

Environment Protection Authority

Lower Lakes Benthic Ecosystem Toxicity Assessment (BETA) Pilot Study

**Draft report for the Department of
Environment, Water and Natural Resources**

Benthic Ecosystem Toxicity Assessment (BETA) Pilot Study

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Executive summary

The recent drought in the Lower Lakes lead to severe acidification of the sediments. These sediments were still considered to pose a hazard to the biota of the region in 2011, despite reflooding, with low pH levels and elevated metal pore water concentrations being detected. This study aimed to investigate the pore water chemistry in the lower Finniss River and Currency Creek and determine if any negative effects on sediment biota could be attributed to the sediment condition. This was done by:

1. testing the pore water chemistry through the deployment of multi-chambered dialysis samplers (peepers),
2. assessing the rate of deformities in chironomids (non-biting midges),
3. investigating the diversity and abundance of organisms living in the sediment profile, and
4. investigating the potential for dissolution of mussel shells in the sediment.

The field work was undertaken between the 7th May and the 21st May 2012 at three locations. One site in the lower section of each of the Finniss River and Currency Creek were chosen as 'impacted' sites, sites known to be effected by acid sulfate soils through a previous study (Fitzpatrick et al. 2011), and one site on the Finniss River (upstream of the causeway on Winery Rd) was chosen as a reference site.

The key findings from this study were:

- The sediment profiles of Finniss River, south and Currency Creek had pH decreasing to less than the ANZECC/ARMCANZ trigger value (TV) of 6.5 below depths of 8 cm
- The total ammonia-N concentrations were above the pH adjusted toxicant TV of 0.9 mg/L in the sediment below a depth of 4 cm at Finniss River, south and Currency Creek and above the pH adjusted stressor TVs in all sediment profiles, and in Currency Creek surface water
- Concentrations of other toxicants, such as metals and metalloids were below TVs suitable for the protection of 95% of species, except at depths below 15 cm in the Currency Creek sediment profile, where boron (TV = 0.37 mg/L), chromium (TV = 1.0 µg/L) and manganese (TV = 1.9 mg/L) were elevated
- Deformity rates in chironomids were low at all sites, although the deformities of more major structures seen in the chironomids collected from Currency Creek in comparison with the reference site (Finniss River, north) may suggest sub-lethal impacts to biota at this site
- A good diversity of taxa was found in the top 2 cm of sediment at all sites sampled, with diversity remaining high at the two sites in the Finniss River further down the profile, but declining considerably at Currency Creek. Very little biota was found below 5 cm at any of the sites.
- The Currency Creek site showed more evidence of impacts than the 'impacted' Finniss River site. This could be a legacy of the degree to which this site was affected during the drought
- The greatest reductions in mussel shell weight were recorded 6 cm below the sediment surface and corresponded with a decrease in pH in the pore water. However, as only one trial was conducted, these results should be treated with caution.

The sediment cores collected in this study showed that most organisms living in the sediment will be found in the top 5 cm with only a few individuals found deeper. However, low pH levels and high ammonia concentrations were seen at deeper levels in the sediment profile. Although the pore water chemistry

suggested generally low concentrations of toxicants at all sites, bioaccumulation or bioconcentration of substances may still be occurring in the biota.

Recommendations

The following investigations are recommended to help determine if acid sulfate soils continue to pose a hazard to the benthic biota in the region:

- sediment toxicity tests be conducted,
- further investigations into the deformity rates seen in chironomids in the Lower Lakes region should occur, and
- metal concentrations within the chironomids themselves should be tested to gain an understanding of any potential bioaccumulation issues in this common group of benthic invertebrates.

1 Introduction

During the recent drought in the Murray-Darling Basin water flow to the Lower Lakes was reduced to unprecedented low levels (as low as – 1 m AHD). This resulted in significant drying of the lakes, exposure of pyrite-containing sediments (acid sulfate soils), oxidation and severe acidification (Fitzpatrick *et al.* 2008). Sediment in the Lower Lakes region which was exposed in the drought in 2008 but has since been re-inundated has been found to still pose a hazard to the biota in the Coorong, Lower Lakes and Murray Mouth (CLLMM) region due to acidification still persisting in the sediments (Fitzpatrick *et al.* 2011). Fitzpatrick *et al.* (2011) also found the pore water of 75% of sites had a pH <7 and 21% had a pH <4, with only the top 5 cm or less of the sediment profile being neutralised to a pH >4. They also found ANZECC/ARMCANZ (2000) trigger values for many metals in the pore water were exceeded, including aluminium, arsenic, boron, cadmium, chromium, copper, manganese, nickel, lead and zinc and that concentrations of most of these metals were exceeded at all sites. Hicks *et al.* (2009) studied metal concentrations in the sediment using peepers (a method to obtain the profile of bioavailable metals in the sediment) and made similar conclusions.

A recent DENR-convened Acid Sulfate Soils and Ecological Risk workshop (December 2011) was held to determine the future directions of research into the recovery of the Lower Lakes following their refilling in 2009-2010 after the drought. The report from this workshop concluded that *“as there is still acidic sediment and pore water present under the Lower Lakes there is potential for the recovery of the ecosystem, in particular the benthic organisms, to be hindered”* (Cugley 2011). Monitoring of the macroinvertebrate community in the surface sediment of the region has found that while improvements in health occurred as water levels returned to normal, molluscs and some crustaceans that were present pre-drought were still missing (Giglio 2011). It may be that these taxa are slower to recolonise than others but it is also possible that these taxa are potentially affected by ongoing acidity and elevated metal concentrations due to their calcium carbonate exoskeletons and shells making them very susceptible to acidification effects (Cubillas *et al.* 2005). During previous acidification events in the Lower Lakes mussel shell dissolution was observed. Research in other regions of Australia has shown that acid and metals from oxidised acid sulfate soils can lead to severe ecological damage (Sammot *et al.* 1995).

This study was conducted to explore the sub-lethal impacts on sediment dwelling invertebrates, particularly chironomids. Chironomids, along with worms, make up the major part of sediment-dwelling fauna and are therefore useful for sediment quality assessments. They are commonly used as test organisms in sediment toxicity tests and are useful bioindicators of contaminated sediment. Many studies have assessed deformities in the mouthparts (mentum, ligula, mandibles or maxillary palps) or antennae in chironomids as an indication of toxic effects resulting from polluted sediment, including metal contamination (e.g. Groenendijk *et al.* 1998, Janssens de Bisthoven *et al.* 1998, Martinez *et al.* 2001, Martinez *et al.* 2002, Swansburg *et al.* 2002, Bervoets *et al.* 2004) and acidity (e.g. Janssens de Bisthoven *et al.* 2004, Janssens de Bisthoven *et al.* 2005). Deformities in chironomids are known to occur naturally at a low rate, however, in contaminated sediment (polluted by metals, pesticides, or acid drainage) the rate of deformities can often be much higher. This investigation is also being paired with a study into the pore water chemistry, particularly focussing on acidity and metal concentrations. Sites found in previous studies that have been impacted by acid sulfate soils were used as monitoring sites in this investigation.

The aims of this study were to investigate the pore water chemistry at particular locations within the lower Currency Creek and Finniss River region and determine if any negative effects on sediment biota could be attributed to the sediment condition. This comprised of four main research areas:

- **Pore water toxicity assessment** - Determining the variability of pH, alkalinity and acidity in the pore water to a depth of 31 cm and major, minor and trace element concentrations to a depth of

15 cm at three locations in the lower Finniss River and Currency Creek region with comparisons made against the ANZECC/ARMCANZ (2000) trigger values.

- **Chironomid deformities** - Assessing the rate of deformities occurring in the mouthparts and antennae of chironomids found at these three locations
- **Screening of benthic community composition** - Determining the diversity and abundance of macroinvertebrates living in the sediment profile to a depth of 10 cm at the three locations
- **Mussel shell dissolution** - Determining the potential for dissolution of mussel shells in the acidic layers of the sediment.

2 Methods

Site selection

Three sites were selected for this study; two found to be impacted by low pH values in previous studies (Fitzpatrick *et al.* 2011) and one reference site. The sites chosen included one “impacted” site in each of the Finnis River and Currency Creek and a “reference” site in the Finnis River (Figure 1). The reference site was chosen in a previously untested location, however, it was presumed that the presence of acid sulfate soils at that location was unlikely and it would therefore be a suitable reference site for this study.

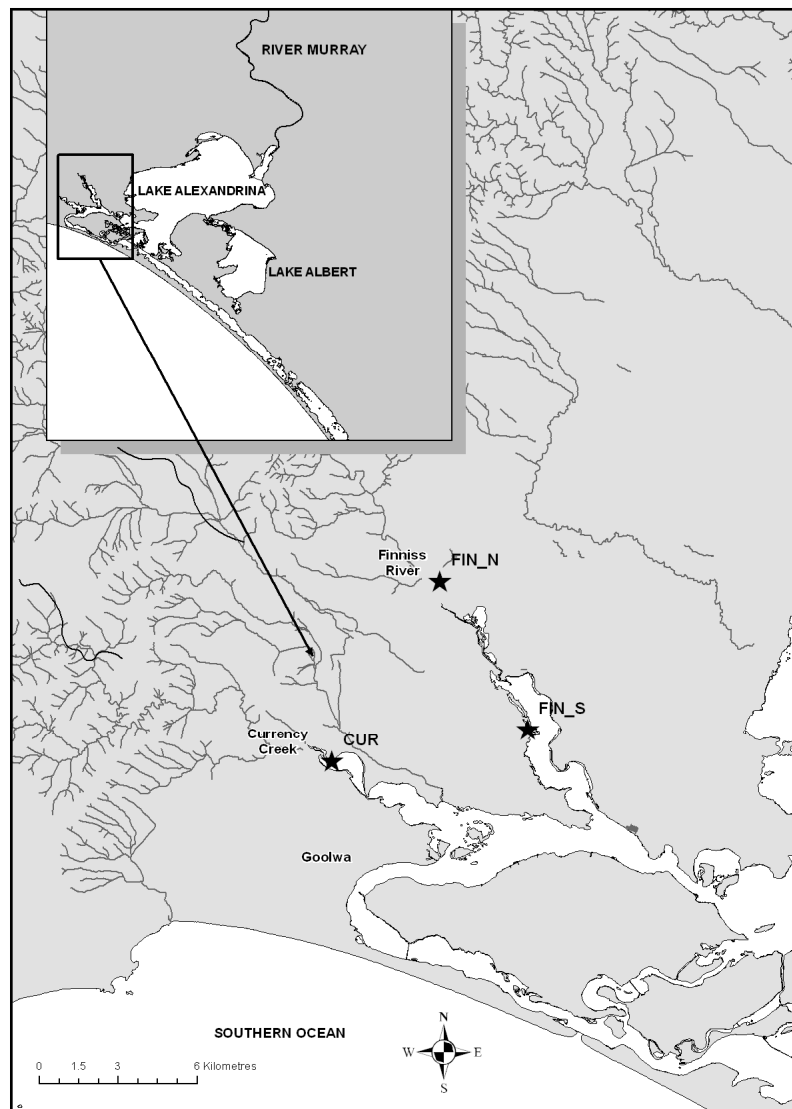


Figure 1 Map showing the locations of sites selected for this study. Site considered impacted by acid sulfate soils were CUR (Currency Creek) and FIN_S (Finniss River, south). FIN_N = Finniss River, north, the reference site.

Water sampling and sediment profiles

Sub-surface grab samples of water were collected at each site in clean acid washed bottles which were rinsed three times with the sample before the bottles were filled. The bottles were inverted until the mouth was approximately 5 cm below the surface and then allowed to fill. Samples were stored in cool insulated boxes for transport to the laboratory where they were filtered through a 0.45 µm membrane filter (Sartorius) and divided into acidified and unacidified sub-samples. Samples were stored at 4 °C until analysed.

