

Lower Lakes groundwater acidification risk project: monitoring report 2012–14



Lower Lakes groundwater acidification risk project: monitoring report 2012-14

Authors: Ben Hamilton, Luke Mosley, Karl Fradley, Dylan Stone & Peter Mettam

For further information please contact:

Information Officer
Environment Protection Authority
GPO Box 2607
Adelaide SA 5001

Telephone: (08) 8204 2004

Facsimile: (08) 8124 4670

Free call (country): 1800 623 445

Website: <www.epa.sa.gov.au>

Email: <epainfo@epa.sa.gov.au>

This project is part of the South Australian Government's Murray Futures program funded by the Australian Government's Water for the Future program.

ISBN 978-1-921495-60-1

November 2014

Cover photo credit: EPA Murraylands Team member Peter Mettam sampling a submerged piezometer in Campbell Park, Lake Albert. An extension tube and capping is used to separate groundwater from surface water, after piezometers were inundated following a return of flow through the Murray-Darling Basin.

© Environment Protection Authority

This document may be reproduced in whole or part for the purpose of study or training, subject to the inclusion of an acknowledgement of the source and to it not being used for commercial purposes or sale. Reproduction for purposes other than those given above requires the prior written permission of the Environment Protection Authority.

Contents

Acknowledgements	1
Abbreviations	2
Executive summary	3
1 Introduction	5
2 Methods	6
2.1 Site selection	6
2.2 Description of groundwater parameters	6
2.3 Groundwater sampling	7
3 Results	8
3.1 Campbell Park (Lake Albert)	8
3.2 Point Sturt (Lake Alexandrina).....	10
3.3 Currency Creek (Tributaries)	12
4 Discussion	17
5 Conclusion	19
6 References	20

List of figures

Figure 1 Lower Lakes groundwater acidification risk project sampling locations	6
Figure 2 Laboratory parameters from four piezometers (P1 to P4) in Campbell Park.....	9
Figure 3 Soluble metals from four piezometers (P1 to P4) in Campbell Park	10
Figure 4 Field parameters from four piezometers (P1 to P4) in Point Sturt.....	11
Figure 5 Soluble metals from four piezometers (P1 to 4) in Point Sturt.....	12
Figure 6 Field parameters from four piezometers (P1 to P4) in Currency Creek	13
Figure 7 Soluble metals from four piezometers (P1 to P4) in Campbell Park	14
Figure 8 The sulfate:chloride ratio in a) Campbell Park, b) Point Sturt and c) Currency Creek.	15
Figure 9 The oxidative reduction potential of groundwater in (a) Campbell Park, (b) Point Sturt and (c) Currency Creek.	16

Acknowledgements

We wish to acknowledge the local landholders including Phil and Yvonne Giles, Anne Hartnett and Trevor Ferguson who kindly gave permission to access sampling locations.

We wish to thank EPA field staff for groundwater sampling, data processing and analysis. The support of Department of Environment, Water and Natural Resources (in particular Dr Liz Barnett and Ann-Marie Jolley) is kindly acknowledged. This work was conducted under funding from the South Australian Government's Murray Futures program.

Abbreviations

ANZECC	Australian and New Zealand Environment Conservation Council
ASS	acid sulfate soils
CLLMM	Coorong, Lower Lakes, Murray Mouth
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DEWNR	Department of Environment, Water and Natural Resources
EPA	South Australian Environment Protection Authority

Executive summary

The 2007 to 2009 drought and water over-allocation in the Murray–Darling Basin led to large areas of sediment containing acid sulfate materials being exposed along the margins of the Coorong, Lower Lakes and Murray Mouth. Piezometers were installed at multiple locations throughout the Lower Lakes including Point Sturt (Lake Alexandrina), Currency Creek (Tributaries) and Campbell Park (Lake Albert) to assess the risks to surface and ground water from sediment acidification.

The aim of this report is to provide an update on the groundwater quality in the Lower Lakes from 2012–14, and includes data from earlier periods for comparison purposes. Strong variation exists between sites and among piezometers in the Lower Lakes, with numerous piezometers showing varied response since 2012. Despite an overall increase in pH and alkalinity in groundwater across the Lower Lakes, there was evidence of residual acidity in all piezometers, and average acidity varied strongly between sites.

Monitoring in 2013 provided some interesting anomalies—acidity values peaking higher in December 2013 in Currency Creek than at any time during the drought, with an associated decline in pH. Sites such as Point Sturt in Lake Alexandrina had a remarkable drop in acidity, to some of the lowest recorded values since monitoring began. Alkalinity increased in the groundwater, although not evenly across all sites within each location.

After several years of post-drought conditions, the variation in groundwater results indicates a continuing slow recovery process via natural remediation, which is highly unpredictable. Any predictions on future trends remain difficult due to inherent variability on small and large scales. We recommend monitoring continues, as the data set is becoming a long-term asset which may provide insightful information on future groundwater acidification events and recovery timescales in the River Murray and Lower Lakes.

1 Introduction

From 2007 to 2009 the Coorong, Lower Lakes and Murray Mouth (CLLMM) experienced record low inflows due to drought induced rainfall reduction and water over-allocation in the Murray–Darling Basin. This led to a major decline in water levels throughout the region, falling to as low as –1.0 m AHD in Lake Alexandrina during 2009 (DENR 2010).

This exposed large areas of lake sediments, naturally containing sulfidic (pH>4) acid sulfate soil materials. These then oxidized from exposure to oxygen to form sulfuric material (pH<4) [Fitzpatrick *et al* 2010]. When these exposed sulfuric sediments were rewet either from local rainfall or a return to regular inflows, surface water provided the pathway for acidity and heavy metals (such as Cd, Cu, Fe, Ni, Pb and Zn) present in acid sulfate soils (ASS) to enter overlying surface water, leading to the acidification of significant marginal lake areas (Mosley *et al* 2014).

In 2009, the Department of Environment, Water and Natural Resources (DEWNR) commissioned Earth Systems Consulting Pty Ltd to quantify acidity flux rates from acid sulfate soils into the surface waters of Lake Alexandrina and Lake Albert. The key objectives of the study (Earth Systems 2009) were to:

- develop an improved understanding of acidity generation, neutralisation and groundwater transport processes within the lake sediments
- quantify acidity flux rates during wetting events by assessing the hydrogeology and hydro geo-chemistry of lake sediments
- provide recommendations for future management of the Lower Murray Lakes.

Piezometers were initially installed throughout the region including Lake Albert, Lake Alexandrina and the Tributaries, and groundwater and hydrological parameters at Point Sturt (Lake Alexandrina), Campbell Park (Lake Albert), Windmill (Lake Albert) and Currency Creek (Tributaries). These sites form the basis of a regular monitoring program which has continued under the South Australian Environment Protection Authority (EPA) from May 2010 to the present day. The Windmill site was decommissioned in April 2011.

During 2013, water levels in the Lower Lakes remained between 0.56–0.87 m AHD, continuing to inundate once exposed groundwater sites which had been installed during the drought. A modified technique, using flanges and extension tubing is used to access the existing submerged piezometers with much success.

The aim of this report is to describe changes in groundwater parameters from the 2012–14 monitoring season, with specific reference to recent historical data. Further context to the study background, aims and methodologies (including acidity generation and modelling) can be found in the report by Earth Systems (2009).

The data collected during this monitoring program assisted in the assessment of potential risks posed by acidified groundwater fluxes to the lake bodies and has been used by Commonwealth Scientific and Industrial Research Organisation (CSIRO) to conduct detailed research into acid mobilisation and fluxes (Cook *et al* 2011).

2 Methods

2.1 Site selection

Three locations, Point Sturt (Lake Alexandrina), Campbell Park (Lake Albert) and Currency Creek (Tributaries) [Figure 1] are monitored quarterly. Prior to piezometer installation, these sites were identified as representative areas which had undergone significant sediment acidification in the drought.

