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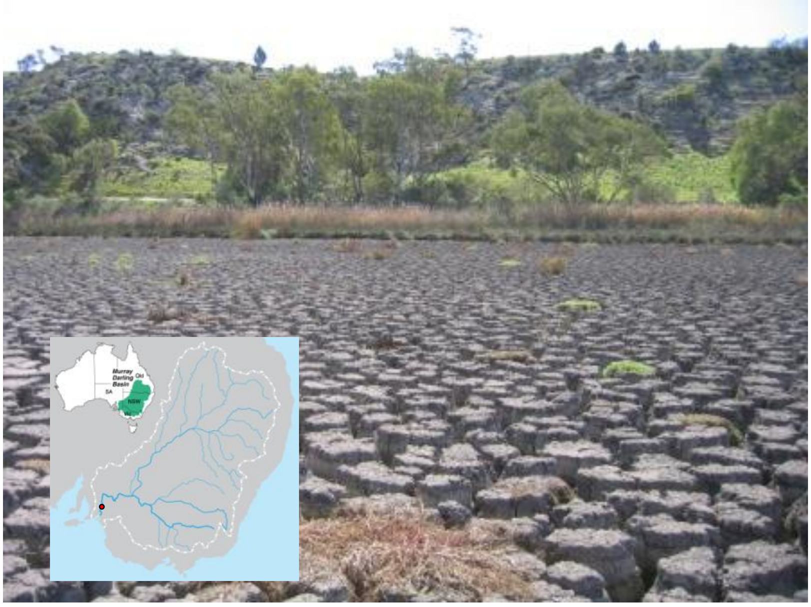

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Assessment of Acid Sulfate Soil Materials (Phase 2)
Teal Flat Hut wetland, South Australia

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Cover Photograph:

Teal Flat Hut wetland
Photographer: Gerard Grealish
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EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of the Teal Flat Hut wetland during 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 Teal Flat Hut wetland to determine the nature, severity and the specific risks associated with acid sulfate soil materials.

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 concentrations were below the sediment quality guidelines (SQG) and soil ecological investigation levels (EIL) for those elements where guidelines are available. The concentrations for this reactive metals partial extraction are considered to be moderately high for aluminium (Al), iron (Fe), manganese (Mn) and vanadium (V).

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 ANZECC/ARMCANZ environmental protection guideline values was used to characterise the degree of hazard. For Teal Flat Hut wetland, iron (Fe) was assigned a high hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 100 times, while aluminium (Al), arsenic (As), cobalt (Co), copper (Cu), nickel (Ni) and zinc (Zn) were assigned a moderate hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 10 times. The dominant control on metal solubility is the pH of the extractions. Three of the four soils analysed had very low pH, and the highest concentrations of both metals and metalloids which breached ANZECC/ARMCANZ environmental protection guideline values. All samples showed a decrease in Eh, but only the acidic soils decreased sufficiently for iron (Fe) to become soluble. The Eh was not low enough for sulfate reduction and the extent of decrease was different in the two profiles studied. The most acidic sample showed little change in Eh. Iron (Fe) increased with time only in one sample after 35 days, probably due to a decrease in Eh and this may have led to the release of arsenic (As) and vanadium (V) from the reductive dissolution of iron oxides and oxyhydroxides. The concentrations of a number of metals were higher than ANZECC/ARMCANZ environmental protection guidelines, largely controlled by the low pH in a sulfuric layer of one profile.

The Teal Flat Hut 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 **very high** risk rating for ***acidification*** and a **very high *contaminant*** risk rating for **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, from very low flows (highest risk) to very high flows (lowest risk), the risk to surface waters in the wetland has been allocated a **medium to very high** risk rating for ***acidification*** and ***contaminant mobilisation***. The risk associated with **deoxygenation** was determined to be **medium** due to the high water soluble sulfate values.

In designing a management strategy for dealing with acid sulfate soils in Teal Flat Hut 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 soils studied were largely dry at the time of sampling, therefore management options considered should relate to controlling or treating acidification and the protection of connected or adjacent wetlands. Due to the medium to very high risks to the wetland values associated with acidification and contaminant mobilisation, and medium risks associated with deoxygenation in Teal Flat Hut wetland, a monitoring program is strongly recommended during any disturbance to the soils.

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).

Following the Teal Flat Hut wetland Phase 1 assessment (Grealish *et al*. 2011) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1), Teal Flat Hut wetland was selected for Phase 2 detailed assessment.

The Phase 1 assessment sampled 3 sites (Figure 1-1) from the wetland which comprised cracking clay soils. Sites TFH 1 and 2 were from the western part of the wetland and TFH 3 was from the east, and the wetland was dry at the time of sampling, although water was present in cracks. The Phase 1 assessment identified two high priority sites based on the presence of sulfuric materials, no high priority sites based on the presence of hypersulfidic materials, one high priority site based on hyposulfidic materials with $S_{CR} \geq 0.10\%$ and one moderate priority site based on the presence of hyposulfidic materials with $S_{CR} < 0.10\%$. Phase 2 investigations were carried out on selected surface soil samples from two sites (TFH 1 and TFH 3) identified in the Phase 1 assessment.

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.

Figure 1-1 Teal Flat Hut wetland aerial photograph with Phase 1 sampling sites identified.

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 Teal Flat Hut wetland is presented in Table 1-3.

