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Assessment of Acid Sulfate Soil Materials (Phase 2)
Lake Carlet, South Australia

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Lake Carlet
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EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of Lake Carlet 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 Lake Carlet 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 and soil ecological investigation levels 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) and manganese (Mn) and to a lesser degree arsenic (As), nickel (Ni) 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 Lake Carlet, aluminium (Al), cobalt (Co) and iron (Fe) 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 neutral to slightly acidic pH which limits the solubility of many metals. One sampled was sulfuric, remaining acidic over the 35 day duration of the tests. High aluminium (Al) was found in the acidic layer, and also in one sample with circumneutral pH, significantly above equilibrium concentrations. It is concluded that much of this aluminium (Al) exists as colloidal particles, thus less toxic than Al^{3+} the dominant form at lower pH. All samples showed a decrease in Eh, but 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. 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.

Lake Carlet 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 **medium** risk rating for **acidification** and a **medium 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 **low** risk rating for **acidification** and **low to medium** risk rating for **contaminant mobilisation** respectively. The risk associated with **deoxygenation** was determined to be **low** as the hazard associated with monosulfide formation was considered low and there was no evidence of monosulfides in the subaqueous soils of the wetland at the time of the Phase 1 field survey.

In designing a management strategy for dealing with acid sulfate soils in Lake Carlet, 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 comprised both dry marginal soils and subaqueous soils at the time of sampling that were soon to commence drying associated with falling river levels, therefore management options considered should relate to controlling or treating acidification and the protection of connected or adjacent wetlands. Due to the medium risks to the wetland values associated with soil acidification and contaminant mobilisation in Lake Carlet, a monitoring program is 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 Lake Carlet Phase 1 assessment (Fitzpatrick *et al*. 2008) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1), Lake Carlet was selected for Phase 2 detailed assessment.

The Phase 1 assessment sampled from 3 sites (Figure 1-1). Sites LCA 1 and 2 were from the dried margins of the wetland and LCA 3 was subaqueous at the time of sampling. The Phase 1 assessment identified one high priority site based on the presence of sulfuric materials, one high priority sites based on the presence of hypersulfidic materials, 2 high priority sites based on hyposulfidic materials with SCR ≥ 0.10% and 2 moderate priority sites based on the presence of hyposulfidic materials with SCR < 0.10%. Phase 2 investigations were carried out on selected surface soil samples from sites 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 Lake Carlet 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 Lake Carlet 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 Lake Carlet samples analysed for Phase 2 assessment.

Soil Laboratory Test	Lake Carlet samples	Sample depth (cm)	Number of samples analysed
Reactive metals	LCA1.1	0-5	4
	LCA1.2	5-15	
	LCA3.1	0-5	
	LCA3.2	5-15	
Contaminant and metalloid dynamics	LCA1.1	0-5	4
	LCA1.2	5-15	
	LCA3.1	0-5	
	LCA3.2	5-15	
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 and 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 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 values and soil ecological investigation levels 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) and manganese (Mn) and to a lesser degree arsenic (As), nickel (Ni) and vanadium (V) (Table 3-1).

Table 3-1 Lake Carlet 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
LCA 1.1	5.3	270	1.1	21	2.0	104	2.8	408	27	2.9	1.7	< 3.0	21	8.4	3.3
LCA 1.2	1.9	103	1.1	10	1.6	57	1.4	280	21	1.7	0.78	< 1.9	11	3.4	1.4
LCA 3.1	12	403	2.1	40	1.4	107	5.7	1298	89	6.1	2.9	< 3.6	33	10	5.0
LCA 3.2	12	611	2.6	33	2.3	96	4.2	1775	212	7.9	2.5	< 3.2	37	6.7	1.7
[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 four Lake Carlet soil materials examined are presented in Appendix 2, summarised in Table 3-2 and plotted against time in Figure 3-1 to 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	Lake Carlet		
			Min.	**Median**	**Max.**
pH		6.5-8.0	**3.7**	**6.1**	6.8
EC*	µS cm^{-1}	2200	185	423	**2274**
Eh	mV	-	87	409	639
Ag	µg l^{-1}	0.05	<0.01	<0.01	<0.1
Al^{A}	mg l^{-1}	0.055	0.05	**0.12**	**0.81**
As^{B}	µg l^{-1}	13	<0.2	2.0	10
Cd	µg l^{-1}	0.2	<0.01	<0.13	**0.30**
Co	µg l^{-1}	2.8	0.17	1.2	**41**
Cr^{C}	µg l^{-1}	1	<0.07	<1	<3
Cu^{H}	µg l^{-1}	1.4	<0.20	<3	**7**
Fe^{I}	mg l^{-1}	0.3	<0.10	<0.10	**4.0**
Mn	µg l^{-1}	1700	0.44	298	**4058**
Ni^{H}	µg l^{-1}	11	<1.0	2.2	**97**
Pb^{H}	µg l^{-1}	3.4	0.20	0.60	<6
Sb	µg l^{-1}	9	<0.60	<2.0	<20
Se	µg l^{-1}	11	<0.04	<0.11	<0.42
V	µg l^{-1}	6	<0.20	<2.0	**6.3**
Zn^{H}	µg l^{-1}	8	<1	1.3	<10

