

Acid Sulfate Soils **Research Program**

Summary Report | October 2010





Australian Government



Government of South Australia

WATER EGOOD

For further information please contact:

Email:	cllmm@deh.sa.gov.au
Phone:	1800 226 709 (free call during normal business hours)
Post:	Coorong, Lower Lakes and Murray Mouth Program Department of Environment and Natural Resources Reply paid 1047 ADELAIDE SA 5001
Website:	www.environment.sa.gov.au/cllmm

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Printed on recycled paper October 2010 ISBN 978-1-921735-06-6

Citation

This report should be cited as:

DENR 2010, *Acid sulfate soils research program summary report*. Prepared by the Lower Lakes Acid Sulfate Soils Research Committee for the SA Department of Environment and Natural Resources, Adelaide.

Cover image

Currency Creek, June 2009 (DENR 2009)

Acid Sulfate Soils Research Program Summary Report

L. Mosley, L. Barnett, J. Cugley, R. Bush, R. Fitzpatrick, W. Hicks, M. Hipsey, S. Pape, R. Seaman, P. Shand, L. Sullivan and J. Taylor

Prepared by the Lower Lakes Acid Sulfate Soils Scientific Research Committee for the SA Department of Environment and Natural Resources, as part of the South Australian Government's \$610 million Murray Futures program funded by the Australian Government's Water for the Future initiative.

October 2010





Acknowledgements

We thank Colin Grundy, Mike South, Anne Hartnett for allowing access through their land and assistance with field sampling and experimentation.

Funding for this project, through the South Australian Government's \$610 million Murray Futures program, by the Australian Government's Water for the Future initiative is gratefully acknowledged.

We also thank various government agency staff, Ann-Marie Jolley (DENR), Benjamin Zammit (EPA), Clive Jenkins (EPA), and Shaun Thomas (EPA) for their assistance.

Executive Summary

Extensive areas of acid sulfate soils have been exposed in the Lower Lakes as a result of unprecedented low water levels. This has resulted in soil acidification (pH<4) over large areas. Acidification of surface waters has also occurred in some localised areas where acidity has been transported from the soil profile.

To inform management decision making, a research program has been undertaken to fill critical knowledge gaps related to the risks posed by exposure of acid sulfate soils in the Lower Lakes. Five research areas were examined:

- an acid sulfate soil spatial heterogeneity/mapping survey
- measurement of acid generation rates
- assessment of the in-situ contaminant generation, transport and neutralisation processes
- laboratory and field studies of the potential for mobilisation of contaminants following inundation with seawater compared to river water
- geochemical modelling of lake water quality.

Detailed findings from these projects will be published in separate reports. This report is a summary of the major findings from these studies.

In addition to these research projects, air quality monitoring was undertaken to assess possible community health impacts arising from the exposure of acid sulfate soils.

Key Messages

The key messages from the research projects undertaken to date are:

- There is an extensive and considerable long-term acid sulfate soil hazard in the Lower Lakes.
- Acidity is being generated rapidly in drying sandy and clayey lake margins, increasing the risk of waterbody acidification when rewetted.
- The exposure of clay-rich sediments in the deeper inundated regions must be avoided.
- The use of fresh water as a management option to keep sediments submerged is a lower risk than seawater.

Major findings

The research program has greatly increased the knowledge of acid sulfate soils in the Lower Lakes and how to manage them. The major findings of the work undertaken are as follows:

- There is a large variability, or heterogeneity, in soil properties. Acid sulfate soils comprising sulfuric materials with severe acidification (pH <4) have occurred over a large area around the margins (18,389 ha, which accounts for about 20% of the 89,219 ha in the Lower Lakes). Acid sulfate soils comprising potential (hypersulfidic and hyposulfidic materials) acidity are also widespread throughout the Lower Lakes study area (up to 70,829 ha). The highest net acidities (>500 mol H⁺/tonne) are in the clay-rich sediments in the middle of Lakes Albert and Alexandrina.
- The rate of oxidation of the acid sulfate soils was found to be high with up to 2% of available pyrite able to be oxidised per day in the sandy sediments.
- Acidity, metals and nutrients already mobilised are being transported to the lakes via shallow groundwater processes following major rainfall events. However, there is a complex flux pattern due to influences of lake seiching (ie wind driven movement of water across the lakes) and other factors; while sandy sediments generally have lower available acidity compared to clay-rich sediments, they are more permeable so have a greater ability to flux contaminants.

- In field and laboratory experiments, introducing seawater on soils with sulfuric materials (pH <4, which formed by oxidation of exposed hypersulfidic material) increases contaminant (acid, metal, metalloid and nutrient) release compared to freshwater. This occurs, despite seawater having a greater alkalinity than river water, due to the higher salinity of seawater mobilising acidic cations off the sediment.
- Data from this research and other monitoring projects have been combined to refine the existing hydrodynamic geochemical 3-D model (ELCOM-CAEDYM). This includes model calibration using data from the Currency-Finniss region before, during and after the acidification events that occurred around April to June 2009.
- The model simulations suggest that fringing regions around both lakes (in addition to those already acidified) are susceptible to acidification in response to local drying and large rainfall events as early as autumn 2010.
- The modelling indicates broad-scale acidification of Lake Albert at water levels of -0.75 m AHD or below, whereas for Lake Alexandrina, this could occur after 2012 if water levels are maintained below -1.75 m AHD due to acidity building up in the sediment and shallow groundwater.
- There was little difference in the overall rates of sulfate reduction (ie the process that neutralises acidity via the reformation of sulfide minerals in the soils) when seawater or river water was used to inundate soils in laboratory experiments. This appears to be due to relatively low organic carbon content in much of the sandy acid sulfate soils limiting the sulfate reduction rate.

The preliminary air quality monitoring results suggested a low risk to community health from breathing dust or drinking rain water. The dust was not acidic and there was little indication of elevated metal levels or presence of acid sulfate soil minerals. However, the risk level will change if water levels decline further, especially during the hot and dry summer periods. Monitoring and evaluation is ongoing.

Management implications

The main management implications of these findings are:

- Some exposed sulfuric (pH<4) materials from acid sulfate soil "hotspots" can be managed or treated locally. Various factors (with respect to acidity generation, neutralisation and transport processes) will determine the type and appropriateness of management actions required.
- The risk of broad-scale lake acidification is reduced if water levels are stabilised at or above <u>minus</u> 1.5 m AHD in Lake Alexandrina and <u>minus</u> 0.5 m AHD in Lake Albert¹. The risk profile substantially increases past these water levels and/or with prolonged time near these levels.
- While seawater addition is a valid option to prevent drying out and acidification of currently submerged sediments, it is a higher risk management option compared to freshwater as enhanced contaminant (acid and metals) mobilisation will occur over oxidised lake marginal sediments.
- Recovery of water quality following lake acidification could take months-years, whereas recovery from soil acidification will take much longer and achieving previous conditions may not be possible.

The acid sulfate soils research program has been highly successful in addressing essential information needs to underpin management of acidification risks in the Lower Lakes. As a consequence, greater certainty is provided for modelling and prediction of water management levels required to prevent acidification. The success of the program has also meant the identification of additional critical knowledge gaps. It is therefore

¹ It is important to continue soil and water quality monitoring to assess the accuracy of the model predictions and, due to their inherent uncertainty, to not rely completely on these predictions for management decisions.

recommended that research and monitoring particularly on acidity fluxes in clay-rich soils/sediments, localised surface groundwater interactions, and sulfate reduction/organic carbon cycling be continued.

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1 Introduction

1.1 Environmental context

The Coorong, Lower Lakes and Murray Mouth (CLLMM) region is recognised as one of Australia's most significant wetlands and is designated a wetland of international importance under the Ramsar Convention. The region is also very important culturally and economically for local communities. The Murray-Darling Basin has been experiencing the worst drought conditions in recent record, and the Coorong, Lower Lakes and Murray Mouth (CLLMM) are under extreme stress. The prolonged low flows out of the Murray-Darling catchment have been insufficient to counter evaporative losses from the large and shallow Lower Lakes. The consequence of this is that water levels have fallen over 1.5 m from pre-drought levels and are now approximately 1m below sea level.

The lowering water levels in the Lower Lakes have resulted in the extensive exposure of acid sulfate soils (Fitzpatrick et al. 2008a,b; 2009a,b). Acid sulfate soils accumulate under waterlogged conditions where there is a supply of sulfate, the presence of organic matter that can be metabolised and iron containing minerals (Dent 1986). Under reducing conditions sulfate is bacterially reduced to sulfide, which reacts with reduced iron to form iron sulfide minerals.

These sulfide minerals are generally stable under reducing conditions, however, on exposure to air the acidity produced from sulfide oxidation can impact on soil quality, water quality, crop production, and corrode concrete and steel structures (Dent 1986). In addition to the acidification of both ground and surface waters, a reduction in water quality may result from low dissolved oxygen levels when monosulfidic materials are mobilised into the water column (Sammut et al. 1993), through the release of high concentrations of aluminium and iron (Ferguson and Eyre 1999), and through the mobilisation of other potentially toxic metals and metalloids (Preda and Cox 2001; Sundström et al. 2002; Simpson et al. 2010). Mobilisation may also result in the release of nutrients into the water column (Sullivan et al. 2008) which can contribute to algal blooms.