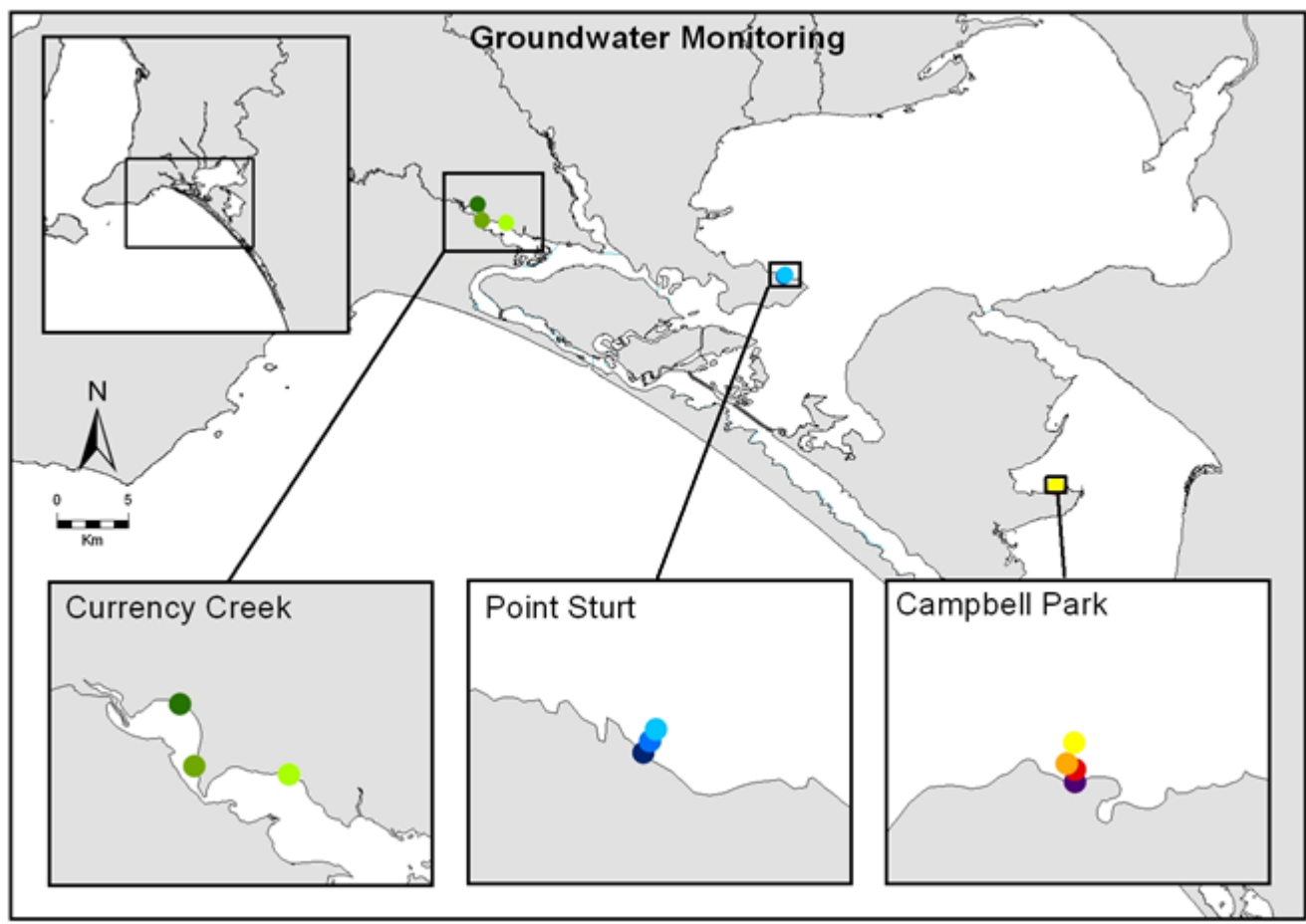


Figure 1 Lower Lakes groundwater acidification risk project sampling locations including Currency Creek, Point Sturt and Campbell Park.

2.2 Description of groundwater parameters

Multiple parameters have been recorded in groundwater consistently since 2009 including pH, electrical conductivity (EC), temperature, alkalinity, acidity and oxidation reduction potential (ORP).

pH is recorded as a useful indicator of whether the groundwater is acidic or alkaline.

Alkalinity (the measure of the buffering capacity of water to neutralise acids and resist pH change) and acidity (a measure of the amount of hydrogen ions, and dissolved Al, Mn and Fe in the water) are also measured in post-purge groundwater. Acidity is not normally present in high concentrations in groundwater unless impacted by acid sulfate soils.

The oxidation reduction potential of groundwater is measured as ORP (the affinity of groundwater to transfer electrons between chemical species) and a general guide to overall salinity is measured by electrical conductivity.

Metals such as Fe, Al and Mn can be released when soil pH is reduced. Local ecology can be sensitive to these metals, so monitoring dissolved metals is an important indicator for the impact of acid sulfate soils.

Parameters such as dissolved oxygen, specific conductivity and total dissolved oxygen have been recorded more recently. Data presented within this report are National Association of Testing Authorities (NATA) accredited laboratory results. NATA accreditation requires maintenance and documentation of strict quality control procedures.

2.3 Groundwater sampling

Groundwater sampling is conducted as per methods outlined in regulatory guidelines (Johnston 2007), which set out to create a standardised approach to sampling groundwater in South Australia. When the drought was in full effect, groundwater piezometers were installed on dry lake beds. When the drought broke and normal flows resumed, sites such as Campbell Park and Point Sturt became submerged and Currency Creek was part submerged. A modified sampling technique was improvised, and involved attaching a water tight extension tube to the existing piezometer.

This extension tube effectively isolated surface water from groundwater within the piezometer. The extension tube is constructed from a commercially available double-ended PVC compression fitting, approximately 250 mm in length, with a screw flange and o-ring at each end. One end is attached to the existing piezometer, and the other end of the fitting is connected to an extension pipe (approximately 500 mm in length) that extends above the water level. To attach the compression fitting to the piezometer, one end of the screw-in section is removed, along with the rubber o-ring seal, and placed on the piezometer underwater. The fitting is then screwed into the end section. Once the fitting is attached, the following sampling procedure is undertaken based on EPA guidelines:

- Each piezometer is purged using a Solonist peristaltic pump connected to a 12V battery. Three to five well volumes are pumped from each piezometer according to established groundwater sampling techniques (Appelo & Postma 2005). Groundwater is monitored during pump out with an YSI multi-meter (any leakage of the fitting can be determined as groundwater is considerably more saline than the overlying surface water, as well as through visual inspection down the piezometer tube) and samples are taken when fluid properties are stable.
- Groundwater flowing into the purged piezometer is tested in the field for general water quality parameters—pH, EC, temperature, ORP and acidity/alkalinity.

pH, EC, temperature and ORP are measured using a calibrated YSI multi-meter. Acidity is measured with a Hanna® Acidity Testing kit using phenolphthalein indicator and HI 3820–0 solution. Alkalinity is tested using a HACH® Test Kit, bromocresol green-methyl red indicator power and a range-specific H₂SO₄ titration cartridge.

- New sample bottles, pre-washed and rinsed with deionised water, were used for all samples destined for laboratory analyses. These bottles were first rinsed with the groundwater that is to be collected, and filled according to a standard method (APHA 2005).

Water samples were transported to the laboratory on ice where analyses are undertaken at the Australian Water Quality Centre (AWQC), a NATA) accredited laboratory. Bottled samples were collected for laboratory analysis of:

- general water quality parameters (pH, EC, ORP, acidity and alkalinity)
- ions (Cl, SO₄, F & Ca)
- metals (Al, Mn, Fe & K).

3 Results

3.1 Campbell Park (Lake Albert)

The pH of groundwater inside Campbell Park piezometers reached a low of 3 in 2009, but has steadily increased since inundation in late September 2011 to pH 5–7 (Figure 2a). pH across all piezometers increased in 2013. The pH in the two most acidic piezometers, P2 and P4, stayed relatively constant in the nine months after April 2011. But since January 2013, both piezometers have recorded notable increases in pH, reaching their highest values since recording began, of 5.9 and 5.3 respectively.

These pH values are still below the ANZECC guideline of 6.5. The pH in P1 has remained one of the only piezometers above the ANZECC (2000) guidelines (pH 6.5), averaging 7.05 since mid-2010. P1 reached a high of 7.4 in March 2014, above any previously recorded pH by piezometers in Currency Creek. P3 rose above the ANZECC guideline of 6.5 in April 2013 for the first time, remaining at an average of 6.53 after April. The range in pH values between piezometers at Campbell Park continues to decline.

In the last 12 months, acidity has remained present throughout all Campbell Park piezometers (Figure 2b). Acidity in P2 and P4 dropped by half since April 2013, but remain at 'high to very high' levels (above 300 mg/L as CaCO₃) as based on ANZECC guidelines. In the later half of 2013, the variation in acidity between piezometers had reduced to its lowest since monitoring began. P1 and P3 remain the most stable, between the 'low' levels stated by the ANZECC guidelines (Figure 1b). P2 has seen a rise in acidity in the first two sampling periods during 2014 (Figure 2b).

In combination with the observed decrease in acidity, was the consistent increase in alkalinity over all four piezometers in 2013 (Figure 2c). In January 2013, P2 had recorded its highest (although very modest alkalinity total) of 14 mg/L since monitoring. By September, alkalinity had reached 111 mg/L, after the first four consecutive recordings of alkalinity in the groundwater. P3 has also shown a gradual rise in alkalinity beginning in January 2014 and peaking at 165 mg/L in September (Figure 2c). Since January this year, alkalinity in Campbell Park has declined however, recording an average of just 15 mg/L over March and June in P2, P3 and P4.

