COORONG, LOWER LAKES & MURRAY
MOUTH RECOVERY PROJECT

Acid Sulfate Soils Research Priorities Review 2010 to 2016

June 2016

Government of South Australia
Department of Environment,
Water and Natural Resources

For further information please contact

Department of Environment, Water and Natural Resources
GPO Box 1047, Adelaide SA 5001
Telephone National (08) 8463 6946
International +61 8 8463 6946
Fax National (08) 8463 6999
International +61 8 8463 6999
Website www.environment.sa.gov.au

Disclaimer

ISBN 978-1-921800-95-5.

Preferred way to cite this publication

DEWNR 2016, Acid sulfate soils research priorities review 2010 to 2016. Government of South Australia, through the Department of Environment, Water and Natural Resources, Adelaide pp.

Acid Sulfate Soils Research Priorities Review 2010 to 2016

June, 2016

Prepared by the South Australian Department of Environment, Water and Natural Resources as part of the Coorong, Lower Lakes and Murray Mouth Recovery Project, funded by the South Australian Government's Murray Futures program and the Australian Government.

Government of South Australia
Department of Environment,
Water and Natural Resources

Foreword

The Department of Environment, Water and Natural Resources (DEWNR) is responsible for the management of the State's natural resources, ranging from policy leadership to on-ground delivery in consultation with government, industry and communities.

High-quality science and effective monitoring provides the foundation for the successful management of our environment and natural resources. This is achieved through undertaking appropriate research, investigations, assessments, monitoring and evaluation.

DEWNR's strong partnerships with educational and research institutions, industries, government agencies, Natural Resources Management Boards and the community ensures that there is continual capacity building across the sector, and that the best skills and expertise are used to inform decision making.

Sandy Pitcher
CHIEF EXECUTIVE
DEPARTMENT OF ENVIRONMENT, WATER AND NATURAL RESOURCES

Acknowledgements

Project Team

Many Department of Environment, Water and Natural Resources staff were involved in the achievements of the 'Research Priorities' Management Action. In particular, we would like to thank agency staff Liz Barnett, Jason Higham, John Howard, Ann-Marie Lush, Stephen Madigan, Paul McEvoy, Ross Meffin, Ceridwen Synnett and Russell Seaman for their efforts in the design and implementation of the research program.

Lower Lakes Acid Sulfate Soils Scientific Research Committee

Expert technical advice obtained from the 'Lower Lakes Acid Sulfate Soils Scientific Research Committee' during the June 2016 acid sulfate soil Workshop was used to review a draft of this document. Contributions enthusiastically provided by the committee members greatly improved the accuracy and completeness of this document. Our thanks goes to: Andrew Baker, Freeman Cook, Tracy Corbin, Rob Fitzpatrick, Matt Hipsey, Tim Hoar, Anu Kumar, Peter Mettam, Luke Mosley, Dan Rogers, Hafiz Stewart and Dylan Stone.

Land holders and community

We thank the landholders and community members that participated in this research program for kindly allowing access through their land and providing assistance with field sampling, experimentation, and knowledge of the CLLMM region. We also thank the region's traditional owners, the Ngarrindjeri, for sharing their knowledge of the CLLMM region and in guiding field activates to avoid the disturbance of culturally significant areas

Nathan Leonard Creeper and Paul Shand are recognised for their contribution to compiling this report.

Executive Summary

The Coorong, Lower Lakes and Murray Mouth (CLLMM) is an iconic region at the terminus of the Murray-Darling Basin (MDB) and recognised as a wetland of international importance under the Ramsar convention. Prolonged hydrological drought conditions in the MDB from approximately 1997 to 2009 (i.e. the 'Millennium Drought') led to the rapid lowering of water levels in the Lower Lakes. Record low water levels resulted in the exposure and oxidation of extensive areas of acid sulfate soils (ASS), forming sulfuric acid in the soils around the margins of Lakes Alexandrina and Albert and along the banks of the Finniss River, Currency Creek and Goolwa Channel. Following the end of the Millennium Drought in 2010, the return of flows rewetted acid sulfate soils that had acidified during the Millennium Drought. In a number of isolated areas, acidity and metals were transported from the soils when they were rewet, causing surface waters to become acidic.