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 Teal Flat Hut wetland samples analysed for Phase 2 assessment.

Soil Laboratory Test	Teal Flat Hut wetland samples	Sample depth (cm)	Number of samples analysed
Reactive metals	TFH1.1	0-5	4
	TFH1.2	5-10	
	TFH3.1		
	TFH3.2	5-20	
Contaminant and metalloid dynamics	TFH1.1	0-5	4
	TFH1.2	5-10	
	TFH3.1	0-5	
	TFH3.2	5-20	
Monosulfide formation potential	-		0
Mineral identification by X-ray diffraction (XRD)	-		0

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 and 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 where guidelines are available. The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (Al), iron (Fe), manganese (Mn) and vanadium (V) (Table 3-1).

Table 3-1 Teal Flat Hut wetland reactive metals data.

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

Sample	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
TFH 1.1	8.3	849	1.6	55	3.7	225	6.4	1610	130	8.3	0.54	< 1.8	45	15	6.3
TFH 1.2	7.6	823	1.3	44	3.1	241	6.4	2028	135	6.6	2.4	< 2.0	44	18	5.3
TFH 3.1	5.0	661	4.3	63	4.7	255	3.8	1767	85	8.4	2.5	9.7	57	24	4.9
TFH 3.2	2.7	283	1.3	46	1.0	69	2.8	609	29	4.1	1.8	< 1.8	32	8.5	3.2
[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 Teal Flat Hut 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	Teal Flat Hut		
			Min.	**Median**	**Max.**
pH		6.5-8.0	🟥 **3.4**	🟥 **3.7**	6.9
EC*	µS cm^{-1}	2200	294	953	2181
Eh	mV	-	227	573	714
Ag	µg l^{-1}	0.05	<0.01	<0.1	<0.1
Al^{A}	mg l^{-1}	0.055	<0.05	🟧 **1.7**	🟧 **5.1**
As^{B}	µg l^{-1}	13	<2	2.8	🟧 **258**
Cd	µg l^{-1}	0.2	<0.03	🟨 **1.1**	🟨 **1.8**
Co	µg l^{-1}	2.8	0.35	🟧 **100**	🟧 **172**
Cr^{C}	µg l^{-1}	1	<0.09	🟨 **2.5**	🟨 **4.0**
Cu^{H}	µg l^{-1}	1.4	<1	<10	🟧 **44**
Fe^{I}	mg l^{-1}	0.3	<0.10	🟧 **8.2**	🟥 **142**
Mn	µg l^{-1}	1700	41	🟨 **3912**	🟨 **4928**
Ni^{H}	µg l^{-1}	11	2.3	🟧 **169**	🟧 **227**
Pb^{H}	µg l^{-1}	3.4	<0.30	<6	<6
Sb	µg l^{-1}	9	<1.0	<10	<20
Se	µg l^{-1}	11	<0.40	0.51	1.0
V	µg l^{-1}	6	<0.90	3.8	🟨 **17**
Zn^{H}	µg l^{-1}	8	1.3	🟧 **113**	🟧 **230**

🟨 ***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.

Three of the samples had very low pH after 24 hours, and although the pH did increase slightly, after 35 days they were still very acidic (pH 3.63 to 4.28; Figure 3-1). The fourth sample from Teal Flat Hut wetland had a slightly acidic pH, which increased to circumneutral by day 35. The SEC was variable, and in all samples showed a general increase with time (Figure 3-1). The lowest SEC was in sample TFH 2.2, which had the highest pH.

The Eh showed a slight increase in all samples between day 1 and day 14, but subsequently decreased. The final Eh values varied from moderately reducing to oxidising.

Iron (Fe) concentrations were initially low after day 1, but increased significantly in the three acidic samples, especially after day 14 (Figure 3-2). Although the Eh values were not particularly low, at these pH's there was enough change to move the acidic waters into the stability field of dissolved ferrous iron (Fe^{2+}), whilst the higher pH sample (TFH 3.2) remained in the stability field for insoluble iron hydroxide throughout the 35 days, i.e. the pH-Eh data are consistent with the trends in iron seen. Manganese (Mn) concentrations were consistently high in the acidic samples (above the ANZECC/ARMCANZ environmental protection guideline value) and low in the more acidic sample.

Aluminium (Al) concentrations remained low in TFH 3.2, but were high in the acidic soils. In the latter samples, aluminium (Al) was high during day 1 and reached a maximum on day 7. It subsequently decreased with time (Figure 3-2), possibly in response to the increase in pH, albeit the increase in pH was small. Arsenic (As) concentrations increased significantly in all soils over time (Figure 3-1), although an increase in concentrations to above the ANZECC/ARMCANZ environmental protection guideline value only occurred in the acidic soils. Vanadium (V) increased above the ANZECC/ARMCANZ environmental protection guideline value in the more acidic soils, especially on day 35 (Figure 3-3).

For the metals, concentrations were related to pH, being much higher in the more acidic soils (Figure 3-1 to Figure 3-3). Those metals breaching the ANZECC/ARMCANZ environmental protection guideline values in the acidic soils were cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn). For these metals, concentrations peaked prior to day 35, or the rate of increase was smaller with time. The trends were dissimilar to iron (Fe), and more similar to manganese (Mn).

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) EC; 8) clay content; 9) microbial activity; 10) temperature, and; 11) porosity (MDBA 2010).

