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Assessment of Acid Sulfate Soil Materials (Phase 2) Paiwalla wetland, South Australia

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Cover Photograph:

Paiwalla wetland
Photographer: Paul Shand
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CONTENTS

LIST OF FIGURES

LIST OF TABLES

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EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of the Paiwalla wetland in March 2008 showed acid sulfate soils to be a priority concern within this wetland complex. Based on Phase 1 recommendations, a Phase 2 investigation was undertaken for the Paiwalla wetland to determine the nature, severity and the specific risks associated with acid sulfate soil materials. The wetland had dried during previous drought conditions, but had been refilled at the time of sampling.

The 24 hour **reactive metals** tests were undertaken to determine those metals and metalloids extractable with a moderately strong acid i.e. potentially available from binding sites on soil minerals such as iron (Fe), manganese (Mn) and aluminium (Al) oxides. Although comparisons can be made with soil and sediment quality guidelines, these are defined for total concentrations and not partial extractions. The results showed that manganese (Mn) was the only element above the soil ecological investigation level (EIL). Although concentrations of other elements did not breach sediment quality guidelines (SQG) and soil ecological investigation level trigger values, the concentrations of many elements were high enough that they may impact water quality if mobilised, particularly for aluminium (Al) and iron (Fe).

The **contaminant and metalloid dynamics** tests were undertaken to assess the release of metals during a water extraction, and to assess dynamics in response to saturation over time by incubating soil materials for periods of 1, 7, 14 and 35 days. The degree to which metal and metalloid concentrations exceed guideline values (ANZECC/ARMCANZ 2000) was used to characterise the degree of hazard. For Paiwalla wetland, aluminium (Al), arsenic (As), copper (Cu), iron (Fe) and vanadium (V) were assigned a low hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by less than 10 times. The surface soil layer from the profile studied showed the biggest change towards reducing conditions and the release of iron (Fe) from this layer correlated with increases in arsenic (As) and a number of other trace metals and metalloids. The dominant control on metal solubility is the pH and Eh of the sediments at the time of the extractions, with the reductive dissolution of iron (Fe) and manganese (Mn) oxides/oxyhydroxides probably controlling the high concentrations of metalloids at high pH. Although metal concentrations were generally low, increasing concentrations of arsenic (As) and vanadium (V) suggest that these elements form the greatest hazard to soil and surface waters over time.

The Paiwalla wetland has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al*. 2010). The main hazards considered in this study that may impact on wetland values are acidification, contaminant mobilisation and deoxygenation. The wetland has been allocated a **low** risk rating due to **acidification** and **contaminant mobilisation** of **soils**. For **surface waters**, the risk is largely dependent on surface and sub-surface hydrology and is thus scenario dependent. Taking into account the range of likely scenarios, and that the wetland is separated from the river by a control structure, the risk to surface waters in the wetland has been allocated a **low** (minor consequence) risk rating due to **acidification** and **contaminant mobilisation**. The risk rating for **deoxygenation** is **medium** due to high concentrations of monosulfides present in the surface soil layer.

In designing a management strategy for dealing with acid sulfate soils in Paiwalla wetland, other values and uses of the wetland need to be taken into account to ensure that any intervention is compatible with other management plans and objectives for the wetland.

The wetland had been refilled at the time of sampling following a dry period and since the wetland has a control structure, management options can focus on reinstating a more natural wetting and drying regime for the wetland to prevent the build-up of sulfidic sediments, and preventing oxidation if required. Due to the lower risks to the wetland values associated with acid sulfate soils in Paiwalla wetland, routine condition monitoring is recommended for this wetland.

1. INTRODUCTION

At its March 2008 meeting, the Murray–Darling Basin Ministerial Council discussed the emerging issue of inland acid sulfate soils and the associated risks to Murray–Darling Basin waterways and agreed that the extent of the threat posed by this issue required assessment. The purpose of the Murray–Darling Basin Acid Sulfate Soils Risk Assessment Project was to determine the spatial occurrence of, and risk posed by, acid sulfate soils at priority wetlands in the River Murray system, wetlands listed under the Ramsar Convention on Wetlands of International Importance and other key environmental sites in the Murray–Darling Basin. The project involved the selection of wetlands of environmental significance, as well as those that may pose a risk to surrounding waters. These wetlands were then subjected to a tiered assessment program, whereby wetlands were screened through a desktop assessment stage, followed by a rapid on-ground appraisal, and then detailed on-ground assessment if results of previous stages indicated an increased likelihood of occurrence of acid sulfate soils.

Detailed assessments of acid sulfate soils within the Murray-Darling Basin (MDB) are conducted as a two-phase process under the MDB Acid Sulfate Soils Risk Assessment Project (ASSRAP). Phase 1 investigations are initially undertaken to determine whether or not acid sulfate soil materials are present in the study area, and provide characterisation of the properties and types of acid sulfate soils. Phase 2 investigations are only conducted if the acid sulfate soil materials from Phase 1 are determined to be a priority concern for the study area and, based on Phase 1 recommendations, selected samples undergo further investigations to determine the nature, severity and the specific risks associated with the acid sulfate soil materials. Phase 2 activities include: (i) soil laboratory analysis to confirm and refine the hazards associated with contaminant mobilisation and/or deoxygenation, (ii) a risk assessment, and (iii) interpretation and reporting, including discussion on broad acid sulfate soil management options.

Detailed Phase 1 acid sulfate soil assessments were undertaken at almost 200 wetlands and river channels throughout the Murray-Darling Basin. In South Australia, 56 wetlands along the River Murray between Lock 1 and Lock 5 were investigated by CSIRO Land and Water (Grealish *et al*. 2010). From these Phase 1 investigations, 13 wetlands were selected for further investigation. Nearly all of the wetlands along the River Murray between Wellington and Blanchetown (Lock 1) in South Australia also received detailed Phase 1 acid sulfate soil assessments (Grealish *et al*. 2011) and of these 23 wetlands were selected for further investigation in Phase 2. This included some wetlands below Lock 1 from earlier studies (Fitzpatrick *et al.* 2008; Fitzpatrick *et al.* 2010).

This report outlines the results of Phase 2 activities on selected surface soil samples from the Paiwalla wetland.

Paiwalla wetland was selected for Phase 2 detailed assessment following analysis of results from the Phase 1 detailed assessment (Fitzpatrick *et al*. 2010) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1). Sampling sites from Phase 1 are shown on Figure 1-1. The Phase 1 assessment focussed on one site (PAI 4) which was sulfidic and samples were taken after the wetland had refilled after a previous drying phase in early 2008 (Fitzpatrick *et al*. 2010). During a preliminary visit in 2007, black soil materials similar to monosulfidic black ooze were identified during a drying phase.

A summary of the soil laboratory analyses undertaken as part of the Phase 2 assessment and the sample selection criteria for each analysis is given in Table 1-2. Soil samples identified to undergo Phase 2 laboratory analysis are primarily from the surface and near-surface layers, as these are the soils most likely to have initial contact with water. A list of the samples selected for Phase 2 analysis for the Paiwalla wetland is presented in Table 1-3.

Table 1-1 Priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project, from MDBA (2010).

Priority	Soil material
High Priority	All sulfuric materials. All hypersulfidic materials (as recognised by either 1) incubation of sulfidic materials or 2) a positive net acidity result with a Fineness Factor of 1.5 being used). All hyposulfidic materials with S_{CR} contents ≥ 0.10% S. All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents ≥100 mg kg^{-1} SO_4. All monosulfidic materials.
Moderate Priority	All hyposulfidic materials with S_{CR} contents < 0.10% S.
No Further Assessment	Other acidic soil materials. All other soil materials.

Table 1-2 Rationale for Phase 2 sample selection, from MDBA (2010)

Parameter	Samples selected
Reactive metals	Conducted on selected upper two surface samples
Contaminant and metalloid dynamics	Conducted on selected upper two surface samples
Monosulfide formation potential	Conducted on surface samples of dry sites that meet the water extractable sulfate criteria for monosulfides
Mineral identification by X-ray diffraction (XRD)	Conducted on a limited number of selected crystals and minerals (if present). Most likely to be associated with sulfuric layers to confirm acid mineral presences
Acid base accounting data	Conducted only on samples from wetlands below Lock 1 and Burnt Creek/Loddon River if not previously analysed and pH_{KCl}<4.5

Table 1-3 Summary of Paiwalla wetland samples analysed for Phase 2 assessment.