🟨 ***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 soil water pH was variable in the samples studied. One sample (LCA 3.2) from 5-15 cm was very acidic and remained so over the 35 day period. The others were slightly acidic, with two showing a dip in pH during day 14 experiments. The sample originally had a pH$_{w}$ of 5.4, and has probably oxidised in storage since sampling in 2008 (Fitzpatrick *et al*. 2008). The two surface soil layers studied showed a decrease in pH, reaching a minimum at day 14 but were recovering by day 35 (Figure 3-1). The SEC was variable, showing little change over time. The highest SEC was in sample LCA 1.1 and possibly represents some evaporative concentration of salts.

The Eh showed a significant and consistent decrease over the day 35 period for all samples, however, the decrease was much less for sulfuric material LCA 3.2, which retained a high Eh (Figure 3-1).

Iron (Fe) remained below the ANZECC/ARMCANZ environmental protection guideline value in all but one sample (LCA 1.1). This sample showed a slight increase up to 14 days followed by a large increase to more than 4 mg l^{-1}. Manganese (Mn) was highest in the sulfuric sample, above the ANZECC/ARMCANZ environmental protection guideline value throughout the duration of the experiment.

Aluminium (Al) concentrations were high in the sulfuric sample, but also present at concentrations above the ANZECC/ARMCANZ environmental protection guideline value in sample LCA 1.1 which had circumneutral pH. For the latter, it is likely that the aluminium (Al) present in the sample is in colloidal form as it is too high for dissolved equilibrium concentrations. The moderately high aluminium (Al) in LCA 3.2 is a function of it's low pH where aluminium (Al) as the Al^{3+} species is soluble. Arsenic (As) concentrations increased in some samples, but remained below the ANZECC/ARMCANZ environmental protection guideline value. Vanadium (V) showed no consistent trend in the samples, and only one sample exceeded the ANZECC/ARMCANZ environmental protection guideline value (Figure 3-3).

The sulfuric sample LCA 3.2 was significantly different from the higher pH samples in terms of metal concentrations with consistently high cadmium (Cd), cobalt (Co), nickel (Ni) and zinc (Zn), with cadmium (Cd), cobalt (Co) and nickel (Ni) being higher than ANZECC/ARMCANZ environmental protection guideline values.

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).

Many metals display a clear trend with pH (Figure 3-4), being higher at $pH < 4.5$. This reflects the higher metals in the sulfuric sample LCA 3.2. Arsenic (As) (Figure 3-4) and vanadium (V) showed a much greater tendency to be high at circumneutral pH, reflecting their different behaviour to the metals due to the formation of oxyanion species. The solubility of iron (Fe) and manganese (Mn) are often controlled by Eh where pH is high, but the samples do not appear to be sufficiently reducing for iron (Fe) dissolution to be significant. There is thus a complex interplay between pH, Eh and metal availability in the samples.