Most metals displayed a clear trend with pH (Figure 3-4), being higher in the acidic soils. A similar trend was also noted for the oxyanions arsenic (As) and vanadium (V), suggesting a source control e.g. derivation from soils which previously contained abundant pyrite.

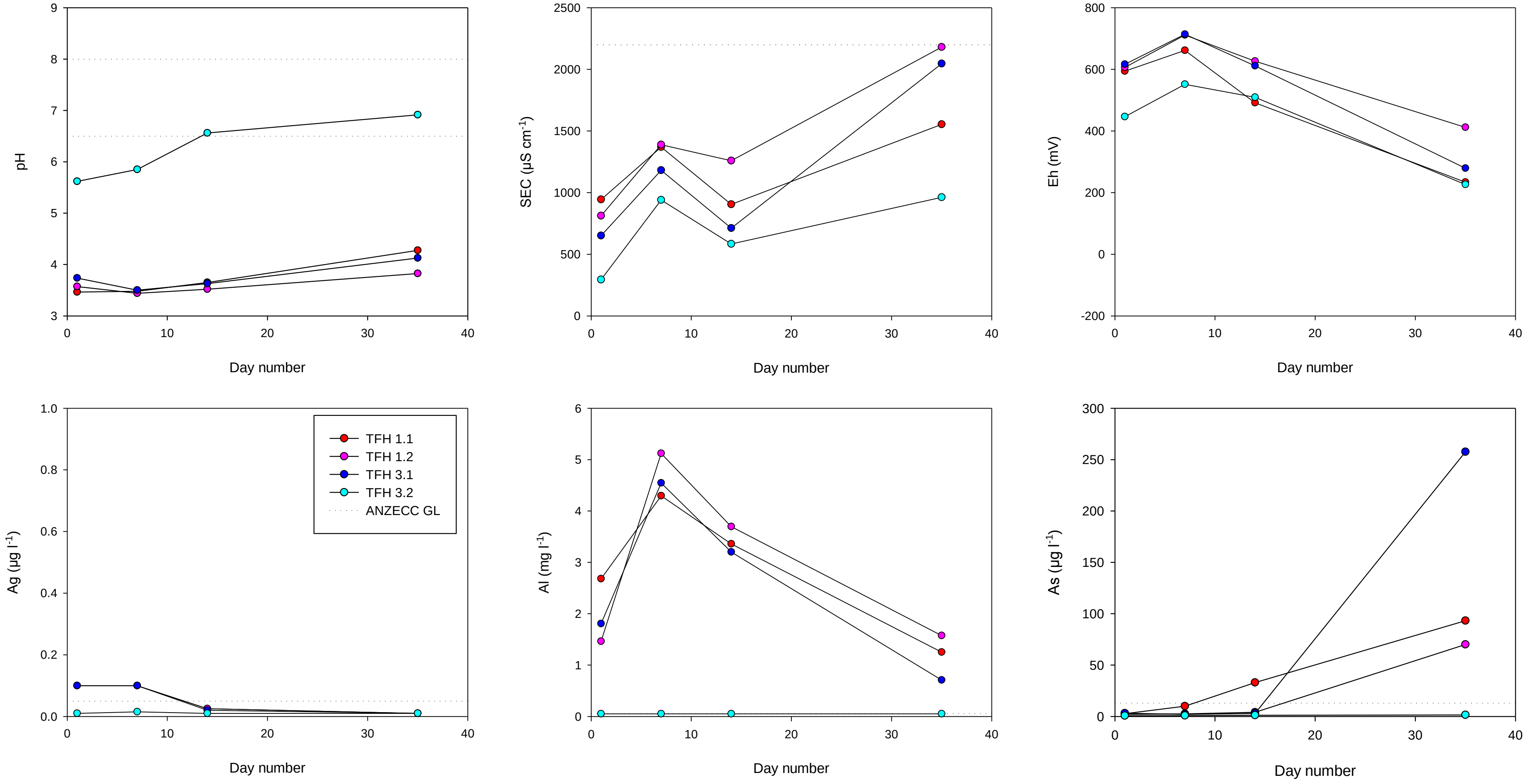

Figure 3-1 Contaminant and metalloid dynamics results for Teal Flat Hut wetland soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al) and arsenic (As).