Soil Laboratory Test	Paiwalla wetland samples	Sample depth (cm)	Number of samples analysed
Reactive metals	PA1a4.1	0-5	3
	PA1a4.2	5-10	
	PA1a4.3	10-20	
Contaminant and metalloid dynamics	PA1a4.1	0-5	3
	PA1a4.2	5-10	
	PA1a4.3	10-20	
Monosulfide formation potential	PA1a4.1	0-5	1
Mineral identification by X-ray diffraction (XRD)	-		0

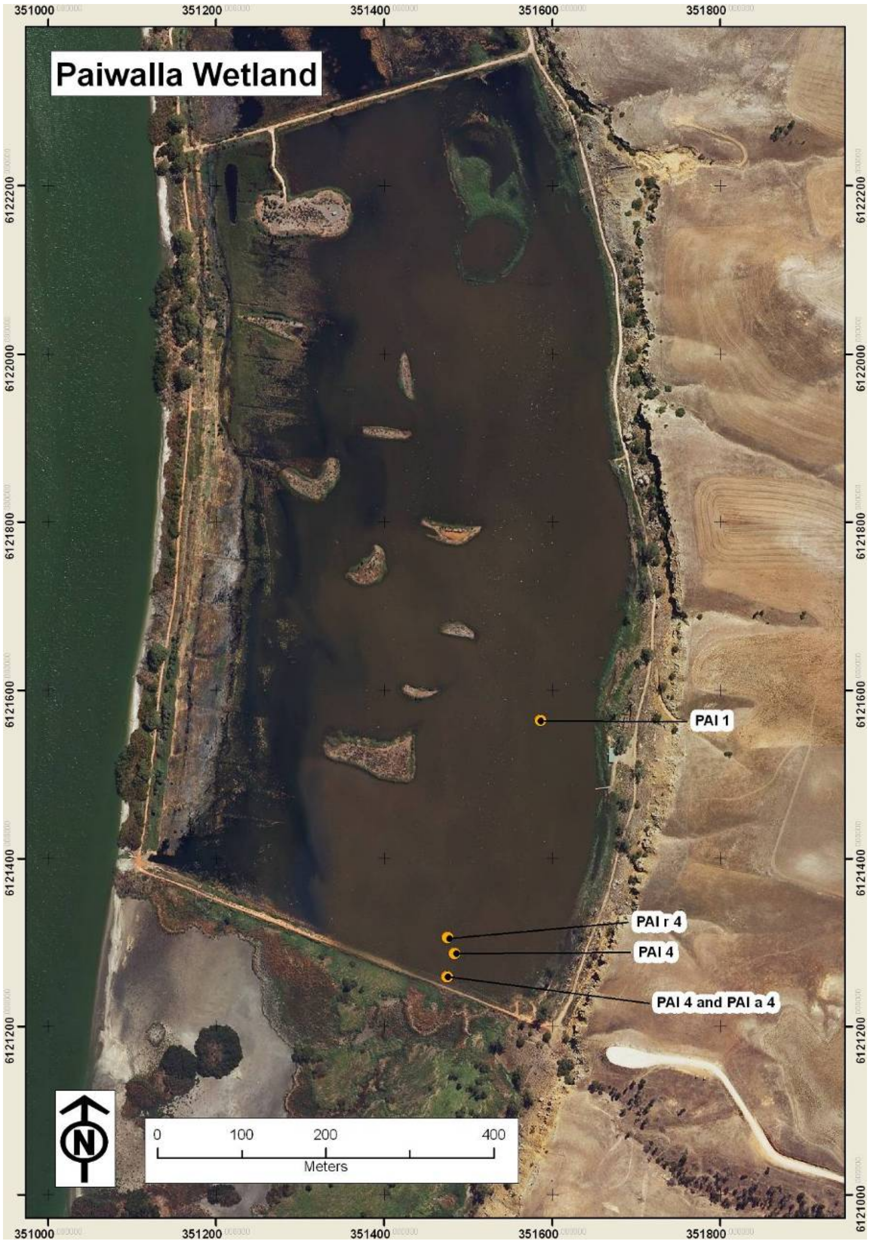

Figure 1-1 Paiwalla wetland aerial photograph with Phase 1 sampling sites identified.

2. LABORATORY METHODS

2.1. Laboratory analysis methods

2.1.1. Summary of laboratory methods

A list of the method objectives for the Phase 2 assessment are summarised below in Table 2-1. All soil samples analysed in this Phase 2 assessment were collected and subsequently stored as part of the Phase 1 field assessment.

Table 2-1 Phase 2 data requirements - list of parameters and objective for conducting the test, from MDBA (2010).

Parameter	Objective
Reactive metals	Assists with determining impacts on water quality by determining weakly to moderately strongly bound metals.
Contaminant and metalloid dynamics	Assists with determining impacts on water quality by simulating longer time frames that create anaerobic conditions. Identifies metal release concentrations that may occur over a 5 week time frame.
Monosulfide formation potential	Determine relative propensity for monosulfides to form following inundation.
Mineral identification by X-ray diffraction (XRD)	Characterisation and confirmation of minerals present.

Guidelines on the approaches that were followed as part of this Phase 2 assessment are presented in full in the detailed assessment protocols (MDBA 2010).

2.1.2. Reactive metals method

The guidelines for the reactive metals method are outlined as an addendum to the detailed assessment protocols (MDBA 2010). In this method, samples were prepared by disaggregation (not grinding) using a jaw crusher, and then sieved to include only the <2 mm fine earth fraction. A total of 2.5 g soil was added to 40 ml of 0.1 M HCl, gently mixed for 1 hour and filtered through a pre-acid washed 0.45 µm nitro-cellulose filter. The metals examined comprised silver (Ag), aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

2.1.3. Contaminant and metalloid dynamics method

The guidelines for the contaminant and metalloid dynamics method are outlined in Appendix 7 of the detailed assessment protocols (MDBA 2010). The contaminant and metalloid dynamics method was designed to determine the release of metals and metalloids in soils after 24 hours. The data represent the availability of metals and metalloids from a weak extraction (water, and thus easily bioavailable) of saturated soils, and for dry wetland soils, those easily mobilised from mineral surfaces and readily soluble mineral phases (such as salts). The exercise was repeated in a batch process for longer time periods (7 days, 14 days, 35 days). The latter approach was aimed at understanding changes in concentrations over time. This is particularly important for dried soils which have been in contact with the atmosphere. The soil materials and the release/uptake of metals/metalloids are expected to change as the chemical environment changes from oxidising to reducing. The data can be compared to existing water quality guidelines, although care should be taken when extrapolating to surface waters without knowledge of hydrological conditions and natural chemical barriers. The impact on surface waters will be governed by the upward chemical flux which is a function of soil type, water flow, diffusion and the chemistry of the soils near the sediment-water interface.

Redox potential (Eh) and pH were determined using calibrated electrodes linked to a TPS WP-80 meter; Eh measurements were undertaken in an anaerobic chamber to minimise the rapid changes encountered due to contact with the atmosphere, and are presented relative to the standard hydrogen electrode (SHE). Specific electrical conductance (SEC) was determined using a calibrated electrode linked to a TPS WP-81 meter. All parameters were measured on filtered (0.45 µm) water samples.

2.1.4. Monosulfide formation potential method

The guidelines for the monosulfide formation potential method are outlined in Appendix 8 of the detailed assessment protocols (MDBA 2010). In this study 3.6 g/L sucrose was used as an organic substrate instead of the 7.2 g/L outlined in the protocols. In addition to sampling after seven weeks, water samples were collected and analysed immediately after inundating the soils (i.e. Day 0). The pore-water pH and Eh were determined at Day 0.

The reactive iron (Fe) fraction in field moist sediments was extracted using 1.0 M HCl (Claff *et al.* 2010). The ferrous iron (Fe^{2+}) and total iron (Fe^{2+} + Fe^{3+}) fractions were immediately fixed following extraction. The ferrous iron trap was made up from a phenanthroline solution with an ammonium acetate buffer (APHA 2005), and the total iron trap also included a hydroxylamine solution (APHA 2005). The iron species were quantified colorimetrically using a Hach DR 2800 spectrophotometer.

Redox potential and pH were determined using calibrated electrodes linked to a TPS WP-80 meter; Eh measurements are presented versus the standard hydrogen electrode. In this study the solid phase elemental sulfur fraction was extracted using toluene as a solvent and quantified by high-performance liquid chromatography (HPLC) (McGuire and Hamers 2000). Pore-water sulfide was preserved in zinc acetate prior to determination by the spectrophotometric method of Cline (1969).

2.1.5. Mineral identification by x-ray diffraction

The guidelines for mineral identification by x-ray diffraction are outlined in the detailed assessment protocols (MDBA 2010).

2.2. Quality assurance and quality control

For all tests and analyses, the quality assurance and quality control procedures were equivalent to those endorsed by NATA (National Association of Testing Authorities). The standard procedures included the monitoring of blanks, duplicate analysis of at least 1 in 10 samples, and the inclusion of standards in each batch.

Reagent blanks and method blanks were prepared and analysed for each method. All blanks examined here were either at, or very close to, the limits of detection. On average, the frequencies of quality control samples processed were: 10% blanks, 10% laboratory duplicates, and 10% laboratory controls. The analytical precision was ±10% for all analyses. In addition, for all samples, reactive metals and contaminant metalloid dynamics tests were duplicated. For the reactive metals, two International standards (Reference Stream Sediment STSD-2 and STSD-3 Canadian Certified Reference Materials) were processed in an identical manner to the samples. Precision was excellent with the coefficient of variation (standard deviation/mean*100) typically being in the range < 1 to 2 %.