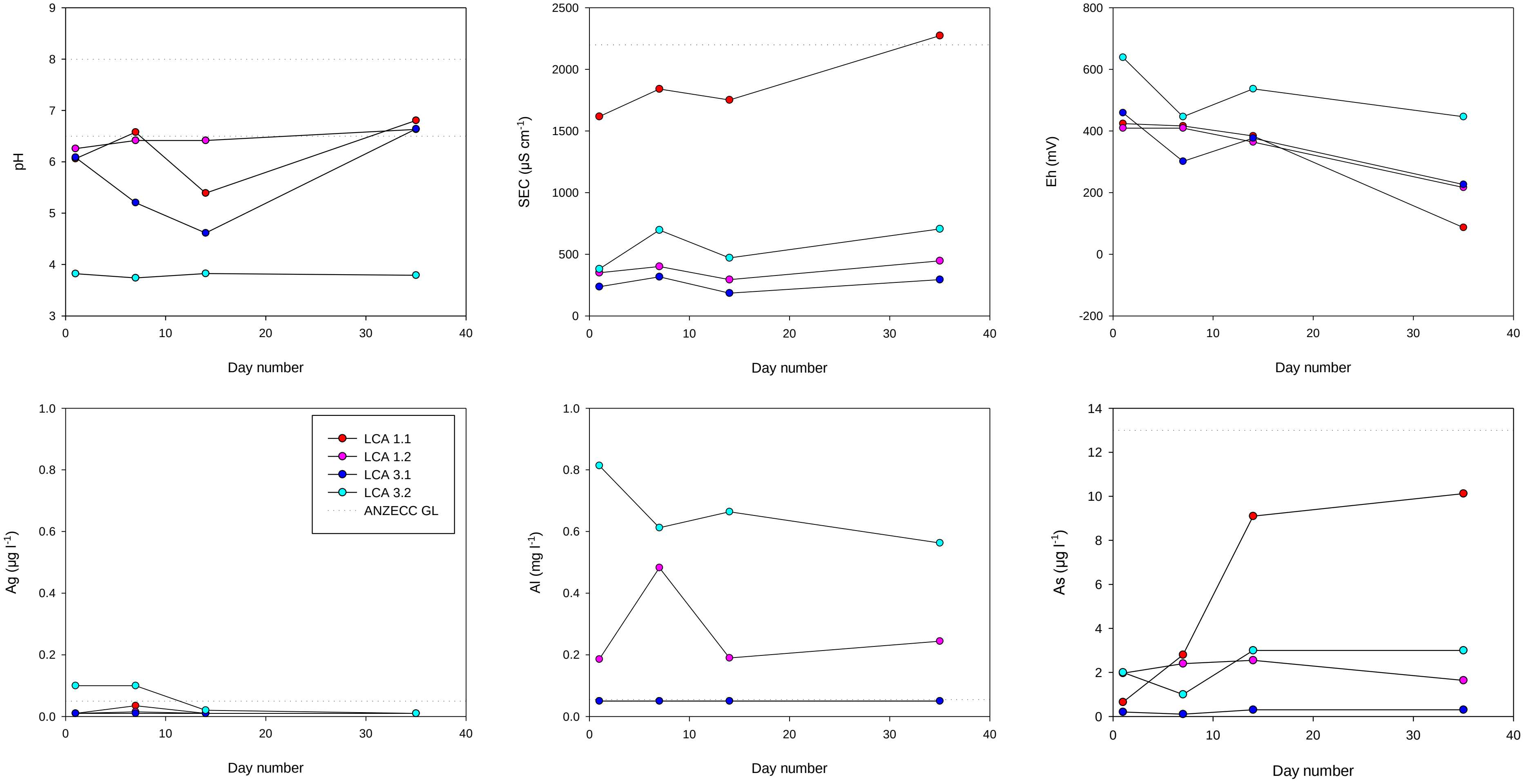

Figure 3-1 Contaminant and metalloid dynamics results for Lake Carlet soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al), and Arsenic (As).

