to accommodate subaqueous conditions (e.g. Wassepts; i.e. Inceptisols that have a positive water potential at the soil surface for more than 21 hours of each day in all years). In contrast, Wassists with sulfuric horizons could easily be accommodated by modifying Keys to Soil Taxonomy (Soil Survey Staff 2010) to incorporate a new Great Group in Wassists as follows:

> Key to Great Groups
>
> BBC. Other Wassists that have a horizon or horizons, with a combined thickness of at least 15 cm within 50 cm of the soil surface, that contains a sulfuric horizon.
>
> Sulfowassists