Pore water at each site was collected using a dialysis chamber sampler (or peeper Teasdale *et al.*, 1995). These peepers are constructed of polymethylmethacrylate with a 0.45 µm polysulfone dialysis membrane (Pall Scientific) as the chamber window. Assembled peepers were placed in acid washed plasticiser free polyvinylchloride (uPVC) transport cylinders filled with Type 1 reagent grade water (APHA, 1995). The cylinders were flushed with nitrogen for 72 hours prior to being installed in the field. The nitrogen flushing continued while the peepers were sealed for transport, creating a nitrogen head space in the cylinder. The peepers were deployed on the 7th May 2012 and retrieved on the 21st May 2012. A 14-day deployment accounts for the possibility of sandy sediments with saline pore water where salinity gradients between the peeper filling solution and the pore water can result in vertical mixing along the peeper face, increasing the equilibration time (Grigg *et al.* 1999). Three peepers were deployed at each site providing samples representative of the sediment water interface, and pore water at 1 cm intervals to a depth of around 32 cm. The peepers were installed in open water to avoid interference with the root structures of the reeds growing along the edge of the water.

Following retrieval, the peepers were cleaned of biological growth and adhering sediment and rinsed with deionised water. The chambers were pierced and the filling solution transferred to acid washed vials. For each depth, the three peeper samples were combined to give a composite sample. This provided a spatially averaged composite sample and increased the volume available for analysis. Below -7 cm, two depth intervals were combined which provided a pore water sample set giving 1 cm resolution to -7 cm and 2 cm resolution to -32 cm. Samples were stored in cool insulated boxes for transport to the laboratory where they were split into sub-samples. All samples were analysed for electrical conductivity (EC), pH and alkalinity but only pore water to a depth of 17 cm was submitted for comprehensive analysis. Where samples were undergoing comprehensive analysis, one sub-sample was acidified with 50 µL of analytical reagent grade hydrochloric acid for major, minor and trace element analysis. Unacidified sub-samples were analysed for EC, pH, alkalinity, chloride and nutrients. Three additional peepers were prepared and transported to the field to be used as field blanks. These were opened and samples prepared in an identical manner to the peepers deployed in the sub-aqueous soil. The results are provided in Table 15 and Table 16. The detection limit for the procedure was calculated as 3 x standard deviation of the blank, however where the procedure detection limit was greater than the instrumental detection limit the procedure detection limit has been used.



Figure 2 Some of the peepers after retrieval.



Figure 3 A peeper following retrieval, ready to be rinsed and the filling solution in the chambers extracted.



Figure 4 Extracting the pore water from the chambers of the peeper.

EC was measured with a TPS WP-81 meter fitted with a K-1.0 conductivity cell. Alkalinity and pH were determined using an Orion 960 autotitrator fitted with an Orion micro pH electrode according to APHA standard methods 2320 and 2510 respectively (APHA, 1995). Nutrients (reactive phosphorus, nitrate + nitrite and ammonia-N) and chloride were determined by automated flow colorimetric analysis according to USEPA methods (USEPA 1997). Major and minor elements including sulphur were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Trace elements plus bromine were determined by inductively coupled plasma-mass spectrometry (ICP-MS). All samples were filtered and acidified prior to analysis.

The flux at the sediment-water interface was estimated using the flux equation (Appendix 1).

Sediment chemistry results from this study were assessed as slightly to moderately disturbed ecosystems and values for the protection of 95% of species applied as recommended by ANZECC/ARMCANZ (2000) (Table 1). It should be noted though that this level of protection still may not protect key or indicator species. Where no or only low reliability values were available data has not been discussed in terms of water quality. Hardness corrections for extremely hard water (400 mg CaCO_3/L) were applied to metals whose toxicity is known to be influenced by hardness, and for which hardness algorithms are available (i.e. Cd, Cu, Ni, Pb and Zn). The hardness algorithms were derived using effects data for fish using toxicity data spanning a water hardness from 25-400 mg CaCO_3/L (ANZECC/ARMCANZ 2000). Their applicability at higher hardness is unknown. The toxicity of other metals, such as manganese, is known to be reduced as water hardness increases, however, no algorithms were available for hardness corrections. For freshwater physical and chemical stressors ANZECC/ARMCANZ (2000) water quality trigger values for south-central Australian lakes have been applied for pH, total ammonia- N, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ (Table 2).

Table 1 Trigger values for toxicants applied to data (ANZECC/ARMCANZ 2000; 95% of species, very hard water). ID means that no or only low reliability data is available and no guideline value has been recommended.

Toxicant	Guideline value (µg/L) (freshwater)
	95% of species
Ammonia ^a	900 ^b
Nitrite ^d	700
Ag	0.05
Al pH>6.5, pH<6.5	55, ID
As (III), (V)	24, 13
B	370
Cd ^c	2.0
Co	ID
Cr (III), (VI)	ID, 1.0
Cu ^c	12.7
Fe	ID
Mn	1900
Ni ^c	99.4
Pb ^c	91.2
Se (Total), (IV) ^b	11, ID
V	ID
Zn ^c	72.3

^a = WQ values quoted for pH 8 must be adjusted for the pH of the water being assessed. Ammonia as TOTAL ammonia as [NH₃-N] at pH 8. ^b = this value increases as pH decreases, ammonia was therefore assessed at each depth according to the pH recorded at that depth. ^c = hardness-dependent algorithms have been used to modify trigger values (assuming a hardness of 400 mg CaCO₃/L). ^d = value is relevant for protection against toxicity but does not relate to eutrophication issues.

Table 2 Trigger values (ANZECC/ARMCANZ 2000) for physical and chemical stressors for south-central Australian lakes.

Parameter	Guideline value (mg/L)
pH	6.5-9.0
Total ammonia-N ^a	0.025 ^a
NO _x -N	0.1
PO ₄ -P	0.01

^a This value is for NH₄⁺, values for total ammonia-N at the sample pH values have been calculated using the formulae in ANZECC/ARMCANZ (2000) Section 8.3.7.2.

Chironomid deformities

Sweep net samples were collected on the 7th and 8th of May 2012 from each site using a 30 cm sided triangular dip net with a mesh size of 250 µm. Samples collected in the net were deposited on a white tray in the field and live chironomids were picked out of the sample and placed in a small plastic container and preserved in 75% ethanol. Samples were searched for 2-3 hours at each site. A minimum of 50 individuals from the tribe Chironomini were aimed for, although other late instar chironomid larvae were also collected.

Fewer individuals were collected from the Finnis River, south site with only 17 individuals collected despite searching for three hours. In the laboratory, the head of each individual chironomid was removed and mounted on a slide using Hoyer's medium to help clear the head capsule and enable better examination. Only 3rd and 4th instar larvae were examined. Each individual was identified to genus level and examined for mouthpart and antennal deformities using a compound microscope.

Sediment core samples

Two core samples were collected from each of the "impacted" sites on 7th May 2012, one near the peeper and one closer to the bank near reed beds. As the peepers at each of the two "impacted" sites were deployed in open water but the chironomids were collected near the reed beds it was deemed suitable to collect sediment cores at both these locations to determine any differences due to a change in water depth or habitat. Due to the homogenous habitat present at the "reference" site, only one sediment core sample was collected from this location. The core samples were collected with a spade and divided into three sections; the top 2 cm, 2-5 cm and 5-10 cm. Each section was placed in a plastic screw-topped storage container and preserved with 75% ethanol in the field. Only the top 2 cm could be collected from the Finnis River, south site near the reeds as the root zone was impenetrable and made collecting a deeper core sample impossible. In the laboratory, each section was washed with water through a 250 µm sieve. The contents of the sieve was then examined under a dissecting microscope. All taxa found were identified to the lowest taxonomic level practicable using available identification guides.

Mussel dissolution trial

An approach was trialled to assess the potential risk that the shells of freshwater mussels (*Velesunio ambiguous*) (and other molluscs) dissolve in the acidified sediment of the Lower Lakes region. Mussel shell pieces of known weight were placed into compartments in a peeper at varying depth in the sediment profile from 3 cm above the sediment surface to a depth of -21 cm. This peeper was deployed at Finnis River, south (impacted site) on 7th May 2012 and collected two weeks later on 21st May 2012. The mussel pieces were washed in distilled water and reweighed to determine the change of mass. A loss of mass indicated potential dissolution due to acid effects.

3 Results and discussion

Surface water samples and sediment profile

pH

The pH values for surface water ranged between 7.24 and 7.36. These measurements were lower than those measured just downstream as part of an on-going EPA monitoring program in the region (EPA unpublished data), where pH 7.8 was recorded on the 17th May 2012. The sediment pH of Finniss River, north (the reference site) was found to remain neutral to a depth of 27 cm. In contrast, sediment pH at the other two locations decreased from a depth of 6 cm. At Finniss River, south the pH decreased from 7.56 (at -6 cm) to 5.06 at a depth of 27 cm. In Currency Creek the pH decreased from 7.13 (at -6 cm) to the lowest reading of 5.71 (at -10 cm) and then increased slightly to 6.63 (at -27 cm) (Figure 5).

In December 2009, pH values recorded below a depth of 10 cm at Finniss River, south and Currency Creek were around 3 (Fitzpatrick *et al.* 2011), in comparison with between 5 and 6 measured in May 2012. While some improvement was seen, these values are still below the pH trigger value of 6.5 (TVs, ANZECC/ARMACANZ 2000). At Finniss River, south and Currency Creek, the pH of the pore water decreases to below the TV at around a depth of 8 cm. The pH values recorded at the reference site were within the TV (6.5 to 9.0) throughout the profile (Figure 5). It should also be noted that the 2009 sites were in a slightly different location than the current study sites (which are closer to the shoreline) so these comparisons need to be treated with caution.

Electrical conductivity

The EC of the surface water samples ranged between 1.08 and 2.53 mS/cm, which was higher than the measurement recorded just downstream on the 17th May 2012 through an on-going EPA monitoring program in the region (EPA unpublished data) when an EC of 0.852 mS/cm was measured. The EC results varied little at the reference site, with surface water measurements of 2.53 mS/cm and 2.47 mS/cm measured at a depth of 27 cm. Only slight variations in EC occurred through the profile. However, the two other sites showed increases in EC down the sediment profile (Figure 5). At Finniss River, south, surface water EC was measured at 1.17 mS/cm with an increase beginning at a depth of 7 cm and reaching 2.23 mS/cm by a depth of 27 cm. At Currency Creek the increase was more striking with surface EC measured at 1.05 mS/cm and increasing in a sigmoidal shape up to 12.4 mS/cm at a depth of 27 cm, with the greatest increases occurring between a depth of 6 cm and 13 cm.