Continuing historical trends, electrical conductivity had generally decreased at most sites in early to mid-2013, but only slightly (Figure 2d). In September 2013, EC dropped significantly in all four piezometers from June, most significantly in P2 (from 28,000 to 22,000 uS/cm) and P3 (from 15,000 to 6,830 uS/cm). Salinity picked up again by mid-December, with P2 and P3 showing some consistency in trends (Figure 2d). The exception to the generally decreasing or stable trends is P2, which reached its highest EC reading (29,500 uS/cm) since monitoring commenced (Figure 2d). Electrical conductivity has continued to decline into the 2014 monitoring period in P1 and P4.

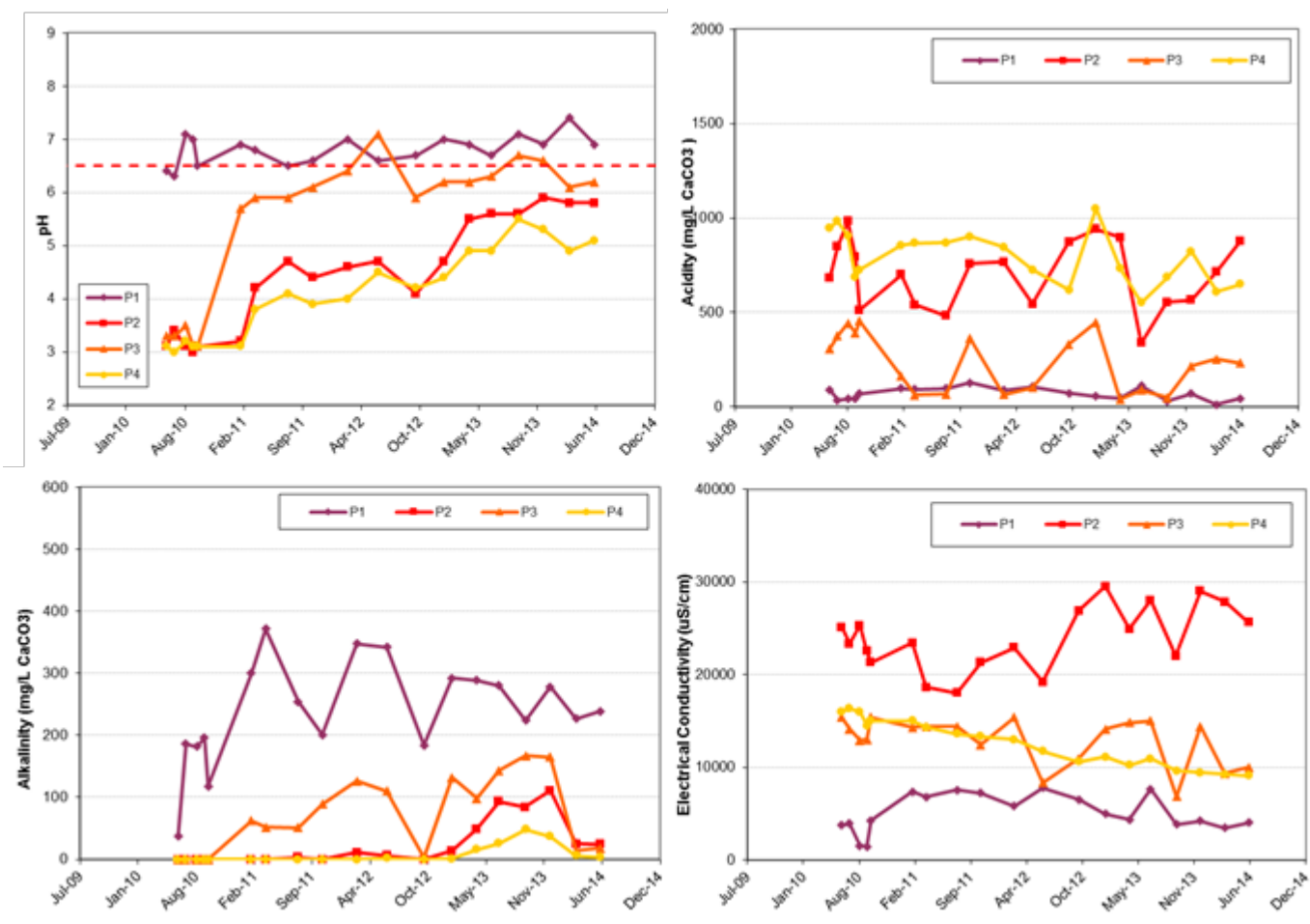


Figure 2 Laboratory parameters from four piezometers (P1 to P4) in Campbell Park—(a) pH, (b) acidity, (c) alkalinity and (d) electrical conductivity.

The AI in Campbell Park showed a marked reduction in 2013, especially in the last several sampling periods (Figure 3a).

AI in P1 and P3 had been below 2.0 mg/L (0.722 and 1.82 mg/L respectively) for the first time since monitoring began, and remained low until the latest monitoring in December 2013. AI at P2 and P4 had remained above the ANZECC guidelines, but had dropped from 32 and 7.76 mg/L in January 2014 to 0.345 and 1.38 mg/L respectively. All four piezometers are still above the ANZECC (2000) guideline of 0.055 mg/L for AI, but have clearly shown a marked improvement since 2012.

Two piezometers (P1 and P3) declined below the ANZECC guideline for Mn (1.9 mg/L), with levels reaching 0.54 and 1.33 mg/L respectively in September 2013 sampling, rising to 1.35 and 2.79 mg/L in December the same year. Mn in P2 and P4 remained variable, consistent with historic values, falling to 9.46 and 6.91 mg/L in September 2013 respectively, before all piezometers uniformly increased in December (Figure 3b).

The presence of Fe has become increasingly abundant across two of the four piezometers, specifically the two which have recorded the highest levels of acidity. Levels of Fe in P2 were almost five times as high in September 2013 (283 mg/L) compared to drought conditions (50.4 mg/L) in August 2009 (Figure 3c). Large spikes were observed in Fe concentrations, more than any other parameter (Figure 3c), and have remained around 300 mg/L into 2014. In January 2013, P2 recorded its highest spike in Fe, reaching 573 mg/L, when compared to a long-term average of 168 mg/L over the previous two years. Fe remains well above ANZECC guidelines (Fe = 0.3 mg/L) in all but one piezometer, with P1 (the piezometer closest to shore) reaching as low as 0.02 mg/L in September 2013.

Despite a recent increase in Fe concentrations in P3, and large concentrations in P2 and P4, piezometer 1 has maintained a negligible iron reading since monitoring began. Concentrations of AI, Mn, and Fe remained greatest in piezometers which have the highest levels of acidity (such as P2 and P4).