3. RESULTS AND DISCUSSION

3.1. Summary of soil laboratory results

3.1.1. Reactive metals data

The data are presented on a dry weight basis (mg kg^{-1}) and shown in Table 3-1. The 24 hour reactive metals studies provide an indication of those metals and metalloids which are more strongly bound to minerals (or weakly soluble with an acid extraction) than would be soluble with a water extraction, and thus have the potential to be released. The use of a moderately strong acid (0.1 M HCl) should provide an indication of “stored metals” and metalloids associated with iron (Fe) and manganese (Mn) oxides and organic materials as well as acid soluble minerals. It is commonly found that the concentrations of metals and metalloids released using extractions are much higher than those found in solution (Gooddy *et al.* 1995). Although guideline values exist for soils and sediments, these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

The concentrations of metals and metalloids were below sediment quality guideline (SQG) values and soil ecological investigation levels (EIL) for those elements for which guidelines are available, with the exception of high manganese (Mn) in sample PAI A4.1 (Table 3-1). The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (Al) and iron (Fe).

Table 3-1 Paiwalla reactive metals data.

Concentrations in mg kg^{-1} and μg kg^{-1} as indicated.

Sample	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
PA1 a4.1	0.41	1032	0.90	68	5.7	958	0.37	17294	978	7.4	1.6	< 23	82	11	17
PA1 a4.2	5.6	662	3.9	100	3.6	494	5.3	3275	267	5.9	3.2	3.9	71	21	17
PA1 a4.3	6.1	363	3.6	45	0.65	185	3.6	1085	14	4.6	2.5	< 2.6	57	12	5.4
[1]SQG	1000	-	20	1500	-	80000	65	-	-	21	50	2000	-	-	200
[2]Soil EIL	-	-	20	3000	-	-	100	-	500	60	600	-	-	50	200

* Units are in μg kg^{-1}

< value is below detection limit

[1] SQG: Sediment Quality Guideline Value (Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000)

[2] Soil EIL: Soil – Ecological Investigation Level (NEPC 1999)

3.1.2. Contaminant and metalloid dynamics data

The contaminant and metalloid dynamics data for the Paiwalla wetland soil materials examined are presented in Appendix 2, summarised in Table 3-2 and plotted against time in Figure 3-1 to Figure 3-3. Table 3-2 also compares the pore-water metal contents to the relevant national water quality guideline for environmental protection (ANZECC/ARMCANZ 2000).

Table 3-2 Summary of contaminant and metalloid dynamics data

Parameter	units	ANZECC Guidelines	Paiwalla		
			Min.	Median	Max.
pH		6.5-8.0	**4.8**	6.5	7.5
EC*	µS cm^{-1}	2200	234	449	2103
Eh	mV	-	44	382	437
Ag	µg l^{-1}	0.05	<0.01	<0.05	<0.05
Al^{A}	mg l^{-1}	0.055	<0.05	**0.06**	**0.19**
As^{B}	µg l^{-1}	13	0.50	2.5	**17**
Cd	µg l^{-1}	0.2	<0.01	<0.2	<0.2
Co	µg l^{-1}	2.8	0.10	0.31	1.4
Cr^{C}	µg l^{-1}	1	<0.3	<0.7	0.90
Cu^{H}	µg l^{-1}	1.4	<1	1.0	**2.0**
Fe^{I}	mg l^{-1}	0.3	<0.1	<0.1	**0.37**
Mn	µg l^{-1}	1700	2.1	29	495
Ni^{H}	µg l^{-1}	11	<1	1.9	4.6
Pb^{H}	µg l^{-1}	3.4	<0.2	<3	<3
Sb	µg l^{-1}	9	<0.6	<10	<10
Se	µg l^{-1}	11	<0.1	<0.2	0.22
V	µg l^{-1}	6	1.9	**6.7**	**12**
Zn^{H}	µg l^{-1}	8	<1	<2	<2

Exceeded ANZECC Guideline (x1)	***Exceeded ANZECC Guideline (x10)***	***Exceeded ANZECC Guideline (x100)***

Notes.

The ANZECC guideline values for toxicants refer to the Ecosystem Protection – Freshwater Guideline for protection of 95% of biota in 'slightly-moderately disturbed' systems, as outlined in the Australian Water Quality Guidelines for Fresh and Marine Water Quality (ANZECC/ARMCANZ 2000).
** ANZECC water quality upper guideline (125-2200 µS cm^{-1}) for freshwater lowland rivers in South-east Australia is provided for salinity (there are currently no trigger values defined for 'Wetlands'.)*

[A] Guideline is for Aluminium in freshwater where pH > 6.5.
[B] Guideline assumes As in solution as Arsenic (AsV).
[C] Guideline for Chromium is applicable to Chromium (CrVI) only.
[H] Hardness affected (refer to Guidelines).
[I] Fe Guideline for recreational purposes.

The pH of the soil materials varied from slightly acidic to neutral and increased slightly over the 35 day incubation period (Figure 3-1). The pH was highest in the shallowest soil layers, decreasing with depth.

The Eh was initially high, and all samples showed a significant decrease, much more in the surface soil layer (Figure 3-1). The SEC showed little variation, with the exception of the deepest sample where SEC dropped significantly on day 7, while the remaining two samples had a maximum on day 14.

Manganese (Mn) concentrations were relatively low in the contaminant and metalloid dynamics tests, with only the surface sample (PAIa4.1) having significant concentrations, but well below the ANZECC/ARMCANZ environmental protection guideline value. Iron (Fe) was also high in the surface sample, but remained close to or below detection limit for the deeper samples (Figure 3-2).

Most other trace elements were below the ANZECC/ARMCANZ environmental protection guidelines (Table 3-2), the exceptions being aluminium (Al), arsenic (As), copper (Cu) and vanadium (V). The highest aluminium (Al) concentration was in the deepest more acidic sample which was released rapidly (1 day test), but subsequently decreased. A spike in aluminium (Al) was also noted in sample PAIa 4.1, but at the circumneutral pH of this sample, it is likely that the aluminium exists in colloidal form. The concentrations of arsenic (As) were low in the sub-surface soil samples, but the top layer had moderately high concentrations, increasing to above the ANZECC/ARMCANZ environmental protection guideline value by day 7, before decreasing again by day 35 (Figure 3-1). The concentrations thus followed that of iron (Figure 3-2). Vanadium increased in all samples over the 35 day period (Figure 3-3). Cobalt (Co), nickel (Ni) and zinc (Zn) also increased with time, but remained below ANZECC/ARMCANZ environmental protection guidelines.

The magnitude of metal mobilisation is affected by many factors that include but are not exclusive to: 1) the abundance and form of metal and metalloid contaminants; 2) the abundance and lability of organic matter; 3) the abundance and reactivity of iron minerals; 4) availability of sulfate; 5) acid/alkalinity buffering capacity; 6) pH; 7) SEC; 8) clay content; 9) microbial activity; 10) temperature; and 11) porosity (MDBA 2010). Overall, the samples displayed little trend with pH (Figure 3-4), but the highest concentrations of iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni) and vanadium (V) were present in the highest pH waters (Figure 3-4), and the correlation of iron (Fe) and manganese (Mn) with these metals suggests a control by reductive dissolution on iron (Fe) and manganese (Mn) oxyhydroxides and mobilisation of the sorbed metals and metalloids, attributed to a decrease in Eh. The decrease in iron (Fe) and arsenic (As) in the 35 day test may also be attributed to incorporation in sulfide minerals.