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

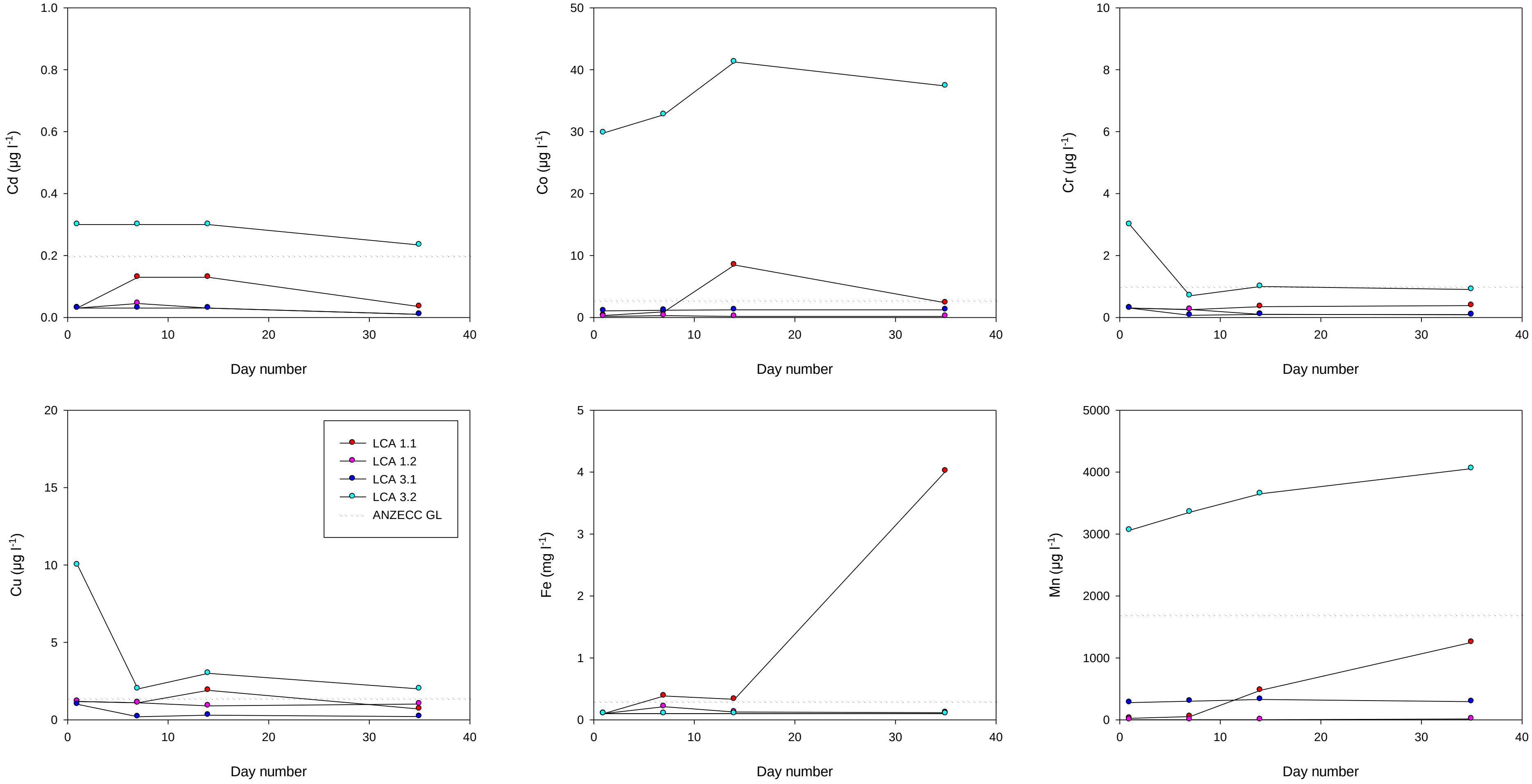

Figure 3-2 Contaminant and metalloid dynamics results for Lake Carlet soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