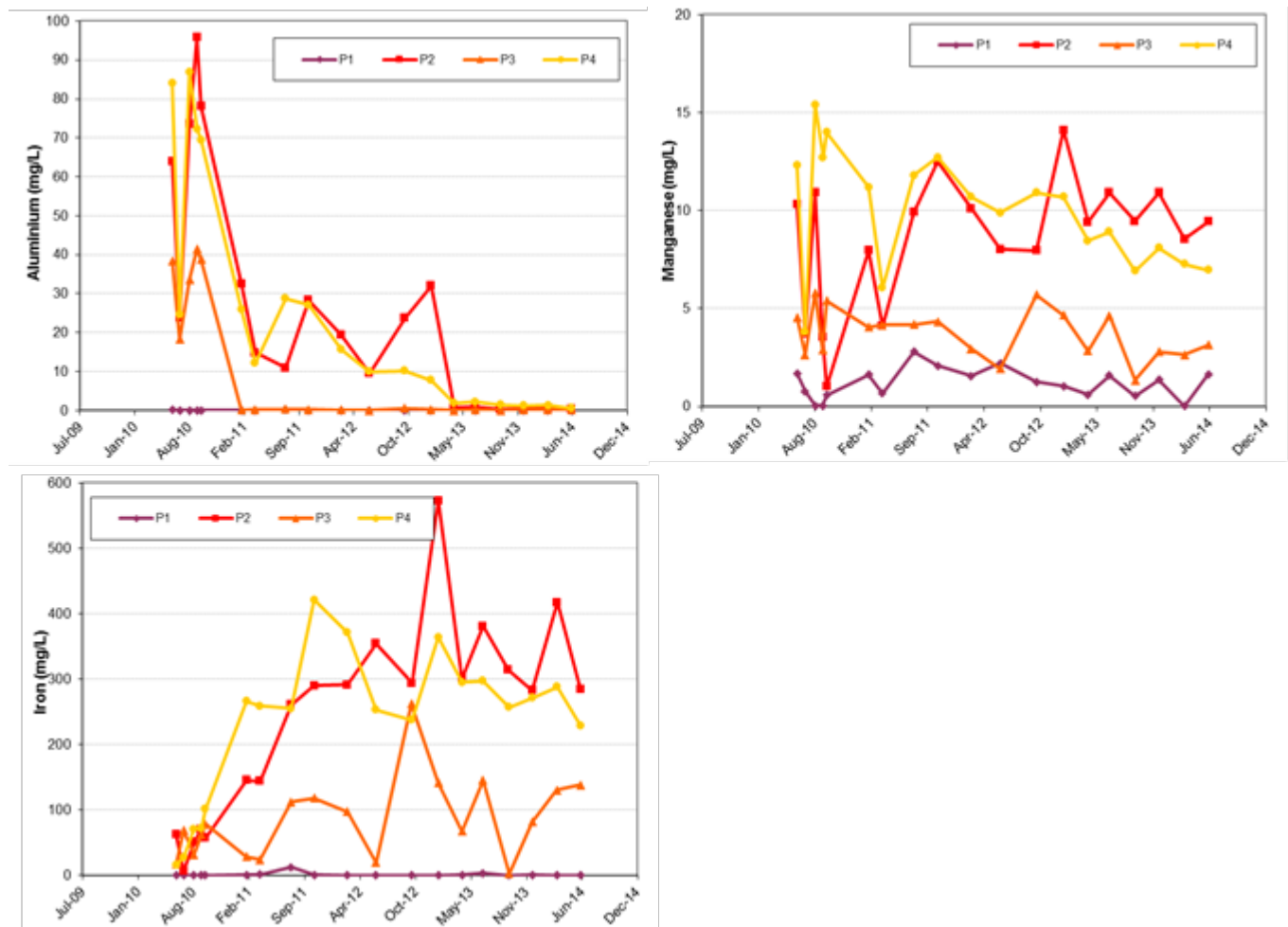


Figure 3 Soluble metals from four piezometers (P1 to P4) in Campbell Park—(a) aluminium, (b) manganese and (c) iron.

3.2 Point Sturt (Lake Alexandrina)

In the last 12 months, the pH of groundwater has remained consistent across all three piezometers in Point Sturt. P1 and P3 remain above the ANZACC guideline of 6.5, and maintained average values of 6.96 (+0.13) and 7.26 (+0.2) for 2013. The more acidic piezometer (P2) became more variable (Figure 4a) in 2013, with an average of 4.28 (+0.35), still well below the ANZECC (2000) guideline of 6.5. In the first half of 2014, P2 showed no sign of consistent pH improvement toward ANZECC guidelines.

In relation to its low pH, P2 has much higher levels of acidity than the other two piezometers (Figure 4b). Despite an average of 842 mg/L between June 2009 and September 2013, pH dropped markedly in December, from 837 to just 51.5 mg/L. This drop did not last however, and increased back to a three-year high of 1,360 mg/L in June 2014. Acidity levels in P1 and P3 also dropped in 2013, to 21.3 and 31.4 mg/L respectively, but nothing not to the extent as changes observed in P2.

With such high acidity recorded in P2, it is no surprise little alkalinity was recorded in 2013 and 2014 with only very small quantities recorded in June and September 2013 of 5 and 2 mg/L respectively. This is markedly less than the relatively large average alkalinity in P1 and P3, of 123 and 262 mg/L respectively for 2013 (Figure 4c). After peaking at around 400 mg/L in May 2011, alkalinity continued to decline in P1 down to a low of 72 mg/L in October 2012. During 2013, alkalinity stabilise in P1 around 123 (+11.4) mg/L, with limited temporal variation.

Electrical conductivity in P2 fell sharply in December 2013, but no other piezometer recorded a decrease. Electrical conductivity actually increased in P3. This drop in salinity was out of character for the site, which has maintained constant salinity in all groundwater piezometers since monitoring began in June 2010. Considering the rise in salinity in

P3 at the same time, the reasons for the rapid decline in P2 is difficult to interpret, but may be due to surface water ingress into the piezometer. During March and June 2014, salinity increased back to baseline conditions, supporting the hypothesis of fresh surface water ingress.

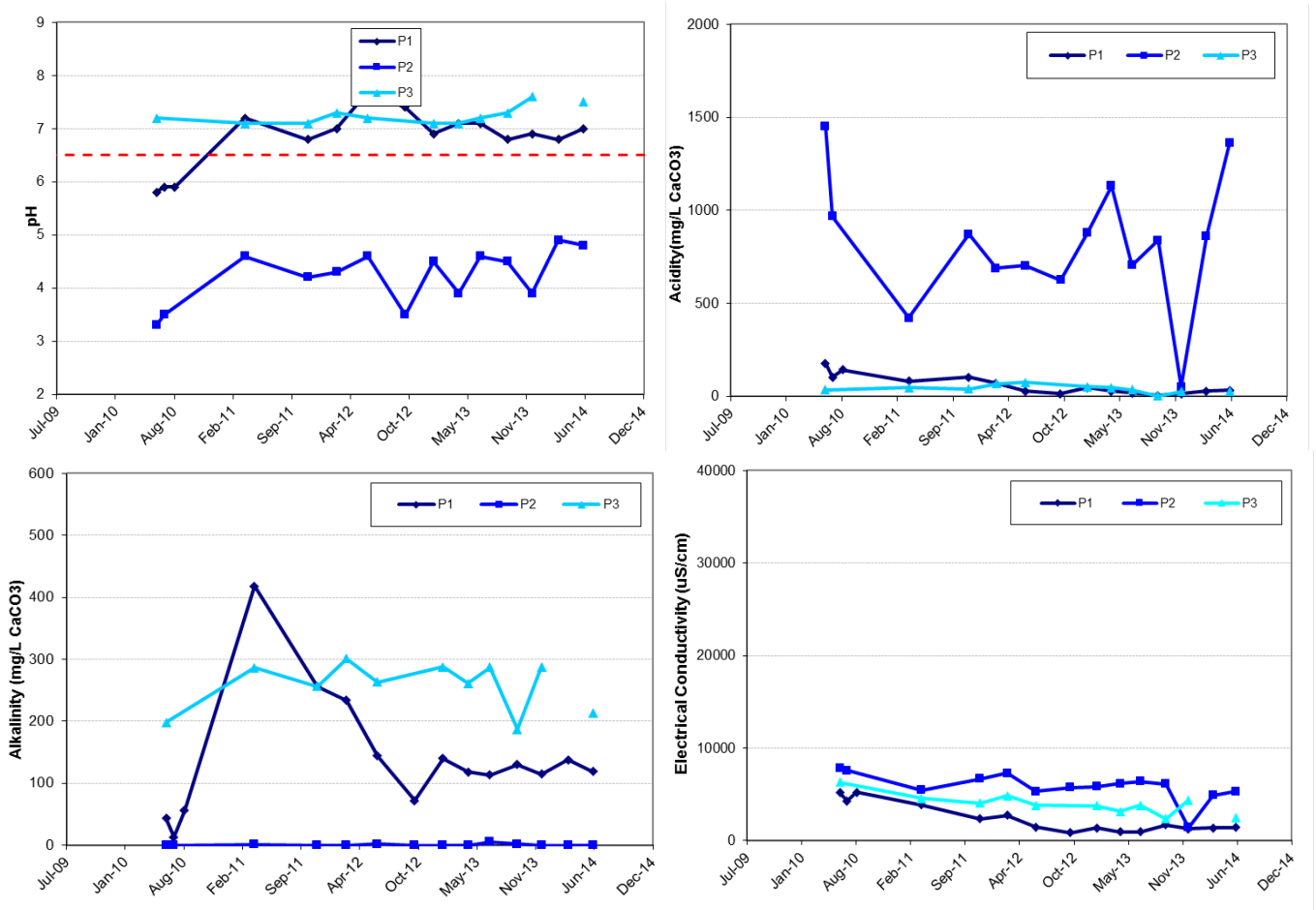


Figure 4 Field parameters from four piezometers (P1 to P4) in Point Sturt—(a) pH, (b) acidity, (c) alkalinity and (d) electrical conductivity.

Soluble metals were highest in the acidified P2, but showed some unique individual characteristics. Soluble Al (Figure 5 showed the most consistency among soluble metals, averaging 11.7 (+7.13) mg/L over 2013. By the end of 2013, Al had dropped to 1.23 mg/L in December. This was a historical low for Al, with the previous low of 9.37 mg/L recorded in April 2011.

Mn continued to show the highest variation between sampling periods compared to any of the soluble metal concentrations (Figure 5b) in Point Sturt. After maintaining an average of 20.4 (+1.7) mg/L with little variability, a sudden drop to 4.20 mg/L in late 2012 has seen values continue to vary erratically, with an average of 15.9 (+7.5) mg/L in 2013. This has not ceased in 2014, with a value of 5.8 mg/L in December 2013 rising to 16.8 mg/L in June 2014.

Fe followed suit, with concentrations maintaining a consistent average of 172 mg/L throughout 2012, dropping to 98 mg/L in October 2012. After falling to this recorded low, variability increased in subsequent sampling throughout 2013 (Figure 5).