Inundation with freshwater has often been proposed to improve the water quality in acid sulfate soil landscapes (Dent 1986), however, the response of acid sulfate soils to submergence is reported to be highly variable (Ponnamperuma et al. 1973; Tuong 1993; Konsten et al. 1994; Johnston et al. 2005). In addition to aiming to prevent further sulfide oxidation, inundation often removes the acidity in partially oxidised sediments as the acidity is consumed from the reduction of iron (III) oxides, sulfates and other oxidised species by anaerobic bacteria (Dent 1986). In some moderately severe acid soils, reduction following inundation causes the pH to rise to approximately 7 within a few weeks, however, some acid sulfate soils may not reach a pH of more than 5 after months of submergence (Ponnamperuma 1972).

1.2 Previous research in the Lower Lakes

Based on previous research in other locations, the most significant risks to water quality in the Lower Lakes were considered likely to occur during re-flooding of oxidised acid sulfate soils. Field investigations by Fitzpatrick et al. (2009a) indicated how various acid sulfate soil materials sequentially changed under subaqueous, waterlogged (saturated) and dried conditions, with further change due to recent re-wetting by winter rainfall events. Laboratory based studies were completed that inundated Lower Lakes acid sulfate soil with freshwater and these demonstrated substantial mobilisation of acidity and other contaminants (Simpson et al. 2008, 2010; Sullivan et al. 2008). A risk assessment was also undertaken which found acid sulfate soil impacts in the Lower Lakes could be severe and potentially lead to damage to

1

the aquatic ecosystem, the broader environment, water supplies, and affect human and livestock health (Stauber et al. 2008).

In response to these concerns and informed with previous research outputs (eg Fitzpatrick et al. 2008a,b; 2009a; Simpson et al. 2008; Sullivan et al. 2008), geochemical and hydrodynamic modelling was undertaken to determine the critical water levels below which acidification of the water bodies was likely to occur (Hipsey and Salmon, unpublished 2008). Based on this modelling the State Government derived "trigger values" which represent the water level that must be maintained in both lakes to prevent acidification. The levels adopted were -0.5 m AHD for Lake Albert and -1.5 m AHD for Lake Alexandrina.

The modelling predictions were found to be highly sensitive to the rate of pyrite oxidation, the potential acidity of the exposed sediment and the diffusion of acidity from the sediment following rewetting (Hipsey and Salmon, unpublished 2008). Given these parameters were not known at the time it was acknowledged there was uncertainty in the trigger levels adopted by the State Government.

The robustness of the various previous acid sulfate soil research studies and acidification triggers derived from the modelling work were also subsequently critically reviewed (Aquaterra, unpublished 2008). The review concluded that:

- In general terms, and with a notable exception, the peer reviewers consider that the studies undertaken and the method and tools employed are basically adequate.
- The notable exception relates to the acidification model in that the biophysical processes in the model are considered to be overly simplistic and "may not adequately represent the rates of transport and reaction".
- The current acidification triggers should not be considered reliable in absolute terms "principally due to the major uncertainties in the modelling process, uncertainty in the selection of parameters and lack of model calibration and validation". Nevertheless, the reviewers comment that "modelling is a valuable tool that can be used to inform the management of the lakes towards best addressing what could be a very real danger to their ecological integrity". In particular, the acidification model "demonstrates that acidification can occur rapidly; that seiching may be a prime contributor to acid release; shows where acidification may become first evident; has the potential to support the on-going diagnosis of monitoring data for the assessment of the lakes condition and possible trajectory towards acidification".

1.3 Current Management

In November 2008 the Murray-Darling Basin Commission agreed to a Real Time Management Strategy to Avoid Acidification in the Lower Lakes consisting of three objectives:

- Avoid irreversible damage through acidification of the Lower Lakes system
- Avoid adverse impacts on the water quality of major water supply off takes
- Use treatments that as far as possible do not compromise mid to long term options.

The Real Time Management Strategy to Avoid Acidification in the Lower Lakes comprises of several components:

- Continuous monitoring of pH and water levels in the Lower Lakes
- Continued pumping from Lake Alexandrina to Lake Albert to ensure the main water body of Lake Albert does not acidify
- Monitoring to provide at least four weeks advance warning of reaching either of the following management triggers:
 - o 25 mg/L of calcium carbonate in either Lake; or
- 2

o -1.5 m AHD in Lake Alexandrina or -0.5 m AHD in Lake Albert.

When either of the latter two management triggers is reached and there are not sufficient freshwater inflows, the minimum quantities of seawater necessary to maintain the lakes above these management triggers was proposed to be immediately introduced through the barrages. The Strategy's management response has not been applied on a large scale and concerns were raised about a possible increase in acidity, and release of contaminants, from oxidised acid sulfate soils exposed to seawater, and additional aquatic ecosystem and water quality impacts (eg hypersalinity).

An Environmental Impact Statement for the Opening of the Barrage Network Separating Lake Alexandrina and the Coorong (Seawater EIS) is being prepared but no decision has as yet been made to proceed with this option. Other options are also under consideration, eg freshwater allocation or buyback, bioremediation and/or other remediation techniques including using ultrafine limestone to treat acidic areas.

The Murray Futures program is developing a long term plan and undertaking actions for the CLLMM region, to ensure the long term health and survival of the CLLMM region. Knowledge of acid sulfate soil risks and how to manage them is important to ensure a long term sustainable future for the region's communities and industries.

1.4 Need for further research

The need for further scientific investigations to better characterise critical processes and provide information to better evaluate various management and treatment options was acknowledged by the South Australian Government.

In response to the Aquaterra (unpublished 2008) review and subsequent discussions, the necessary research to fill the critical knowledge gaps was scoped and the following investigations proposed:

- Determining the spatial extent and severity of various acid sulfate soil types in the lower lakes area.
- Refining the oxidation rate of pyrite (acidity generation rates) is needed to improve the geochemical model and for evaluating alternative remediation options (eg liming).
- Determining the in situ dynamics of the generation, transport and neutralisation of acidity and other contaminants resulting from the pyrite oxidation process.
- Assessing the potential for contaminant (acid, metals, metalloids, nutrients) mobilisation and neutralisation if seawater is used instead of freshwater.
- Improving the framework and parameters used within the current lake geochemical model for the outputs to be used with confidence.
- Quantifying the potential nuisance and health impacts from ASS dust on the community; also the nuisance H₂S gas production as a result of dramatically increasing the concentration of aqueous sulfate in the lakes via seawater flooding.

A series of research projects was contracted to the following organisations:

- CSIRO
- Earth Systems
- Southern Cross University
- University of Western Australia.

The expected outcomes from each program and the linkages between them are shown diagrammatically in Figure 1.



Figure 1: Expected outcomes and linkages between the research projects

Details of the work that was undertaken and the findings of the research will be published in a series of technical reports (currently in preparation) as follows:

- Spatial variability of subaqueous and terrestrial acid sulfate soils and their properties, for the Lower Lakes South Australia by R.W. Fitzpatrick, G. Grealish, A. Chappell, S. Marvanek and P. Shand, CSIRO Land and Water.
- Quantification of acidity flux rates to the Lower Murray Lakes (and Supplementary Report), by Earth Systems Pty Ltd.
- Lower Lakes laboratory study of contaminant mobilisation under seawater and freshwater inundation by L.A. Sullivan, R.T. Bush, N.J. Ward, D.M. Fyfe, M. Johnston, E.D. Burton, P. Cheeseman, M. Bush, C. Maher, M. Cheetham, K.M. Watling, V.N.L. Wong, R. Maher and E. Weber, Southern Cross Geoscience.
- The potential for contaminant mobilisation following acid sulfate soil rewetting: field experiment by W.S. Hicks, N. Creeper, J. Hutson, R.W. Fitzpatrick S. Grocke and P. Shand, CSIRO Land and Water.
- The potential for contaminant mobilisation following acid sulfate soil rewetting: lab experiment by S. Simpson, R. Jung, C. Jarolimek, and I. Hamilton, CSIRO Land and Water.
- Lower Lakes hydro-geochemical model development and assessment of acidification risks by M.R. Hipsey, B.D. Busch, J. Coletti and S.U. Salmon, University of Western Australia.
- Air quality in the Lower Lakes region during a hydrological drought by D. Palmer, R. Mitchell, C. Powell, J. Spencer and L. Mosley, Environment Protection Authority, South Australia.

This report summarises the aims, approach, and findings from each project, provides answers to key management questions posed by the project steering committee, and some commentary on the implications of the research program findings for management of the Lower Lakes.

2 Research Program Summary

2.1 Spatial heterogeneity of acid sulfate soils

Further details of the work undertaken and the findings are provided in the report by Fitzpatrick et al. (2010).

2.1.1 Aim

Map the spatial extent and heterogeneity of potential and available acidity in acid sulfate soils and sediments in the Lower Lakes.

2.1.2 Approach

A soil survey of 330 sites (and 706 soil layers) was undertaken in August 2009 in Lakes Alexandrina and Albert including the lower Finniss River and Currency Creek tributaries. The sampling sites were selected randomly using geostatistical techniques. Time and budgetary constraints meant that the overall density of sampling was reduced from recommended levels. However, this reduction was based on developing relationships between the acid sulfate soil subtypes and other more readily mapped parameters such as bathymetry/elevation, vegetation or some other remotely sensed or airborne technology. Soil parameters measured in the field and laboratory were soil texture, pH_{water}, pH_{peroxide}, pH_{incubation}, electrical conductivity, and full acid base accounting (eg titratable actual acidity, chromium reducible sulfur, acid neutralising capacity, net acidity). Maps of the various soil parameters across the whole Lower Lakes were produced using geostatistical techniques.