This report reviews the findings from acid sulfate soil research activities undertaken as part of the 'Research Priorities' Management Action; for the period 2010 to 2016. Research activities undertaken cover a number of different scientific fields and are categorised into eight key research themes. A number of significant findings are summarised under the relevant key research themes underlined below.

Properties and spatial distribution of ASS materials in the CLLMM region

- Acid sulfate soils are widespread in the CLLMM region and represent an extensive and significant long term acidification hazard.

Air quality impacts related to ASS

- Low lake levels resulted in an increased dust nuisance for communities around the Lower Lakes.
- Dust blown off the dry acidified lake bed during the Millennium Drought was not a public health risk.

Pyrite oxidation rates in the Lower Lake soils

- Pyrite oxidation rates in the CLLMM region were relatively fast.
- Pyrite oxidation rates were generally faster in sandy soils than in clayey soils.
- Pyrite oxidation rates slowed considerably when soils became more saturated. This supports the use of temporary structures to keep soil saturated if not inundated to prevent further acidification.

Contaminant mobilisation and transport

- Ecologically hazardous concentrations of acidity, metals and other contaminants can be mobilised when acid sulfate soils are rewet.
- The most hazardous period for surface water acidification and contamination is immediately following rewetting. Hence, if surface waters do not turn acidic upon rewetting, they are unlikely to do so in the future.

- The rewetting of severely acidified soils with seawater as opposed to freshwater carries a higher risk of surface water acidification and contamination in the short term.
- Surface water is more likely to become acidic above clayey soils than sandy soils.
- A single charge of water can be insufficient to neutralise stored soil acidity. Soils have the potential to remain acidic following rewetting, unless internal alkalinity is generated through reduction reactions.
- Both rainfall and seiche events were the dominate drivers of transport processes that delivered acidity from the soils to lake surface waters.
- Lateral groundwater flow and diffusive fluxes following rewetting were less significant acidity delivery mechanisms.
- Model simulations demonstrated that the fortuitous rapid rate of lake refilling at the end of the Millennium Drought minimised localised manifestations of acidification.
- Where lake refilling is predicted to occur slowly, storing water to permit the rapid inundation of soils should be considered as a potential management option to reduce the risk of surface water acidification.

Post reflooding recovery of sulfuric materials

- Many soils had not returned to pre-drought conditions 3 years after rewetting. Soil monitoring ceased in 2013 and the current status of acid sulfate soils is unknown.
- Despite some improvements in soil pH, the degree of acidification hazard in the Lower Lakes remains high and largely unchanged since the Millennium Drought.
- The recovery or neutralisation of oxidised acid sulfate soils is complex. Under favourable conditions recovery in the surface layers can occur quickly. However, under less favourable conditions and for deeper soil layers, recovery can take several years. The presence of jarosite was a dominant factor slowing the rate of soil neutralisation and recovery.
- The rapid rate of acidification and the potentially long time-scales required for recovery highlight that the best way to manage acid sulfate soils is to prevent them from being disturbed in the first place.
- Phytoremediation (via revegetation) provided a source of organic matter (carbon) to the soil that fuelled internal alkalinity generating reduction reactions. However, results were dependent on the type of vegetation species used;
    - Vegetation species unable to survive prolonged inundation (e.g. Bevy rye) may have helped to 'kick-start' alkalinity generating reduction reactions but were unable to support internal alkalinity generation in the long term.
    - In contrast, vegetation species with greater tolerance to prolonged inundation (e.g. *Phragmites australis* and *Schoenoplectus validus*) were able to support internal alkalinity generation over the long term.
- The use of inundation tolerant plant species (e.g. *Phragmites australis*) may also result in increased acidification and deoxygenation hazards compared to unvegetated sites. These hazards were avoided almost completely when inundation intolerant vegetation was used.

- Revegetation stabilised exposed lake margin soils against erosion by wind and water. This substantially reduced the loss of surface soil layers and prevented highly acidic sub-surface soil layers from becoming exposed and making direct contact with surface waters upon rewetting.
- Overall, the effectiveness of phytoremediation (via revegetation) to aid recovery is uncertain and further work is required to better define the risks and benefits of this management technique.