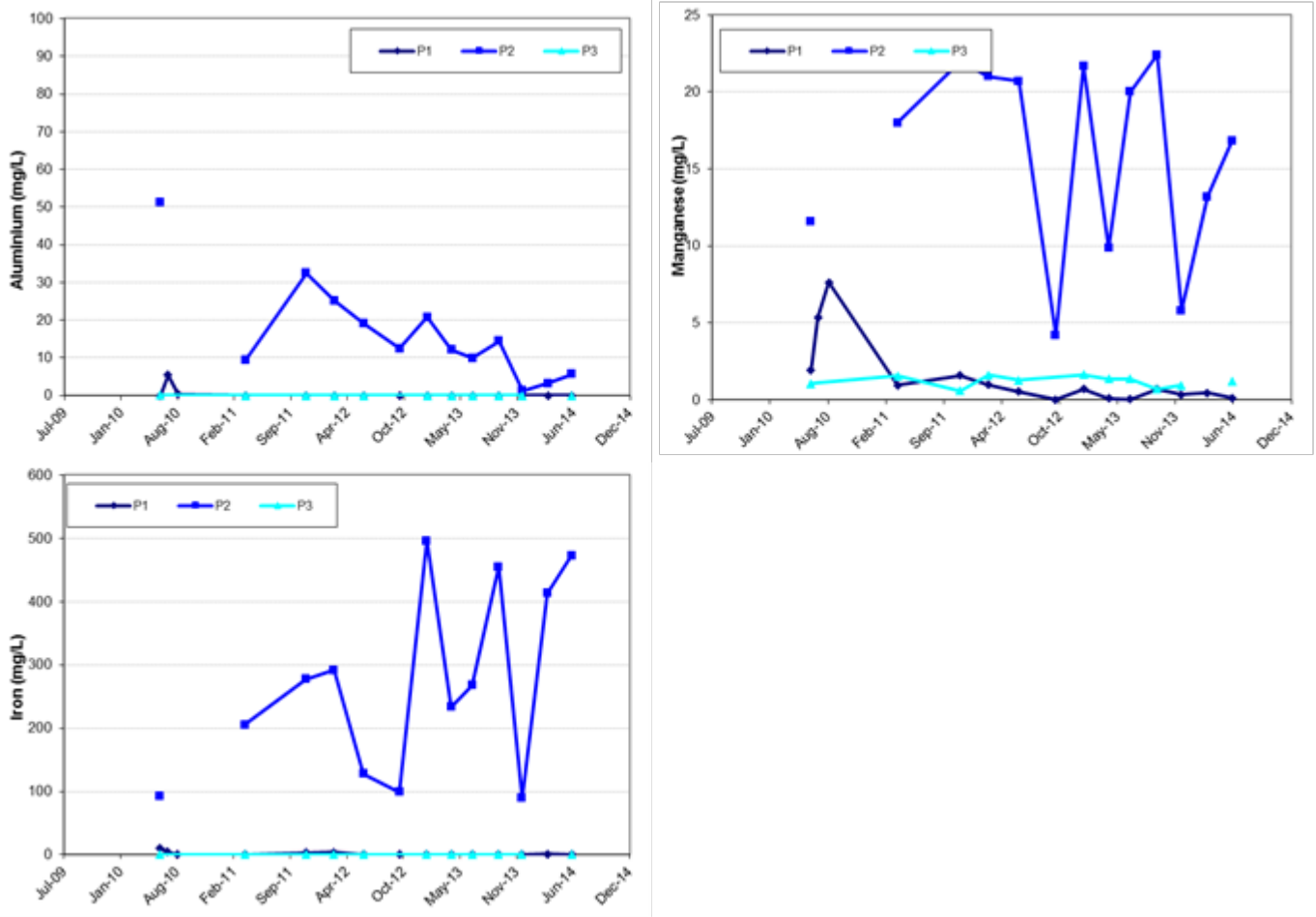


Figure 5 Soluble metals from four piezometers (P1 to 4) in Point Sturt—(a) aluminium, (b) manganese and (c) iron.

3.3 Currency Creek (Tributaries)

During 2013, two out of three Currency Creek piezometers (P1 and P3) maintained an average pH just below ANZECC guidelines of 6.36 and 6.24 respectively. These values were consistent with 2012, with the variation between the two piezometers becoming closer now (Figure 6a) than ever before. The pH in the piezometer situated at the midpoint of Currency Creek, P2, has decreased considerably, from an average of 5.4 between January and June 2013, to a pH of 3.6 in September. This late-year decrease in 2013 has risen back to above pH guidelines in June, averaging a record high 195 mg/L across the three piezometers.

Corresponding with the considerable drop in pH was an equal increase in acidity in P2 (Figure 6b). All piezometers were remarkably similar during 2012, but acidity levels became more variable between piezometers during 2013, with P2 showing a large spike late in the year. Acidity was recorded up to 1,140 mg/L, up from an average of 314 mg/L between January and June. Subsequent monitoring in December 2013 recorded a drop back down to 85.5 mg/L, closer to acidity levels recorded early in the year. An average acidity of 102 mg/L has been maintained over the three piezometers into 2014.

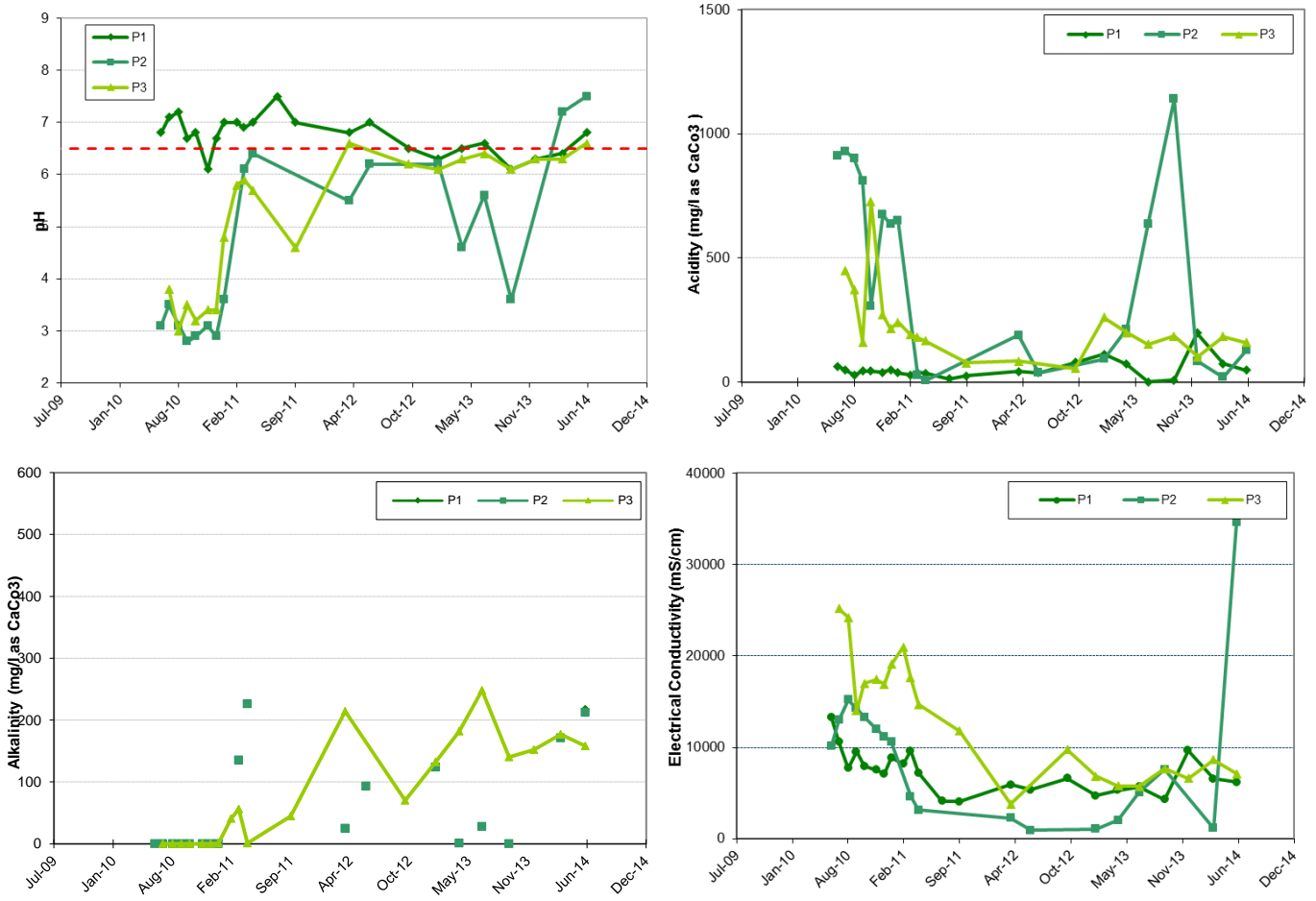


Figure 6 Field parameters from four piezometers (P1 to P4) in Currency Creek—(a) pH, (b) acidity, (c) alkalinity and (d) electrical conductivity.