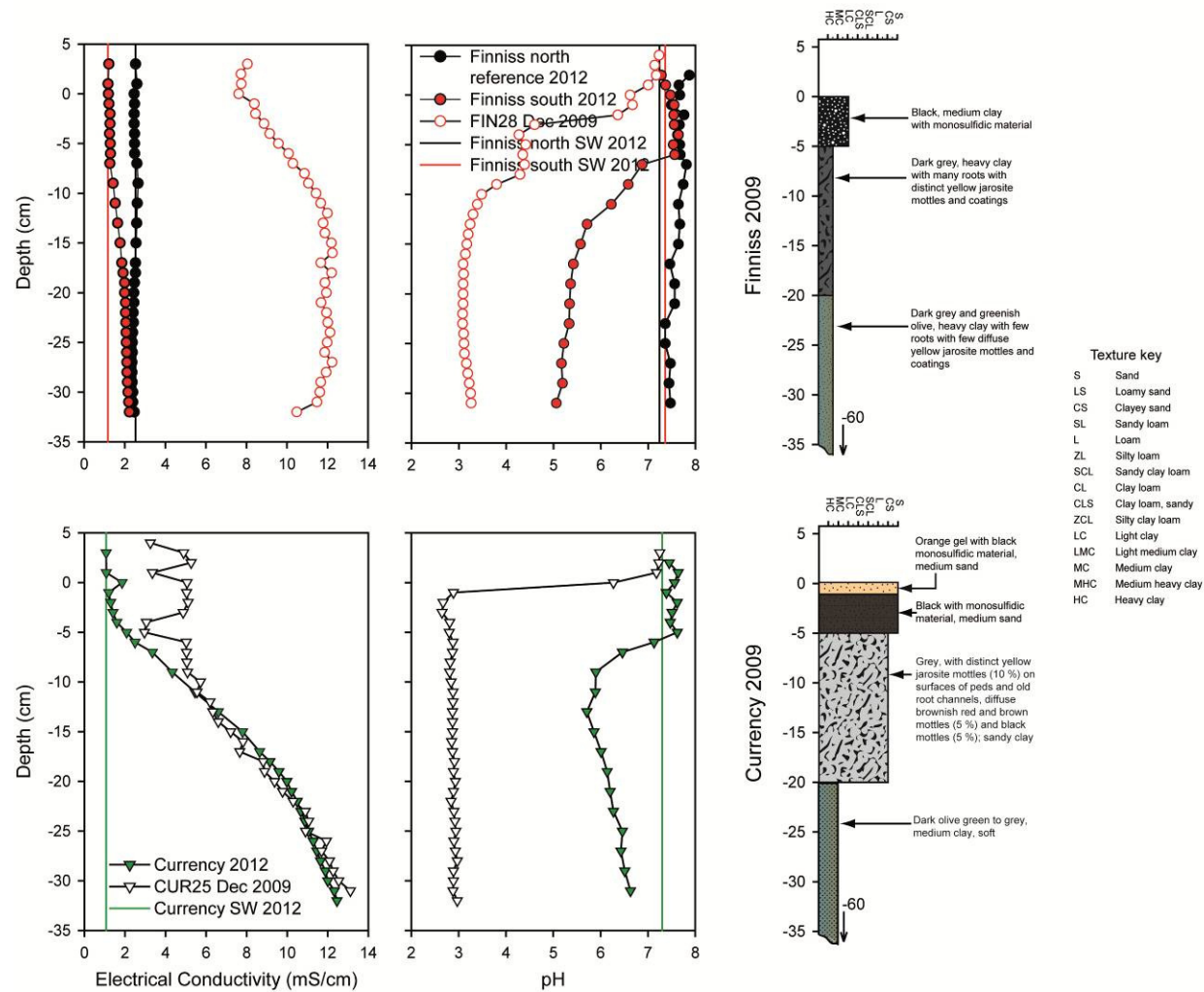


Figure 5 EC and pH profiles for the current (May 2012) and immediate post re-flooding (December 2009) peeper deployments as well as the December 2009 soil profile descriptions. Surface water (SW) values are shown as vertical lines.

Alkalinity and acidity

Alkalinity was measured to a depth of 31 cm and acidity to a depth of 15 cm below the sediment surface. In December 2009 alkalinity measurements recorded from Finniss River, south and Currency Creek were zero 1-2 cm below the surface (Fitzpatrick *et al.* 2011). In this study alkalinity was higher than those measured in 2009 but were still low throughout the profile at Finniss River, south and only beginning to slightly increase at Currency Creek 20 cm below the sediment surface (Figure 6). While alkalinities at these two sites are greater than zero (i.e. pH >4.5), acidities increase once the pH falls below 6.5 primarily due to an increase in the dissolved iron concentrations (Figure 6) and there is insufficient alkalinity to neutralise the acidity. At the reference site, (Finniss River, north) alkalinity increases with depth from around 2 mmol/L (the value of the surface water) to 4-5 mmol/L below 15 cm. While pH values below a depth of 10 cm at Finniss River, south and Currency Creek have increased by around 2 pH units since December 2009, alkalinity is still low at <0.2 mmol/L and acidity is much greater being between 2 and 5 mmol/L.

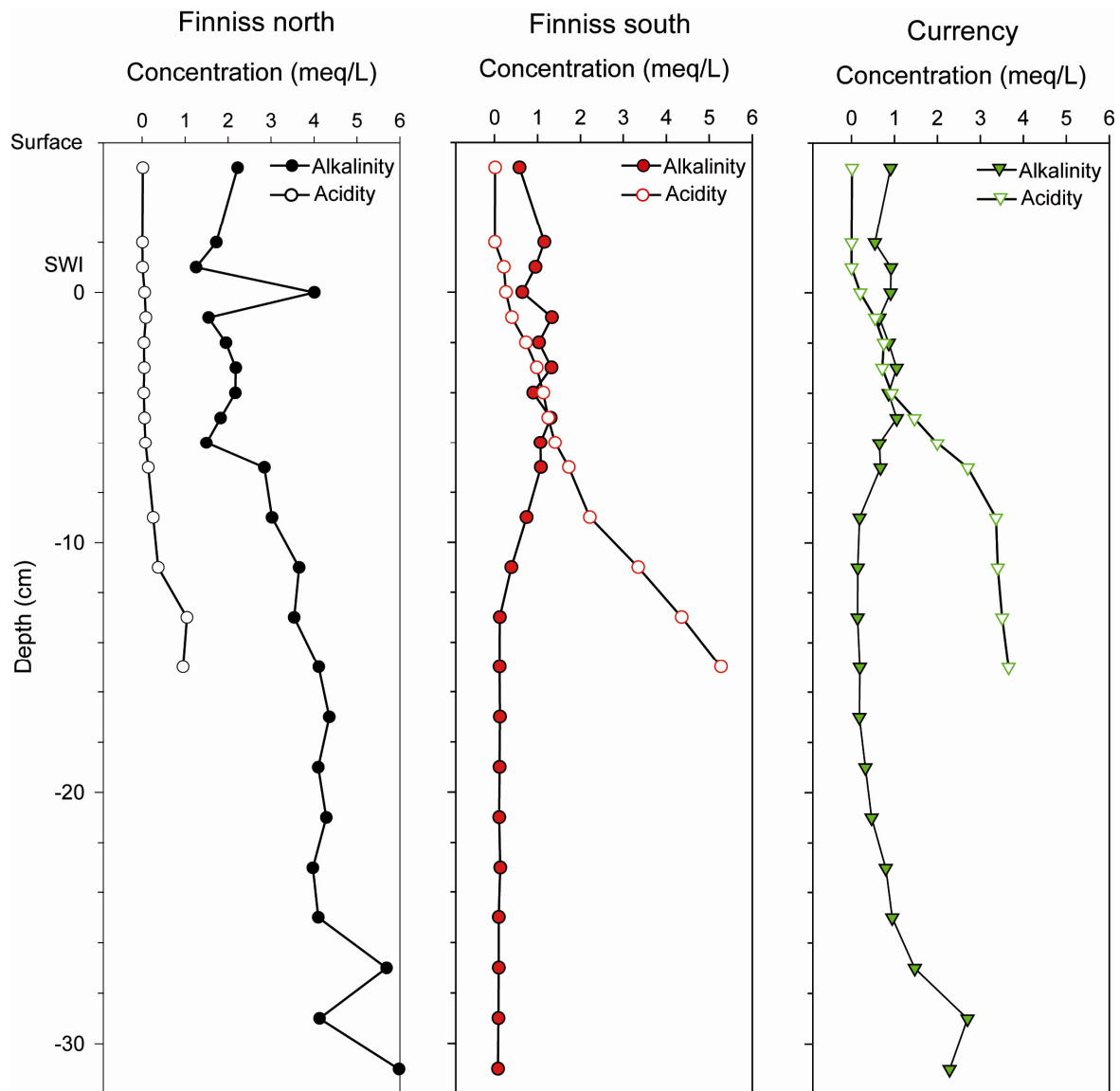


Figure 6 Pore water profiles for alkalinity (filled symbols) and acidity (the sum of acidic cations; open symbols). Depth from sediment-water interface to surface not to scale.

Redox sensitive species

Iron concentrations in the pore water at the reference site was low throughout the profile with concentrations of 0.37 mg/L in the surface water, 0.079 to 0.169 mg/L in the sediment-water interface and around 1-2 mg/L in the top 6 cm of the pore water profile, rising to values of 27 and 25 mg/L at 13 and 15 cm below the soil surface. However, at Finnis River, south iron concentrations increased from 5.7 mg/L at the sediment-water interface to 150 mg/L at a depth of 15 cm (Figure 7 and Table 14). At Currency Creek, concentrations increased from 5.4 mg/L at the sediment surface to 93 mg/L at a depth of 10 cm with concentrations remaining around 90-100 mg/L to the limit of sampling at a depth of 15 cm. Aluminium concentrations were at or below the TV of 55 µg/L at all sites except at the surface-water interface at Finnis River, south. Manganese concentrations were below the TV of 1900 µg/L at all sites except at a depth of 15 cm at Currency Creek (Table 4).

Sulfate concentrations at Finnis River, south and Currency Creek were elevated compared with the reference site at Finnis River, north and Cl:SO₄ ratios are lower than the seawater ratio (Figure 8). This indicates that the elevated sulphate concentrations are not due to 'salt' from a saline groundwater source but from sulfide oxidation and are the remaining signature of the oxidation of sulfidic material during the period of low lake water levels. Detailed results are provided in Table 12.

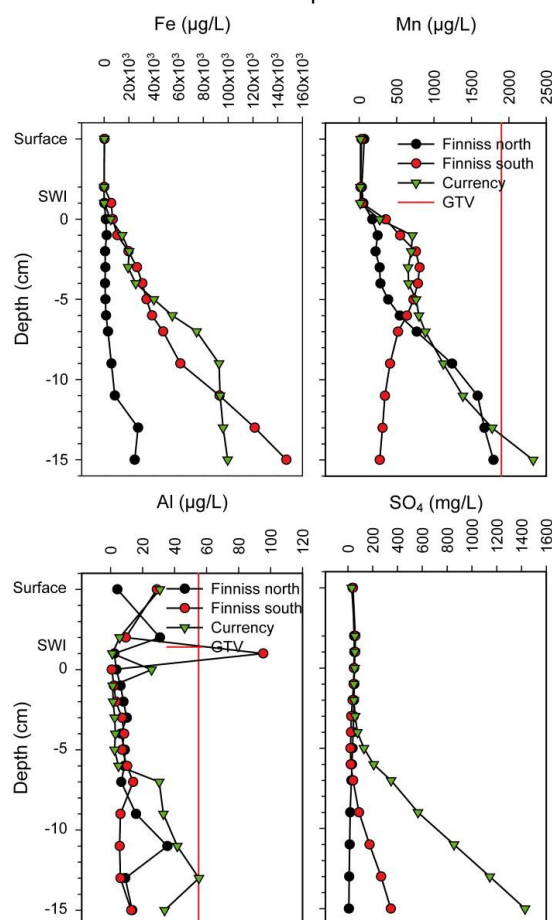


Figure 7 Pore water concentration profile for aluminium and redox sensitive components and the trigger value (TV for the protection of 95% of species; ANZECC/ARMCANZ 2000) for species where a value has been set. Depth from sediment-water interface to surface not to scale.