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

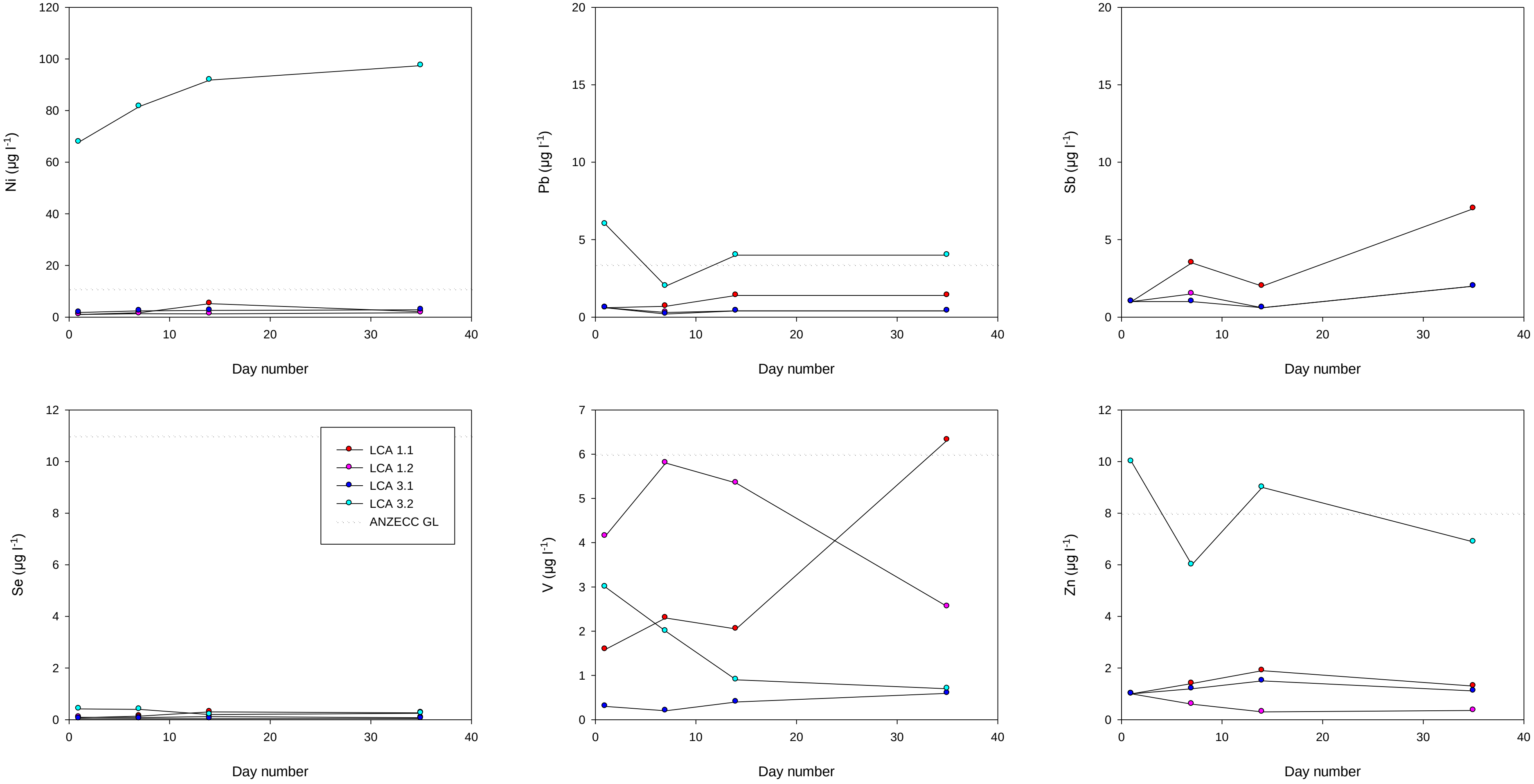

Figure 3-3 Contaminant and metalloid dynamics results for Lake Carlet soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