Between June 2010 and January 2011, alkalinity was not recorded in Currency Creek P2 and P3 (Figure 6c). After January 2011, P2 alkalinity rose consistently to average 120 mg/L over the following 12 months. After January 2013 however, alkalinity fell to an average of just 9.6 mg/L. P3 on the other hand, rose to a similar post-drought average of 106 mg/L since January 2011, without suffering a fall observed in P2. Alkalinity has now become consistent between piezometers, with an average of 195 mg/L in June 2014.

Electrical conductivity has also increased in the last 12 months, with the increases occurring equally across all three piezometers (Figure 6d). Despite the dramatic increase in salinity in P2 into 2014, we believe this is a systematic error, and does not truly represent salinity in Currency Creek P2.

In December 2013, a sufficient sample volume could not be withdrawn from P2. The laboratory could not test for all parameters, and excluded some tests such as pH, but tested for parameters such as acidity. We could infer the trend of falling pH may not have continued into December, and some recovery is predicted in the next quarterly sampling event in 2014, considering the spike in acidity has now reduced to pre-April concentrations (Figure 6b).

Despite the sharp rise in acidity in September 2013, Al did not increase in P2 nor any other piezometer (Figure 7a), all staying below the ANZECC guidelines (<0.0055 mg/L).

Mn increased during 2013 in P1 and P2, together averaging 0.17 mg/L in 2012 compared to 0.86 mg/L in 2013. P3 on the other hand actually decreased in 2013, from an average of 3.18 mg/L in 2012 to 1.78 mg/L across 2013 (Figure 7b).

Fe was the only soluble metal while the trend corresponded to the large acidity spike in P2 during September, increasing from 3.16 mg/L in January to 555.1 mg/L in September, only to fall back to 0.303 mg/L three months later (Figure 7c).

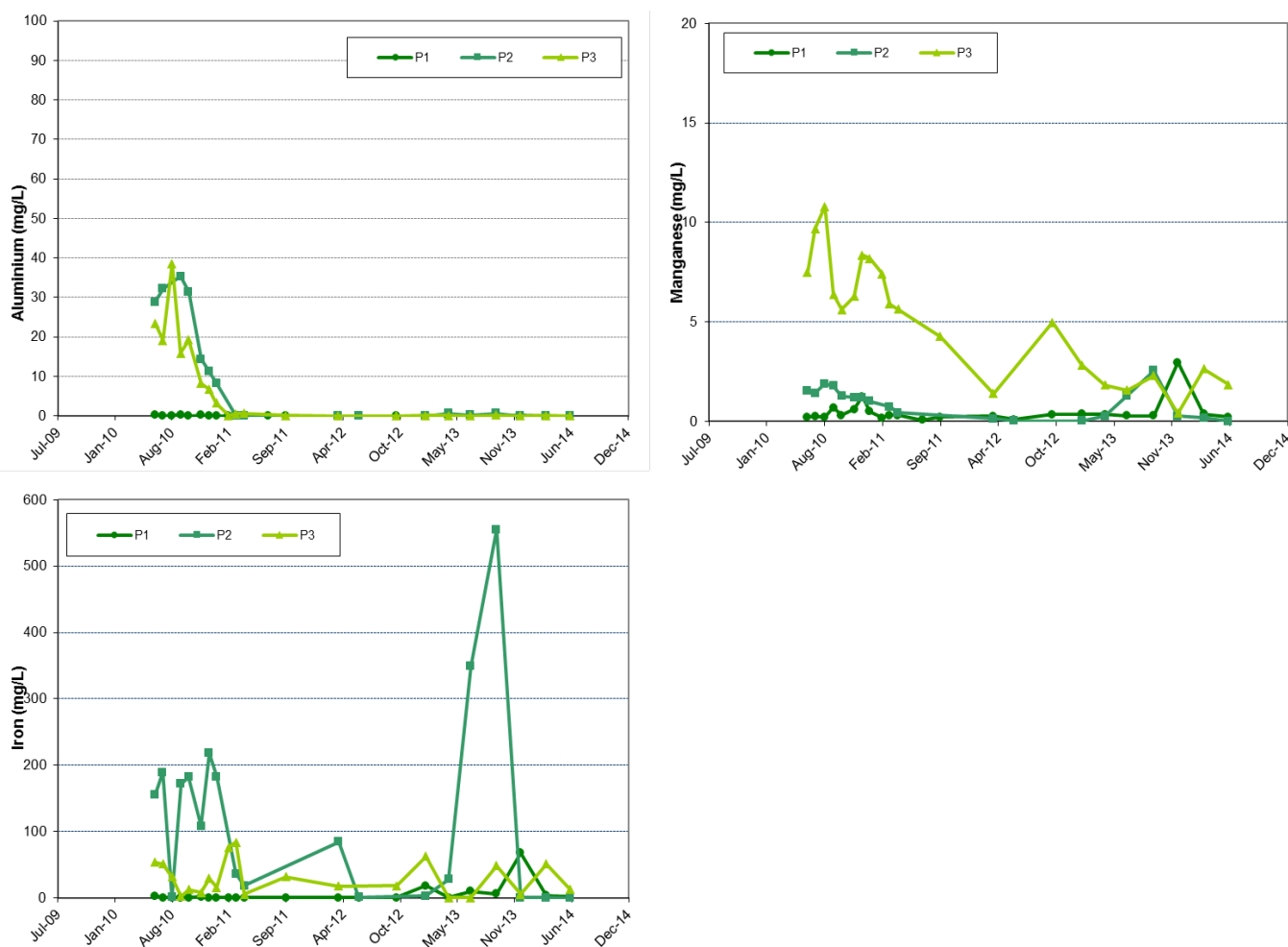


Figure 7 Soluble metals from four piezometers (P1 to P4) in Campbell Park—(a) aluminium, (b) manganese and (c) iron.

Variation in alkalinity of groundwater might be influenced by the reduction of sulfate (Sullivan *et al* 2011), and this was assessed via a sulfate:chloride ratio (Figure 8). The sulfate:chloride ratio has remained markedly constant in Campbell Park (Figure 8a) and Currency Creek (Figure 8c) since July 2010, with a spike in Currency Creek P2 in June 2013. This was observed in conjunction with the increase in acidity within the piezometer in June, and would likely indicate an increase in the oxidation of pyrite.

There are no indications of reducing sulfate:chloride ratios that would indicate sulfate reduction is occurring. Point Sturt (Figure 8b) has the largest variation in the sulfate:chloride ratio of any site, but the ratios in these piezometers have become more stable over the last few years. Spikes of a similar magnitude to that of Currency Creek P2 occurred throughout Point Sturt P1 during 2013, but did not correspond with increases in acidity.