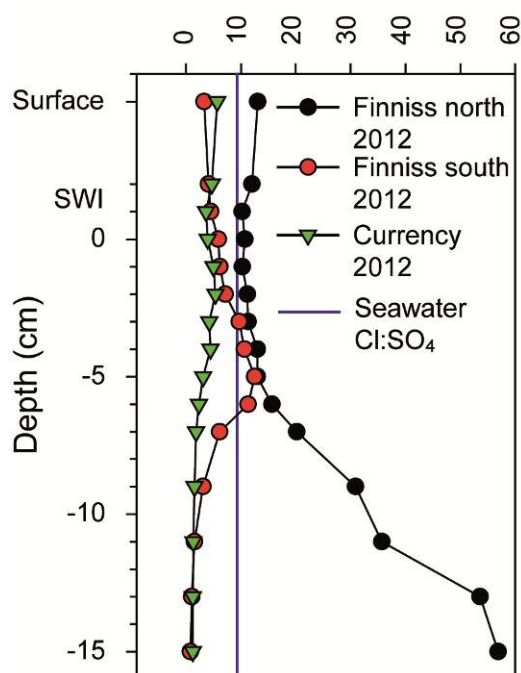


Figure 8 Cl:SO₄ ratio in peeper pore water. Values less than the seawater ratio are indicative of pyrite oxidation. Depth from soil-water interface (SWI) to surface not to scale.

Nutrients and nutrient fluxes

Nitrate and nitrite concentrations below a depth of 11 cm in Finniss River, south and Currency Creek, as well as those measured at the sediment-water interface at Currency Creek were elevated and above the TV (Figure 9 and Table 3). This could favour algal blooms that in turn will provide a source of labile organic carbon which will enhance the formation of monosulfidic black ooze (Bush *et al.* 2004). Total ammonia-N concentrations were elevated and above the TV for toxicants below a depth of 4 cm at both Finniss River, south and Currency Creek (Figure 9 and Table 3). At Finniss River, north, orthophosphate concentrations were above the TV throughout the pore water profile, except between a depth of 10 and 11cm and at Finniss River, south concentrations were above the TV in the surface water and in the pore water from below a depth of 10 cm. At Currency Creek, orthophosphate concentrations were above the TV below a depth of 7 cm. Detailed results and a summary comparison of measured concentrations to the TVs for selected pore water depth intervals are provided in Table 12.

The calculated nutrient flux rates depends on sediment porosity and a combination of the difference in concentration between the overlying water and the 'constant' concentration in the sediment, and the depth to this concentration - the nutrient gradient (Equation 12, Figure 10). The nutrient flux values show a net ammonia-nitrogen flux from the soil to the overlying water indicative of reducing conditions in the sediment and an internal source of nutrient loading in the water body. The diffusive flux of nitrate from the soil-water interface into the soil profile may also indicate oxidation of ammonia in the water column to nitrate and of nitrogen cycling in general. Differences between sites are a combination of the size of the nutrient pool (loading) and the biogeochemical conditions necessary for its mineralisation and release. Additional measurements would be required to determine the relative importance of these factors. Results are shown graphically in Figure 10 and tabulated in Table 13.

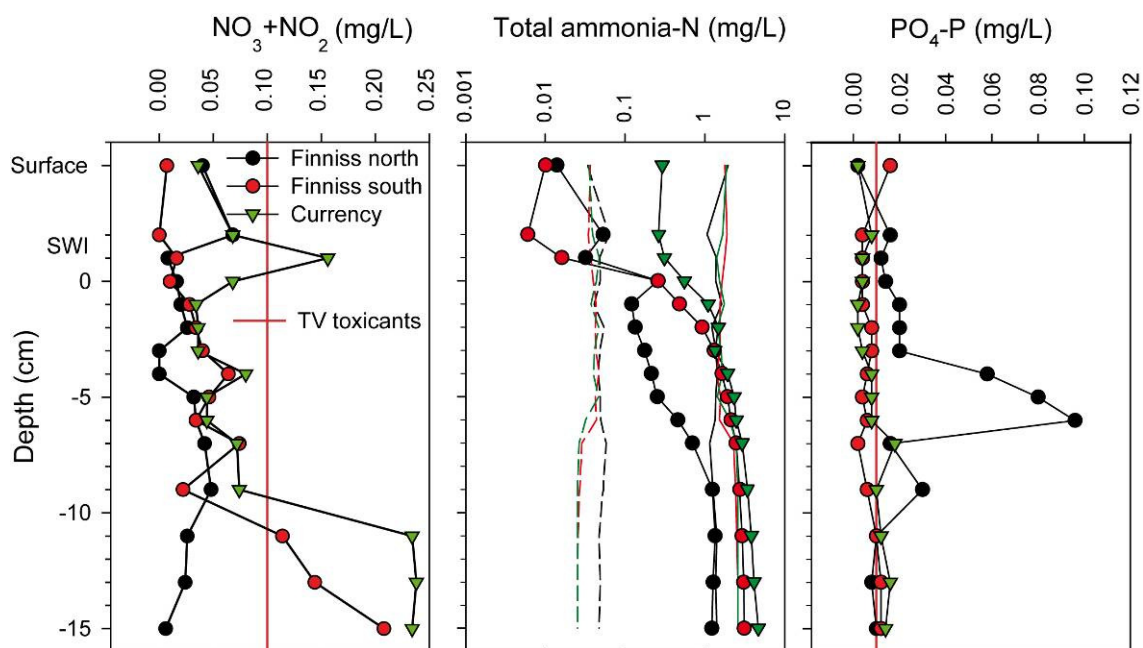


Figure 9 Nutrient concentrations and the trigger value (TV; ANZECC/ARMCANZ 2000) for physical and chemical stressors in south-central Australian lakes. Depth from sediment-water interface to surface not to scale. Note the TV for ammonia varies with pH. Ammonia TVs are shown as a solid line for toxicant values and dashed line for stressor values. Line colours match site symbol colours.

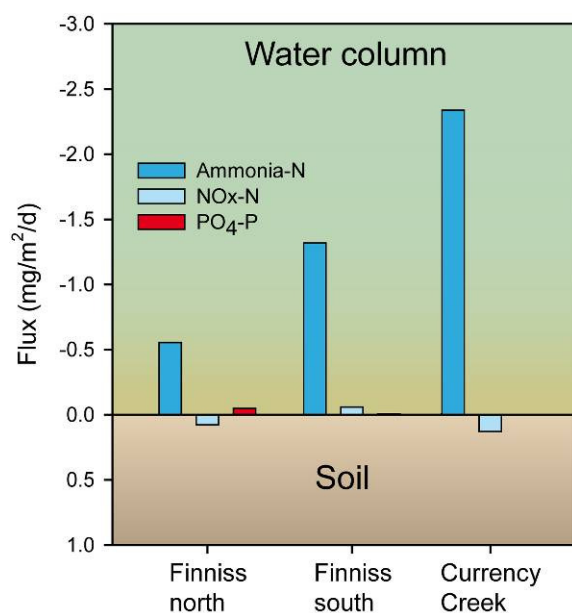


Figure 10 Diffusive nutrient fluxes calculated from peeper nutrient profiles. Negative values indicate flux to the water column from the sediment, positive values flux from the water column to the sediment.

Metals and metalloids

Concentrations of metals and metalloids were generally below the TVs except for the specific sites and pore water depths noted in the following paragraph.

At both Finniss River, north and Currency Creek silver was elevated in the sediment-water interface compared with the pore water and surface water measurements (Appendix 2). The iron concentrations in the pore water of these two sites were also elevated in comparison with the reference site. Arsenic concentrations (measured as total arsenic) were above the TV for As (V) below 10 cm in Finniss River, south and between -4 cm and -10 cm in Currency Creek, although concentrations were still below the TV for As(III). Further investigation would require arsenic speciation studies. Boron was measured at concentrations above the TV below -6 cm at Currency Creek and chromium was also above the TV below 12 cm in Currency Creek (Table 14) and similarly to arsenic, speciation would be required to investigate further. An unusually elevated concentration for zinc (121 µg/L) was measured at -1 cm in Currency Creek. This value was quite different from the measurements recorded at both 0 cm and -2 cm at this site and is also above the hardness-corrected TV of 72.3 µg/L. Given the low readings recorded elsewhere in the sediment profile at this site, this value could be considered to be an anomaly and not indicative of zinc pollution at Currency Creek. A summary comparison of measured concentrations to the TVs for selected pore water depth intervals is provided in Table 4 and more detailed results are provided in Table 14.

Table 3 Summary table showing exceedances for physical and chemical stressors. ➡ = Exceedance, ➡➡ = no exceedance

	pH	Nitrate+ nitrite-N	NH ₃ -N	PO ₄ -P
Finniss River, north (reference)				
Surface water	➡➡	➡➡	➡➡	➡➡
-1 cm	➡➡	➡➡	➡	➡
-5 cm	➡➡	➡➡	➡	➡
-10 cm	➡➡	➡➡	➡	➡
-15 cm	➡➡	➡➡	➡	➡
Finniss River, south (impacted)				
Surface water	➡➡	➡➡	➡➡	➡
-1 cm	➡➡	➡➡	➡	➡➡
-5 cm	➡➡	➡➡	➡	➡➡
-10 cm	➡➡	➡	➡	➡
-15 cm	➡	➡	➡	➡
Currency Creek (impacted)				
Surface water	➡➡	➡➡	➡	➡➡
-1 cm	➡➡	➡➡	➡	➡➡
-5 cm	➡➡	➡➡	➡	➡➡
-10 cm	➡	➡	➡	➡
-15 cm	➡	➡	➡	➡

Table 4 Summary table showing exceedances for toxicants (trigger values to protect 95% of freshwater species, very hard water). ♦ = Exceedance, ➡= no exceedance

	Total NH ₃ - N	Nitrite- N	Ag	Al	As	B	Cd [§]	Cr	Cu [§]	Mn	Ni [§]	Pb [§]	Se	Zn [§]
Finniss River, north (reference)														
Surface water	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-1 cm	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-5 cm	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-10 cm	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-15 cm	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
Finniss River, south (impacted)														
Surface water	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-1 cm	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-5 cm	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-10 cm	♦	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-15 cm	♦	➡	➡	➡	♦	➡	➡	➡	➡	➡	➡	➡	➡	➡
Currency Creek (impacted)														
Surface water		➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡
-1 cm	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	➡	♦
-5 cm	♦	➡	➡	➡	♦	➡	➡	➡	➡	➡	➡	➡	➡	➡
-10 cm	♦	➡	➡	➡	♦	♦	➡	➡	➡	➡	➡	➡	➡	➡
-15 cm	♦	➡	➡	➡	➡	♦	➡	♦	➡	♦	➡	➡	➡	➡

[§] = Values have been adjusted for hardness.

Chironomid deformities

In total, 147 individual chironomids from 8 genera were collected from Finnis River, north, 17 individuals from 5 genera from Finnis River, south and 140 individuals from 10 genera from Currency Creek with deformities detected in 4.1, 0 and 4.3% of the collections respectively (Table 5, Table 6 and Table 7). Deformities were found in both the antennae and mouthparts of the chironomids with 3 antennal and 3 mouthpart deformities detected at the reference site, and 1 antennal and 5 mouthpart deformities detected at Currency Creek. Examples of these deformities are presented in Figure 11 and Figure 12.