2.1.3 Findings

The net acidity² in the surface (0-10 cm) sediments of the Lower Lakes is shown in Figure 2. The results show an extensive acid sulfate soil hazard is present in the Lower Lakes. Approximately 80% (70,829 ha) of the total lake area (89,219 ha) had significant potential for developing sulfuric (pH<4) materials or conditions in the sediments if water levels continue to decline. The median net acidity measured (10 mol H+/tonne) was below guideline levels (18 mol H+/tonne, Dear et al. 2002) for when management of soils is considered to be required. However, a large area of the inundated soil/sediments of both lakes and tributaries, particularly Lake Albert, contain very high levels of net acidity (>250 mol H+/tonne). This is well in excess of the Dear et al. (2002) guideline and indicates a very severe hazard. The southern and north eastern regions of Lake Alexandrina and some margins around both lakes appear to be of a lower hazard.

The map of sediment pH_{water} is shown in Figure 3. This map shows that acid sulfate soil with sulfuric material (pH<4) was found in about 20% of the marginal areas (18,389 ha), generally regions with poor connection to the main lake bodies (eg Currency Creek, Finniss River, Loveday Bay and Boggy Lake). It is important to note that these survey results represent only one point in time (August 2009) and that acidity generation and transportation are variable on both spatial and temporal scales. Based on prior CSIRO acid sulfate soil surveys (Fitzpatrick et al. 2008a,b; 2009a,b), it was established that acidity has been flushed, from several large areas which contained sulfuric materials, during the early winter of 2009.

The acid sulfate soil classification map for the Lower Lakes is shown in Figure 4. This map shows that the areas with a high net acidity in the middle of both lakes are predominantly comprised of clay-rich sediments while the sandier sediments are found on the lake margins.

² A positive net acidity indicates an acid generating potential greater than the acid neutralising capacity of the sediment. A negative net acidity indicates an excess acid neutralising capacity which in theory could prevent sediments becoming a hazard.



Figure 2: Net acidity map showing data grouped into five classes for the upper soil layer (0 to 10cm) (source: Fitzpatrick et al. 2010)



Figure 3: pH_{soit:water} map data grouped into four classes for the upper soil layer (source: Fitzpatrick et al. 2010)



Figure 4: Soil classification map of the distribution of the wide range of acid sulfate soil subtypes. Map legend showing: i) acid sulfate soil materials with sulfuric (pH<4), hypersulfidic (pH<4 after incubation), hyposulfidic (pH>4 after incubation) and monosulfidic (MBO) materials; ii) depth of water with deep water (overlying water >2.5m), subaqueous (overlying water 0 to 2.5m), hydrosols (saturated within 50cm below soil surface); iii) soil texture with sands, loams, and clays. (source: Fitzpatrick et al. 2010)

2.2 Acidity generation

Further details of the work undertaken and the findings are provided in the report by Earth Systems (2010).

2.2.1 Aim

To measure the oxidation rate of pyrite in the Lower Lakes sediments as a function of moisture content, in order to quantify acidity generation rates.

2.2.2 Approach

A specifically designed laboratory-based apparatus, OxCon module, was used to measure oxygen consumption due to pyrite oxidation in representative clay and sand sediments from the Lower Lakes (Figure 5). The OxCon approach was used as it was considered the best available method for direct laboratory measurement of pyrite oxidation rates as a function of moisture content. Moisture content provides a surrogate for the availability of oxygen for pyrite oxidation, due to low oxygen diffusion rates in water relative to air (ie high moisture contents correspond to low oxygen diffusion rates). The OxCon approach is based on conventional industry standard techniques for estimating pyrite oxidation rates via oxygen consumption testwork. Furthermore, the OxCon methodology used for the Lower Murray Lakes testwork was specifically developed to overcome some key limitations of existing techniques, including the ability to isolate the effect of pyrite oxidation on oxygen consumption rates from that of organic carbon oxidation.



Figure 5: The OxCon apparatus used to measure pyrite oxidation rates (source: Earth Systems 2010)

2.2.3 Findings

The rates of pyrite oxidation, derived from the oxygen consumption as a function of moisture content, are shown in Figure 6. Figure 7 plots the same results in comparison to values found in previously published studies. The results show that sulfide oxidation rates in the sands display a complex relationship with moisture content. The oxidation rates for clay appear to increase systematically with decreasing moisture content

over the range tested. The peak sulfide oxidation rate was around 1.2 wt% pyrite per day in sandy sediments (at 15 wt% water content) and 0.8 wt% pyrite per day in clays (at 23 wt% water content). At these rates, the majority of available pyrite could be oxidised within approximately three to four months.

The general association between decreasing oxidation rates with increasing moisture content is related to a decrease in oxygen diffusion rates in water relative to air. There is a wide range (six orders of magnitude) of oxidation rates reported in the literature for pyrite, but a far narrower range associated with the pyrite associated with ASS. The results in the current study are comparable with typical oxidation rates in ASS, which are toward the higher range of rates reported for pyrite. This appears consistent with reports from CSIRO of rapid oxidation in incubated soil samples. The pyrite in the Lower Lakes is of framboidal nature (has a very high surface area) which is conducive to rapid oxidation.



Figure 6: Pyrite oxidation rates vs moisture content for Lower Lakes sand and clay (source: Earth Systems 2010)

Comparison of pyrite equivalent oxidation rates for various sulfidic materials



Figure 7: Comparison of reported pyrite oxidation rates for a variety of sulfidic materials including hard rock mine waste rock, tailings, coal mine overburden material and ASS. Pyrite oxidation rate shown on log scale due to significant range in oxidation rates, from 0.001-0.01 wt% FeS_2 / day (typical of mine environments) to 0.1-10 wt% FeS_2 / day (naturally unconsolidated sediments). Scale of the y-axis ranges from 1.E-06 (10⁻⁶ or 0.000001wt% FeS_2 / day) up to 1.E+02 (10² or 100 wt% FeS_2 / day). (source: Earth Systems 2010)

2.3 Contaminant generation, transport and neutralisation

Details of the work undertaken and the findings are provided in the report by Earth Systems (2010).

2.3.1 Aims

- Develop an understanding of the geology, hydrogeology and hydrogeochemistry of the lake sediments.
- Develop an understanding of the acidity generation rates, acidity transport processes and flux rates within the lake sediments of the Lower Lakes as a function of wetting events.
- Provide recommendations for future management of the Lower Lakes.

2.3.2 Approach

Three transects comprising 24 piezometers were located in Lakes Alexandrina and Albert (Figure 8)³. Sediment moisture probes were also installed at these transects. Geological profiles were produced for each of the three transects. Acid base accounting of sediments was conducted and the hydraulic conductivity of the sediments measured. Data logging of groundwater levels and sediment moisture was also undertaken. Six groundwater quality sampling events were undertaken (August 2009 – April 2010).



Figure 8: Piezometer sites in Lakes Alexandrina and Albert and Currency Creek (source: Earth Systems 2010)

2.3.3 Findings

The geological information gathered from drilling, shallow pitting and transient electromagnetic (TEM) surveys identified a coherent regional near surface stratigraphy across both lakes. The majority of the areas examined contain a thin

³ Three individual piezometers were installed in Currency Creek but did not form part of the transect analysis.

veneer of lake sediments (1-3 m thick) overlying a calcrete/silcrete capped Bridgewater Formation limestone.

Hydraulic conductivity values ranged from 0.09 to >30 m/day for lake sediment sands and 0.5 to >30 m/day for the Bridgewater Formation calcareous sands. Groundwater head levels rose rapidly in response to significant rainfall events (temporary rises of 30 cm are typical in response to 10-15 mm rainfall events), but fell very rapidly over subsequent days.

Figure 9 shows piezometric levels at the Windmill transect site in Lake Albert. Similar data is available for other locations. Piezometric levels at the Windmill location generally decrease with proximity to the lake surface water, indicating the potential for groundwater to flow towards the lake. However, from 7 to 10 September 2009, a hydraulic gradient existed from site 3 to site 1 indicating flow in the reverse direction. This may be attributed to the effects of surface water seiching.



Figure 9: Piezometric (groundwater) and ground levels at the Windmill transect site in Lake Albert. Site 1 is piezometers closest to shoreline with a transect extending to Site 4 closest to the water's edge. Rainfall is also shown at Narrung. The dots indicate possible lake seiching events that influence shallow groundwater levels. Piezometric levels at all sites were around 0.3 m lower than surface water levels measured in Lake Albert near Waltowa Swamp in mid-November 2009. The cause of this discrepancy is currently under investigation, but it may be due to survey errors at the lake level monitoring sites. (source: Earth Systems 2010)

Groundwater quality data have shown variable alkalinity, acidity and pH, and some exceedences of the 80% trigger levels for the protection of aquatic ecosystems (ANZECC/ARMCANZ 2000) for several dissolved metals (eg As and Cd).

Despite water levels decreasing to lower than -0.4 m AHD in Lake Albert and -1.0 m AHD in Lake Alexandrina in March and April 2009, there has been no obvious impact on surface water quality (pH or alkalinity). This indicates that either little acidity has so far been released from exposed sediments or that any acidity that has been released has been neutralised by soluble alkalinity and/or sulfide re-precipitation within the lake sediments or surface water bodies. Overall, the hydraulic gradients in the sediments have been small (eg 0.00 to 0.002 in November 2009) although there is potential for gradients to increase significantly toward the lake if lake levels continue to decline.

The data collected between August and November 2009 show that:

• Prior to the commencement of monitoring, some localised acidity generation had occurred within the upper profile lake sediments, as indicated by acidic

groundwater observed in some piezometers (3 sites at Campbell Park and 2 sites at Point Sturt).