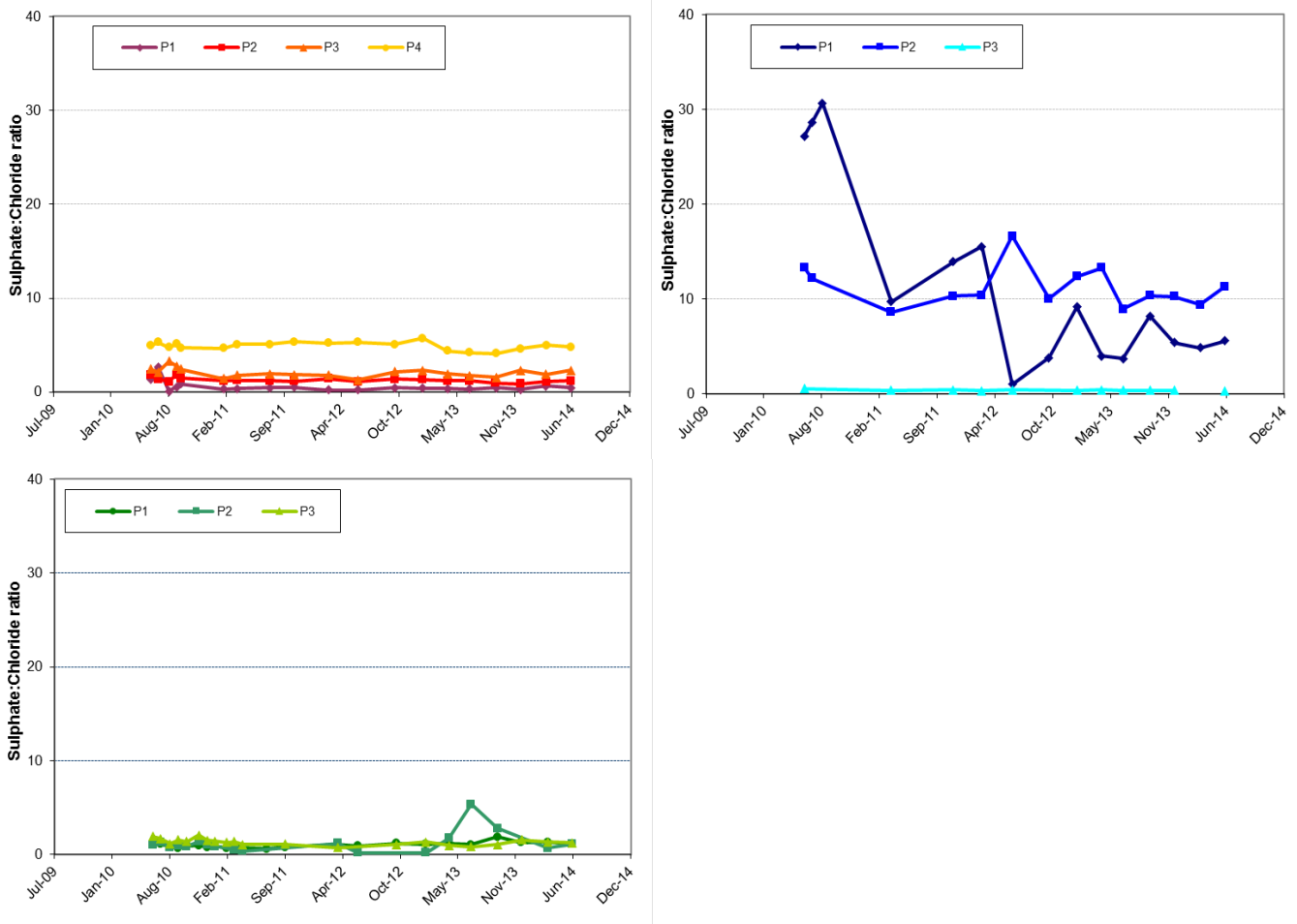


Figure 8 The sulfate:chloride ratio in (a) Campbell Park, (b) Point Sturt and (c) Currency Creek.

After the drought, the oxidative reduction potential (ORP) became increasingly stable, with ORP shifting from strong fluctuating peaks upwards of 200 mV, to below an average of -66.6 mV in Campbell Park (Figure 9), -23.6 mV in Point Sturt (Figure 9) and -34.9 mV in Currency Creek (Figure 9) across 2013. The consistent but slow trends towards more negative values indicate the sediments and groundwater had shifted from a highly oxidising state to a more reducing state, with less recent variability between piezometers than observed in the past.

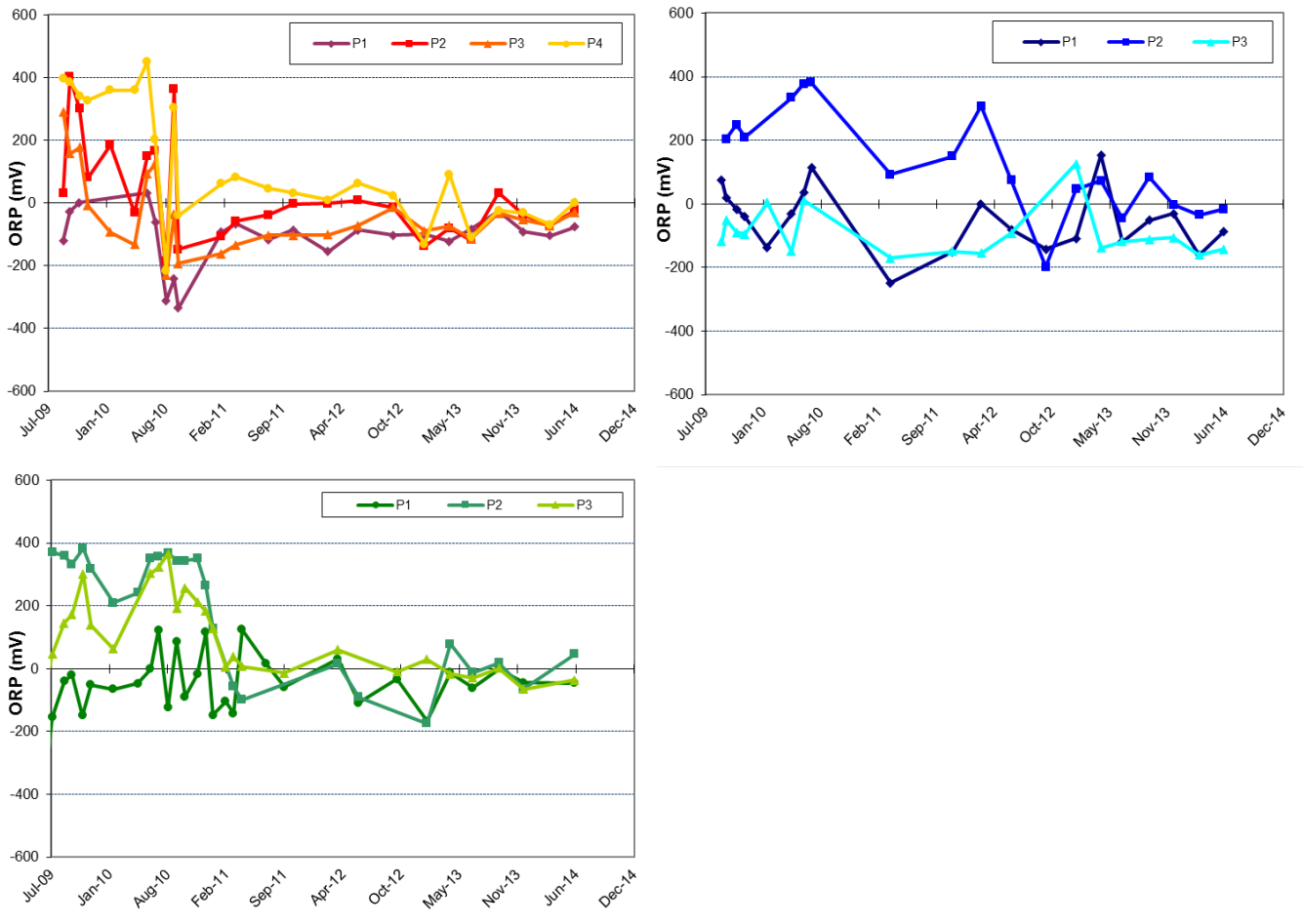


Figure 9 The oxidative reduction potential (ORP) of groundwater in (a) Campbell Park, (b) Point Sturt and (c) Currency Creek. Oxidative reduction potential is represented here by field sampling, and is the only parameter within this report which cannot be verified by laboratory sampling.

4 Discussion

Strong variation exists between sites and among piezometers in the Lower Lakes, with numerous piezometers remaining acidic throughout 2013 and into 2014. There was evidence of residual acidity in all four piezometers in Campbell Park, even though average acidity in 2013 decreased from 2012. This was associated with what was perhaps the most consistent rise in pH among piezometers at any monitored site. This was in direct contrast to Currency Creek, where pH in all piezometers had declined from a high in early 2012, to a large, unexpected and sustained drop in pH at a single piezometer, from 6.2 in January to 3.6 in September, its lowest recorded pH in almost two years.

This led to a large spike in acidity and dissolved Fe, recording a figure higher than at anytime during the drought. Other piezometers at Currency Creek maintained an average pH value consistent with the previous recovery year, but residual acidity was still detected and had increased. Point Sturt piezometers were similar to those in Currency Creek, which showed consistent pH in post-recovery years. But unlike Currency Creek where residual acidity increased, acidity dropped to record low levels.

Alkalinity showed similar variation between sites, with Campbell Park showing a strong and gradual increase in alkalinity, even in piezometers which have had little to no alkalinity since monitoring began part way through 2010. Currency Creek sites showed much more variability, where one piezometer reached both a record high and low alkalinity in 2013 while two other piezometers varied strongly from quarter to quarter.

Compared to the other sites, alkalinity at Point Sturt showed remarkable consistency in previous years. Alkalinity increases may be due to several possible reasons including diffusion and advection of alkaline lake water into the groundwater and sulfate reduction (Sullivan *et al* 2011). With alkalinity still persistent and even increasing in the overlying surface waters of Lake Alexandrina, Lake Albert and Currency Creek, we would predict the continual sequestration of alkalinity into shallow sediment, and eventually aiding recovery deeper in the depth profile.

For sulfate reduction to be favorable there needs to be highly reducing conditions present in the groundwater and the absence of other more favourable electron acceptors such as oxygen, nitrate, and Fe and Mn oxides. Since 2009, the oxidative reduction potential (ORP) of groundwater at all sites had shifted from a heavily oxidising state to a more reducing state. However, the ORP values are still above those which are generally indicative of sulfate reduction (-400 mV ORP ≈ -200 mV Eh). This coupled with the relatively stable sulfate:chloride ratios, suggest Fe oxide/oxyhydroxy sulfate mineral reduction processes, rather than sulfate reduction is occurring deeper in the Lower Lakes sediment and groundwater.

There may also be insufficient labile carbon in the deeper sediments (ie no fresh carbon has been resupplied since drought unlike surface sediment where revegetation and lake productivity cycles resupply carbon) to drive the system far enough towards sulfate reducing conditions. Sulfate reduction might also be prevented by the low pH (<5 , Jong & Parry 2006) in some piezometers. It is interesting to also note, in both 2012 and 2013 monitoring, increases in pH and alkalinity were most common in Campbell Park, and was not previously associated with high levels of organic matter or sulfate reduction (Sullivan *et al* 2011). A piezometer in Currency Creek showed a large but temporary spike in the sulfate:chloride ratio, corresponding to the increase in acidity in that piezometer, which could indicate more oxidation of pyrite. It is unclear why this has occurred but would suggest the temporary presence of oxygen or nitrate in the system.