Benthic ecology and ecotoxicology impacts related to ASS

- Porewaters, analysed four years after rewetting, were considered severely toxic to aquatic organisms.
- The cause of toxicity was attributed to a combination of stressors including low pH, elevated salinities and high metal and nutrient concentrations.
- Surface waters and surface soil layers generally exhibited no acute or chronic toxicity to biota.
- Benthic biota were most abundant in the surface soil layer due to favourable habitat conditions and were spatially distanced from potentially toxic concentrations of contaminants.
- However, the upward flux of contaminants from the severely toxic sub-surface porewaters posed a moderate to high level risk to biota inhabiting surface waters and the surface soil layers. The flux of contaminants from toxic sub-surface layers is expected to persist for several years.

Development of an integrated CLLMM water quality response model

- An integrated modelling platform, able to simulate the hydrodynamics and biogeochemistry of the system from 2008-2015, was developed and validated for the CLLMM region.
- The model utilised findings from concurrent studies that were part of the 'Research Priorities' Management Action. By using data directly associated with the Lower Lakes region modelling outcomes are better supported.
- The model was used to set 'trigger levels' for Lakes Alexandrina and Albert. Water heights should be managed above these levels to prevent surface water acidification;
    - For Lake Albert the 'trigger level' was set at - 0.5 m AHD.
    - For Lake Alexandrina the 'trigger level' was set at - 1.5 m AHD.
- Overall, modelling pointed to a much higher risk to Lake Albert than Lake Alexandrina under Millennium Drought conditions, supporting the decision to maintain water levels in Lake Albert via pumping from Lake Alexandrina.
- Hot-spot locations of surface water acidification observed in the Millennium Drought are unlikely to change in a future drought.
- The model is best employed as a predictive tool within an adaptive monitoring framework, and not used in isolation. Modelling and process studies should be integrated.

Overall, the 'Research Priorities' Management Action successfully addressed essential information needs to underpin the effective management of the threat posed to the ecological character of the CLLMM region by acid sulfate soils. However, knowledge gaps and uncertainties remain. Continued annual to bi-annual monitoring of antecedent conditions and acid sulfate soil status are critical to successfully responding to another drought. Future acid sulfate soil research should prioritise the investigation of linkages between acid and contaminant fluxes, coupled biogeochemical cycles and ecological impacts throughout the food chain.

Table of Contents

List of Tables

List of Figures

1. Introduction

1.1 Preface

This report reviews the findings of acid sulfate soil research conducted as part of the 'Research Priorities' Management Action for the Coorong, Lower Lakes and Murray Mouth (CLLMM) Recovery Project (DEH, 2009). Overall, the CLLMM Recovery Project comprised a suite of 21 management actions, with 'Research Priorities' commencing in 2009. The Management Action aimed to fill key acid sulfate soil knowledge gaps to inform management of the CLLMM region and manage variable lake levels if low inflows returned. This was achieved by undertaking a suite of research activities related to acid sulfate soil processes to provide a foundation for decision making and lead to an improved understanding of the CLLMM Site's ecological character.

The CLLMM Recovery Project ($137 million) was a key component of the South Australian Government's Murray Futures Program ($610 million) and was funded by the Federal Australian Government's Water for the Future Initiative ($12.9 billion). Through the CLLMM Recovery Project, an investment of approximately $1.25 million (plus co-contributions from service providers) was made towards research activities related to acid sulfate soil processes in the region. In addition, approximately $2.25 million was invested towards the monitoring and adaptive management of acid sulfate soils and their impacts.

This review was written to provide a valuable resource for environmental scientists, natural resource managers and community members with an interest in the unique CLLMM environment and/or acid sulfate soils. As an extension to the previous summary report (DENR, 2010), this review consists of a compilation of all acid sulfate soil research conducted in the CLLMM region as part of the 'Research Priorities' Management Action for the period 2010 to 2016. This review individually summarises the aims, approach and findings from each output (e.g. scientific reports) generated. Key findings contained in the individual summaries, and their significance for the management of acid sulfate soils in the CLLMM region, are further synthesised into an overall review and conclusions. Acting as a portal, this review provides a way for readers requiring greater detail to easily access the full scientific reports. Finally, this review incorporates the outcomes from the acid sulfate soils expert workshop held in Adelaide in June 2016, including recommendations for future research priorities.