- There has been no evidence of significant additional acidity generation within the lake sediments during the monitoring program.
- Acidity generated within the upper lake sediments has migrated downward from sandy layers in the unsaturated zone to the groundwater via rainwater infiltration. However, there has been only limited vertical mixing/diffusion within the sediment profile.
- There has been no significant lateral migration of acidity from the sediments towards the lake water, based on relatively consistent water quality over time (at each site) despite significant chemical variations relative to other sites on the same transect. This is attributed to relatively low hydraulic gradients between August and November 2009, as well as the significant near-surface evapotranspiration water losses.
- Groundwater chemistry data shows that some degree of in-situ carbonate dissolution (ANC consumption) has occurred at all sites. At Campbell Park this has clearly been related to acidity generation. However, ANC consumption has been insufficient to counter the acidity in groundwater at Campbell Park. This is despite indications that sandy lake sediments are generally net acid producing potential (NAPP) negative.
- There is evidence of sulfide precipitation (bacterial sulfate reduction) within the upper sediments affected by acidity generation at Campbell Park (although not Point Sturt) based on the progressive increases in pH and CI:SO₄ ratios observed over the last 3 months.

Collection of the data has been directed at developing an acidity flux model (in collaboration with the University of WA) that can predict acidity generation from the unsaturated lake sediments into the water. Increased risk is predicted over the next 1-2 years if lake levels decline (increasing volume of acid sulfate soil exposed, increasing sulfide content with depth, and increasing hydraulic gradient towards lake water). The conclusions of the Earth Systems modelling are consistent with those obtained by the University of WA (see section 2.5 in this report).

2.3.4 Acidity generation potential and rates

In Lake Albert, the total potential acidity generation over 22 months (from 1 September 2009) is estimated at ~50,000 tonnes H₂SO₄ assuming no ANC consumption, or ~38,000 tonnes H₂SO₄ assuming 10% ANC consumption per year. Much of this load is expected to be released into the lake during the autumnal flush (weeks / months) (Figure 10a). Modelling of the duration of this acidity discharge is underway, and results are pending. The acidity generation rate is expected to drop significantly after 9 months due to pyrite depletion in the unsaturated zone.

In Lake Alexandrina, total potential acidity generation over 22 months (from September 2009) is estimated at ~180,000 tonnes H_2SO_4 assuming no ANC consumption, or ~115,000 tonnes H_2SO_4 assuming 10% ANC consumption per year (Figure 10b). Prior to the first autumnal flush, the total acidity generation is estimated at ~40,000 tonnes H_2SO_4 assuming no ANC consumption, or ~28,000 tonnes H_2SO_4 assuming 10% ANC consumption per year. This represents ~20 to 25% of the acidity load generated after 22 months.

These results may be overestimates based on sediment moisture measurements (see Earth Systems 2010) showing limited increase in the oxidation depth over the time period of the study.

2.3.5 Acidity flux rates

The likely rate and duration of acidity release (flux) events in Lake Albert and Lake Alexandrina have been estimated for a range of lake water level, hydraulic conductivity and acidity concentration scenarios, based on hydrogeological modelling conducted by Coletti and Hipsey (2010).

Based on the observed acidity flux event at Currency Creek in 2009, the duration of future acidity flux events is likely to be at the lower end of estimated range, ie closer to two to three months for the first acidity flux event and one to two months for the second event in Lake Albert, and closer to one to two months for the first acidity flux event and three to four months for the second event in Lake Alexandrina. These estimates correspond to the lower minimum lake water level (-1.0 m AHD), hydraulic conductivity of 10 m/day and acidity values of 10,000 mg/L CaCO₃.

Surface runoff and acid salt dissolution associated with high intensity rainfall events (where rainfall intensity exceeds infiltration rate) has not been taken into account as an acidity flux mechanism. Implications for the duration of acidity flux events are currently under investigation.

Key factors that can limit the acidity generation and release into the lake are increases in the hydraulic gradient within the sands, distribution and concentration of sulfides in the upper sandy sediments, and the extent of acid neutralising capacity (ANC) consumption within the sandy sediments.





Figure 10: Preliminary estimates of cumulative acidity generation from Lake Albert (a) and Lake Alexandrina (b) sediments from 1 September 2009 to 30 June 2011 (source: Earth Systems), based on laboratory data and field data collected from August-November 2009. Results may be overestimates based on recent sediment moisture data collected in early 2010. (source: Earth Systems 2010)

2.4 Seawater contaminant mobilisation

Further details of the work undertaken and the findings are provided in the reports by CSIRO (Hicks et al. 2010; Simpson et al. 2010) and Southern Cross University (Sullivan et al. 2010).

2.4.1 Aim

Assess the potential for contaminant mobilisation and/or neutralisation if seawater is used to inundate the Lower Lakes instead of freshwater.

2.4.2 Approach

The mobilisation of contaminants (acid, metals, metalloids and nutrients) if seawater is used in the Lower Lakes instead of freshwater to inundate sediments was studied using laboratory and field based mesocosm experiments (Figure 11). Sediment and overlying water quality was sampled on regular intervals. Changes in the sediment geochemistry upon reinundation with water were also studied (eg via measurement of redox potential, sulfate reduction rates and processes).



Figure 11: Field based mesocosm (LEFT) (source: Hicks et al. 2010) and laboratory (RIGHT) experiments (source: Sullivan et al. 2010)

2.4.3 Findings

Both field and laboratory studies indicated that seawater enhanced mobilisation of contaminants to surface waters.

In the field experiments there was a greater initial mobilisation of acidity and consequent pH decrease with seawater inundation than for the freshwater treatment (Figure 12). This pH decrease occurred despite the alkalinity in the seawater being greater than the freshwater. The acid flux from the clay soil at Boggy Creek was sufficient to acidify the overlying 0.5 m water column within two months of rewetting. This acid flux is attributed to the higher concentrations of cations (eg Ca⁺², Mg⁺², Na⁺) in seawater being exchanged for acidity (H⁺, Al⁺³) on the soil particle surfaces. This cation exchange process creates a higher concentration of acidity in the pore water which then diffuses out to the water column. Increasing salinity may also increase iron and aluminium mineral solubility (Öhman et al. 2006). It is noted that while the trend is very similar, there were significant differences in the magnitude of the pH change between seawater replicates at the Boggy Creek site. The reason for this is unclear but could be due to:

- localised spatial differences in the amount of available acidity present at each replicate site
- localised spatial differences in the cracks and macropores present at each replicate site that could have resulted in different preferential flow pathways giving rise to finger flow and exfiltration (Selker et al. 1996).

In contrast, in the sandy soil material at Point Sturt there was good agreement between all replicates and a downward displacement of acid pore water deeper into the soil profile. This flux creates the potential for the acidification of shallow groundwater and lateral fluxes to the water body. A mass balance of the acidity in the soil profiles at both sites shows that a single charge of water to any feasible depth would be insufficient to neutralise stored soil profile acidity. This indicates that several flushes of dilution water could be required to achieve neutral conditions in the water and sediment.

Similar results were found in the laboratory experiments (Sullivan et al. 2010) where sediment acidity was found to have a greater acidifying effect on overlying water pH and alkalinity when inundated with seawater compared to River Murray water (Figure 13). After 35 days only three of 15 exposed lake soil samples had inundating waters with pH< 6. This general lack of acidification was mainly due to the relatively low acidity stores in the exposed lake sediments at their time of sampling.

Mobilisation of some metals (eg Ni, Zn) and nutrients (ammonia) was also exacerbated with seawater inundation (Figure 13). The companion laboratory experiments by Simpson et al. (2010) also showed enhancement of metal mobilisation with seawater. The simulations of sediment resuspension also showed that this process could enhance metal mobilisation, particularly from the clay soils.

Numerous exceedances (eg Cu, Zn, NH₄) of the ANZECC water quality guidelines were observed in both the field and laboratory experiments, particularly for seawater inundation. The exceedances show that, as well as acidity, there are additional toxicity risks to aquatic ecosystems when exposed soils are reinundated. However many exceedances were relatively minor and therefore the ecological impacts may also be minor or short term, depending on the amount of dilution.

The capacity for acid neutralisation in the sediments to occur via sulfate reduction was researched (Sullivan et al. 2010). There was little difference in the overall rates of sulfate reduction (ie the process that neutralises acidity via the reformation of sulfide in the sediment) when seawater or river water was trialled. This finding appears to be due to the organic carbon content in the sediment being the limiting factor rather than the sulfate concentration in the overlying water (Figure 14).



Figure 12: Changes in overlying water pH when clay (LEFT) and sand (RIGHT) sediments are exposed to freshwater (TOP) and seawater (BOTTOM) in field mesocosm experiments. (source: Hicks et al. 2010)



Figure 13: Changes in overlying water pH, alkalinity, nickel (Ni) and ammonia (NH₄ here expressed as NH₃) when Lower Lakes sediments are exposed to freshwater (LEFT) and seawater (RIGHT) in laboratory experiments. The different coloured lines represent different sampling sites. (source: Sullivan et al. 2010)



Figure 14: Sulfate reduction rate as a function of soil organic carbon content (source: Sullivan et al. 2010)

2.5 Geochemical modelling

Further details of the work undertaken and the findings are provided in the report by the University of Western Australia (Hipsey et al. 2010).

2.5.1 Aim

Undertake spatially resolved hydro-geochemical modelling of various water level scenarios associated with the drying and rewetting of acid sulfate soils in the Lower Lakes for the purposes of unravelling the complex pathways of acidity generation and neutralisation.