Metals such as Al, Mn and Fe still remain variable, with most remaining above the ANZECC guidelines (2000) throughout 2013. At Campbell Park, Al fell below the ANZECC guideline of 0.055 mg/L twice in 2013 (only happening once before, after monitoring began in 2009) and had declined on 2012 averages, along with Mn and Fe. The increase in pH >5 likely resulted in the substantial decrease in Al as little Al is in soluble form above this pH (Bigham & Nordstrom 2000).

Fe and Mn are redox sensitive metals and under reducing conditions may remain in soluble form over a wider range of pH values. Point Sturt showed the most consistent metal concentrations, with Al and Fe in all piezometers remaining below the ANZECC guidelines since May 2012. Only one of the three piezometers in Point Sturt remained above the guideline of 1.9 mg/L for Mn. Groundwater throughout Currency Creek had a large spike in soluble metals during 2013. Despite falling below the guidelines in September 2011, Al spiked in multiple piezometers in April and September 2013,

falling below the guideline of 0.055 mg/L in December 2013. P1 in Currency Creek has not spiked in Al, but has had a constant increase in soluble concentrations since April, and breached the ANZECC guidelines to protect aquatic ecosystems in December. Despite all three Currency Creek piezometers being below the Mn guideline in 2012, measurements peaked in late 2013, with strong variation between piezometers.

Iron was another metal to rise above the ANZECC guidelines in 2013, but all three piezometers remain extremely variable and have not declined below the guideline of 0.3 mg/L for the protection of aquatic ecosystems. These spikes in metal concentrations do not necessarily correspond to a drop in pH at the same piezometer, and are surprising given 2012 data, where a stronger recovery was predicted on improving pH. As noted in previous reports, we believe the reductive dissolution of Fe and Mn oxides, and Fe oxyhydroxysulfate minerals such as jarosite, were leading to the observed high levels of these metals in groundwater.

In terms of risk to surface water arising from the acidified groundwater, the flux of acidity and metals between groundwater and surface water was previously estimated using models and the risk of major impacts was predicted to be low at current water levels/flows (Cook *et al* 2011, Cook & Mosley 2012). In 2013, the EPA used benthic flux chambers (Hamilton *et al* 2013) which directly measured acidity and metal flux between sediment, surface and groundwater in two acidification hotspots on Hindmarsh Island.

The benthic chambers isolated external alkalinity inputs from surface waters, and despite small increases in the flux of acidity and minor drops in pH, the chambers did not acidify. This was likely due to a concurrent alkalinity flux from the sediments to surface water due to sulfate reduction (Shand *et al* 2010) in the shallow organic-rich sediments. Metals (including Mn, Al and Fe) were also fluxing from sediment into surface water (Hamilton *et al* 2013). Increases in ammonia and filterable reactive phosphorous in benthic chambers, along with oxygen consumption and a decrease in nitrate would be indicative of organic matter mineralisation, nitrification and denitrification processes.

While risks to surface water remain low, the persistent low pH and acidity, and presumed lack of sulfate reduction in deeper sediments are concerning as there has already been a long timescale over five years of recovery from the 2007–09 drought. If you considered Campbell Park alone, it appears to be an ideal site indicative of recovery. All piezometers had a gradual rise in pH over the two years post inundation, which promoted further reduction in acidity; likely by encouraging internal alkalinity generation through bacterial processes (Shand *et al* 2010).

This is not reflected across any other site however, and the sheer variation of results between piezometers and among sites suggests this studies' experimental design (replication not only at the site level, but not piezometer level) adequately captures groundwater dynamics.

Predictions from the previous years' monitoring suggested the process of recovery would be slow, considering the persistent high levels of acidity. The evaluation has not changed with monitoring results from 2013, especially considering the lack of an observable decrease in acidity.

We prefer not to make predictions of full recovery timescales, even at a site to site level, based on the large small-scale variation between individual piezometers. A key question is how resilient will the site be to future droughts, particularly if recovery from the 2007–09 drought is incomplete.

5 Conclusion

This monitoring program has demonstrated the continued presence of acidic conditions in groundwater post-drought in the CLLMM region, metals which remain above ANZECC (2000) guidelines for healthy ecosystems and a variable recovery pattern indicated by inconsistent rises and falls in pH and alkalinity.

Natural remediation via downward advection and diffusion of alkalinity from lake water is likely occurring but it appears unlikely sulfate reduction is occurring. We recommend continued groundwater monitoring throughout Campbell Park, Currency Creek and Point Sturt. This groundwater data provides a unique opportunity to quantify temporal and spatial recovery after severe drought, and will inform management decisions during future drought conditions.

6 References

- ANZECC 2000, *Australian and New Zealand guidelines for fresh and marine water quality*, Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- APHA 2005, *Standard methods for the examination of water and waste water*, American Public Health Association, American Water Works Association and Water Environment Federation, District of Columbia.
- Appelo CAJ & Postma D 2005, *Geochemistry, groundwater and pollution*, Balkema Publishers, Netherlands.
- Bigham JW & Nordstrom DK 2000, 'Iron and aluminium hydroxysulfates from acid sulfate waters', *Reviews Mineral Geochemistry* 40:351–403.
- Cook FJ, McLachlan G, Leyden E & Mosley L 2011, *Physical properties of soils/sediments of Lower Murray Lakes and modelling of acid fluxes*, CSIRO: Water for a Healthy Country National Research Flagship, 60 pp, viewed 12 November 2014, www.clw.csiro.au/publications/waterforahealthycountry/2011/wfhc-LowerMurray-acid-fluxes.pdf
- Cook FJ & Mosley LM 2012, *Modelling of acidic solute fluxes from sediments to the water column in the Lower Lakes of South Australia*, prepared by Freeman Cook & Associates and the South Australian Environment Protection Authority for the Department of Environment, Water and Natural Resources, Adelaide, viewed 12 November 2014, www.environment.sa.gov.au/files/006f96bc-f53f-405a-b9bd-a0d60100da17/cllmm-gen-modellingacidicsolutereport.pdf
- DENR 2010, *Acid sulfate soils research program summary report*, prepared by the Lower Lakes Acid Sulfate Soils Research Committee for the Department of Environment, Water and Natural Resources, Adelaide.
- Earth Systems 2009, *Quantification of acidity flux rates to the Lower Murray Lakes: final report*, prepared by Earth Systems Pty Ltd for the Department of Environment, Water and Natural Resources, Adelaide.
- Fitzpatrick RW, Grealish G, Chappell A, Marvanek S & Shand P 2010, *Spatial variability of subaqueous and terrestrial acid sulfate soils and their properties for the Lower Lakes South Australia*, CSIRO Land and Water report, viewed 12 November 2014, www.environment.sa.gov.au/Conservation/Rivers_wetlands/Coorong_Lower_Lakes_Murray_Mouth/The_environment/Acid_sulfate_soils/Research_projects/Acid_Sulfate_Soils_Research_Program_reports
- Hamilton BM, Mosley L, Stone D & Zammit B 2013, *Measurement of sediment acidity fluxes to Boggy and Hunters Creeks*, prepared by the South Australian Environment Protection Authority for the Department of Environment, Water and Natural Resources, Adelaide, 40 pp, viewed 12 November 2014, www.epa.sa.gov.au/xstd_files/Water/Report/fluxes_boggy_hunters_creeks.pdf
- Johnston D 2007, *EPA Guideline: Regulatory monitoring and testing groundwater sampling*, South Australian Environment Protection Authority, Adelaide, viewed 12 November 2014, www.epa.sa.gov.au/xstd_files/Water/Guideline/guide_gws.pdf
- Jong T & Parry DL 2006, 'Microbial sulfate reduction under sequentially acidic conditions in an upflow anaerobic packed bed bioreactor', *Water Research* 40:2561–2571.
- Mosley LM, Zammit B, Jolley AM & Barnett L 2014, 'Acidification of lake water due to drought', *Journal of Hydrology* 511: 484–493.
- Shand P, Merry RH, Grocke S, Thomas M, Fitzpatrick RW, Thomas B, Jayalath N & Creeper N 2010, *Water and soil quality impacts during reflooding of Nelwart Lagoon, South Australia*, CSIRO Land and Water report for the South Australian Murray Darling Basin Natural Resources Management Board, Adelaide.

Sullivan LA, Burton ED, Ward NJ, Bush RT, Coughran J, Cheetham MD, Fyfe DM, Cheeseman PJ & McIntyre T 2011, *Lower Lakes sulfate reduction study*, Southern Cross Geoscience Technical Report 711, prepared for the South Australian Department of Environment, Water and Natural Resources, Adelaide.