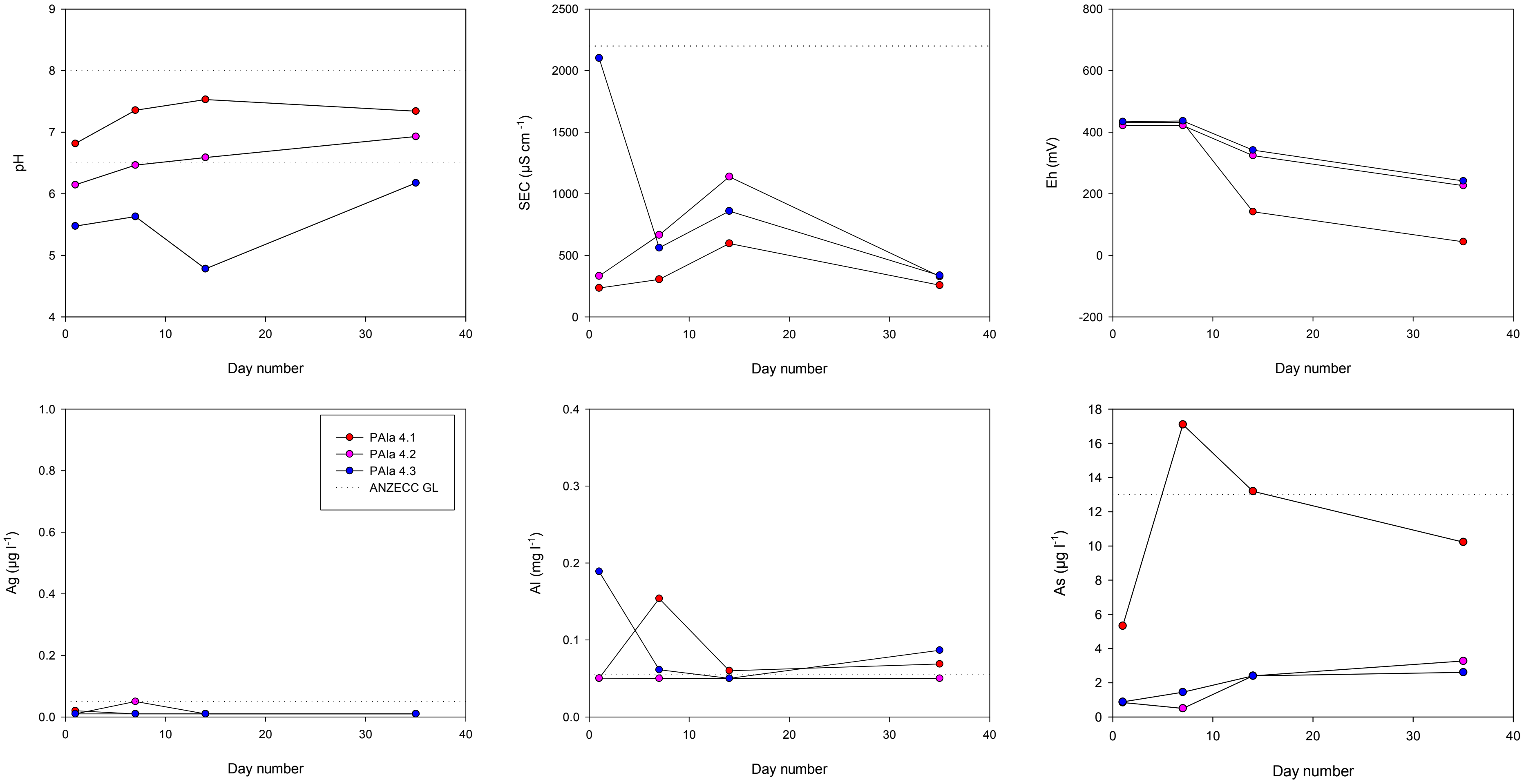

Figure 3-1 Contaminant and metalloid dynamics results for Paiwalla wetland soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al) and arsenic (As).

Note: silver (Ag) was all < detection limit, data represent detection limits which vary according to required dilutions.

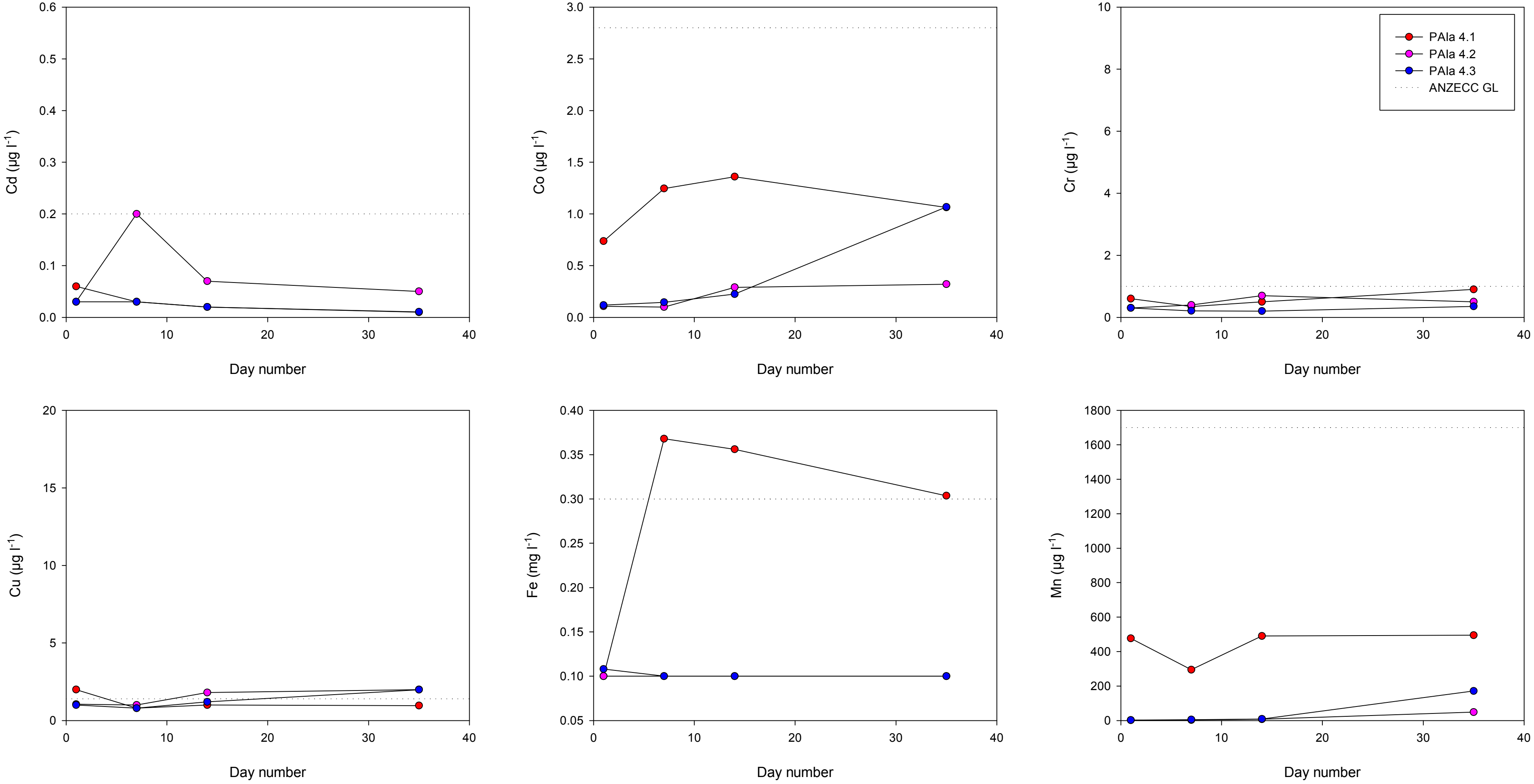

Figure 3-2 Contaminant and metalloid dynamics results for Paiwalla wetland soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

Note: cadmium (Cd) was < detection limit in some samples, data represent detection limits which vary according to required dilutions.

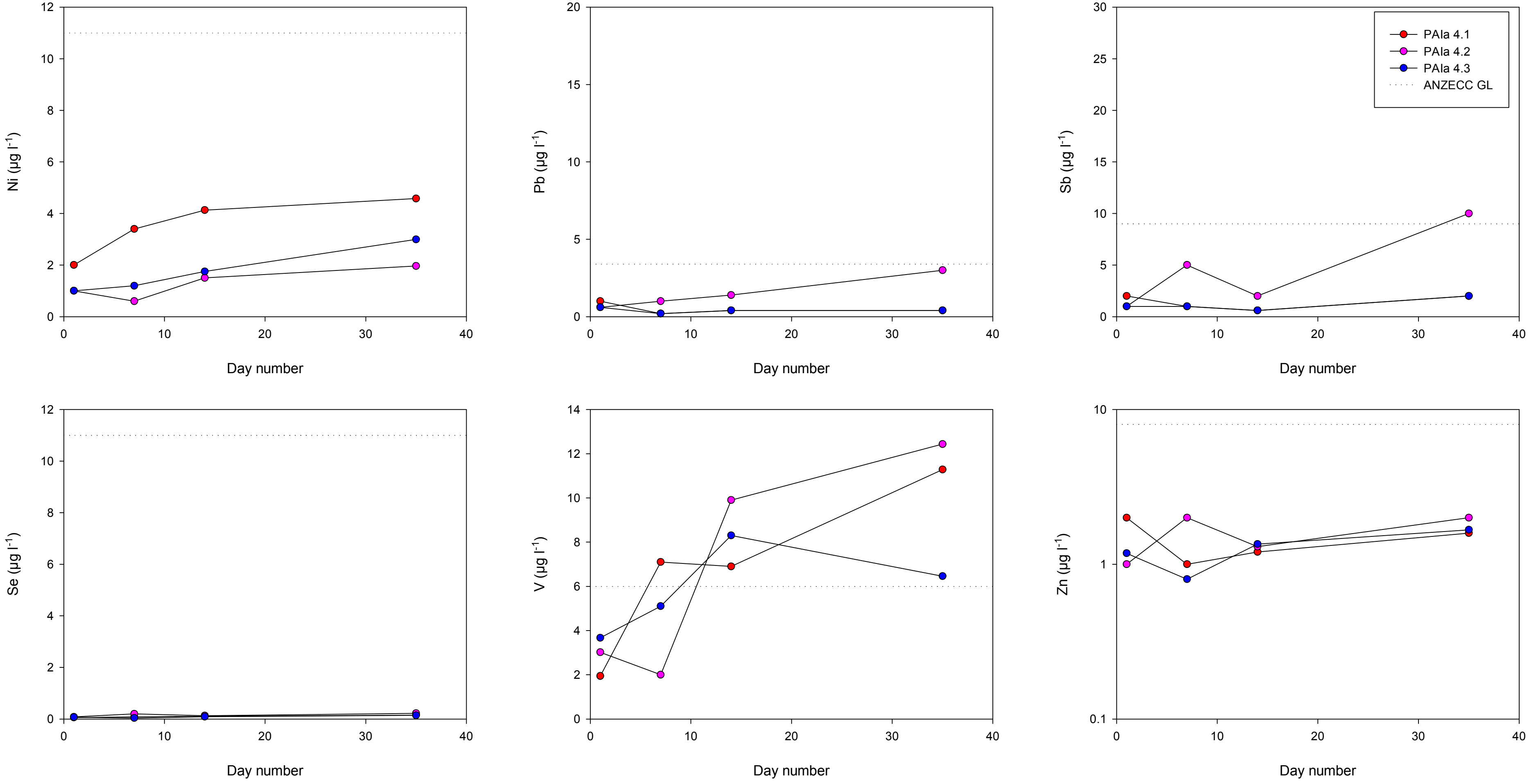

Figure 3-3 Contaminant and metalloid dynamics results for Paiwalla wetland soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

Note: lead (Pb) and antimony (Sb) were all < detection limit, and zinc (Zn) was < detection limit in some samples, data represent detection limits which vary according to required dilutions.