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

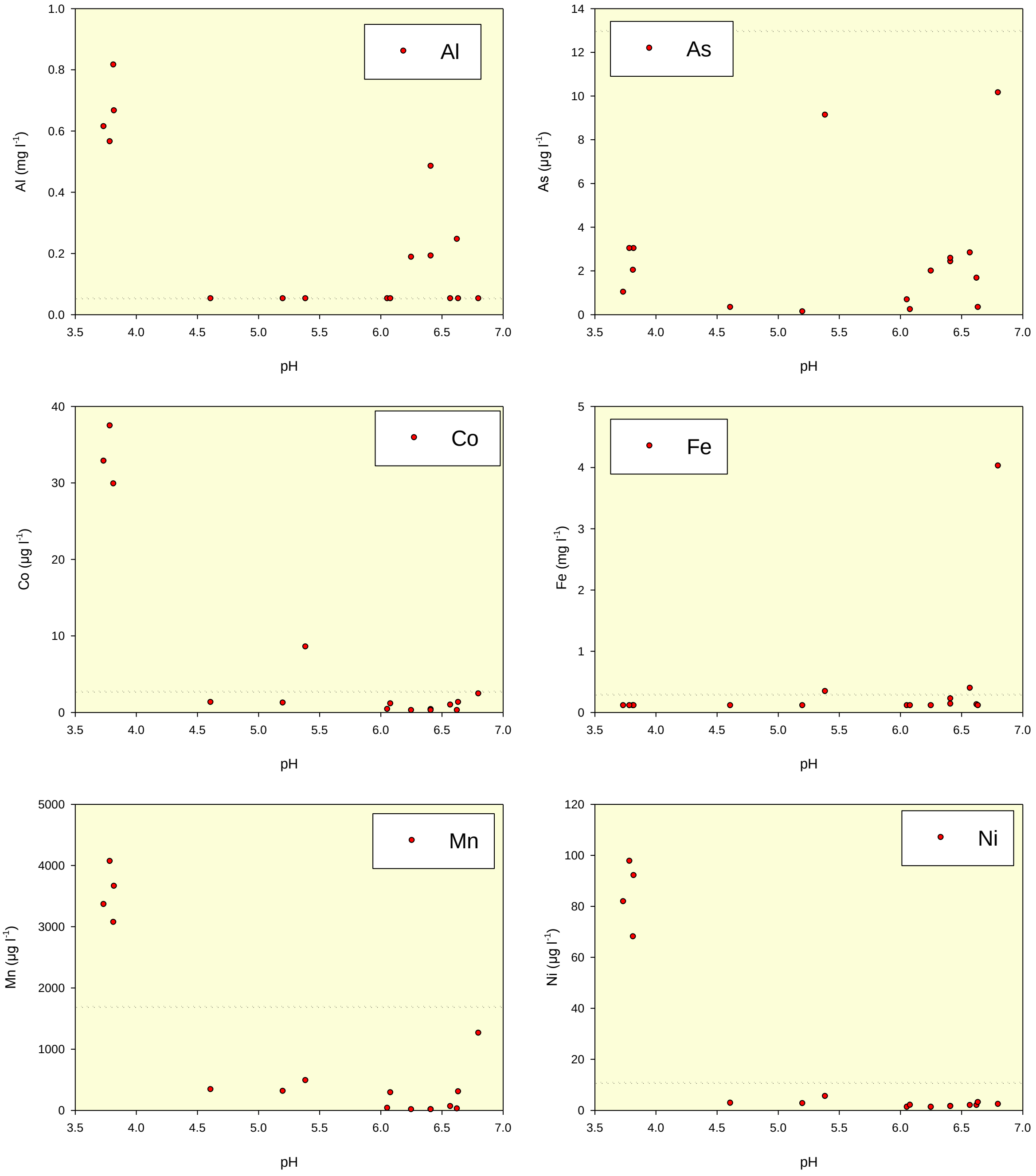

Figure 3-4 Selected trace elements plotted against pH.

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 guidelines and soil ecological investigation levels (Table 3-1). Concentrations of iron (Fe), manganese (Mn) and aluminium (Al), and to a lesser degree arsenic (As), nickel (Ni) 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 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. One sample was very acidic and remained so over the 35 day period. The others were slightly acidic, with two showing a dip in pH during day 14 experiments. All samples showed a significant decrease in Eh (Figure 3-1), but this was limited in the sulfuric sample LCA 3.2. Although Eh did decrease in most samples, iron concentrations remained low. However, the rapid increase in sample LCA 1.1 on day 35 was associated with a lower Eh, and therefore the slow release of iron (Fe) is most likely due to insufficiently low Eh for iron (Fe) to be soluble. The risks associated with metal and metalloid release from iron oxides/oxyhydroxides may be greater with longer time. However, high metal concentrations were not found along with the increase in iron (Fe), indicating limited mobility or availability. The metalloids arsenic (As) and vanadium (V) did increase and may pose further hazard. pH is likely to be the dominant control of metal mobilisation for the acidic soils in the wetland, and for metalloids in the neutral to alkaline soils associated with the reductive dissolution of iron oxides/oxyhydroxides.

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 environmental 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 silver (Ag), chromium (Cr), lead (Pb) and zinc (Zn) in some samples. It is therefore not possible to group these 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 moderately high net acidities noted by Fitzpatrick *et al*. (2008). Nevertheless, the contaminant and metalloid dynamics data suggest that most soils may take little time to recover in terms of acidity. The exceptions are the acidic sub-surface soil materials such as LCA 3.2, where sulfide oxidation has led to the development of sulfuric materials and a source of metals and metalloids. The higher pH in the surface soils will help minimise or ameliorate the upward flux of acidity and metals from these soils. Higher pH will limit the solubilities of most trace metals, although the concentrations in this study suggest that mobilisation will occur but be limited and of short duration. It is likely that the aluminium (Al) exists as colloidal material in some samples and hence may pose less of a risk than truly dissolved aluminium (Al^{3+}). The metalloid elements arsenic (As) and vanadium (V), which form oxyanions are likely to be controlled by the reductive dissolution of iron (Fe) oxides and may be a greater hazard once the Eh falls more in the soils. These may be a problem 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 Lake Carlet.

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

Note: Sb, Ag, Cr, Pb and Zn below detection limits in some samples due to dilutions, and therefore are likely to be classified as a 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.
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	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 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, degree and depth of soil cracking.

Lake Carlet 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 relatively low net acidities in the dried marginal soils of Lake Carlet suggest that the acidification hazard is relatively low. An increased risk is associated with soils towards the centre of the wetland beneath the surface 5 cm depth. These deeper soils evidently have the ability to form sulfuric materials. The higher pH in the surface layers of these soils suggest that there is some buffering capacity which may help ameliorate acid flux towards the surface, but the high net acidities suggest that large areas of the wetland are probe to soil acidification. The high net acidities and contaminant and metalloid dynamics results for the deeper layers suggest that if drying occurs, 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 moderate and probably localised in the wetland.