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

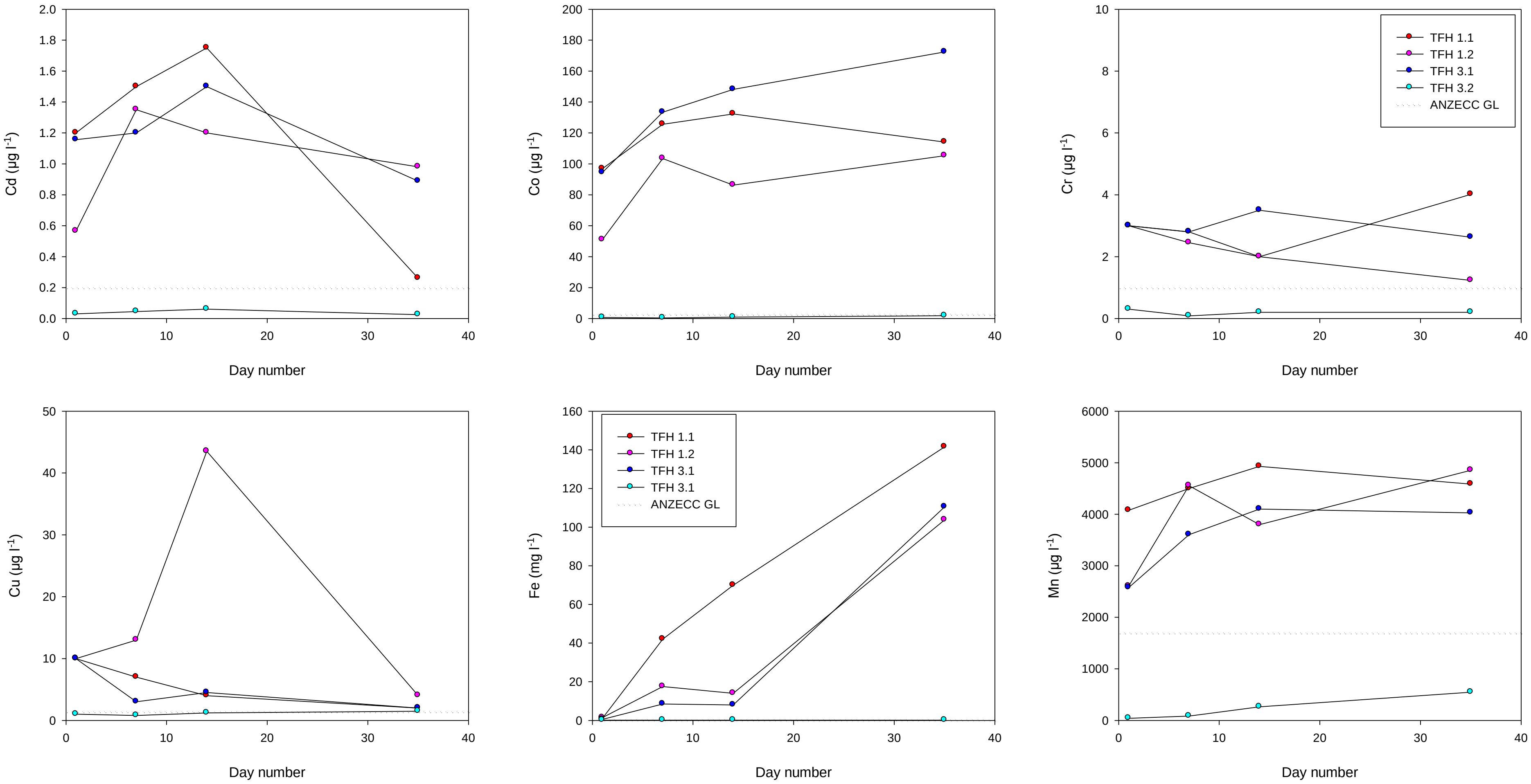

Figure 3-2 Contaminant and metalloid dynamics results for Teal Flat Hut wetland soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