1.2 Environmental context of the CLLMM Region

The CLLMM region is located at the terminus of the Murray-Darling Basin (MDB), about 75 km south east of the city of Adelaide, South Australia. The site encompasses Lake Alexandrina, Lake Albert, the lower reaches of Currency Creek and Finniss River, the Murray Mouth and Coorong lagoon and a number of other ephemeral aquatic ecosystems. Lake Alexandrina (approximately 650 km^2) and Lake Albert (approximately 169 km^2) are large shallow lakes with gently sloping margins. Average depths at full capacity for Lake Alexandrina and Lake Albert are 2.9 m and 1.4 m, respectively. Together they have a capacity of approximately 2015 GL under normal flow conditions.

Currency Creek and Finniss River are considered permanent tributaries. In their lower reaches they broaden from their channels into sheltered wetland habitat and ultimately open water as part of the Goolwa Channel and Lake Alexandrina.

The environmental importance of the CLLMM region is recognised nationally as one of Australia's icon wetlands and internationally as a wetland of international importance under the Ramsar convention. The CLLMM region supports a large number of ecological communities (some threatened) including waterbirds, fish, amphibians, and flora. The area is a popular recreational site and supports a range of economically important commercial activities such as tourism, irrigated agriculture and commercial fishing. The CLLMM region is culturally significant to the Ngarrindjeri people, who have cared for the country for thousands of years.

The freshwaters of the River Murray flow into Lake Alexandria and Lake Albert (via the Narrung Narrows). The Lower Currency Creek and Finniss River tributaries are adjacent to Lake Alexandrina and receive freshwater flows from the eastern Mount Lofty Ranges which then enter the Goolwa Channel (River Murray). The freshwaters of the River Murray, Lakes Alexandrina and Albert, and the Currency and Finniss tributaries are separated from the saline waters of the Coorong and Southern Ocean by a series of barrages that were constructed in the 1930 to 1940s.

1.3 An introduction to acid sulfate soils

1.3.1 What are acid sulfate soils?

Acid sulfate soils are soils that either contain iron-sulfide minerals (e.g. pyrite (FeS2)), or soils that are affected by the transformations of iron-sulfide minerals (e.g. severe acidification). The iron sulfide minerals found in acid sulfate soils accumulate naturally in reducing environments, such as those found in waterlogged soils. If left undisturbed and kept in a reducing environment (e.g. underwater), the accumulated iron-sulfide minerals in acid sulfate soils are generally considered benign. However, if disturbed and exposed to oxidising conditions (i.e. exposed to air) the accumulated iron-sulfide minerals in acid sulfate soils will oxidise, and potentially generate sufficient sulfuric acid to severely acidify the soil (i.e. resulting in a pH of less than 4).

Hence the main distinguishing features of an acid sulfate soils are either:

- The presence of pyrite in sufficient quantities that would result in severe acidification if disturbed and allowed to oxidise. Due to their potential to acidify these soils are commonly termed **potential acid sulfate soils**. Scientifically they are classified as **hypersulfidic materials**

or

- The presence of severe acidification (pH < 4), with the oxidation of iron-sulfate minerals the dominate source of acidity. These soils have realised their acidification potential and are commonly termed **actual acid sulfate soils**. Scientifically they are classified as **sulfuric materials**.

Two other types of acid sulfate soil materials exist. These are **hyposulfidic materials** and **monosulfidic materials**.

- **Hyposulfidic materials** are similar to hypersulfidic materials in that they contain a source of potential acidity (i.e. pyrite). However, unlike hypersulfidic materials, hyposulfidic materials also contain an equivalent source of acid neutralisation capacity. Because of this, the oxidation of hyposulfidic materials does not result in severe acidification.
- **Monosulfidic materials** have high concentrations of iron monosulfide minerals (FeS). The acidification potential of monosulfidic materials is not as great as hypersulfidic materials. This is because, compared with pyrite, iron monosulfide minerals release only 1/8th the amount of acidity when oxidised. However, due to its propensity to form as surface accumulations, monosulfidic materials can be easily resuspended and cause the deoxygenation of surface waters. Monosulfidic material is commonly observed as monosulfidic black ooze, however, it occurs in a range of consistencies.