It is concluded that soil acidification would pose a serious problem in deeper soils over much of the wetland in the sub-surface soils as suggested by the measured low pH over the 35 days of the contaminant and metalloid dynamics tests. The wetland dried following sampling, and due to its location adjacent to the river and connectivity, 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 rapid if there are sufficient flows, as indicated for the surface soil layers in the contaminant and metalloid dynamics experiments. A **minor** 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 **medium** (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 an **insignificant** categorisation is given for consequence. 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 to 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 aluminium (Al), cobalt (Co) and iron (Fe) are the elements with the highest hazard. Although aluminium (Al) was high in the sulfuric soil, high concentrations were also observed in sample LCA 1.1 where pH was high. It is suggested that the aluminium (Al) may be in colloidal form in the latter, hence less toxic than Al^{3+} which is the dominant form at low pH. In addition, aluminium (Al) is likely to precipitate rapidly as pH increases and unlikely to be impacted by a return to reducing conditions since it is not redox-sensitive. Although the majority of samples showed a trend towards more reducing conditions, the change was probably not sufficient to cause mobilisation of metals through the reductive dissolution of iron oxides/oxyhydroxides. The risks are thought to be higher for metalloids, as in the one sample where iron dissolution was significant after 35 days (LCA 1.1; Figure 3-2), metal release was minor, but the release of vanadium (V) and arsenic (As) were significant. These metalloids are mobile at high pH and their increase over the 35 day period suggests that these pose a significant risk. 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.* 2011), 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 **minor** 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 **medium** (Table 4-4).

A rating for surface water impacts from metals and metalloids will depend on surface and sub-surface hydrology. The slightly acidic to circumneutral pH values in this study, however, means that longer term impacts are unlikely. 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 **insignificant** to **minor** consequence is applied. The risk to surface waters from metal mobilisation is therefore considered to be **low to medium** (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 (Fitzpatrick *et al.* 2008), including for soils that were still subaqueous at the time of sampling. Water soluble sulfate concentrations were not measured but are considered likely to be high. However, although there were no water soluble sulfate analyses completed on which to base a hazard categorisation, the monosulfide formation hazard is considered to be low given that monosulfides were not observed in the subaqueous soils of the wetland. As such, the consequence is therefore considered to be ***insignificant*** and as such the risk associated with deoxygenation is **low** (Table 4-4).

Table 4-4 Summary of risks associated with acid sulfate soil materials in Lake Carlet.

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

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 low to medium 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 pH's observed, the increase in pH over the 35 day period and limited metal mobilisation imply that any risks are likely to be localised in nature. The highest risks are likely to be associated with deeper drying and cracking where sulfide minerals may be present at higher concentrations.

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 quite rapid 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

Lake Carlet

Sample	Depth	Analysis	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
LCA 1.1	0-5	a	5.5	262	1.1	20	2.0	110	2.9	426	27	2.9	1.7	< 3.0	19	8.3	3.2
		b	5.2	278	1.0	22	2.0	97	2.7	390	27	2.9	1.7	< 3.0	22	8.5	3.5
LCA 1.2	5-15	a	1.7	90	1.4	9.0	1.5	60	1.5	394	29	1.5	0.73	< 1.9	11	3.9	1.3
		b	2.1	116	0.90	11	1.8	53	1.3	166	12	1.9	0.83	< 1.9	11	3.0	1.4
LCA 3.1	0-5	a	11	383	2.1	39	1.3	100	5.7	1293	79	5.7	2.9	< 3.6	32	10	5.0
		b	13	423	2.1	42	1.4	115	5.7	1303	100	6.4	2.9	< 3.6	34	11	5.0
LCA 3.2	5-15	a	12	613	2.5	33	2.3	89	4.3	1729	207	7.3	2.5	< 3.2	36	6.6	1.7
		b	12	609	2.6	33	2.4	102	4.0	1821	216	8.4	2.5	< 3.2	38	6.9	1.7