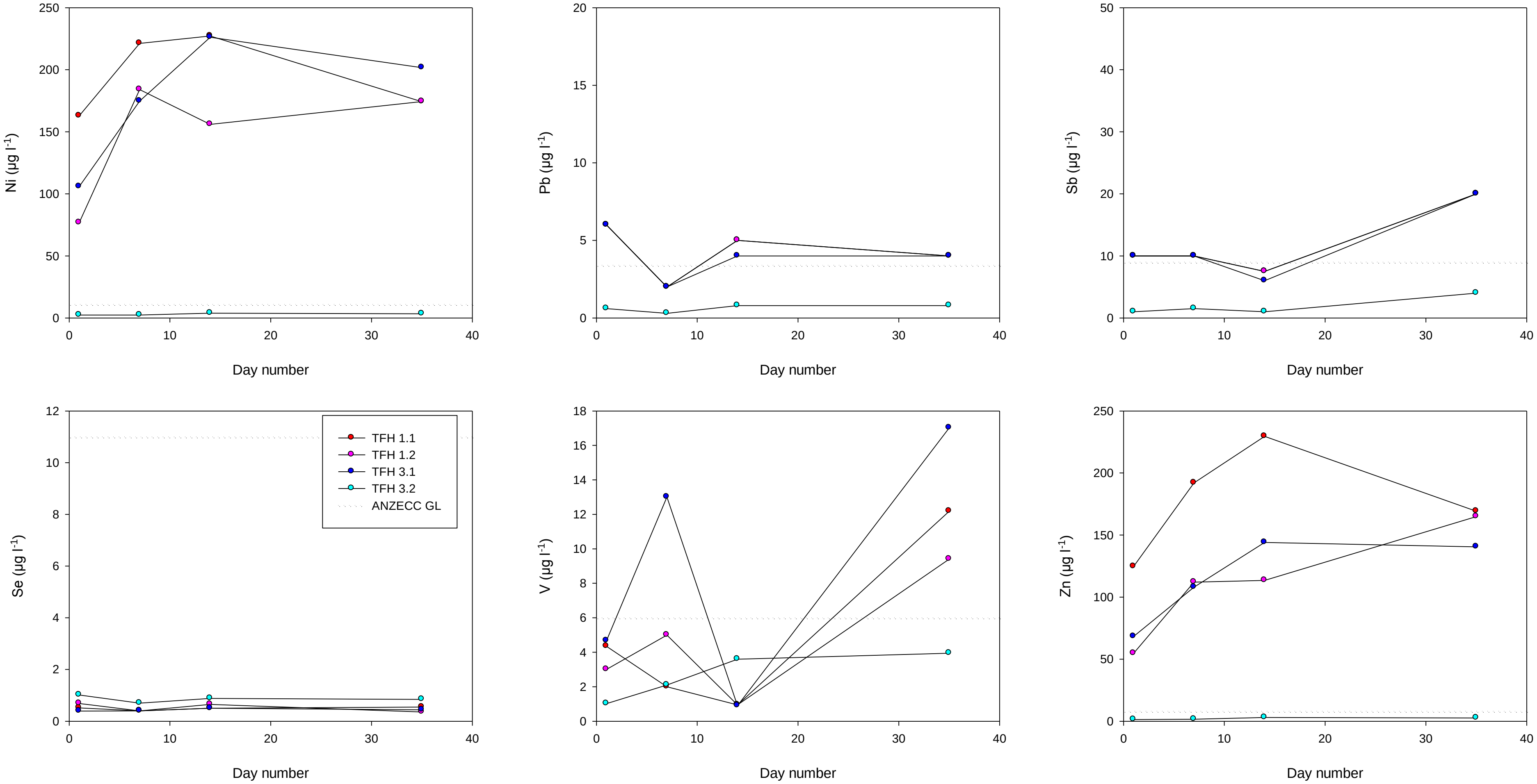

Figure 3-3 Contaminant and metalloid dynamics results for Teal Flat Hut wetland soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

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

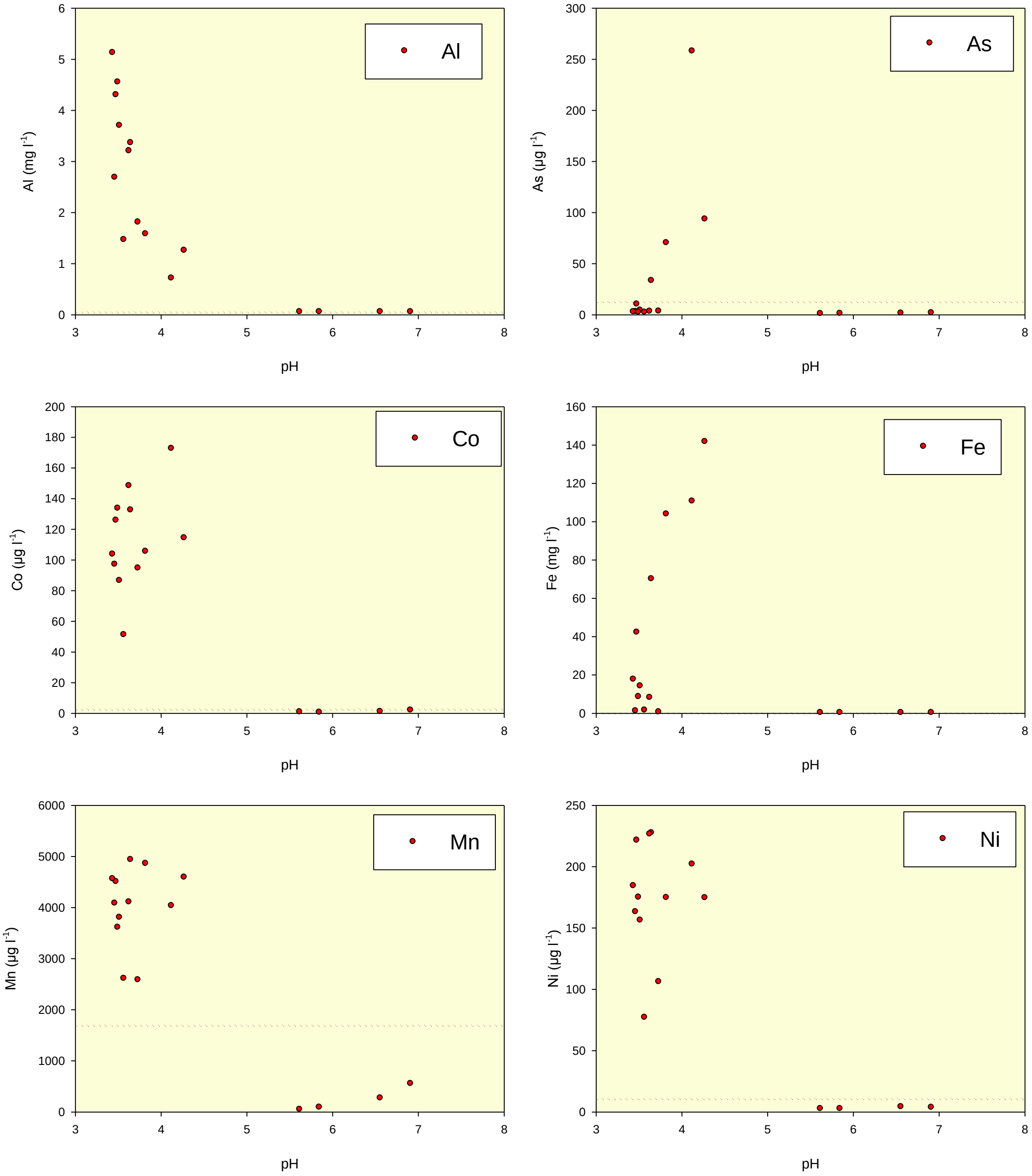

Figure 3-4 Selected trace elements plotted against pH.