1.3.2 The formation of hypersulfidic materials (potential acid sulfate soils) in the CLLMM Region

The formation of hypersulfidic material principally involves the formation of acid generating iron-sulfide minerals. Pyrite is the most abundant and thus the dominant acid generating mineral in acid sulfate soils. The formation of pyrite occurs in waterlogged, reduced environments where sources of sulfate, iron and organic matter are available. Pyrite formation involves a complex series of biogeochemical processes, however the overall reaction is summarised by the equation:

$$15CH_2O + 4FeOOH + 8SO_4^{2-} + CO_2 = 4FeS_2 + 16HCO_3^{-} + 9H_2O$$

Organic matter + iron oxide + sulfate + carbon dioxide = pyrite + alkalinity + water

Two key factors have contributed to the formation of pyrite in the Lower Lakes: continuous waterlogging and salinisation. Since the construction of the barrages water levels in the Lower Lakes have been actively managed at approximately 0.75 m AHD. These high, static water levels were maintained from approximately 1940 until 2006. The construction of regulatory structures, such as barrages downstream and locks in the River Murray upstream to manage water at artificially high levels, resulted in the loss of the natural wetting and drying regime driven by climate variability. Under natural conditions, without the intervention of regulatory structures, climate variability produces regular periods of flooding in years with high rainfall, followed by periods of drying in years with low rainfall. This natural wetting and drying cycle prevents the continuous accumulation of pyrite, whereby each dry period oxidises pyrite accumulated during the previous wet period. The smaller amount of acidity released during the more frequent oxidation of accumulated pyrite is more effectively dealt with in freshwater systems by natural soil and water neutralisation processes. The buffering of seasonal and yearly variations in rainfall, caused by barrages and locks, supports prolonged periods of inundation, in turn favouring reducing conditions and the on-going accumulation of acid generating pyrite.

The salinisation of the MDB, due to primary industry development within the catchment, is another modification that aids the accumulation of pyrite. The formation of pyrite is a naturally occurring process in freshwater inland systems. However, under low sulfate concentrations typical of freshwater systems, sulfate reduction and in turn the production of pyrite is restricted. However, high concentrations of sulfate associated with salinisation can enhance sulfate reduction and result in greater accumulations of pyrite.

These two main anthropogenic disturbances (i.e. the construction of regulatory structures and salinisation) have supported the on-going multi-decade accumulation of pyrite and formation of hypersulfidic materials in the CLLMM region for at least 70 years (approximately 1940 until 2006).

1.3.3 The formation of sulfuric materials (actual acid sulfate soils) in the CLLMM Region

Pyrite will continue to form under reducing conditions as long as there is sufficient iron, sulfate and liable organic matter available. Once formed, pyrite is stable (i.e. benign) as long as reducing conditions are maintained. However, if exposed to air, pyrite will oxidise and release acidity. The process through which FeS_2 contained in hypersulfidic material is oxidised involves a number of geochemical and biogeochemical reactions. However, the complete oxidation of pyrite is summarised by the equation.

$$4FeS_2 + 15O_2 + 14H_2O = 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+$$

pyrite + oxygen + water = iron hydroxide + sulfate + acidity

In a closed system, the amount of acidity released by pyrite oxidation is equivalent to the amount of alkalinity generated when the pyrite was formed (see Section 1.3.2). This means that theoretically the oxidation of pyrite in a closed system will not result in the formation of sulfuric material (i.e. severe acidification) upon oxidation.

However, most natural systems are not closed. In acid sulfate soils, alkalinity, or acid neutralising capacity, is generally found in the form of carbonates ($CaCO_3$) or dissolved alkalinity (HCO_3^-). Carbonate minerals, such as calcite, are common in calcareous environments such as the Lower Lakes. These minerals are readily solubilised and can be transported away from the area of pyrite accumulation. Conversely, pyrite is insoluble and remains within the soil. In natural acid sulfate soil systems, severe soil acidification following the oxidation of hypersulfidic material is often the result of the removal of acid neutralising capacity from the soil. Hence, as pyrite accumulates, the soil develops an acid generation potential. When the acid generation potential is greater than the available acid neutralising capacity, sulfuric material will form following the oxidation of hypersulfidic materials. The oxidation of hypersulfidic material is most often triggered by decreasing surface water levels or lowering of the water table.

In 2006, prolonged hydrological drought conditions in the MDB (i.e. the 'Millennium Drought') led to the rapid lowering of water levels in the Lower Lakes. The Millennium Drought (approximately 1997 to 2009) is the worst drought to affect the MDB in recorded history. Water levels in Lake Alexandrina reached their lowest level of approximately -1.0 m AHD in late 2009. As a consequence of unprecedented low water levels, extensive areas of previously inundated soils around the margins of Lakes Alexandrina and Albert and along the banks of the Finniss River, Currency Creek and Goolwa Channel became exposed. Many of the exposed soils contained acid sulfate soil materials that underwent their first major drying phase for at least 70 years. The exposure and drying of acid sulfate soil materials during the period 2006 to 2010, resulted in the en masse oxidation of multi-decade pyrite accumulations, in turn forming sulfuric acid in the wetland, lake and river systems of the CLLMM region.