Many of the genera analysed showed no deformities at any of the sites. This finding is consistent with others studies (e.g. Martinez *et al.* 2002 and Swansburg *et al.* 2002) which have shown that some genera are more likely to exhibit deformities than others. Martinez *et al.* (2002) suggest that different feeding habits may influence the pollution tolerance of genera and therefore the likelihood of mouthpart deformities occurring. The sediment type, variation in tolerance between species within the same genus and the degree of exposure to pollutants for each individual will also influence the degree of deformities seen in a population. The genus *Chironomus* has been found to exhibit deformities in contaminated sediment and is often the genus used in deformity studies, particularly in laboratory and mesocosm studies. In this study *Chironomus* were only collected from two sites (the reference site and Currency Creek) with deformities occurring in 3.4 and 6.5% of the collection respectively. As the deformity rate measured at Currency Creek is only slightly higher than the reference site it is difficult to determine if this is indicative of sediment contamination, or if it is still low enough to be considered within the range of natural deformities. However, the more interesting result is in the deformities themselves. The two deformed *Chironomus* specimens from the reference site had additional teeth on the pecten epipharyngis, a small structure within the mouth of the chironomid which naturally has a variable number of teeth on it anyway. In contrast, the deformities seen at Currency Creek occurred on more major structures of the mouth and antennae. These more major deformities could be suggestive of impacts from sediment pollution.

Chironomid deformities have been found elsewhere in the Murray-Darling Basin (including interstate) at varying rates throughout but averaging around 4-5% (Chris Madden, pers. comm.). Townsend *et al.* (2009) studied sediment contamination at 14 sites along the River Murray, between Jingellic, in New South Wales and Murray Bridge. They found deformities of the chironomid *Procladius* to be between 0 and 70% with a 9% deformity rate occurring at their reference site. Further research is needed to confirm the natural rate of deformities in chironomids in the River Murray and Lower Lakes region.

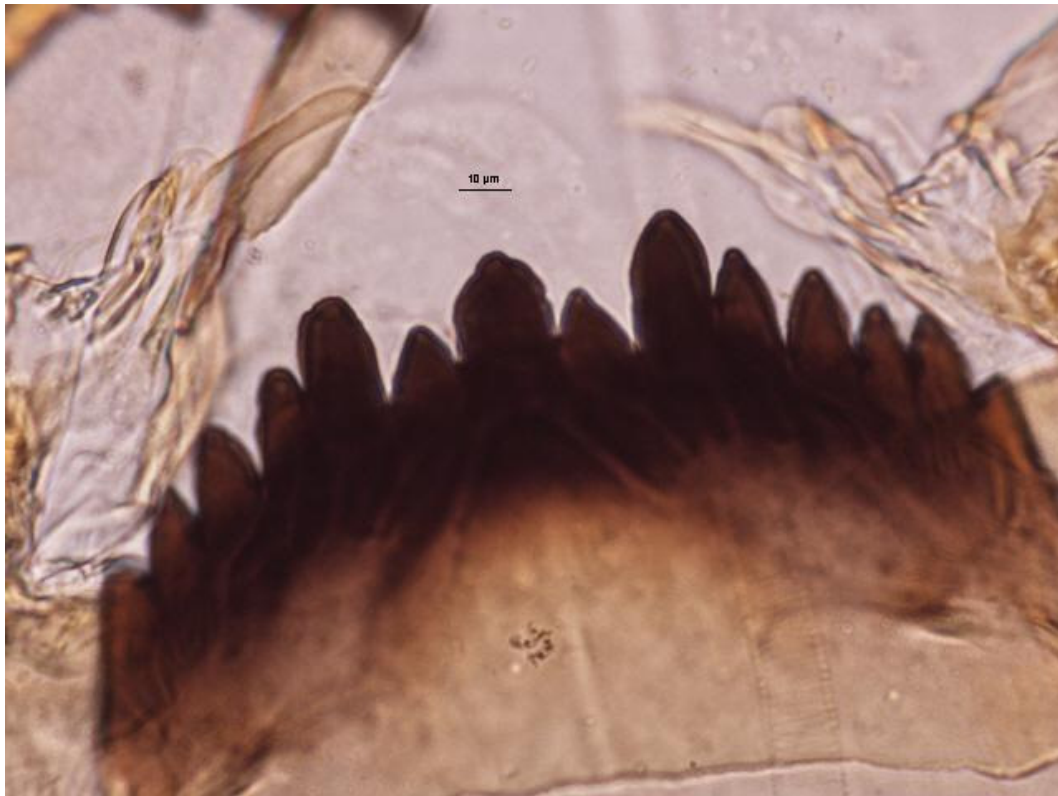


Figure 11 A deformed mentum of a *Chironomus* individual with a missing lateral tooth on the left-hand side.



Figure 12 A deformed antenna of a *Paratanytarsus* individual with a reduced number of antennal segments (circled antenna).

Table 5 Number of chironomid deformities at the Finniss River, north (reference) site

Genus	Number of Individuals	Number of deformities	% deformities	Type of deformity
<i>Paramerina</i>	2	0	0	-
<i>Procladius</i>	1	0	0	-
<i>Corynoneura</i>	1	0	0	-
<i>Paralimnophyes</i>	4	0	0	-
<i>Paratanytarsus</i>	50	2	4.0	1 mouthpart and 1 antennal ^a
<i>Chironomus</i>	59	2	3.4	2 mouthpart ^b
<i>Dicrotendipes</i>	11	2	18.2	2 antennal ^c
<i>Kiefferulus</i>	19	0	0	
Total	147	6	4.1	

^a = deformities seen include misshapen mentum tooth, and missing antennal segment and misshapen basal segment. ^b = extra tooth on pecten epipharyngis. ^c = missing segments on both antennae and antenna with misshapen basal segment and fused 2nd and 3rd segments.

Table 6 Number of chironomid deformities at the Finniss River, south (impacted) site.

Genus	Number of Individuals	Number of deformities	% deformities
<i>Paralimnophyes</i>	1	0	0
<i>Cladotanytarsus</i>	7	0	0
<i>Tanytarsus</i>	1	0	0
<i>Cladopelma</i>	1	0	0
<i>Kiefferulus</i>	7	0	0
Total	17	0	0

Table 7 Number of chironomid deformities at the Currency Ck (impacted) site.

Genus	Number of Individuals	Number of deformities	% deformities	Type of deformity
<i>Procladius</i>	2	0	0	-
<i>Cricotopus</i>	2	0	0	-
<i>Nanocladius</i>	1	0	0	-
<i>Paralimnophyes</i>	10	0	0	-
<i>Paratrichocladius</i>	1	0	0	-
<i>Paratanytarsus</i>	18	0	0	-
<i>Chironomus</i>	77	5	6.5	1 antennal and 4 mouthpart ^a
<i>Cladopelma</i>	1	0	0	
<i>Kiefferulus</i>	15	0	0	
<i>Parachironomus</i>	13	1	7.7	mouthpart ^b
Total	140	6	4.3	

^a = deformities seen include three-segmented antennae, missing lateral tooth on mentum, extra tooth on pecten epipharyngis, deformed premandible and asymmetric pecten epipharyngis. ^b = extra tooth on mandible.

Sediment cores

Invertebrates identified in the sediment cores included mostly segmented worms, non-biting midges (chironomids) and round worms (nematodes). However, many other taxa were also collected, including microcrustaceans (seed shrimps (ostracods), copepods (harpacticoids and cyclopoids) and a water flea (*Ilyocryptus*)), the amphipod family Corophiidae, one larval specimen from the caddis-fly genus *Ecnomus*, a water mite (Oribatida), a springtail (Hypogasturidae) and a fly larva from the family Muscidae. A detailed list of the taxa collected is provided in Table 18.

Table 8 Number of individuals and diversity of taxa collected in sediment cores from three sites in the lower Finnis River and Currency Creek. Note: Only a surface sample was collected from the Finnis River, south, in the reeds, due to difficulty in collecting sediment at depth around the roots of the reeds.

Site Name	Profile depth	Sediment Composition	Number of individuals	Number of taxa
Finniss River, north (reference)	0-2 cm	Mostly organic matter and sand	37	11
	2-5 cm	Mostly organic matter and sand	34	7
	5-10 cm	Mostly clay, some organic matter	15	3
Finniss River, south (impacted) – near peeper	0-2 cm	Mostly clay, some fine detritus and sand	32	10
	2-5 cm	Mostly clay, some fine detritus	54	5
	5-10 cm	Mostly clay, some fine detritus	0	0
Finniss River, south (impacted) – in reeds	0-2 cm	Mostly organic matter	53	13
Currency Ck (impacted) – near peeper	0-2 cm	Mostly sand, some clay	78	8
	2-5 cm	Mostly sand, some clay and detritus	4	2
	5-10 cm	Mostly clay, some sand	1	1
Currency Ck (impacted) – in reeds	0-2 cm	Mostly detritus (anaerobic and black)	50	7
	2-5 cm	Mostly sand	4	2
	5-10 cm	Mostly sand	1	1

As expected, most biota were found in the top 2 cm of the sediment with between 7 and 13 different taxa being identified from the three sites (Table 8). Many invertebrates, including chironomids were also found in the 2-5 cm layer at the two sites in the Finnis River. However, at Currency Creek only 5 individuals were found below 2 cm in the sediment both near the reeds and near the peeper at this site (Table 8). As the sediment chemistry at this site suggests acidity and metal concentrations within this depth of the sediment profile are at concentrations that should not impact the ecosystem, it is likely that the difference between this site and those in the Finnis River is a legacy of the severe impacts that occurred at this site during the drought. Much of this section of Currency Creek dried completely during the drought leaving large and very deep cracks in the sediment. Acidic pools were also found along this section and a limestone trial was carried out in this section in 2010 in attempt to ameliorate the acidity (Barter 2010). Very few invertebrates

were found at any site below 5 cm. This is possibly due to poor habitat, including unsuitable substrate, reduced oxygen levels and lack of food.

Mussel dissolution study

Mussel shells were placed at 3 cm, 2, 0, -1, -5, -6, -10, -11, -20 and -21cm with all shells showing a decrease in mass except the shells placed at -5cm. These shells were found to be coated with a black substance which was then easily rubbed off under running water. It is possible that the substance was iron precipitate, perhaps due to an increase in oxygen availability in comparison with the deeper sediment. The shells in the surface water (>0 cm) showed only a very slight decrease in mass. The greatest decrease in mussel shell mass (at -6 cm) (Figure 13) corresponded with a decrease in pH in the pore water (at -7 cm) at this site (Figure 5), suggesting the health of mussels could be compromised at this depth. Below 7 cm the loss of mass varied between 0.17 g and 0.028 g. Given only one profile was studied (another one broke as it was installed) these results should be treated with caution.