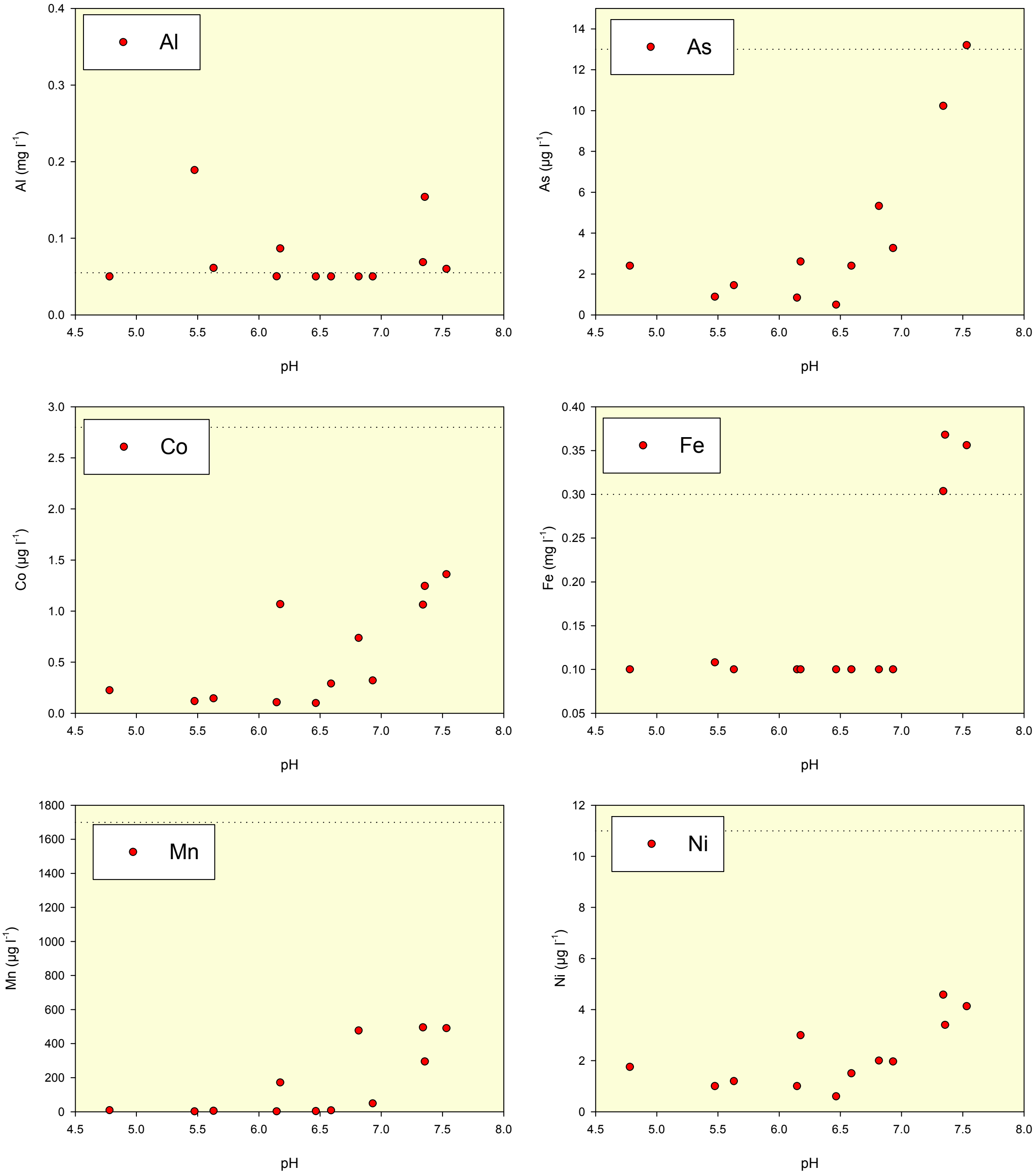

Figure 3-4 Selected trace elements plotted against pH.

3.1.3. Monosulfide formation potential data

The monosulfide formation potential data for the single sample analysed for Paiwalla wetland (PAIa4.1) are shown in Table 3-3. The pH of the soil water changed from 8.97 to 5.77 over the seven week incubation period (Figure 3-5). The decrease in pH is different from the contaminant and metalloid dynamics tests, where pH remained high (Figure 3-1). This may be due to fermentation of organic substrate added (sucrose), which caused acidification of the pore-waters.

The Eh decreased significantly from 366 to 69 mV (Figure 3-5) indicating a change to more reducing conditions. The Eh data are consistent with the contaminant and metalloid dynamics experiments where Eh decreased from 437 to 44 mV (Table 3-2).

Table 3-3 Summary of monosulfide formation potential data for the Paiwalla wetland surface soil material PAIa 4.1 after 7 weeks (3.6 g/L sucrose).

Inundation Time	Parameter	Units	Paiwalla (PAIa 4.1)
Day 0	Total Fe	mg/kg	16239
	$Fe(II)^{-}$	mg/kg	19090
	Sulfate*	mg/kg	938
	pH		8.97
	Eh	mV	366
Week 7	pH		5.77
	Eh	mV	69
	S_{AV}	Wt. %S	0.74
	S^{o}	Wt. %S	0.13
	Pyrite-S	Wt. %S	0.13
	Dissolved S^{2-}	µg/L	6791

*completed during Phase 1

The sample originally contained 0.9% S_{CR} and 9% acid neutralising capacity (ANC) (Fitzpatrick *et al*. 2010). Acid volatile sulfide (S_{AV}) of the sample analysed at the time of the tests was 0.85 % S. After 7 weeks, S_{AV} was 0.74 %, with 0.13 S^{0} and 0.13 pyrite-S (Table 3-3). Taking into account sample variability and analytical errors it appears that there has been little change in the reduced sulfide component. Dissolved sulfide concentrations were high at 6.8 mg l-1 (6791 µg/L, Table 3-3), reflecting the reducing nature of the soils.

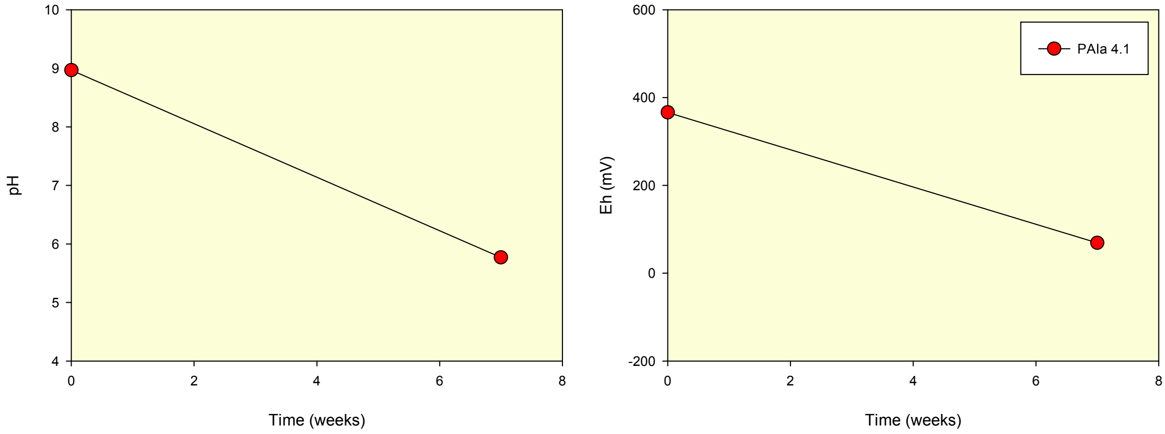

Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample PAIa4.1 from Paiwalla wetland.

3.1.4. Mineral identification by x-ray diffraction

No surface mineral efflorescences were identified or sampled at this wetland during the Phase 1 field survey.

3.2. Interpretation and discussion of results

The reactive metals and contaminant and metalloid dynamics tests undertaken as part of this Phase 2 assessment assist in determining the impacts on water quality by simulating the release of metal and metalloid concentrations that may occur under saturated conditions.

The 24 hour **reactive metals** studies provide an indication of those metals and metalloids which are more strongly bound to minerals (or weakly soluble with an acid extraction), and thus have the potential to be released. The use of a moderately strong acid (HCl) should provide an indication of "stored metals" and metalloids associated with iron (Fe) and manganese (Mn) oxides and organic materials as well as acid soluble minerals. It is commonly found that the concentrations of metals and metalloids released using extractions are much higher than those found in solution (Gooddy *et al*. 1995). Although guideline values exist for soils and sediments, these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

All metal and metalloid concentrations in the acid extracts were below the sediment quality guidelines and the soil ecological investigation level values (Table 3-1), except for manganese (Mn). Although the concentrations were generally less than guideline values, the concentrations of some metals were moderately high for this partial extraction technique, particularly for aluminium (Al) and iron (Fe). Nevertheless, the concentrations of many metals are sufficiently high (mg kg^{-1}) compared to water quality guidelines (generally µg kg^{-1}) that significant release could pose a risk to soil and surface water quality.