2.5.2 Approach

An existing 3D lake geochemical model (ELCOM-CAEDYM) was refined using data and process information from the other research projects (eg spatial variability of actual and net acidity, oxidation rates, moisture content of sediment, acid flux mechanisms and rates, neutralisation processes; Figures 15 and 16). The model includes a spatially resolved ASS module that is able to connect soil dynamics with that of the surface waters. Key developments included incorporating a dynamic and vertically resolved soil profile into the ASS module. This allowed calculation of moisture content, pyrite oxidation, and sulfate reduction rates with depth in the soil profile, and also spatially across the lake bed.

A 2D HYDRUS water transport model of the exposed lake-bed was developed and informed by the field measurements of Earth Systems (2010). This model was used to estimate groundwater seepage rates from the sediment to the lake as a function of the hydraulic head gradient (which varies in response to rainfall, evaporation and lake level) and the results were used within the 3D model for predicting acid flux rates.

The lake geochemical model was calibrated for the period from January 2008 to September 2009 against monitoring data from the various sites in the region, including from the Currency-Finniss region where large-scale acid impacts have occurred. The model has then been used to forecast the lake conditions from October 2009 to January 2013. Various water level management scenarios were run including augmentation of lake volumes with additional freshwater or with seawater, and the acidification trigger levels have been revised.

2.5.3 Findings

After development of the soil model in line with the new experimental data available, the model was calibrated against historical data collected until September 2009 for both Lakes Albert and Alexandrina, and the acidification event in the Currency-Finniss region. The revised model accurately predicted the timing, severity and recovery of the acidification of Currency Creek, although several uncertainties remained.

Various model scenarios were then run for Lake Albert and Lake Alexandrina to determine the critical water levels ("trigger levels") when lake acidification could occur. It should be noted that these scenarios are hypothetical only for the purposes of testing lake response to the acid sulfate soils impacts.

For Lake Albert, the lake went acidic for all simulations that went below a water level of -1.0 m AHD (Figure 17). Sensitivity testing of the model did not change this outcome. Stabilisation at either -0.75 and -0.5 m AHD appeared to prevent any large scale deterioration in pH or alkalinity (ie dissolved inorganic carbon - DIC) until the end of 2012. However, pH instabilities at the lake margins were observed even at -0.5 m AHD. This is also reflected in the observational record of soil and water acidification in localised areas around the lake margins over the winter of 2009. Based on these modelling results the key management recommendation to prevent lake acidification is to maintain water levels above minus 0.75 m AHD in Lake Albert (Hipsey et al. 2010). Seawater scenarios have not been modelled for Lake Albert as yet.

For Lake Alexandrina, the main lake body maintained satisfactory pH and alkalinity up until the end of 2012 for all stabilisation and drawdown scenarios (Figures 18 and 19). However the model does indicate several issues:

- The north western region shows temporary acidification during lake drawdown and then seasonal rewetting (and this was consistent with observations sin Boggy Lake)
- Seawater intrusion does create some acidification in the south reach of the lake around Pt Sturt and alkalinity declined over the whole lake area. Seawater salinities are rapidly established across the whole lake area in the -1m AHD water level stabilisation scenario
- A high accumulation of available acidity in the soil and increasing cumulative loadings of acid in baseflow/shallow groundwater are evident. This indicates that longer simulations beyond 2012 could eventually deteriorate if levels were maintained below -1.5m. Longer term simulations are being run as part of the Seawater EIS.

Based on these issues, the key management recommendation to prevent lake acidification is to maintain water levels above minus 1.75 m AHD in Lake Alexandrina (Hipsey et al. 2010). Fringing waterbody regions with poor connection to the lake will continue to acidify in response to rainfall.

The model outputs suggest the potential acidification process for both lakes is either lateral movement of shallow groundwater and acidity from sandy sediments, or raindriven ponding of acidic material which washes into the lake margin. Major rainfall events also mobilise acidity from the unsaturated zone (top layers of exposed sediment) down into the saturated zone (shallow groundwater) and this moves laterally towards the lake due to the increased hydraulic gradient.

Lake refill and seasonal scale re-inundation of acidified soil contributed to the acidity flux to the water column, but this was not as significant as acidity mobilised following heavy rains. Variability in the flux depends on sensitivity to the vertical percolation of acidity in response to rain, generation of lateral flow from saturated soil, and the in situ soil neutralisation processes. Continued research and modelling of infiltration processes, groundwater transport and neutralisation processes are warranted given that these are the proposed main drivers in the model.

In all simulations conducted, the area of sulfuric soil is large and acidity levels in the soil remain high despite fluxes to the lake (Figures 20 and 21). Therefore a soil hazard will continue to remain around the margins of the lake.

It is important to continue to improve the geochemical model to further reduce uncertainty in its predictions. It is also important to continue water quality monitoring to assess the accuracy of model predictions and, due to their inherent uncertainty, to not rely completely on these predictions for management decisions.



Figure 15: Example of grids used to configure the Lake Albert model showing a) the base validation bathymetry, b) the soil classification (sand/clay) map, c) the soil potential acidity map and d) the soil acid neutralising capacity (ANC) map (source: Hipsey et al. 2010)



Figure 16: Example of grids used to configure the model showing a) the base validation bathymetry (including the Currency/Finniss region), b) the modified domain used for the forecast simulations, c) the domain used to examine the seawater entrance (including Wellington Weir), d) the soil classification (sand/clay etc) map, e) the soil potential acidity map and f) the soil acid neutralising capacity (ANC) map. (source: Hipsey et al. 2010)



Figure 17: Time series of water level, pH, dissolved carbonate alkalinity (DIC) and salinity predicted by the model for the middle of Lake Albert for the continued drawdown (yellow line) scenario compared with water level stabilisation (via pumping freshwater from Lake Alexandrina) at approximately -1.0 m AHD (green line), -0.75 m AHD (blue line) and -0.5 m AHD (red line) scenarios. (source: Hipsey et al. 2010)



Figure 18: Time series of water level, pH, dissolved carbonate alkalinity (DIC) and salinity predicted by the model for Lake Alexandrina for the continued drawdown (blue and black line, note: includes additional 170 GL allocated to lakes in 2009, DN1considers no continued pumping to Lake Albert following Oct 2010, DN2 assumes continued pumping to Lake Albert), partial refill with freshwater (red line, 170 GL and 500 GL additional allocation during 09-10), and stabilisation at -1.0 m AHD with either freshwater (green line) or seawater (yellow line) scenarios. The measured water quality data are shown as the circles. (source: Hipsey et al. 2010)



Figure 19: Example of plot from Lake Alexandrina model with continued drawdown assumed for pH in June 2012. (source: Hipsey et al. 2010)













Figure 20: Summary of integrated acid sulfate soil model outputs for the Lake Alexandrina drawdown scenario showing a) soil acidity stores, potential acidity (PASS) and available acidity (AASS), b) acidity production and consumption/neutralisation, c) lake areas that are wet and dry, d) baseflow contribution to lake water body, e) soil neutralisation rate, f) acid load to lake water body during seiching/sediment rewetting and acid consumption by neutralisation in lake sediment. (source: Hipsey et al. 2010)

Lake Alexandrina: Acidity Fluxes 2012



Lake Albert: Acidity Fluxes 2012



Figure 21: Example of acidity output budgets from the Lake Alexandrina model (TOP) and Lake Albert model (BOTTOM) highlighting approximate annual fluxes and stores of acidity for 2012 should continued drawdown assumptions occur. UZ is the unsaturated zone and SZ is the saturated zone. (source: Hipsey et al. 2010)

2.6 Air quality study

This work is being undertaken by the Environment Protection Authority. The study will continue over the 2009-10 summer before a technical report is completed.

2.6.1 Aim

Assess possible human health risks arising from the drying and wind mobilisation of acid sulfate soils around the Lower Lakes.

2.6.2 Approach

Two high volume dust samplers were re-installed at the Goolwa and Meningie communities during March-May 2009. Sampling was triggered when the wind was blowing off the lake at >2m/s. Photographs of a sampler and dust storm are shown in Figure 22. Acidity and metals were analysed on the filters with additional mineralogy analyses conducted by the CSIRO. Rainwater tanks were also sampled around the Lower Lakes following the first rainfall event of the 2008 winter. High volume dust samplers have been installed at Milang and Meningie for monitoring over the 2009-10 summer.



Figure 22: A high volume sampling unit (left) and dust storm (right) near Goolwa

2.6.3 Findings

The dust on the filters in the preliminary sampling (late 08-09 sampling) was found to be non-acidic. A health risk assessment on the metals data by Golder Associates indicated "ambient air levels of metals in Meningie and Goolwa are unlikely to be a cause for concern for the health of residents who might be exposed". However, there were a number of uncertainties noted that need to be addressed. These include uncertainties about the air monitoring analytical results, uncertainties about the species of chromium in the air, uncertainties about variability of particle (PM10) and metals concentrations in different seasons and different locations in the two areas.

These uncertainties are now being addressed in the further dust monitoring now underway at Meningie and Milang (Goolwa sediments have been re-inundated). Preliminary results are shown in Figure 23 for 24 hours and wind-switched (when wind is off the lake bed) samples. Relatively low levels of particles (PM10) have been found on the filters and there is no evidence of acidic dust particles. Chromium results showed some exceedance of guidelines but these were not related specifically to acid sulfate soils (as 24hr results similar to wind-switched results). Archival surface soil samples from the lake bed were examined by CSIRO for speciation of chromium and found that chromium III was the dominant species. This is the low toxicity form of chromium. The Health Department have stated that "these results and the chromium

speciation analyses confirm the previous assessment that the dust does not represent a significant risk to public health in terms of acidity or heavy metals."