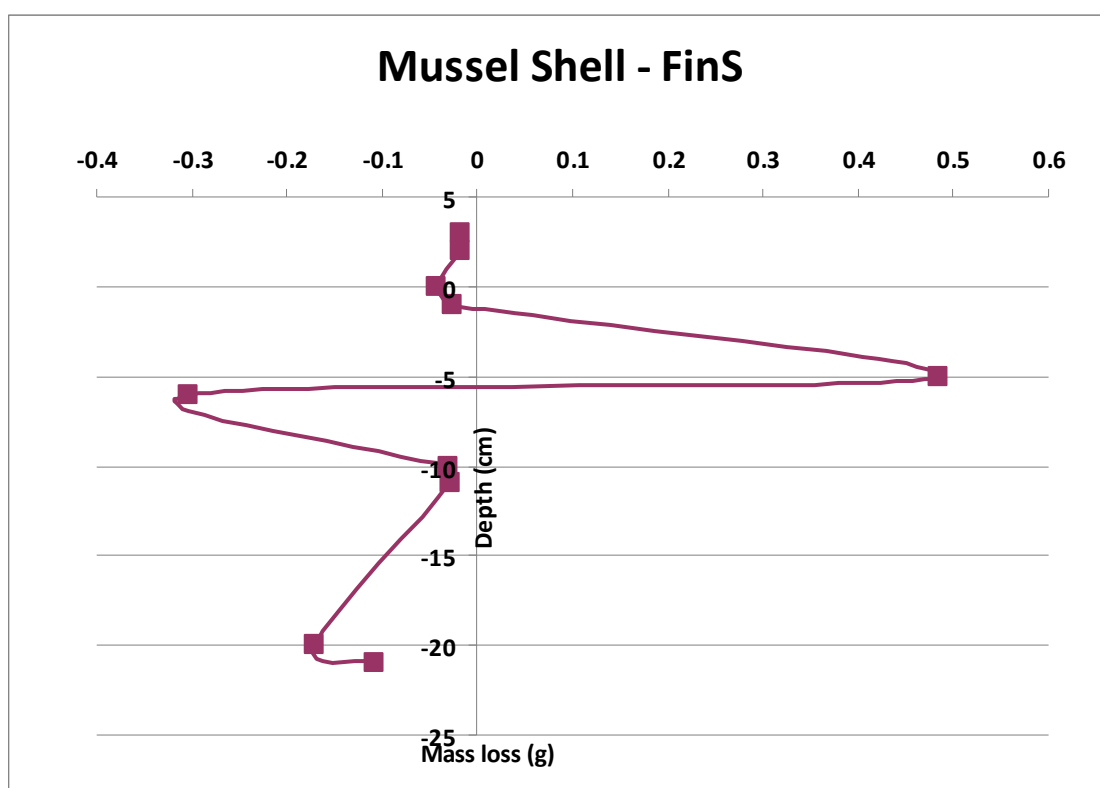


Figure 13 Change in mass of mussel shells deployed at varying sediment depths at Finnis River, south.

4 Conclusions

The results from this study showed that acidity is still of concern in the sediment of the lower reaches of the Finnis River and Currency Creek, with pH values below 6.5 (the ANZECC/ARMCANZ trigger value for south-central Australian lakes) below depths of 8 cm. Below a depth of 5 cm ammonia concentrations were also at toxicant levels and could potentially be harmful to biota. However, the sediment cores collected in this study showed that most organisms living in the sediment will be found above a depth of 5 cm with only a few individuals found deeper than this. Concentrations of other toxicants, such as metals and metalloids were found to be below trigger values suitable for the protection of 95% of species, except below a depth of 15 cm in Currency Creek, where boron, chromium and manganese were elevated. Although the pore water chemistry suggested generally low concentrations at all sites, bioaccumulation of substances may still occur in some biota. The possibility of this occurring is highlighted by the differences in deformities in *Chironomus* specimens seen between the reference site and Currency Creek, where more major structures were deformed. However, further research is needed to confirm if deformities are higher at sites affected by acid sulfate soils than unaffected sites and whether they can be an important measure of environmental harm in the region. The greatest decrease in mussel shell weight was recorded 6 cm below the sediment surface and corresponded with a decrease in pH in the pore water. However, mussels will not generally be found living this deep. As only one trial was conducted these results should be treated with caution.

5 Further research and recommendations

The findings from this pilot study have raised further questions and research ideas that could help discern if acid sulfate soils are having a sub-lethal impact on biota in the Lower Lakes region. It would be worthwhile investigating the following issues:

- Using the Sediment Quality Triad to complete an assessment of the sediment condition of the Lower Lakes. This Triad combines sediment chemistry, benthic monitoring and sediment toxicity assessments. The former two have been investigated briefly in this study, however sediment toxicity tests have not been conducted to date. Two possible options might be:
 - Conducting whole sediment toxicity testing.
 - If Chironomids were used as a test organism then the endpoints to the toxicity test could be deformity rates of those chironomids as well as testing for metal concentrations within the bodies of the chironomids to gain an understanding of potential metal bioaccumulation
 - Conducting interstitial water toxicity identification evaluation, where the reason for the toxicity (if any is exhibited) is also determined through manipulation of the sample, (i.e. addition of EDTA to mask metal toxicity, aeration to remove volatile or oxidisable contaminants etc.)
- Investigating the change over time in deformity rates of *Chironomus* at specific locations to determine if exposure to pollutants varies over time
- Determining deformity rates in chironomids at a variety of sites elsewhere in the Lower Lakes region to determine the variability across the region
- Undertake more mussel shell dissolution experiments *in situ*
- Undertake more detailed transects of pore water chemistry over a wider spatial scale but also investigate the variability within a smaller reach (e.g. within a 50 m zone away from the edge of the water (more habitable zone for aquatic invertebrates))
- Undertake detailed chemical speciation modelling to inform ecological risk assessments. This could include parameterisation of HYDRUS/PHREEQC to account for chemical transformations and provide detailed flux estimates including speciation
- Transplanting live mussels and testing body burden of metals of mussels left *in situ* for 6 weeks (would need a considerable number as some would need to be tested as a reference group to obtain background levels of metals).

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Appendix 1 Method for flux calculations

The flux at the sediment-water interface was estimated using the flux equation. The equation was parameterised using measured and literature values as described below.

The equation for the flux across the sediment-water interface can be formulated according to the equation (Stumm and Morgan 1996):

$$F_{z=0} = F_d + F_a + F_s \quad 1$$

Where the flux is due to:

molecular diffusion in pore water $F_d = -\phi D \frac{dC}{dz}$ 2

advection in pore water $F_a = \phi UC$ 3

and sedimentation or solid (mineral) phases $F_s = \phi U_s C_s$ 4

so that $F_{z=0} = \phi(-D \frac{dC}{dz} + UC + U_s C_s)$ 5

Where:

ϕ is the sediment porosity

C and C_s are the concentrations in the solution and solid

U and U_s are the rates of pore water advection and of sedimentation and

D is the sediment diffusion coefficient (Stumm and Morgan 1996).

Krom and Berner (1980) use the following equation to convert from diffusion at infinite dilution D_0 to sediment diffusion D_s :

$$\frac{D_0}{D_s} = \phi F \quad 6.$$

Where F is the formation factor which can be estimated using Archie's factor (Manheim 1970) so that $F = \phi^{-2}$ and substituting and rearranging $D_s = \phi D_0$ and equation so that:

$$F_{z=0} = \phi(-D \frac{dC}{dz} + UC + U_s C_s) \quad 7$$

becomes

$$F_{z=0} = -D_s \frac{dC}{dz} + \phi(UC + U_s C_s) \quad 8.$$

If C_d is the concentration at depth d where the concentration becomes constant and C_0 is the concentration at the sediment-water interface, then:

$$F_{z=0} = -D_s \frac{C_d - C_0}{d} + \phi(UC + U_s C_s) \quad 9$$

a further simplification can be introduced by assuming $D_0=10^{-9}$ m/s for simple electrolytes (Appelo and Postma 2005). D_0 is adjusted for temperature using the equation:

$$D_{0,T} = \frac{D_{0,298} T \eta_{298}}{298 \eta_T} \quad 10$$

where η is the viscosity of water (Mortimer *et al.* 1999).

The rate of pore water advection or linear interstitial advection velocity (LIV) is obtained by dividing the measured seepage flux by the sediment porosity (Mortimer *et al.* 1999) so that:

$$U = \frac{\text{measured seepage}}{\phi} \quad 11.$$

Assuming no advective flux i.e. no flux through the sediment profile to or from groundwater, the flux at the sediment-water interface becomes the diffusive flux, so that:

$$F_{z=0} = -D_s \frac{C_d - C_0}{d} \quad 12$$

Sediment porosity values used were those measured by Hicks *et al.* (2009), values of C_d and d for each species were determined from dialysis chamber sampler concentration profiles and literature values were used for other parameters.

Appendix 2 Tables of results

Electrical conductivity, pH and alkalinity

Surface water

Table 9 Surface water EC, pH and alkalinity. Samples were taken 5 cm below the water surface.

Sample	EC (dS/m)	pH	Alk (meq/L)
Finniss River, north (reference site)	2.53	7.24	2.22
Finniss River, south	1.17	7.36	0.58
Currency Creek	1.08	7.30	0.91

Pore water

Table 10 Pore water EC. Negative depth values indicate the depth below the sediment surface.

Finniss River north		Finniss River south		Currency Creek	
Depth (cm)	EC (dS/m)	Depth (cm)	EC (dS/m)	Depth (cm)	EC (dS/m)
2	2.54	3	1.22	3	1.07
1	2.60	1	1.18	1	1.08
0	2.47	0	1.19	0	1.86
-1	2.48	-1	1.23	-1	1.20
-2	2.47	-2	1.27	-2	1.30
-3	2.47	-3	1.28	-3	1.41
-4	2.48	-4	1.25	-4	1.60
-5	2.48	-5	1.29	-5	2.08
-6	2.49	-6	1.30	-6	2.50
-7	2.60	-7	1.27	-7	3.35
-9	2.66	-8	1.43	-8	4.33
-11	2.62	-9	1.53	-9	5.45
-13	2.59	-10	1.65	-10	6.60
-15	2.56	-11	1.77	-11	7.80
-17	2.53	-12	1.86	-12	8.64
-18	2.53	-13	1.92	-13	9.15
-19	2.48	-14	2.00	-14	9.59
-20	2.44	-15	2.00	-15	9.98
-21	2.45	-16	2.04	-16	10.21
-22	2.41	-17	2.04	-17	10.49
-23	2.43	-18	2.06	-18	10.67
-24	2.39	-19	2.07	-19	10.87
-25	2.37	-20	2.08	-20	11.05
-26	2.37	-21	2.10	-21	11.28
-27	2.36	-22	2.11	-22	11.46
-28	2.36	-23	2.11	-23	11.64
-29	2.37	-24	2.14	-24	11.88
-30	2.40	-25	2.16	-25	12.00
-31	2.39	-26	2.20	-26	12.32
-32	2.47	-27	2.23	-27	12.45

Table 11 Pore water pH and alkalinity. Negative depth values indicate the depth below the sediment surface. na = not analysed.