The **contaminant and metalloid dynamics** was designed to determine the release of metals and metalloids in soils. The data represent the availability of metals and metalloids from a weak extraction (water, and thus easily bioavailable) of saturated soils, and for dry wetland soils (especially below Lock 1), those easily mobilised from mineral surfaces and readily soluble mineral phases (such as salts). The exercise was undertaken in a batch process for time periods of 1 day, 7 days, 14 days and 35 days. This approach was aimed at understanding changes in concentrations over time. This is particularly important for dried soils which have been in contact with the atmosphere. The soil materials and the release/uptake of metals/metalloids are expected to change as the chemical environment changes from oxidising to reducing. Typical changes would be a reduction in redox potential (Eh), providing sufficient organic matter or other reducing agents are present, and an increase in pH (providing the soils contain or have the capacity to generate acid neutralising agents). The data can be compared to existing water quality guidelines, although care should be taken when extrapolating to surface waters without knowledge of hydrological conditions and natural chemical barriers. The impact on surface waters will be governed by the upward chemical flux which is a function of soil type, water flow, diffusion and the chemistry of the soils near the sediment-water interface. The mobility of most metals is commonly related to the stability of iron (Fe) and manganese (Mn) minerals. Under oxidising conditions iron (Fe) and manganese (Mn) oxide minerals are important sorbents for trace metals, whilst under very reducing conditions they may be incorporated into sulfide minerals. However, under moderately reducing conditions i.e. during the transition (suboxic) from oxidising to reducing conditions, iron (Fe) and manganese (Mn) are soluble and this is the period where metals may be released into solution and pose the greatest hazard.

It would appear that reductive processes have begun in the samples analysed with a slight decrease in Eh for most samples by day 35. The largest decrease in Eh was in surface sample PAIa4.1 (Figure 3-1), which also displayed the largest increase in pH. The monosulfide formation potential tests also suggest that the precipitation of monosulfides is occurring. The pH was relatively low only in the deepest sample analysed, but this had increased to pH 6.2 by day 35. At the pH values observed, it is unlikely that dissolved aluminium will be a problem, and any dissolved aluminium will likely precipitate as pH increases. The high iron may also decrease over time as precipitation of sulfides occurs in the shallow soil layers, consistent with a return to a monosulfidic surface layer as first observed by Fitzpatrick *et al*. (2010) before the wetland dried completely. A similar fate is likely for cobalt (Co) and nickel (Ni), although these are not likely to increase significantly at the pH values observed in the contaminant and metalloid dynamics tests. The metalloids arsenic (As) and vanadium (V), which can be mobile at high pH may represent the highest potential hazard and were found to increase with time. Although arsenic (As) peaked at 7 days, vanadium (V) showed a continuous increase. Both metalloids are likely to be controlled by the precipitation of sulfide minerals, which would scavenge these elements from solution.

The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-4). For some samples which required dilution, the detection limits were slightly above ANZECC/ARMCANZ environmental protection guideline values due to required dilution. Antimony (Sb) was below detection limit for all samples (detection limits varying between 0.6 and 10 µg l^{-1}). It is therefore not possible to determine hazard classifications for antimony (Sb) in Figure 3-4, although it can be concluded that it either sits in the No hazard or Low Hazard grouping.

Of particular significance for Paiwalla wetland are the low hazards for a number of elements (Table 3-4). However, the metalloids pose the greatest potential hazard at the likely pH of the soils and surface waters. The data are consistent with the generally low net acidities noted by Fitzpatrick *et al*. (2010), which varied from -678 up to 35 mol H^+/tonne, which means that the soils are likely to take little time to recover from drying and any associated local acidification.

Table 3-4 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in the Paiwalla wetland.

Degree of Hazard	Guideline Threshold	Metal/Metalloid
No Hazard	Value below ANZECC/ARMCANZ guideline threshold	Ag, Cd, Co, Cr, Mn, Ni, Pb, Se, Zn
Low Hazard	Value exceeds ANZECC/ARMCANZ guideline threshold, but is less than 10x exceedance	Al, As, Cu, Fe, V
Moderate Hazard	Value exceeds ANZECC/ARMCANZ guideline threshold by 10x or more, but is less than 100x exceedance	
High Hazard	Value exceeds ANZECC/ARMCANZ guideline threshold by 100x or more	

Note: Sb is below detection limits due to dilutions, and is therefore likely to be in the low or no hazard classification.

The monosulfide formation potential test assists in determining the propensity for monosulfides to form during future inundation. The sample used for this test contained high concentrations of acid volatile sulfide (S_{AV}), and also elemental sulfur (S^0) and S_{CR}. The concentration of acid volatile sulfide (S_{AV}) ranks the monosulfide formation potential hazard as high (Table 3-5).

Table 3-5 Guideline thresholds for the degree of hazard associated with acid volatile sulfide (S_{AV}) concentrations.

Degree of Hazard	Guideline Threshold
No Hazard	< 0.01 % S_{AV}
Low Hazard	0.01 % S_{AV}
Moderate Hazard	>0.01 – 0.05 % S_{AV}
High Hazard	>0.05 % S_{AV}

4. Risk assessment

4.1. Risk assessment framework

Risk is a measure of both the consequences of a hazard occurring, and the likelihood of its occurrence (MDBA 2011). According to the National Environment Protection Measures (NEPM), risk is defined as "*the probability in a certain timeframe that an adverse outcome will occur in a person, a group of people, plants, animals and/or the ecology of a specified area that is exposed to a particular dose or concentration of a hazardous agent, i.e. it depends on both the level of toxicity of hazardous agent and the level of exposure*" (NEPC 1999).

The MDB Acid Sulfate Soils Risk Assessment Project developed a framework for determining risks to wetland values from acid sulfate soil hazards (MDBA 2011). The risk assessment framework has been applied in this study to determine the specific risks associated with acidification, contaminant mobilisation and de-oxygenation. In this risk assessment framework, a series of standardised tables are used to define and assess risk (MDBA 2011). The tables determine the consequence of a hazard occurring (Table 4-1), and a likelihood rating for the disturbance scenario for each hazard (Table 4-2). These two factors are then combined in a risk assessment matrix to determine the level of risk (Table 4-3).

Table 4-1 determines the level of consequence of a hazard occurring, ranging from insignificant to extreme, and primarily takes account of the environmental and water quality impacts, to the wetland values and/or adjacent waters.

Table 4-1 Standardised table used to determine the consequences of a hazard occurring, from MDBA (2011).

Descriptor	Definition
Extreme	Irreversible damage to wetland environmental values and/or adjacent waters; localised species extinction; permanent loss of drinking water (including stock and domestic) supplies.
Major	Long-term damage to wetland environmental values and/or adjacent waters; significant impacts on listed species; significant impacts on drinking water (including stock and domestic) supplies.
Moderate	Short-term damage to wetland environmental values and/or adjacent waters; short-term impacts on species and/or drinking water (including stock and domestic) supplies.
Minor	Localised short-term damage to wetland environmental values and/or adjacent waters; temporary loss of drinking water (including stock and domestic) supplies.
Insignificant	Negligible impact on wetland environmental values and/or adjacent waters; no detectable impacts on species.

Table 4-2 determines the likelihood (i.e. probability) of disturbance for each hazard, ranging from rare to almost certain. This requires an understanding of the nature and severity of the materials (including the extent of acid sulfate soil materials, the acid generating potential and the buffering capacity of wetland soil materials) as well as contributing factors influencing the risk (MDBA 2011). Examples of disturbance include: (i) rewetting of acid sulfate soil materials after oxidation, (ii) acid sulfate soil materials that are currently inundated and may be oxidised, or (iii) acid sulfate soil materials that are currently inundated and may be dispersed by flushing (e.g. scouring flows) (MDBA 2011). As mentioned previously, the consequence of a hazard occurring and the likelihood rating for the disturbance scenario for each hazard are then ranked using a standardised risk assessment matrix (Table 4-3).

Table 4-2 Likelihood ratings for the disturbance scenario, from MDBA (2011).

Descriptor	Definition
Almost certain	Disturbance is expected to occur in most circumstances
Likely	Disturbance will probably occur in most circumstances
Possible	Disturbance might occur at some time
Unlikely	Disturbance could occur at some time
Rare	Disturbance may occur only in exceptional circumstances

Table 4-3 Risk assessment matrix, adapted from Standards Australia & Standards New Zealand (2004).

Likelihood category	Consequences category				
	Extreme	Major	Moderate	Minor	Insignificant
Almost certain	Very High	Very High	High	Medium	Low
Likely	Very High	High	Medium	Medium	Low
Possible	High	High	Medium	Medium	Low
Unlikely	High	Medium	Medium	Low	Very low
Rare	High	Medium	Low	Low	Very low

It is suggested that:

- For very high risk immediate action is recommended.
- For high risk senior management attention is probably needed.
- Where a medium risk is identified management action may be recommended.
- Where the risk is low or very low, routine condition monitoring is suggested.