3.1.3. Monosulfide formation potential data

No samples were selected from this wetland for monosulfide formation potential studies.

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.

The metal and metalloid concentrations were all below sediment quality guideline (SQG) values and soil ecological investigation levels (Table 3-1). The concentrations for most reactive metals and metalloids are relatively low, however concentrations of iron (Fe), manganese (Mn), aluminium (Al) and vanadium (V) are considered high for this partial extraction, consistent with the relatively low initial pH.

The **contaminant and metalloid dynamics** method 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 is 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.

The soil water pH was variable in the samples studied, but three out of four samples were very acidic, maintaining similar pH over the 35 day period. All samples showed a significant decrease in Eh (Figure 3-1), and for the acidic samples, this was sufficient to allow iron (Fe) to be soluble. Iron (Fe) concentrations increased over time, and appear to be strongly controlled by the decrease in Eh. The Eh and pH conditions were sufficiently low, that manganese (Mn) remained in solution in most of the samples. The risks associated with metal and metalloid release are probably related to the dissolution of iron (Fe) and manganese (Mn) compounds. The trends for most metals are similar to manganese (Mn), whilst those for the metalloids are more similar to iron (Figure 3-1 to Figure 3-3). The dominant control on the risks of metals and metalloids is likely to be pH: the highest concentrations were present in the acidic soil materials in contaminant and metalloid dynamics experiments.

The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-3). For some samples which required dilution, the detection limits were slightly above ANZECC/ARMCANZ environment protection guideline values due to required dilution. Antimony (Sb), for example, was below detection limit for all samples (detection limit varying between 1 and 20 µg l^{-1}), as was lead (Pb). It is therefore not possible to group either lead (Pb) or antimony (Sb) in Table 3-3, although it can be concluded that they either sit in the 'No hazard' or 'Low Hazard' grouping. The data are shown in Appendix 1 which displays the detection limits for individual analyses.

The data are consistent with the moderate to high net acidities noted by Grealish *et al*. (2011). The contaminant and metalloid dynamics data suggest that most soils may take a significant time to recover in terms of acidity. The higher pH in the surface soils of one profile (TFH 3) will help minimise or ameliorate the upward flux of acidity and metals from this area. Higher pH will also limit the solubilities of most trace metals. The main control on metal and metalloid availability appears to be pH in the Teal Flat Hut wetland soils. The source of many metals appears to be closely related to manganese (Mn) which may imply a source from manganese oxides/oxyhydroxides. Alternatively, both may simply be controlled by pH. The metalloids show more similarities to iron (Fe) and therefore a link to dissolution of an iron-bearing mineral appears likely. This may be an iron oxide/oxyhydroxide or an oxyhydroxysulfate mineral such as natrojarosite. The mobility of both metals and metalloids may be a significant hazard over longer timescales, at least until further reduction into the field of iron sulfide stability, in which case they may be scavenged by precipitating iron (Fe) sulfides.

Table 3-3 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in the Teal Flat Hut wetland.

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

Note: Pb and Sb are below detection limits in some samples due to dilutions, and therefore are likely to be classified as low or no hazard.

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 the acid sulfate soils, the net acid generating potential and the buffering capacity of the 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	Low	Low
Unlikely	High	Medium	Medium	Low	Very low
Rare	High	Medium	Low	Very 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 metal 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, degree and depth of soil cracking.

The Teal Flat Hut 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 to high net acidities in the dry soils Teal Flat Hut wetland (Grealish *et al*. 2011) suggest that the acidification hazard is variable. However, the majority of samples had a moderate to high risk of acidification based on net acidity. The high net acidities for many samples imply that the acidified soils may some time to recover, but this will depend largely on hydrological conditions e.g. high flows will provide some buffering and allow the acidity flux to move downwards in the soil profile. The acidification hazard is therefore considered to be significant but spatially variable in the wetland.

It is concluded that soil acidification would pose a serious problem in the soils over much of the wetland as suggested by the measured low pH over the 35 days of the contaminant and metalloid dynamics tests. The wetland was dry during sampling, and due to its location adjacent to the river, the likelihood of disturbance is considered **almost certain** as flows return to normal in the future. The consequences for soil ecology are likely to be short term and localised in nature and the timescale for soil recovery from acidification will probably be of the order of at least months even if there are sufficient flows, as indicated in the contaminant and metalloid dynamics experiments. A **major** rating is therefore applied for consequence as short-term damage to soil water chemistry is considered likely. This provides a *risk rating for soil acidification* of **very high** (Table 4-4). A rating for surface water acidification will depend on surface and sub-surface hydrology. The highest risk is likely to be during low flows where the soil to water ratio is high: acidity will be most concentrated. The risk to surface water acidification is considered lowest where high flows are available to both dilute acidity and transport acidity downwards in the soil profile. Surface water acidification is likely to be lower than soil acidification, due to limited transport and buffering reactions at the soil/water interface (where recovery may be rapid), therefore a **minor to major** categorisation is given for consequence. The *risk to surface water acidification* is therefore likely to be **medium to very high** (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 high acidification hazard due to the oxidation of sulfide minerals means that metals and metalloids are likely to be present at moderately high concentrations in some soils, depending on availability. The data suggest that iron (Fe), aluminium (Al), arsenic (As), cobalt (Co), copper (Cu), nickel (Ni) and zinc (Zn) are the elements with the highest hazard. The samples showed a trend towards more reducing conditions, and at the pH's observed this was sufficient to mobilise iron (Fe) and manganese (Mn) which are often related to trace metals and metalloids through acid dissolution and redox processes. The hazards may be higher for metalloids if the pH increases, as these may be mobile even once pH increases. Arsenic (As) was very high during the contaminant and metalloid dynamics experiments for one sample (258 µg l^{-1}) suggesting that this element may pose a significant hazard once the soils partially recover. However, further reduction processes may lead to reincorporation of metals and metalloids into sulfide minerals (following sulfate reduction).