The CSIRO mineralogy results showed limited amounts of acid sulfate soil minerals in the dust on the filters (mostly sand and salt dominated, Table 1). These findings are consistent with the low levels of acidity and metals noted above.

Rainwater tank sampling in the first rainfall after summer also indicated no health concerns.

Dust issues may be expected to increase substantially if larger areas of lakebed are exposed in the event that water levels continue to fall.

Sample ID and location	Mineralogical Composition
T-00783 Meningie	Halite (NaCl) – dominant;
	Gypsum (CaSO4.2H2O) - sub-dominant
T-00788 Goolwa	Halite – dominant; Gypsum - minor,
	Quartz, feldspar (albite) and possible natrojarosite - trace
T-00786 Meningie	Halite - dominant
T-00887 Goolwa	Halite - dominant, Gypsum - minor

Table 1: Mineralogical composition of samples (source: CSIRO)

*Dominant (>60%), co-dominant (sum of phases >60%), sub-dominant (20-60%), minor (5-20%), trace (<5%)



Figure 23: Selected dust results for particle concentrations (PM10), pH, aluminium and chromium at Milang and Meningie over 2009-10 summer. The air quality guideline value is shown as the red dashed line. Both wind-switched (WS) and 24hr sampling results are shown.

3 Management Questions

The Coorong, Lower Lakes and Murray Mouth Projects Steering Committee identified a number of key management questions to be answered by the research work program. These questions cover outcomes such as "If the lakes do acidify how long will recovery take" and "Will seawater solve the problem in the short to longer term" as well as process-related questions such as "How far down into the sediments is mobilisation occurring".

The researchers involved in undertaking the investigations met as a Scientific Research Committee on five occasions (including a teleconference) over a period of four months. At each of these meetings the management questions were discussed in depth.

The information provided below represents the consensus views of the group based on the findings of the research projects and the extensive experience of the experts involved.

3.1 How extensive and severe is the problem?

3.1.1 In the sediments

New mapping of the spatial heterogeneity of the acid sulfate soils around the lakes, coupled with previous work undertaken by CSIRO has reliably determined within quantified statistical confidence limits the spatial extent of the problem (Fitzpatrick et al. 2010). The work has found that there are extensive acid sulfate soils throughout the Lower Lakes although there is large variability, or heterogeneity, in their properties.

Greater than 80% (70,829 ha) of the total lake area (89,219 ha) had considerable potential for developing sulfuric (pH<4) conditions in the sediment if water levels continue to decline (Fitzpatrick et al. 2010). This highlights the extensiveness of the hazard. The mean net acidity measured (124 mol H+/tonne) greatly exceeded guideline levels (18 mol H+/tonne, Dear et al. 2002) for when management of soils is considered to be required. This highlights the severity of the hazard present in both lakes. The hazard is particularly severe in the clay sediments in Lake Albert which comprise a very large area in the middle of the lake. A large-scale soil acidification issue will occur if these sediments start to dry out and oxidise. Significant hazards are also present in the deeper area clay-rich sediments of Lake Alexandrina and in the tributaries. In contrast, there are areas near the Tauwitchere and Ewe Island Barrages and around both lake margins that have negative net acidity, ie excess neutralising capacity.

Sullivan et al. (2010) found that the level of acidity in many of the marginal (0-15 cm) sandy soil materials was generally very low. Only two of the fifteen sites studied had total available acidity that exceeded the value usually used to trigger further acid sulfate soil investigations, even though sediment pH was low (pH 2.6 in one case). This highlighted that soil pH is not a good indicator of the ability of sediment to supply acidity to the Lower Lakes. It is noted that these exposed marginal sediments have undergone flushing from rainfall during the early winter of 2009 that may have removed acidity prior to the sampling being undertaken. It is noted that some areas that have acidified already in the Lower Lakes such as Currency Creek contained largely sandy surface sediments.

3.1.2 In the drying phase versus the wetting phase?

The drying phase creates the problem by exposing acid sulfate soils to the air. Oxidation of the sulfidic material in the soils generates soil acidification and dissolution of potential contaminants, eg metals such as aluminium in the soils. When these soils are rewetted by rainfall, wind seiching or lake refill, the acidity and contaminants are mobilised. New problems can then occur such as accumulation of mono-sulfidic black ooze material and metalloid release (such as arsenic). Indications are that presently the drying phase has posed a lower overall risk to lake water quality as despite substantial lake drawdown (2006-present) and rainfall rewetting of the marginal sediments, there has not been any major change in alkalinity in the main bodies of the lakes (see reports on the EPA website⁴). The drying has posed a high risk to soil quality through generation of acidity (Fitzpatrick et al. 2008a,b; 2009). The flux studies and geochemical modelling results suggest that further lake drawdown/drying will begin to increase the risk of lake acidification. The impacts already observed in Loveday Bay and Finniss River (Fitzpatrick 2009a) and predicted relate to rewetting of soils/sediments following rainfall once very large sediment areas are exposed. This could be analogous to the considerable localised water acidification that has occurred following rainfall events in areas which have mostly dried and generated large amounts of acidity (eg Currency Creek and Loveday Bay). There could also be substantial risks upon lake refill, particularly with seawater. Laboratory-scale testing and field work has found the response of the inundating waters to the underlying soils varies considerably in terms of pH and alkalinity. Inundation by seawater generally has a greater acidification effect, and consequent increased levels of contaminant release, than inundation by River Murray water (Sullivan et al. 2010, Hicks et al. 2010, Simpson et al. 2010).

3.2 How far down into the sediments is acid mobilisation occurring?

As at August 2009, the depth of the soil oxidation (acid mobilisation) front varies from 10 cm to 1 metre below the soil surface depending on the location and the soil type. The spatial heterogeneity study report provides cross sections at different sites with information on soil status (Fitzpatrick et al. 2010).

Piezometers installed at sites in Lake Alexandrina, Lake Albert and Currency Creek have been used to remotely monitor groundwater levels. Sediment moisture profiles and sulfide oxidation rates have been determined as a function of soil moisture content. Findings from this work show that sulfidic soils 30 cm above the water table are oxidising/acid generating (Earth Systems 2010).

Field experiments have assessed acid mobilisation at two sites under freshwater and seawater inundation (Hicks et al. 2010). The work has found that for clay soils net solute flux is from the soil to the surface water whereas for sandy soils the flux is from the water to the soil. This indicates that clay soils are a potentially greater threat to water quality than sandy soils based solely on acidity levels. However sandy soils pose a significant threat to groundwater and to surface water under due to their permeability.

3.3 What are the trigger levels and are they appropriate⁵?

The revised water level management targets to prevent lake acidification are >-1.75m AHD for Lake Alexandrina and >-0.75m AHD for Lake Albert (Hipsey et al. 2010, see Figure 18). These revised figures are similar to the previous trigger levels of -1.5m and -0.5m AHD for Lakes Alexandrina and Albert respectively (MDBA and state government adopted levels based on Hipsey and Salmon, unpublished 2008⁴). There were significant uncertainties around the earlier figures due to insufficient information in a number of critical areas. While there is less uncertainty in the current trigger levels, model refinement is ongoing. However it is clear the risk profile substantially increases past these water levels and/or with prolonged time that the water level is near these levels.

⁴See website

http://www.epa.sa.gov.au/environmental_info/water_quality/lower_lakes_water_quality_monitoring

⁵ The Murray-Darling Basin Commission (now Authority) agreed to a management strategy with triggers relating to: 1) water levels and 2) alkalinity of 25 mg/L as calcium carbonate in either lake – whereby minimum quantities of seawater would be introduced. In a broader context, trigger levels could also be contemplated for soils and ecological impacts but these are not specifically considered here.

Sediment acidification is an important issue as it will impact the ability of benthic ecosystems to recover. No trigger levels have been considered for sediment acidification.

3.4 How long have we got until water acidification?

Timescales for potential water acidification are based on many factors, particularly water level trends which can not be predicted far in advance. Based on the above trigger levels and DWLBC lake water level predictions, there could have been a major acidification as early as winter 2010 in Lake Albert if it was allowed to dry out. Lake Alexandrina did not go acidic until the end of the current model run in 2012. However, substantial lake margin areas were acidic and there was evidence of significant acid groundwater transport which, if of sufficient magnitude, could acidify the lake at some future time.

As noted above there are still uncertainties in the modelling which must be taken into account in any management decisions using the new trigger values.

The modelling, laboratory and field flux studies demonstrate that acidity flux rates using seawater inundation are greater than for freshwater (Sullivan et al. 2010; Hicks et al. 2010, Hipsey et al. 2010). During the first 1-2 days after inundation there is an initial fast acidity flux with a slower but on-going long-term flux.

As at October 2009, EPA monitoring has found that the main lakes have satisfactory and stable alkalinity. Nevertheless acidification, covering several hundred hectares has occurred in some localised areas (Loveday Bay, Currency Creek, upper Finniss River and Dunn's lagoon).

3.5 How reliable are the predictions?

Previous predictions were based on the stage 1 lake geochemical model with limited data. As a result, these predictions had a significant degree of uncertainty. Nevertheless, despite the uncertainties the earlier modelling successfully predicted Loveday Bay and Currency Creek acidification in winter 2009 assuming average oxidation rate scenarios (Hipsey and Salmon, unpublished 2008).