Finniss River north					Finniss River south					Currency Creek				
Depth range (cm)		pH	Alkalinity (mmol/L)	Acidity [§] (mmol/L)	Depth range (cm)		pH	Alkalinity (mmol/L)	Acidity [§] (mmol/L)	Depth range (cm)		pH	Alkalinity (mmol/L)	Acidity [§] (mmol/L)
3	1	7.87	1.73	0.007	3	1	7.28	1.16	0.007	3	1	7.45	0.55	0.002
1	0	7.65	1.25	0.009	1	0	7.37	0.95	0.22	1	0	7.64	0.92	0.002
0	-1	7.67	4.01	0.057	0	-1	7.47	0.64	0.27	0	-1	7.56	0.91	0.21
-1	-2	7.49	1.55	0.086	-1	-2	7.55	1.34	0.40	-1	-2	7.39	0.65	0.55
-2	-3	7.76	1.95	0.040	-2	-3	7.54	1.03	0.73	-2	-3	7.62	0.87	0.75
-3	-4	7.66	2.18	0.049	-3	-4	7.55	1.32	0.98	-3	-4	7.51	1.05	0.72
-4	-5	7.62	2.17	0.038	-4	-5	7.64	0.90	1.1	-4	-5	7.47	0.86	0.94
-5	-6	7.67	1.83	0.054	-5	-6	7.53	1.31	1.2	-5	-6	7.62	1.05	1.5
-6	-7	7.68	1.50	0.076	-6	-7	7.56	1.07	1.4	-6	-7	7.13	0.65	2.0
-7	-9	7.81	2.84	0.14	-7	-9	6.87	1.08	1.7	-7	-9	6.46	0.67	2.7
-9	-11	7.74	3.02	0.26	-9	-11	6.58	0.75	2.2	-9	-11	5.90	0.19	3.4
-11	-13	7.64	3.65	0.37	-11	-13	6.22	0.39	3.3	-11	-13	5.89	0.14	3.4
-13	-15	7.67	3.54	1.0	-13	-15	5.71	0.12	4.4	-13	-15	5.71	0.14	3.5
-15	-17	7.64	4.11	0.95	-15	-17	5.57	0.12	5.3	-15	-17	5.86	0.20	3.7
-17	-19	7.46	4.36	na	-17	-19	5.42	0.13	na	-17	-19	6.01	0.18	na
-19	-21	7.56	4.10	na	-19	-21	5.36	0.12	na	-19	-21	6.14	0.32	na
-21	-23	7.56	4.28	na	-21	-23	5.34	0.11	na	-21	-23	6.20	0.47	na
-23	-25	7.36	3.97	na	-23	-25	5.33	0.13	na	-23	-25	6.27	0.80	na
-25	-27	7.36	4.10	na	-25	-27	5.22	0.10	na	-25	-27	6.46	0.95	na
-27	-29	7.47	5.69	na	-27	-29	5.17	0.10	na	-27	-29	6.43	1.47	na
-29	-31	7.44	4.13	na	-29	-31	5.19	0.09	na	-29	-31	6.51	2.70	na
-31	-32	7.47	5.98	na	-31	-32	5.06	0.08	na	-31	-32	6.63	2.28	na

[§] = Sum of acidic cations Fe, Al, Mn and H

Table 12 Surface and pore water major elements and nutrient concentrations in mg/L (mg CaCO₃/L for hardness). Negative depth values indicate the depth below the sediment surface. Values in red are in exceedance of the ANZECC/ARMCANZ trigger value for physical and chemical stressors for south-central Australian lakes. Red shading indicated the TV for the protection of 95% of species is exceeded.

	Depth (cm)	Na	K	Ca	Mg	Hardness	Cl	Stot	SO ₄	Br	Ptot	Si	PO ₄ -P	NO _x	NO ₃ -N	NO ₂ -N	NH ₃ -N
Finniss River north	8	210	5.4	46	27	230	500	13	38	1.5	0.033	5.5	0.002	0.04	0.04	0.002	0.014
	2	340	9.6	69	48	370	600	17	50	2.6	0.022	7.5	0.016	0.07	0.06	0.008	0.053
	1	340	9.5	70	47	370	530	17	52	2.5	0.028	7.5	0.012	<0.01	<0.01	0.006	0.032
	0	320	9.3	69	47	370	520	16	48	2.5	0.16	7.4	0.014	0.02	0.01	0.004	0.26
	-1	330	9.5	73	47	380	530	17	52	2.5	0.29	8.0	0.020	0.02	0.02	0.002	0.12
	-2	330	9.2	72	45	370	540	16	49	2.5	0.18	8.0	0.020	0.03	0.02	0.006	0.13
	-3	330	9.4	77	47	390	540	16	48	2.5	0.28	8.7	0.020	<0.01	<0.01	0.002	0.18
	-4	350	9.3	75	47	380	550	14	42	2.5	0.26	9.0	0.058	<0.01	<0.01	0.006	0.21
	-5	330	9.3	79	49	400	490	13	38	2.5	0.41	9.2	0.080	0.03	0.03	0.004	0.25
	-6	340	8.8	84	48	410	510	11	33	2.5	0.53	10	0.096	0.03	0.03	0.006	0.46
	-7	320	9.4	94	53	450	570	9.4	28	2.5	0.60	13	0.016	0.04	0.04	0.006	0.70
	-9	320	8.9	110	60	510	570	6.2	18	2.5	1.0	15	0.030	0.05	0.04	0.004	1.3
	-11	300	8.8	110	63	540	530	5.0	15	2.5	0.99	16	0.010	0.03	0.02	0.006	1.3
	-13	290	8.7	130	67	590	540	3.3	10	2.5	1.0	18	0.008	0.02	0.02	0.006	1.3
	-15	280	9.7	120	66	580	500	2.9	8.7	2.3	1.0	19	0.010	<0.01	<0.01	0.004	1.2
Finniss River south	SW	120	7.6	26	19	140	130	14	41	0.85	0.014	1.9	0.016	<0.01	<0.01	0.001	0.010
	2	150	9.9	35	24	190	240	20	60	1.1	0.009	2.7	0.004	<0.01	<0.01	0.006	<0.009
	1	160	10	35	24	190	260	20	59	1.1	0.046	3.5	0.004	0.02	0.01	0.004	0.016
	0	150	9.3	36	25	190	300	17	50	1.1	0.056	4.7	0.004	0.01	<0.01	0.004	0.26
	-1	160	10	39	27	210	280	15	45	1.2	0.17	7.6	0.004	0.03	0.02	0.004	0.48
	-2	160	10	40	27	210	270	13	38	1.2	0.40	13	0.008	0.03	0.03	0.006	0.93
	-3	160	11	40	29	220	270	9.2	27	1.3	0.64	16	0.008	0.04	0.03	0.006	1.3
	-4	160	12	41	29	220	260	8.1	24	1.3	0.81	19	0.006	0.06	0.06	0.006	1.6
	-5	160	12	39	29	210	270	7.1	21	1.3	0.83	21	0.004	0.05	0.04	0.006	1.9
	-6	160	14	37	29	210	260	7.6	23	1.3	0.81	22	0.006	0.03	0.03	0.006	2.1
	-7	160	17	36	29	210	260	14	42	1.3	0.83	24	0.002	0.07	0.07	0.004	2.5
	-9	160	21	34	30	210	280	30	90	1.4	0.74	24	0.006	0.02	0.01	0.008	2.7
	-11	170	27	34	31	210	270	58	180	1.4	0.56	25	0.010	0.11	0.10	0.014	2.9
	-13	180	32	34	32	220	280	89	270	1.4	0.40	27	0.012	0.14	0.13	0.016	3.1
	-15	180	37	33	32	220	270	120	350	1.4	0.23	30	0.012	0.21	0.19	0.020	3.1

Table 12 (continued)

	Depth (cm)	Na	K	Ca	Mg	Hardness	Cl	Stot	SO ₄	Br	Ptot	Si	PO ₄ -P	NO _x	NO ₃ -N	NO ₂ -N	NH ₃ -N
	SW	65	4.9	16	11	87	180	10	31	0.43	0.008	0.57	0.002	0.04	0.03	0.004	0.29
Currency	2	130	10	31	22	170	270	19	57	0.93	0.010	0.96	0.008	0.07	0.06	0.006	0.26
	1	130	10	31	21	170	210	19	56	0.93	0.010	0.79	0.004	0.16	0.14	0.020	0.31
Creek	0	130	10	33	22	170	220	18	54	0.95	0.030	1.7	0.004	0.07	0.06	0.006	0.56
	-1	140	11	36	24	190	250	16	49	1.1	0.080	4.6	0.002	0.03	0.03	<0.001	1.1
	-2	160	12	37	26	200	260	16	49	1.2	0.26	6.4	0.002	0.04	0.03	0.006	1.5
	-3	170	14	40	28	210	250	19	58	1.4	0.33	6.6	0.004	0.04	0.03	0.004	1.3
	-4	210	16	43	33	240	340	26	77	1.6	0.50	9.1	0.008	0.08	0.07	0.006	1.9
	-5	250	19	48	41	290	410	43	130	2.0	0.87	13	0.008	0.04	0.04	0.006	2.3
	-6	320	22	52	50	340	480	70	210	2.5	1.4	17	0.008	0.04	0.04	0.008	2.5
	-7	430	28	59	65	420	640	120	350	3.3	2.5	24	0.018	0.07	0.05	0.018	3.0
	-9	550	35	72	91	550	880	190	570	4.3	3.3	31	0.010	0.07	0.06	0.010	3.4
	-11	720	43	92	120	730	1100	290	860	5.6	3.1	35	0.012	0.23	0.21	0.020	3.9
	-13	880	49	120	160	940	1400	380	1100	6.9	2.2	38	0.016	0.24	0.21	0.024	4.1
	-15	1000	59	150	200	1200	1700	480	1400	8.2	1.7	42	0.014	0.23	0.21	0.024	4.7

Table 13 Calculated diffusive nutrient flux at soil-water interface ($F_{z=0}$) mg/m²/d.

	Finniss north	Finniss south	Currency Creek
Ammonia-N	-0.55	-1.3	-2.3
NO _x -N	0.077	-0.06	0.13
PO ₄ -P	-0.049	-0.007	0.00

Table 14 Surface and pore water minor and trace element concentrations in µg/L. Negative depth values indicate the depth below the sediment surface. Values in red indicated exceedance over the ANZECC/ARMCANZ trigger value to protect 95% of freshwater species.

	Depth (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Pb	Hg	Mn	Mo	Ni	Se	Zn	V
Finniss River north	SW	<0.005	4.2	2.1	140	60	<0.002	0.018	0.15	<0.001	0.41	370	0.20	0.005	67	<0.001	0.24	0.24	8.4	0.37
	2	0.039	31	2.8	200	89	0.005	0.019	0.089	0.017	1.3	79	0.073	0.007	34	0.047	0.75	0.00	2.0	0.005
	1	0.073	2.3	2.4	200	88	0.002	0.003	0.097	<0.001	0.71	190	0.091	0.007	55	0.067	0.67	0.72	0.9	0.005
	0	0.084	3.6	3.1	200	93	<0.002	0.014	0.19	<0.001	0.88	1400	0.10	0.014	170	0.063	0.89	0.98	2.0	0.005
	-1	<0.005	6.2	4.1	200	96	<0.002	0.024	0.24	<0.001	0.95	2100	0.84	0.001	250	0.062	0.67	0.78	121	0.005
	-2	<0.005	8.0	4.1	200	94	<0.002	0.009	0.15	<0.001	0.87	860	0.097	0.001	220	<0.001	0.62	0.72	1.5	0.16
	-3	<0.005	10	4.1	210	100	<0.002	0.008	0.17	<0.001	0.64	1000	0.068	0.003	270	<0.001	0.45	0.055	1.8	0.44
	-4	<0.005	6.4	3.8	210	93	<0.002	0.011	0.14	<0.001	0.67	770	0.068	0.004	280	<0.001	0.44	1.1	2.7	0.000
	-5	<0.005	8.9	2.8	210	93	<0.002	0.019	0.16	<0.001	0.81	1100	0.077	0.005	390	<0.001	0.68	0.57	2.0	0.005
	-6	<0.005	8.7	3.4	190	100	<0.002	0.013	0.21	<0.001	0.67	1600	0.065	0.006	540	<0.001	0.45	0.29	2.0	0.45
	-7	<0.005	6.6	2.6	180	120	<0.002	0.017	0.41	<0.001	0.77	3200	0.41	0.002	770	<0.001	0.43	0.75	2.1	0.005
	-9	<0.005	16	3.3	160	140	<0.002	0.011	0.57	<0.001	0.83	5900	0.075	0.055	1200	<0.001	0.24	0.51	2.2	<0.005
	-11	<0.005	35	1.8	150	160	<0.002	0.011	0.59	<0.001	1.0	8700	0.13	0.024	1600	<0.001	0.55	1.0	1.6	0.005
	-13	<0.005	9.2	3.0	150	190	<0.002	0.013	0.53	<0.001	1.1	27000	0.090	0.001	1700	<0.001	0.33	0.86	3.0	0.005
	-15	<0.005	14	4.0	140	200	<0.002	0.011	0.53	<0.001	1.2	25000	0.13	0.012	1800	<0.001	0.24	1.3	1.9	0.005
Finniss River south	SW	<0.005	29	1.3	94	35	<0.002	0.013	0.23	0.074	1.1	290	0.32	0.004	32	0.335	1.1	0.69	15	0.88
	2	<0.005	9.4	1.6	120	47	<0.002	0.033	0.12	<0.001	1.7	150	0.21	0.001	16	0.526	1.7	0.49	4.2	0.45
	1	<0.005	95	3.0	120	49	<0.002	0.009	0.15	<0.001	1.2	5700	0.13	0.002	40	0.599	1.5	0.43	1.8	0.56
	0	<0.005	0.8	4.5	110	48	<0.002	0.010	0.20	<0.001	0.86	7000	0.062	0.002	350	0.818	1.1	0.73	1.2	2.8
	-1	<0.005	2.1	4.8	120	47	<0.002	0.022	0.38	<0.001	1.0	11000	0.12	0.004	550	1.246	1.5	0.67	1.7	0.56
	-2	<0.005	3.3	6.4	120	45	<0.002	0.016	0.48	<0.001	0.89	20000	0.099	<0.001	760	1.341	1.4	0.91	3.8	4.7
	-3	<0.005	7.2	11	120	42	<0.002	0.009	0.39	0.041	0.73	27000	0.15	0.075	810	1.403	1.4	0.73	1.6	7.0
	-4	<0.005	8.5	11	120	31	<0.002	0.012	0.35	0.11	0.90	31000	0.12	0.005	780	1.377	1.2	1.4	2.7	7.3
	-5	<0.005	7.2	11	130	25	<0.002	0.009	0.31	0.81	0.73	34000	0.095	0.005	730	1.040	1.2	0.95	2.1	9.5
	-6	<0.005	10	8.3	140	20	0.010	0.018	0.32	0.40	1.0	39000	0.13	0.008	640	1.035	1.3	0.88	2.4	6.6
	-7	<0.005	14	8.8	150	18	<0.002	0.010	0.31	1.0	1.0	48000	0.19	0.003	520	1.494	1.3	1.1	2.6	7.3
	-9	<0.005	6.2	10	170	17	<0.002	0.021	0.31	0.96	1.1	62000	0.17	0.016	410	3.960	1.3	1.5	3.6	7.6
	-11	<0.005	5.6	15	190	15	<0.002	0.051	0.35	1.0	1.2	93000	0.18	0.001	340	7.961	1.2	1.7	7.2	4.5
	-13	<0.005	6.1	16	200	10	<0.002	0.076	0.38	0.87	1.6	120000	0.17	0.012	310	14.191	1.2	2.3	5.2	1.4
	-15	<0.005	13	17	210	7.1	<0.002	0.073	0.39	0.64	2.0	150000	0.26	0.001	270	18.235	1.2	1.8	7.7	1.2