These categories of management responses have been kept quite broad to acknowledge that jurisdictional authorities and wetland managers may choose to adopt different approaches in dealing with acid sulfate soils. The imprecise nature of these management responses is intended to provide flexibility in jurisdictional and wetland manager responses to the risk ratings associated with the acid sulfate soil hazards (MDBA 2011).

4.2. Assessment of risks

Realisation of the main risks associated with acid sulfate soil hazards (acidification, contaminant mobilisation and deoxygenation) is highly dependent on transport and therefore on the surface and sub-surface hydrology. The risks are thus scenario dependent, and difficult to quantify without predicted changes of water flows and inputs and hydrogeological controls.

The consequences of a hazard, as outlined in Table 4-1, relate to reversible or irreversible damage to wetland values. Few studies have documented in sufficient detail the short or long term damage to inland wetland ecosystems and values caused by acid sulfate soil hazards, but short term consequences have been clearly illustrated e.g. for water quality and ecosystem impacts (McCarthy *et al*. 2006; Shand *et al*. 2010). Irreversible damage is difficult to assess due to lack of sufficient data over longer timescales and lack of knowledge, for example, on sub-surface soil recovery and contaminant mobilisation impacts on benthic organisms. Nevertheless, the following sections detail the hazards and likelihood of a number of scenarios and discuss consequences based on limited previous work (e.g. McCarthy *et al*. 2006; Shand *et al.* 2010). The risks to soil water quality and surface water quality are necessarily different. The risks to soil water quality in terms of acidification and contaminant release are easier to assess from the tests carried out in this study than the risks posed to surface water quality. The impacts on surface water quality will be largely controlled by upward flux of acidity and metals from the soils and sediments into the water column. This will be controlled by *inter alia* surface water volume and groundwater connectivity and level, soil type, hydraulic conductivity, and degree and depth of soil cracking.

The Paiwalla wetland has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al*. 2010).

4.2.1. Risks associated with acidification

The low net acidities in samples from Paiwalla wetland indicate that the acidification hazard is very low. Net acidities were very low in many of the soils where oxidation had taken place due to high acid neutralising capacity (ANC up to 9%: due to high amounts of carbonate). Incubation of the soils (Fitzpatrick *et al*. 2010) showed pH to vary from 7.82 in the upper surface layer to 5.92 at depth. Most of the acidity in the soil samples was as potential sulfidic acidity (S_{CR}), but with minor titratable actual acidity (TAA) in the deepest soil layer studied.

The probability of soil acidification is considered low as evidenced by the generally negative net acidities in most samples studied in the wetland. The wetland is connected to the river by a control structure and therefore can be managed in terms of water level. The likelihood is therefore classed as **possible**. The consequences of soil acidification are likely to be insignificant for soil ecology, and the timescale for soil recovery from any localised acidification is likely to be rapid at the pH observed in the contaminant metalloid dynamics studies. Studies in other wetlands e.g. Nelwart Lagoon (Shand *et al.* 2010) indicate that, once pH is moderate to neutral, that local pH increase can be rapid. A **minor** rating is therefore applied for consequence as long-term damage to soil water chemistry is considered likely. This provides a *risk rating for soil acidification* of **low**. A rating for surface water acidification will depend on surface and sub-surface hydrology. However, taking into account the very low net acidity in the surface soils the consequences are likely to be **insignificant**. The *risk to surface water acidification* is, therefore, likely to be **low** (Table 4-4).

4.2.2. Risks associated with contaminant mobilisation

The risks of metal and metalloid mobilisation are controlled primarily by metal abundance and availability, geochemical controls on speciation and transport mechanisms. The master variables pH and Eh exert a direct major influence on the solubility of individual metals and metalloids and minerals such as iron (Fe) and manganese (Mn) oxides and hydroxides which are important sorbents of metal and metalloids species. The low acidification hazard due to the oxidation of sulfide minerals means that if metals and metalloids have been released they are likely to be mobile. Although reduction processes may lead to reincorporation of metals and metalloids into sulfide minerals (following sulfate reduction), at intermediate redox, potential mobility may be high where iron (Fe) and manganese (Mn) are soluble. The reactive metals and contaminant and metalloid dynamics test results attest to the availability and mobility of a number of metals, particularly aluminium (Al), iron (Fe), arsenic (As) and vanadium (V). The risks from aluminium are likely to be minor as precipitation and flocculation are likely to occur at the pH values observed in the contaminant and metalloid dynamics experiments after a few days. The main risks come from those metalloids which are mobile at higher pH, in this case arsenic (As) and vanadium (V). At the concentrations measured, the consequences are likely to be moderate for soil pore-waters and soil/sediment ecology. However, the soils which released most arsenic are those which appear to form monosulfides relatively easily and this may limit arsenic (As) in soil and surface waters. A consequence rating of **minor** is thus selected. This provides a risk rating for contaminant mobilisation in soils of **low** (Table 4-4).

A rating for surface water impacts from metals and metalloids will depend on surface and sub-surface hydrology. The consistently high pH values and reformation of monosulfidic materials in the surface soils in this study, however, means that only short term impacts are likely i.e. prior to strong reduction in the surface soils. The risk, based on **minor** consequence, is therefore **low**.

4.2.3. Risks associated with de-oxygenation

Monosulfidic materials are considered the main cause of deoxygenation risk in acid sulfate soils. Monosulfidic black ooze was identified in the wetland prior to the Phase 1 survey (Fitzpatrick *et al*. 2010). The water soluble sulfate concentrations were also high and above the trigger value for monosulfidic black ooze formation (MDBA 2010).

The hazard for monosulfidic formation potential is high (Table 4-4) with acid volatile sulfide (S_{AV}) being very high with a concentration of 0.74%. This suggests that risks from deoxygenation could be significant. The risk of deoxygenation is most significant if the surface soils are disturbed and the soils have a consistency that will allow rapid movement and transport to areas of high value. The soils had a gel-like consistency prior to drying and the reformation of low density black monosulfidic surface soils was observed at the time of sampling. Paiwalla wetland is separated from the River Murray by a control structure and risks are therefore limited to the wetland itself. The consequence of deoxygenation is considered to be **moderate** as disturbance may lead to short term deoxygenation, particularly as the low density surface monosulfidic soils can be mobilised easily. Taking into account the **possible** likelihood of disturbance and the **moderate** consequence, a risk rating of **medium** is attributed for deoxygenation potential.

Table 4-4 Summary of risks associated with acid sulfate soil materials in Paiwalla wetland.

Acidification Risk		Contaminant mobilisation		Deoxygenation
Soil	*Water*	*Soil*	*Water*	
Low	Low	Low	Low	Medium

5. BROAD ACID SULFATE SOIL MANAGEMENT OPTIONS

The options available for rehabilitation of inland waterways containing acid sulfate soils has recently been reviewed (Baldwin & Fraser 2009) and incorporated into the *National guidance on managing acid sulfate soils in inland aquatic ecosystems (*EPHC & NRMMC 2011; see Table 5-1). The national guidance document provides a hierarchy of management options for managing acid sulfate soils in inland aquatic ecosystems including:

1. *Minimising the formation of acid sulfate soils in inland aquatic ecosystems.*
2. *Preventing oxidation of acid sulfate soils, if they are already present in quantities of concern or controlled oxidation to remove acid sulfate soils if levels are a concern but the water and soil has adequate neutralising capacity.*
3. *Controlling or treating acidification if oxidation of acid sulfate soils does occur.*
4. *Protecting connected aquatic ecosystems/other parts of the environment if treatment of the directly affected aquatic ecosystem is not feasible.*
5. *Limited further intervention.*

In designing a management strategy for dealing with acid sulfate soils in affected inland wetlands, other values and uses of a wetland need to be taken into account to ensure that any intervention is compatible with other management plans and objectives for the wetland. The medium conservation status for this wetland suggests that the management responses required should align with those suggested following the risk assessment ratings (Table 4-3).

A number of options for treating acid sulfate soils in inland wetlands have been identified (see Table 5-1). By far the best option is not to allow acid sulfate soils to build up in the first instance. This requires removing the source of sulfate from the wetland, for example, by lowering saline water tables and/or introducing frequent wetting and drying cycles to the wetland so that the amount of sulfidic material that can build up in the sediments during wet phases is limited, hence reducing the likely environmental damage (acidification, metal release or deoxygenation) that would occur as a consequence of drying.

If acid sulfate soils have formed, prevention of oxidation, usually by keeping the sediments inundated to sufficient depth, is a potential strategy. If oxidation of acid sulfate soils occurs and the sediment and/or water column acidifies, neutralisation may be necessary.

The main risk identified in this study is due to deoxygenation from disturbance of monosulfides. However, the probability of physical disturbance to the monosulfidic surface layer is less than in channels where flows are higher, and can therefore be more easily managed. Since the wetland is managed with a control structure and acid sulfate soils are re-forming, options 1-2 in Table 5-1 form important management options. Management of the wetland may focus on reinstating a more natural wetting and drying regime to prevent the build-up of sulfidic sediments, and also preventing oxidation if required.

The impacts on surface and sub-surface ecosystems are not well understood and are worthy of further work, particularly long term impacts on ecosystem functionality and diversity.

Table 5-1 Summary of management options and possible activities, from EPHC & NRMMC (2011).