Although the timescales cannot be assessed with existing information, the data suggest that metal availability is significant for some metals. Comparisons with other studies (e.g. Nelwart Lagoon, Shand *et al*. 2010), suggest that at the pH levels noted in the contaminant and metalloid dynamics experiments for most samples, reductive processes may occur rapidly once initiated, and soil recovery may be rapid. A **major** rating is applied for consequence due to the presence of a number of metals in deeper acidic soil layers and metalloids in surface soils, along with a likelihood of disturbance of **almost certain** as flows return to normal in the future. This provides a risk rating for contaminant mobilisation in soils of **very high** (Table 4-4).

A rating for surface water impacts from metals and metalloids will depend on surface and sub-surface hydrology. The acidic to circumneutral pH values in this study, however, means that longer term impacts are possible. Chemical reactions with soils and interactions at the soil/water interface are likely to diminish any minor hazards from metal flux. The highest risk is likely to be during low flows where the soil to water ratio is high: metals will be most concentrated. The risk to surface metal and metalloid flux is considered lowest where high flows are available to both dilute metal and metalloid concentrations and transport these downwards in the soil profile. Due to enhanced mobility of metalloids at higher pH, the hazard cannot be assumed to be insignificant with the limited time series data available in this study, hence an **minor** to **major** consequence is applied. The risk to surface waters from metal mobilisation is therefore considered to be **medium to very high** (Table 4-4).

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 not identified in the wetland during the Phase 1 survey (Grealish *et al*. 2011). However, water soluble sulfate concentrations were high (up to 768 mg kg^{-1}). Given that monosulfides were not identified during the Phase 1 field sampling which was made more difficult as the wetland was dry, and even though no monosulfide formation potential tests were completed, the consequence cannot be assumed to be insignificant due to the elevated water soluble sulfate levels. Therefore a minor consequence is applied and as such the risk rating for deoxygenation from monosulfide disturbance is **medium** (Table 4-4).

Table 4-4 Summary of risks associated with acid sulfate soil materials in the Teal Flat Hut wetland.

Acidification Risk		Contaminant mobilisation		Deoxygenation
Soil	*Water*	*Soil*	*Water*	
Very high	Medium-very high	Very high	Medium-very high	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 medium to very high risks identified in this study are due to soil and water acidification and contaminant mobilisation. The likelihood of water refilling the wetland is high as flows return to normal levels. The limited number of case studies on refilling wetlands makes prediction of risk difficult in terms of determining whether reversible or irreversible damage is likely to occur. However, at the low pH's observed, the limited increase in pH over the 35 day period along with metal and metalloid mobilisation imply that any risks are likely to be significant.

As the wetland has previously dried and undergone oxidation, management options 1 and 2 in Table 5-1 are not relevant to the current study, although minimising further oxidation could have been an option prior to recent high flows down the River Murray. Treatment options currently remain a viable option should water quality impacts e.g. acidification of surface water and/or high metal concentrations be seen. Since the risks are scenario dependent, it is recommended that surface water monitoring be undertaken at this wetland. Based on the data from this study and elsewhere (Shand *et al*. 2010), it is likely that soil recovery will be relatively slow in the sub-surface soils as pH is relatively high in three of the four samples. It is anticipated, however, that for deeper soil layers which remain sulfuric, soil acidity may remain for periods of several months. 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

Teal Flat Hut wetland

Sample	Depth	Analysis	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
TFH 1.1	0-5	a	8.4	841	1.6	54	3.7	225	6.5	1624	128	8.3	0.54	< 1.8	45	15	6.3
		b	8.3	857	1.5	55	3.8	225	6.2	1596	131	8.3	0.54	< 1.8	45	15	6.2
TFH 1.2	5-10	a	7.5	819	1.3	44	3.1	237	6.5	1998	135	6.7	2.4	< 2.0	43	18	5.7
		b	7.7	827	1.3	44	3.1	245	6.3	2057	136	6.4	2.5	< 2.0	44	19	4.8
TFH 3.1	0-5	a	4.8	643	4.1	59	4.5	239	3.8	1647	83	8.0	2.5	7.7	56	23	4.6
		b	5.2	678	4.4	67	5.0	270	3.9	1887	87	8.9	2.5	12	59	26	5.2
TFH 3.2	5-20	a	2.7	281	1.3	43	0.93	66	2.7	614	27	3.8	1.8	< 1.8	32	7.9	3.0
		b	2.7	285	1.4	49	1.1	73	2.9	605	31	4.3	1.9	< 1.8	32	9.0	3.4