The refined model outputs (Hipsey et al. 2010) are based on more reliable data and sensitivity testing has been undertaken so that the model is able to provide firmer predictions (ie a lower degree of uncertainty). The degree of uncertainty in the modelled trigger levels for Lake Alexandrina is approximately \pm 0.25m AHD based on the ranges for model parameters determined from the spatial extent and flux work as well as values published in the scientific literature. The revised model successfully predicted the acidification in Boggy Lake on the date that it occurred (Figure 24).



Figure 24 – Modelled (TOP) and measured (BOTTOM) pH in Boggy Lake area of Lake Alexandrina on 19/5/10. The blue area in the model shows the acidification in Boggy Lake was successfully predicted (source: University of WA and EPA).

Predictions on soil acidification have proved reliable and have been confirmed by more extensive mapping of acid sulfate soils (Fitzpatrick et al. 2008; Fitzpatrick et al. 2010).

3.6 If the lakes do acidify, how long will recovery take?

Based on local case studies from the Finniss River (Fitzpatrick et al. 2009a) and Loveday Bay (Fitzpatrick et al 2010), as well as other locations (eg East Trinity Inlet Queensland and Nelwart wetland) it is likely that recovery from a severe acidification would take years to decades but this depends on many factors (eg how long sediments have been oxidised, flushing rate, severity of soil and water acidification and effectiveness of sulfate reduction). A severe acid sulfate soil site at East Trinity Inlet in Queensland has taken several years of tidal flushing to initially restore soil/sediment and water quality with further remediation still necessary.

The laboratory and field mobilisation experiments showed that sulfate reduction could reduce acidity in the sediments and water column over the timescale of months but the rate is limited by organic carbon availability in the sediment (eg Sullivan et al. 2010).

Forecast refilling scenarios for freshwater and seawater inundation are being simulated using the geochemical model for short and long time frames. This will allow determination of the flushing/recovery rate. The preliminary results suggest return of entitlement flows does not result in any flushing for at least 2-3 years (Hipsey et al. 2010).

Recovery of sediment quality to enable benthic ecosystem recovery could be much longer than surface water recovery. Some changes to sediment may be irreversible.

3.7 Are there any lead indicators?

Water alkalinity (or acidity) and pH are appropriate lead indicators. Alkalinity and pH triggers have been developed previously for the Lower Lakes and endorsed by the Murray Darling Basin Ministerial Council.

Fortnightly water quality monitoring is being undertaken to assess if any primary (alkalinity declines) or secondary (increases in Aluminium, Iron or Arsenic concentrations or the Sulfate to Chloride concentration ratio) indicators of acidification are evident.

Soil acidity is being monitored at fifty exposed shoreline sites by CSIRO as water levels change. Sulfate reducing bacteria (SRB) operate under reducing conditions so pore water pH and redox⁶ potential are also important indicators of sediment conditions, eg SRB activity is limited by pH<4.5 and low Oxidation Reduction Potential (ORP).

It would be useful to develop soil acidity triggers (as a function of soil texture and organic matter content) as additional lead indicators.

3.8 What are the practical management options and their likely effectiveness?

This management question is being addressed through the Seawater EIS alternative options study which is assessing the feasibility of bioremediation or other alternative options versus introduction of seawater. This work is yet to be completed. The spatial heterogeneity data as well as geochemical modelling work will help to inform this work. Uncertainties still exist as to the effectiveness of some options. There are several previous reports available on potential alternative management options (Earth Systems unpublished 2008a; Earth Systems unpublished 2008b, Earth Systems unpublished 2009).

Based on the research program's findings, prevention using freshwater is clearly the preferred management option.

3.8.1 Is localised prevention or treatment an option?

Localised prevention has already been shown to be a feasible option. For example, the previous Lake Albert pumping and the Goolwa Channel Water Level Management Project have prevented acidification in localised areas. The difficulty is that it could become increasingly problematic to undertake localised prevention unless fresh water is available.

Localised treatment using limestone was reasonably successful in Currency Creek although alkalinities remain relatively low and the longer term effect of metal

⁶ reduction-oxidation reaction

precipitates is unknown. Treatment options are being tested as part of Currency-Finniss region and Lake Albert management.

The middle of Lake Albert requires prevention due to the large amount of acid that would be generated if the sediments dried out. Treatment alone is not considered by the scientific research committee to be a viable option for dealing with the very large potential acid generation in Lake Albert.

3.8.2 If so what is best (eg saturation, liming, bioremediation, revegetation, other) and what are the impacts and implications (eg costs)?

This management question is being addressed through the Seawater EIS project's alternative options study which is identifying the feasibility of bioremediation or other alternative options versus introduction of seawater. This work is yet to be completed.

Based on the results from the current research program, inundation with fresh water is clearly the best option as this prevents acid developing and minimises contaminant release. Other options are possible depending on circumstances on a case by case basis.

A range of management options (prevention using saturation, control and treatment) are being evaluated and trialled as part of the Currency-Finniss region and Lake Albert management assessments and the alternative options study in the Seawater EIS but uncertainties still exist as to the effectiveness of some options. For example, the potential impacts of metals and metalloids, and whether treatment and removal options are viable will need to be investigated.

Spatial mapping of acid sulfate soils and modelling work will be used to inform the viability of different management options by estimating the amount of acidity generated and thereby the amount of acid neutralising that could be required.

3.8.3 Is there significant variation in the risk profile of different parts of the lakes that will require different types of remediation?

The risk profile depends on a number of factors including:

- the extent and severity of acid sulfate soils around the lakes;
- the likelihood that sulfidic soils will be exposed on drying down;
- the rate of oxidation and mobilisation of acidity; and
- the release rate of contaminants from the soil.

Spatial heterogeneity mapping has shown considerable variation in the vertical and horizontal extent of acid sulfate soils and their net acidity, pH and Titratable Actual Acidity (or readily available acidity) around the Lower Lakes (Fitzpatrick et al. 2010). Therefore, the risk profile does show significant variation around the lakes.

The research investigations indicate the highest potential acid sulfate soil hazards are in the clay-rich areas in the centre of both lakes; consequently these areas should be kept inundated to prevent extensive soil and water acidification. Sand-rich areas also represent a threat due to their low buffering capacity and high permeability to transport acid. Laboratory and field studies have shown that seawater inundation is more of a risk than freshwater (Sullivan et al. 2010; Hicks et al. 2010).

To avoid large-scale soil and water acidification, the clay-rich areas in the middle of Lakes Albert and Alexandrina will require preventative measures rather than relying on treatment. Treatment is not considered to be a viable option for these areas due to the extent of the acid sulfate soils hazard and the potential for existing water alkalinity to be overwhelmed. Localised treatment may be possible for less severe hazard areas.

3.9 Will seawater input solve the problem in the short term or the longer term?

Indications from the geochemical modelling are that seawater may result in the increased risk of acidification relative to freshwater (Hipsey et al. 2010). Rewetting by

seawater of oxidised soils on the lake margins (eg by wind seiching or rainfall) resulted in increased mobilisation of acidity and other potential contaminants from oxidised soils (Sullivan et al. 2010, Hicks et al. 2010). Seawater could be useful in the absence of sufficient freshwater to prevent high-risk sediments (eg in middle of lakes) from becoming exposed.

This research program focuses only on the geochemical aspects of acid sulfate soils and does not cover important ecological, social and economic issues being considered as part of the Seawater EIS.

3.9.1 How effective is seawater as an option to reverse the acidification (as opposed to its use as a preventive measure by keeping the soils wet)?

Laboratory experiments using 15 randomly selected exposed soil samples from around the lakes, and field experiments at two different sites, have demonstrated that seawater inundation can increase acidity and release greater levels of contaminants from the soils compared with River Murray (fresh) water inundation (Sullivan et al. 2010).

Based on these findings seawater is not considered to be effective over weeks to months to reverse soil acidification as it results in a greater amount of acid mobilisation from sediments containing acidity.

The overall effectiveness of seawater in reversing lake acidification would likely depend on the amount of seawater dilution/alkalinity provided and the ability to flush away contaminants. Lake geochemical modelling (Hipsey et al. 2010) has determined that seawater stabilisation at -1.5m AHD may import additional alkalinity to temporarily reverse acidification, but this may be insufficient to counter ongoing acid fluxes at lake levels of -1.5m AHD or lower.

3.9.2 The exchange rate with the ocean is slow – what happens if/when carbonate from an initial seawater input is used up but acidification continues?

If carbonate system buffering in the initial seawater inundation is used up, lake acidification would continue until such time that sufficient additional neutralising capacity and/or dilution water was added to the lake.

Field experiments undertaken at two different sites indicate that, without tidal exchange, seawater has less neutralising ability than freshwater when oxidised/acidic sediments are inundated. A mass balance of the acidity in the soil profiles at both sites showed that a single charge of water to any feasible depth was insufficient to neutralise stored soil profile acidity even for a site such as Point Sturt where the intensity of acidity is high but the amount relatively low (Hicks et al. 2010). This implies that very large volumes of flushing water could be required if acidification occurred on a large scale. However the geochemical modelling results suggested seawater may be able to be used to temporarily recover from a low pH condition in Lake Alexandrina (see Figure 17, Hipsey et al. 2010)

Model simulations will be run with different seawater input rates to assess the impact of using seawater and whether sufficient neutralising capacity can be generated or enough ocean exchange is possible. These will be completed as part of the Seawater EIS project.

3.9.3 Will seawater input create other problems, ie metal/acid release, importing of sulfate?

Further more in-depth modelling and assessment of these issues is being undertaken as part of the Seawater EIS.