Table 14 (continued)

	Depth (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Pb	Hg	Mn	Mo	Ni	Se	Zn	V
Currency	SW	<0.005	31	0.9	63	20	<0.002	0.010	0.10	<0.001	0.74	210	0.22	0.001	18	0.216	0.85	0.37	16	0.41
Creek	2	0.353	5.6	1.8	110	43	<0.002	0.021	0.14	<0.001	1.7	20	0.11	0.176	18	0.964	1.5	0.43	3.2	0.005
	1	0.108	1.1	1.0	110	38	<0.002	0.012	0.11	<0.001	1.0	25	0.065	0.025	16	1.005	1.4	0.00	1.4	0.005
	0	0.048	26	2.2	110	44	<0.002	0.038	0.35	<0.001	1.3	5400	0.12	0.015	270	1.732	2.1	0.45	3.9	0.005
	-1	<0.005	1.3	5.7	120	52	<0.002	0.010	0.42	<0.001	0.85	15000	0.10	0.006	710	1.833	1.3	0.75	1.5	1.1
	-2	<0.005	1.6	11	130	56	<0.002	0.015	0.30	<0.001	0.72	20000	0.093	0.009	700	1.829	0.96	0.63	5.8	0.84
	-3	<0.005	2.6	11	140	57	<0.002	0.008	0.32	<0.001	0.70	19000	0.18	0.013	650	1.835	0.93	0.85	1.6	<0.005
	-4	<0.005	3.0	13	170	61	<0.002	0.013	0.37	<0.001	0.88	26000	0.11	0.002	660	1.547	0.99	0.29	2.7	2.0
	-5	<0.005	2.5	15	210	67	<0.002	0.013	0.47	0.24	2.1	40000	0.13	0.002	760	1.515	0.94	1.2	2.1	3.7
	-6	<0.005	4.9	17	270	62	<0.002	0.016	0.50	0.51	1.0	55000	0.16	0.006	800	1.259	1.6	2.2	4.9	5.5
	-7	<0.005	30	17	380	70	<0.002	0.035	0.60	0.51	1.6	75000	0.33	0.008	880	1.770	1.8	2.0	5.9	5.1
	-9	<0.005	33	19	490	73	0.017	0.023	0.65	0.73	2.6	93000	0.39	0.161	1100	1.891	2.2	3.6	7.1	5.6
	-11	<0.005	42	11	610	66	<0.002	0.011	0.47	0.71	2.7	94000	0.29	0.020	1400	1.237	1.8	3.8	9.3	3.1
	-13	<0.005	55	10	720	77	0.047	0.016	0.38	1.4	2.8	96000	0.38	0.002	1800	0.330	0.30	4.0	13	4.5
	-15	<0.005	34	12	850	85	0.019	0.022	0.38	1.2	3.1	100000	0.23	<0.001	2300	0.206	0.00	3.2	15	4.3

Table 15 Quality control results for peeper field blanks. Measurements recorded in mg/L.

Sample	PO ₄ -P	NO _x	NO ₃ -N	NO ₂ -N	Ammonia-N	Na	K	Ca	Mg	Cl	Stot	SO ₄	Br	Ptot	Si
Blank 1	0.000	0.052	0.050	0.002	0.006	0.31	0.16	0.12	0.03	11	1.2	3.6	0.006	0.000	0.40
Blank 2	0.000	0.046	0.045	0.001	0.009	0.30	0.17	0.12	0.03	6	1.0	3.1	0.005	0.000	0.50
Blank 3	0.000	0.051	0.049	0.002	0.003	0.28	0.21	0.13	0.03	2	1.3	3.9	0.004	0.000	0.41
Mean	0.0	0.050	0.048	0.0017	0.0060	0.30	0.18	0.12	0.033	6.7	1.2	3.5	0.0052	0.0	0.44
Std Dev	0.0	0.0032	0.0026	0.00058	0.0030	0.014	0.027	0.0034	0.0019	4.6	0.13	0.39	0.00077	0.0	0.056

Table 16 Quality control results for peeper field blanks. Measurements recorded in µg/L.

Sample	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Pb	Hg	Mn	Mo	Ni	Se	Zn	V
Blank 1	0.000	0.000	0.000	48	0.53	0.000	0.035	0.032	0.010	2.7	0.000	0.16	0.000	0.50	0.000	0.85	0.04	13	0.000
Blank 2	0.000	0.000	0.000	56	0.21	0.000	0.028	0.032	0.042	2.5	0.000	0.33	0.000	0.54	0.000	0.48	0.15	12	0.000
Blank 3	0.000	0.000	0.000	49	0.29	0.000	0.026	0.029	0.014	2.4	0.000	0.25	0.005	0.49	0.000	0.72	0.02	12	0.000
Mean	0.0	0.0	0.0	51	0.35	0.0	0.030	0.031	0.022	2.5	0.0	0.25	0.0017	0.51	0.0	0.68	0.068	12	0.0
Std Dev	0.0	0.0	0.0	4.7	0.17	0.0	0.0047	0.0017	0.018	0.16	0.0	0.087	0.0029	0.024	0.0	0.19	0.071	0.69	0.0

Table 17 Morphology of soil samples collected on 19th and 21st December 2009 that correspond to May 2012 peeper deployment sites (from Fitzpatrick *et al.* 2011). Note care should be taken with this comparison as the deployment sites in 2012 were closer to banks than in 2009.

Site ID May 2012	Sample ID	Site Label	Locality description	Sampling tool	Upper depth (cm)	Lower depth (cm)	Morphology
FIN_S	FIN28-M2	FC1001	Finniss River: Finniss River Estate (Peter Elmes) site –nearest site from main bank; in main wetland or back swamp with many cracks evident under 120 cm water. Subaqueous.	Spade/ Gouge Auger/ D-Augur	0	5	Black, medium clay with monosulfidic material.
		FC1002			5	20	Dark grey, heavy clay with many roots with distinct yellow jarosite mottles and coatings (30 %) along root channels and on surfaces of subangular blocky structures, very soft.
		FC1003			20	60	Dark grey and greenish olive, heavy clay with few roots with few diffuse yellow jarosite mottles and coatings (15 %) along root channels and on surfaces of subangular blocky structures, very soft.
CUR	CUR25-M2	FC1062	Currency Creek: high, 20m in wetland from step up to reeds along water edge under 50 cm water. Subaqueous.	Spade/ Gouge Auger	0	1	Orange gel with black monosulfidic material, medium sand , very soft.
		FC1063			1	5	Black with monosulfidic material, medium sand , soft.
		FC1064			5	20	Grey, with distinct yellow jarosite mottles (10 %) on surfaces of peds and old root channels, diffuse brownish red and brown mottles (5 %) and black mottles (5 %); sandy clay , subangular blocky, soft.
		FC1065			20	60	Dark olive green to grey, medium clay , soft

Appendix 3 Sediment cores

Table 18 Macroinvertebrate taxa identified in sediment cores collected from the study sites.

	Finniss River, north (reference)			Finniss River, south (peeper)			Finniss River, south (reeds)	Currency Creek (peeper)			Currency Creek (reeds)		
Taxa Name	0-2cm	2-5cm	5-10cm	0-2cm	2-5cm	5-10cm ^a	0-2cm	0-2cm	2-5cm	5-10cm	0-2cm	2-5cm	5-10cm
Naididae	5			2	4			4					
Dero sp.	1												
Pristina sp.							2						
Pristina longiseta							2						
Tubificidae							6						
Branchiura sowerbi		1	2										
Oligochaeta unidentified	8	4	3					18	2	1	10		
Nematoda	3	5	10	8	42		8	28			27	2	
Procladius sp.				1									
Chironomus sp.	5	8									8		1
Dicrotendipes conjunctus	7												
Dicrotendipes sp.	3	3											
Kiefferulus sp.		11					2						
Polypedilum sp.				2			16	8					
Cryptochironomus sp.								2					
Cladopelma sp.				5	1		2						
Paratanytarsus sp.	1											2	
Cladotanytarsus sp.				1			3						
Tanytarsus sp.				1									
Chironomini		2		9	1		1				2		
Chironominae							1	5					
Oribatida									2				
Hypogastruridae											1		
Muscidae	1												
Corophidae				2			7						
Culicoides					1								
Ecnomus cygnitus							1						
Ilyocyptus sp.				1									
Ostracoda	1							3			1		
Harpacticoida							2						
Cyclopoida											1		

^a = no taxa found in sample.

Appendix 4 Photos of monitoring sites

Site: Currency Creek (impacted)



Figure 14 The site at Currency Ck.



Figure 15 Deploying the peeper at the Currency Ck site.



Figure 16 Sediment core collected from Currency Ck.



Figure 17 Jarosite in sediment sample collected from Currency Ck.

Site: Finniss River, south (impacted)



Figure 18 The site at Finniss River, south.



Figure 19 Peeper at Finniss River, south two weeks after being deployed.

Site: Finniss River, north (reference)



Figure 20 The site at Finniss River, north.