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

Teal Flat Hut 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
TFH 1.1	1	0-5	a	589	945	3.46	<0.1	2.9	2.0	1.0	92	<3	<10	1.0	3978	159	<6	<10	0.53	4.6	124
			b	599	943	3.47	<0.1	2.4	3.3	1.4	101	<3	<10	0.94	4170	166	<6	<10	0.50	4.1	125
	7		a	649	1350	3.48	<0.1	4.3	9.0	1.5	126	2.8	8.0	42	4524	222	<2	<10	<0.4	<2	188
			b	674	1389	3.48	<0.1	4.3	11	1.5	126	2.8	6.0	42	4476	220	<2	<10	<0.4	<2	196
	14		a	489	918	3.65	<0.03	3.6	30	2.0	137	2.0	<5	72	5136	233	<6	<9	0.60	<1	240
			b	494	892	3.65	<0.02	3.1	36	1.5	128	2.0	3.0	68	4721	221	<4	<6	0.40	<0.9	219
	35		a	229	1644	4.24	<0.01	2.0	90	0.35	127	4.1	<2	143	5009	202	<4	<20	0.58	14	189
			b	239	1464	4.31	<0.01	0.48	96	0.17	101	3.9	<2	140	4161	147	<4	<20	0.51	11	149
TFH 1.2	1	5-10	a	604	878	3.55	<0.1	1.6	<2	0.68	52	<3	<10	1.6	2625	77	<6	<10	0.68	<3	52
			b	609	747	3.59	<0.1	1.3	<2	0.45	50	<3	<10	1.3	2581	76	<6	<10	0.70	<3	58
	7		a	709	1386	3.45	<0.1	4.9	2.0	1.5	102	2.1	14	16	4493	178	<2	<10	<0.4	4.0	108
			b	714	1392	3.43	<0.1	5.4	3.0	1.2	105	2.8	12	19	4616	190	<2	<10	<0.4	6.0	116
	14		a	619	1593	3.53	<0.03	5.1	<5	1.5	106	<2	75	24	4926	194	<6	<9	0.30	<1	140
			b	634	926	3.51	<0.02	2.3	<3	0.90	66	2.0	12	3.7	2672	118	<4	<6	1.0	<0.9	87
	35		a	409	1925	3.88	<0.01	1.3	67	0.93	107	1.2	3.7	111	5018	178	<4	<20	0.32	13	170
			b	414	2436	3.77	<0.01	1.9	72	1.0	103	1.2	4.4	97	4689	171	<4	<20	0.40	5.5	160
TFH 3.1	1	0-5	a	614	641	3.74	<0.1	2.1	3.5	0.87	96	<3	<10	0.59	2555	104	<6	<10	0.29	5.1	71
			b	619	661	3.73	<0.1	1.5	2.6	1.4	93	<3	<10	0.54	2600	107	<6	<10	0.49	4.3	65
	7		a	719	1265	3.44	<0.1	5.8	3.0	1.5	143	3.5	4.0	11	4065	199	<2	<10	<0.4	20	120
			b	709	1098	3.56	<0.1	3.3	<1	0.90	124	2.1	2.0	6.1	3143	150	<2	<10	<0.4	6.0	96
	14		a	609	554	3.66	<0.02	2.9	<3	1.2	148	2.0	3.0	4.7	4214	174	<4	<6	0.60	<0.9	141
			b	614	869	3.60	<0.02	3.5	<3	1.8	149	5.0	6.0	11	3985	278	<4	<6	0.40	<0.9	147
	35		a	274	2064	4.09	<0.01	0.53	275	0.79	176	3.1	<2	111	4071	202	<4	<20	0.47	17	137
			b	284	2029	4.16	<0.01	0.89	240	0.99	169	2.2	<2	110	3980	202	<4	<20	0.41	17	144
TFH 3.2	1	5-20	a	449	276	5.49	<0.01	<0.05	0.56	<0.03	0.77	<0.3	<1	<0.1	47	2.6	<0.6	<1	1.1	0.78	1.5
			b	444	312	5.75	<0.01	<0.05	0.70	<0.03	0.53	<0.3	<1	<0.1	34	2.1	<0.6	<1	0.96	1.3	<1
	7		a	559	898	5.88	<0.01	<0.05	1.0	<0.03	0.33	<0.07	0.80	<0.1	74	2.3	<0.2	<1	0.68	2.2	1.6
			b	544	983	5.82	<0.02	<0.05	0.80	<0.06	0.36	<0.1	0.81	<0.1	96	2.4	<0.4	<2	0.72	2.0	1.6
	14		a	519	579	7.04	<0.01	<0.05	1.2	<0.06	0.86	<0.2	1.2	<0.1	259	3.9	<0.8	<1	0.88	3.6	3.0
			b	499	587	6.08	<0.01	<0.05	1.2	<0.06	0.83	<0.2	1.2	<0.1	267	3.8	<0.8	<1	0.88	3.6	3.0
	35		a	229	892	7.18	<0.01	<0.05	1.7	0.03	1.9	<0.2	1.6	<0.1	570	3.7	<0.8	<4	0.78	4.1	2.9
			b	224	1032	6.65	<0.01	<0.05	1.1	<0.02	1.6	<0.2	1.4	<0.1	521	2.9	<0.8	<4	0.91	3.8	2.2

< value is below detection limit

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