The potential for mobilisation of contaminants (acid, metals, metalloids and nutrients) following rewetting of acid sulfate soils with seawater and freshwater has been investigated in laboratory and field studies (Sullivan et al. 2010; Hicks et al. 2010).

Compared with fresh River Murray water, seawater enhances metal, nutrient and acid mobilisation from oxidised soils.

Seawater has a much higher sulfate concentration than river water but the sulfate reduction experiments undertaken by Southern Cross University showed little difference in rates between the two water types. This was because organic carbon was limiting the reaction rate rather than sulfate. This suggests seawater inundation is not likely to increase sulfide production in the lakes relative to freshwater.

Without tidal exchange or sufficient river flows, salinity would build up in the lake quickly and hypersaline conditions are likely to develop over time.

3.9.4 What will be the likely properties of the lake post seawater input (ie salinity, pH, metals) and the ecological challenges that will require management?

The research work is not specifically targeted at the ecological challenges but will help to identify the magnitude of the problem. Ecological assessment is part of the EIS for the Opening of the Barrage Network Separating Lake Alexandrina and the Coorong (Seawater EIS).

Laboratory studies of 15 randomly selected exposed soil samples collected from around the lakes and field studies at two different sites found that water quality guidelines were exceeded for protection of aquatic ecosystems in a number of the seawater inundation experiments (Sullivan et al. 2010). However, these had limited depth of standing water.

It is noted that Lake Albert could become hypersaline during 2010 (even with freshwater pumping) and Lake Alexandrina will have substantial salinity if low inflows continue. Increasing saline conditions in the lakes will likely induce even greater cation exchange processes to seawater input.

Preliminary modelling results for Lake Alexandrina show that salinity propagates across the lake to create near seawater salinities at the river entrance near Wellington within 3-6 months but hypersalinity did not develop within a 2-3 year timeframe under 896GL inflow at SA Border (Hipsey et al. 2010)

Higher salinity will result in less turbid water in the lakes and this, coupled with salinityinduced nutrient release from the sediments and warm conditions with ample sunlight, could create algal blooms.

The short-medium term geochemical stability of the system is unknown.

3.9.5 Is partial seawater input a viable option or should it be all or nothing?

Use of freshwater to maintain lake levels above the trigger levels is clearly preferred. If freshwater is not available then prevention and/or treatment using part ("shandied") seawater may be an option. As noted above even partial seawater input will result in seawater salinities in large areas of the lakes within 6 months.

3.10 Is it possible for the lakes to recover naturally?

Long-term recovery of acid sulfate soils can occur naturally although hydrological and geochemical conditions will control sulfur cycling. Under anoxic conditions, sulfur can reduce back to sulfide, however research from East Trinity Inlet (eg Johnston et al. 2009) indicates that acid-volatile sulfide can form with geochemical changes (eg sediment morphology and composition) to an altered rather than previous state. Oxidation of acid sulfate soils and subsequent pH increase will liberate metals and metalloids that can then be either deposited as precipitates and/or taken up in the foodchain.

The ecological issues associated with either freshwater or seawater inundation could be very significant. The research currently underway does not cover this but will help to inform further work. This is part of the Seawater EIS project.

3.10.1 If so what is the minimum that we need to do without compromising recovery?

Acid base accounting of acid sulfate soils, monitoring of water quality and linking into ecological surveys are fundamental for the real-time management of the Lower Lakes. It is also necessary that the data are used to verify and inform hydrological and biogeochemical modelling.

Long-term freshwater refilling scenarios of different flow rates from the CSIRO sustainable yields study suggest that we are in a severe drought and increased freshwater flows to the lakes will return at some point. How well the lake water quality might recover from acid sulfate soil issues and/or seawater ingress will depend on how well flows are able to flush out salinity and acidity. This could take years judging on experiences at other sites (eg East Trinity). Recovery of the soil condition is also possible but could take a much longer timescale (years to decades) and the system could end up in an altered state (eg formation and persistence of iron precipitates).

3.11 Are odour and other air quality problems likely to occur?

The EPA undertook air quality monitoring over late summer 2008 to assess risks from breathing in airborne dust off the Lower Lakes and drinking rainwater collected on roof tanks. Based on these initial findings the Department of Health has advised of a low health risk. Monitoring is ongoing and no additional risks have been noted.

It is possible that there may be localised odour issues, particularly in areas where mono-sulfidic black ooze (MBO) is present. Sediment re-inundation may also cause odour problems (eg hydrogen sulfide, sulfur dioxide).

Sand drift has been noted to be a major issue in some areas and a revegetation program is being trialled in some areas to stabilise sands.

4 Further research and monitoring

Various ideas for further research and monitoring are contained in the research project reports. The priority areas to inform management of the Lower Lakes, and improve modelling predictions, are considered to be:

- Improved information on the amount of retained acidity in sediment profiles is required with better estimates of the conversion and mobility between different forms of acidity.
- Key parameters (pH, acidity, Eh, salinity) should be monitored in sediments and shallow groundwaters around the lakes, including transects and whole of system surveys, with more intensive analysis if screening indicates problem areas. This information can provide an early warning of acidity problems.
- Continued monitoring and research of the percolation and baseflow of acidity, in particular groundwater movement following rainfall events, as a critical pathway for lake acidification. Better information is required on the magnitude and variability of this effect for example by using isotope tracers.
- The behaviour of clays during drying, oxidisation, and rewetting under a range of conditions needs to be better understood. The field and laboratory experiments carried out to date were undertaken after some rewetting, by rainfall, of dried mostly sandy sediments.
- The oxidation rates of acid sulfate soil materials requires further research, particularly the oxidation of clay materials and the *in situ* dynamics of sediment moisture and oxygen diffusion. Column leaching experiments could also be undertaken as another simple and independent check on oxidation rates.
- Bioremediation is a proposed management option in some localised areas but the requirements for it to be effective are not well understood. In particular the effects of carbon addition on sulfate reduction rates need to be determined.
- Continued monitoring of whole of lake water quality is required while there is a significant risk of acidification. The current monitoring program should be reviewed and assessed to ensure that it is effective and meets objectives.
- Continued soil monitoring (twice per annum) of the current fifty CSIRO monitoring sites in Lakes Albert, Alexandrina and tributaries. At 5 selected sites undertake additional research: installing peepers for geochemical modelling and conducting more detailed mineralogical analyses.
- Analyse and reinterpret the existing CSIRO spatial mapping data on a volume basis, rather than a layer basis, (suggest volume could be top 10cm, upper 0 to 30cm, or/and 0 to 50cm). This removes the complication of samples coming from different sampling depth intervals. Also provides information on capacity.
- Redo the CSIRO mapping survey of the whole regions but suggest restricting the survey (to save on resources) to the areas above and below the water level (say +-0.5m either side of the current water level) where change would be expected, number of sites could be trimmed down because CSIRO now has prior quantitative information to produce a statistical sound sample site placement design.
- Longer term (5 years+) geochemical model simulations for Lake Alexandrina are recommended to explore the potential lag effects in the delivery of acidic groundwater. The geochemical model should continue to be developed and informed by further research and monitoring work.

5 Conclusion

The Lower Lakes acid sulfate soil research program has substantially increased knowledge of the extent and severity of acid sulfate soils, processes leading to the development and transport of acidity and other contaminants, and the potential water quality impacts.

There is an extensive and considerable acid sulfate soil hazard in the Lower Lakes. The acidity in the soils is heterogeneous and dynamic. The research investigations indicate particularly severe acid sulfate soil hazards are in the clay-rich areas in the centre of both lakes; consequently these areas should be kept inundated to prevent acidification.

Once exposed to the atmosphere, oxidation of the acid sulfate soils in the Lower Lakes occurs rapidly. Significant quantities of acid and contaminants (metals, metalloids and nutrients) have already formed in the sediment around exposed margins of the Lower Lakes.

Currently the acidity flux to the lake via groundwater seepage (following rain events) is not substantial relative to the amount of acid neutralising capacity (alkalinity) in the main lake water body. The current low flux appears to be due to the generally low hydraulic head gradient of the shallow groundwater. However, shallow groundwater flux is predicted to greatly increase if water levels decline further, potentially posing risks to the main lake water body. Sand-rich areas pose a particular threat for groundwater transport due to their low buffering capacity and high permeability to transport acid. Acidification of surface water has already occurred in localised areas containing sands.

Geochemical modelling indicated that acidification of the main lake areas could occur under seawater and freshwater scenarios if water levels fall below approximately -1.75m AHD for Lake Alexandrina and -0.75m AHD for Lake Albert. This is due to the acidic groundwater seepage/baseflow becoming much greater due to much greater exposed sediment area and higher hydraulic head gradient. Localised acidic "hotspots" will continue around the lake margins.

Inundation with seawater will increase the acidity of oxidised acid sulfate soils and release increased levels of contaminants compared with inundation by freshwater. It is preferable to maintain water levels with freshwater and seawater should be considered as a last resort option (if freshwater is not available) to keep high-acidity sediments from oxidising. Other recovery issues surrounding seawater use (eg possible hypersalinity) have not been considered in the present study.

Current indications are that the dust blowing off the exposed lake beds is non-acidic and does not pose a risk to community health. Ongoing monitoring is required to confirm this, particularly if water levels decline further.

The Terms of Reference for the review of the Real Time Management Strategy to Avoid Acidification in the Lower Lakes are currently being scoped following the outcomes of this research and the Seawater EIS project. Any future strategy should be adaptive and informed by ongoing research and soil, water quality and ecological monitoring.

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