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

Lake Carlet

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
LCA 1.1	1	0-5	a	230	1760	6.43	<0.01	<0.05	0.62	0.03	0.31	<0.3	1.4	<0.1	23	<1	<0.6	<1	0.07	1.8	<1
			b	220	1473	5.69	<0.01	<0.05	0.68	0.03	0.33	<0.3	<1	<0.1	24	<1	<0.6	<1	0.09	1.4	<1
	7		a	220	1340	7.09	<0.02	<0.05	2.6	<0.06	0.18	<0.1	1.2	<0.1	4.8	1.4	<0.4	<2	<0.08	3.6	<0.8
			b	215	2342	6.06	<0.05	<0.05	3.0	<0.2	1.6	<0.4	<1	0.67	101	2.0	<1	<5	<0.2	1.0	<2
	14		a	195	1702	3.60	<0.01	<0.05	10	<0.06	6.4	<0.2	1.8	0.19	348	4.7	<0.8	<1	0.20	2.6	1.8
			b	175	1800	7.18	<0.01	<0.05	8.0	<0.2	11	<0.5	<2	0.48	602	5.7	<2	<3	0.40	1.5	<2
	35		a	-110	2323	6.96	<0.01	<0.05	11	<0.02	2.3	0.27	<0.4	4.0	1237	2.2	<0.8	<4	0.22	6.1	<0.6
			b	-115	2224	6.65	<0.01	<0.05	9.4	<0.05	2.4	<0.5	<1	4.0	1263	2.0	<2	<10	0.31	6.6	<2
LCA 1.2	1	5-15	a	210	331	6.61	<0.01	0.19	2.3	<0.03	0.12	<0.3	1.4	<0.1	0.89	<1	<0.6	<1	0.09	3.0	<1
			b	210	368	5.90	<0.01	0.18	1.7	<0.03	0.21	<0.3	<1	<0.1	<0.6	<1	<0.6	<1	0.10	5.3	<1
	7		a	200	394	6.42	<0.02	0.59	2.2	<0.06	0.32	0.30	1.2	0.27	0.80	1.4	<0.4	<2	<0.08	6.0	<0.8
			b	220	407	6.41	<0.01	0.37	2.6	<0.03	0.25	0.21	1.0	0.16	0.70	1.3	<0.2	<1	0.08	5.6	<0.4
	14		a	170	285	6.33	<0.01	0.06	2.1	<0.03	0.17	<0.1	0.90	<0.1	0.56	1.2	<0.4	<0.6	0.10	3.9	<0.3
			b	160	303	6.50	<0.01	0.32	3.0	<0.03	0.16	<0.1	0.90	0.15	0.32	1.3	<0.4	<0.6	0.14	6.8	0.30
	35		a	20	435	6.58	<0.01	0.26	1.6	<0.01	0.18	<0.09	1.0	0.13	13	1.7	<0.4	<2	0.08	2.4	0.42
			b	15	457	6.68	<0.01	0.22	1.7	<0.01	0.16	<0.09	1.0	0.10	14	1.6	<0.4	<2	0.07	2.7	<0.3
LCA 3.1	1	0-5	a	230	221	5.51	<0.01	<0.05	<0.2	<0.03	0.90	<0.3	<1	<0.1	232	1.3	<0.6	<1	0.04	<0.3	<1
			b	290	253	6.66	<0.01	<0.05	<0.2	<0.03	1.2	<0.3	<1	<0.1	326	2.3	<0.6	<1	0.04	<0.3	<1
	7		a	100	319	5.19	<0.01	<0.05	0.10	<0.03	1.1	<0.07	<0.2	<0.1	303	2.6	<0.2	<1	<0.04	<0.2	1.2
			b	105	315	5.22	<0.01	<0.05	0.10	<0.03	1.2	<0.07	<0.2	<0.1	300	2.2	<0.2	<1	<0.04	<0.2	1.2
	14		a	175	181	5.50	<0.01	<0.05	<0.3	<0.03	1.2	<0.1	<0.3	<0.1	330	2.5	<0.4	<0.6	0.04	0.40	1.5
			b	180	189	3.73	<0.01	<0.05	<0.3	<0.03	1.3	<0.1	<0.3	<0.1	328	2.7	<0.4	<0.6	0.04	0.40	1.5
	35		a	25	297	5.69	<0.01	<0.05	<0.3	<0.01	1.3	<0.09	0.21	<0.1	304	2.3	<0.4	<2	0.05	0.71	1.2
			b	30	292	7.59	<0.01	<0.05	<0.3	<0.01	1.1	<0.09	<0.2	<0.1	285	3.4	<0.4	<2	0.04	0.48	1.1
LCA 3.2	1	5-15	a	430	362	3.82	<0.1	0.59	<2	<0.3	29	<3	<10	<0.1	2947	66	<6	<10	0.54	<3	<10
			b	450	399	3.82	<0.1	1.0	<2	<0.3	31	<3	<10	<0.1	3174	70	<6	<10	0.29	<3	<10
	7		a	225	702	3.72	<0.1	0.61	<1	0.30	33	<0.7	<2	<0.1	3379	82	<2	<10	<0.4	<2	8.0
			b	270	691	3.76	<0.1	0.62	<1	<0.3	33	<0.7	<2	<0.1	3327	81	<2	<10	<0.4	<2	4.0
	14		a	325	403	3.83	<0.02	0.55	<3	0.30	32	<1	<3	<0.1	3210	83	<4	<6	<0.2	<0.9	9.0
			b	350	539	3.82	<0.02	0.78	<3	0.30	51	<1	<3	<0.1	4090	101	<4	<6	<0.2	<0.9	9.0
	35		a	235	724	3.73	<0.01	0.60	<3	0.35	38	<0.9	<2	<0.1	4204	100	<4	<20	0.30	<0.7	7.6
			b	260	687	3.85	<0.01	0.53	<3	0.11	36	<0.9	<2	<0.1	3911	95	<4	<20	0.19	<0.7	6.2

< value is below detection limit

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