Management Objective	Activities
1. Minimising the formation of acid sulfate soils in inland aquatic ecosystems	**Reduce secondary salinisation through:** • Lowering saline water tables • Maintaining the freshwater lens between saline groundwater and the aquatic ecosystem • Stopping the delivery of irrigation return water • Incorporating a more natural flow regime.
2. Preventing oxidation of acid sulfate soils or controlled oxidation to remove acid sulfate soils	**Preventing oxidation:** • Keep the sediments covered by water • Avoid flow regimes that could re-suspend sediments. **Controlled oxidation:** • Assess whether neutralising capacity of the sediments and water far exceeds the acidity produced by oxidation • Assess the risk of deoxygenation and metal release. Monitor intervention and have a contingency plan to ensure avoidance of these risks.
3. Controlling or treating acidification	• Neutralise water column and/or sediments by adding chemical ameliorants • Add organic matter to promote bioremediation by micro-organisms • Use stored alkalinity in the ecosystem.
4. Protecting adjacent or downstream environments if treatment of the affected aquatic ecosystem is not feasible	• Isolate the site • Neutralise and dilute surface water • Treat discharge waters by neutralisation or biological treatment.
5. Limited further intervention	• Assess risk • Communicate with stakeholders • Undertake monitoring • Assess responsibilities and obligations and take action as required.

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APPENDICES

APPENDIX 1 REACTIVE METALS DATA

Paiwalla wetland

Sample	Depth	Analysis	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
PA1 A4.1	0-5	a	0.04	1055	0.95	73	5.8	943	0.15	17970	1009	7.7	1.6	< 23	81	11	17
		b	0.77	1009	0.85	63	5.6	974	0.58	16618	947	7.1	1.7	< 23	83	10	17
PA1 A4.2	5-10	a	5.0	572	3.3	89	2.9	402	4.4	2611	209	5.6	2.9	< 3.9	62	19	14
		b	6.2	753	4.6	110	4.2	587	6.2	3938	325	6.2	3.5	3.9	80	22	19
PA1 A4.3	10-20	a	6.4	384	3.6	49	0.63	180	3.4	1093	11	4.8	2.4	< 2.6	57	12	5.3
		b	5.8	341	3.5	41	0.67	191	3.7	1077	16	4.5	2.5	< 2.6	57	11	5.6

Units are mg kg^{-1} unless indicated otherwise as below

* Units are in µg kg^{-1}

< value is below detection limit*

APPENDIX 2 CONTAMINANT AND METALLOID DYNAMICS DATA

Paiwalla wetland

Sample	Day	Depth cm	Analysis	Eh mV	EC µS/cm	pH	Ag µg/L	Al mg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Fe mg/L	Mn µg/L	Ni µg/L	Pb µg/L	Sb µg/L	Se µg/L	V µg/L	Zn µg/L
PA1 A4.1	1	0-5	a	235	231	7.12	<0.02	<0.05	4.3	<0.06	0.71	<0.6	<2	<0.1	474	<2	<1	<2	0.06	1.7	<2
			b	230	237	6.51	<0.02	<0.05	6.4	<0.06	0.76	<0.6	<2	<0.1	479	<2	<1	<2	0.06	2.2	<2
	7		a	240	284	7.47	<0.01	0.23	19	<0.03	1.2	0.42	0.80	0.44	227	3.4	<0.2	<1	0.08	9.0	1.2
			b	225	323	7.24	<0.01	0.08	15	<0.03	1.3	0.28	0.80	0.30	363	3.4	<0.2	<1	0.08	5.2	0.80
	14		a	-30	585	7.50	<0.01	<0.05	12	<0.02	1.4	0.60	0.80	0.31	516	4.0	<0.4	<0.6	0.09	6.5	1.2
			b	-85	606	7.56	<0.01	0.07	14	<0.02	1.3	0.40	1.2	0.40	464	4.3	<0.4	<0.6	0.12	7.3	1.2
	35		a	-150	262	7.39	<0.01	0.07	10	<0.01	1.1	0.94	0.85	0.27	500	4.6	<0.4	<2	0.16	11	1.7
			b	-160	252	7.29	<0.01	0.07	10	0.01	1.1	0.87	1.1	0.34	489	4.6	<0.4	<2	0.15	11	1.5
PA1 A4.2	1	5-10	a	220	283	6.15	<0.01	<0.05	0.73	<0.03	0.12	<0.3	1.1	<0.1	1.8	<1	<0.6	<1	0.09	3.7	<1
			b	225	382	6.14	<0.01	0.05	0.96	<0.03	0.10	<0.3	<1	<0.1	2.4	<1	<0.6	<1	0.07	2.3	<1
	7		a	225	645	6.43	<0.05	<0.05	0.50	<0.2	0.10	<0.4	1.0	<0.1	3.5	0.80	<1	<5	<0.2	2.0	<2
			b	220	685	6.50	<0.05	<0.05	<0.5	<0.2	0.10	<0.4	<1	<0.1	2.5	0.40	<1	<5	<0.2	2.0	<2
	14		a	130	1425	6.43	<0.01	<0.05	2.0	<0.1	0.32	<1	<2	<0.1	14	1.6	<2	<3	<0.2	7.0	<2
			b	120	852	6.75	<0.01	<0.05	2.8	<0.04	0.26	<0.4	1.6	<0.1	0.80	1.4	<0.8	<1	0.06	13	<0.6
	35		a	25	338	6.98	<0.01	<0.05	4.4	<0.05	0.35	<0.5	2.0	<0.1	51	1.9	<2	<10	0.25	12	<2
			b	30	318	6.88	<0.01	<0.05	2.1	<0.05	0.29	<0.5	2.0	<0.1	46	2.0	<4	<10	0.20	13	<2
PA1 A4.3	1	10-20	a	230	279	5.36	<0.01	0.25	0.90	<0.03	0.11	<0.3	<1	0.12	2.3	<1	<0.6	<1	0.08	3.8	<1
			b	240	3925	5.59	<0.01	0.13	0.87	<0.03	0.13	<0.3	<1	<0.1	2.9	<1	<0.6	<1	0.06	3.5	1.4
	7		a	240	574	5.62	<0.01	0.07	1.5	<0.03	0.16	0.21	0.80	<0.1	4.7	1.3	<0.2	<1	0.04	5.6	0.80
			b	235	548	5.64	<0.01	<0.05	1.4	<0.03	0.13	0.21	0.80	<0.1	4.9	1.1	<0.2	<1	0.04	4.6	0.80
	14		a	140	852	5.89	<0.01	<0.05	2.6	<0.02	0.22	<0.2	1.2	<0.1	7.7	1.7	<0.4	<0.6	0.09	8.7	1.2
			b	145	866	3.67	<0.01	<0.05	2.2	<0.02	0.23	<0.2	1.2	<0.1	9.0	1.8	<0.4	<0.6	0.09	7.9	1.5
	35		a	40	344	6.17	<0.01	0.07	2.6	<0.01	1.2	0.33	2.1	<0.1	191	3.1	<0.4	<2	0.15	6.2	1.7
			b	45	329	6.18	<0.01	0.10	2.6	0.01	0.89	0.37	1.9	<0.1	152	2.9	<0.4	<2	0.14	6.8	1.7

< value is below detection limit

APPENDIX 3 MONOSULFIDE FORMATION POTENTIAL DATA

Paiwalla wetland

MBO Formation Potential (MBO FP) - DAY 0 **IRON DATA** **DAY 0**

				Total Reactive Fe (mg/kg)				**Fe(II) (mg/kg)**				**Eh (mV)**				**pH**			
Sample No.	org	Site Name	**Site ID**	Replicate 1	Replicate 2	**Mean**	+/-	Replicate 1	Replicate 2	**Mean**	+/-	Replicate 1	Replicate 2	**Mean**	+/-	Replicate 1	Replicate 2	**Mean**	+/-
17	csiro	Paiwalla	PA1A4.1	18119	14359	**16239**	*1880*	20197	17983	**19090**	*1107*	358	375	**366**	*9*	8.96	8.97	**8.97**	0.00
32	-	Blank	-	0.3	0.1	**0.2**	*0.1*	<0.1	<0.1	**<0.1**	*<0.1*	183	186	**185**	*2*	6.17	6.10	**6.14**	0.04

MBO Formation Potential (MBO FP) - Week 7

				AVS (%S)				**Pyrite (%S)**				**ES (%S)**				**pH**				**Eh (mV)**				**Aqueous Sulfide (µg/L)**			
Sample No.	**org**	**Site Name**	**Site ID**	Replicate 1	Replicate 2	**Mean**	*+/-*	Replicate 1	Replicate 2	**Mean**	*+/-*	Replicate 1	Replicate 2	**Mean**	*+/-*	Replicate 1	Replicate 2	**Mean**	*+/-*	Replicate 1	Replicate 2	**Mean**	*+/-*	Replicate 1	Replicate 2	**Mean**	*+/-*
17	csiro	Paiwalla	PA1A4.1	0.66	0.83	**0.74**	*0.08*	0.11	0.14	**0.13**	*0.02*	0.11	0.15	**0.13**	*0.02*	5.81	5.73	**5.77**	*0.04*	133	6	**69**	*63*	6322	7261	**6791**	*469*
32	csiro	Blank														5.45	5.42	**5.44**	*0.02*	325	338	**331**	*6*	< 0.1	< 0.1	< 0.1	<0.1

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