1.3.4 Post-drought rewetting of sulfuric materials in the CLLMM Region

In 2010, the Millennium Drought broke and large volumes of freshwater entered Lake Alexandrina causing a rapid rise in water levels. The water levels in Lake Alexandrina stabilised first, then the temporary Narrung bund (Section 1.4.1) separating Lake Albert from Lake Alexandrina was breached in late 2010. This led to an equalisation of water levels in both lakes, returning to approximately 0.7 m AHD. The temporary flow structures installed near Clayton (Goolwa Channel) and in Currency Creek were also breached in late 2010. However, this region also experienced an earlier partial refilling (approximately 0.5 m AHD) in November 2009 as a result of pumping from Lake Alexandrina and tributary flows (i.e. large unseasonal catchment rainfall).

The return of high flow conditions, following the end of the Millennium Drought, resulted in the rewetting of sulfuric materials that formed around lake margins and river banks during the Millennium Drought. When sulfuric materials are rewet they can release metals and cause surface water to turn acidic (Section 1.4.1). Since being rewet in 2010, high water levels have been maintained in the Lower Lakes, and soils have remained underwater.

1.3.5 Environmental hazards associated with acid sulfate soils

The majority of environmental impacts posed by acid sulfate soils are associated with sulfuric materials. As well as low pH and severe acidity, the porewaters of sulfuric materials often contain high concentrations of mobile metals and metalloids. These acidic and metal rich porewaters can be transported from the acid sulfate soil to surface waters and cause significant ecological impacts such as:

- Severe stunting or death of acid or metal intolerant vegetation.
- Detrimental effects on fish and other aquatic and benthic organisms including habitat degradation, fish kills, infection and disease, community structures changes due to the removal or suppression of species and benthic smothering due to the formation of iron precipitates.

1.4 Historical acid sulfate soil research in the CLLMM Region

In Australia, acid sulfate soils are estimated to cover 22 million ha (Fitzpatrick, *et al.*, 2008a). Approximately 6 million ha can be found along Australia's coast in low lying areas such as mangroves and estuaries. The remaining approximately 16 million ha is located in inland environments such as the rivers, lakes, wetlands, and floodplains in the MDB. Historically, acid sulfate soils have been considered a coastal issue and consequently coastal systems have been the focus of the majority of published research since the 1970s. In contrast, the full extent of inland acid sulfate soils was only beginning to be recognised in the late 1990s (Fitzpatrick and Shand, 2008a).

In the CLLMM region, the earliest scientific recording of acid sulfate soils was in 1931, when J.K. Taylor and H.G. Poole encountered a soil that acidified to a pH of 3.9 while surveying the suitability of Lake Albert for pasture or cropping (Fitzpatrick and Shand, 2008b). This was identified as a hypersulfidic material 78 years later when the original soil samples were retrieved from the CSIRO soil archive and retested. However, it was not until 2008 that the occurrence and potential risks posed by acid sulfate soils in the CLLMM region began to be investigated and documented. These early investigations corresponded with or occurred just prior to the rapid lowering of water levels in the CLLMM region during the Millennium Drought. Hence, at a time where acid sulfate soils in the CLLMM region were already undergoing rapid transformations (from hypersulfidic to sulfuric) relatively little was known about their properties, distribution and controlling processes.

A full account of research activities that occurred prior to the initiation of the 'Research Priorities' Management Action in 2009 is beyond the scope of this report. However, a brief background of how these earlier investigations of acid sulfate soils and their impacts in the CLLMM region influenced the creation of the 'Research Priorities' Management Action is provided below.

Field soil surveys conducted by CSIRO in 2007 to 2008 identified that a range of acid sulfate soil materials were present in the Lower Lakes (Fitzpatrick*, et al.*, 2008b, Fitzpatrick*, et al.*, 2008c) and the lower reaches Finniss River and Currency Creek tributaries (Fitzpatrick*, et al.*, 2009a, Fitzpatrick*, et al.*, 2009b, Fitzpatrick*, et al.*, 2011). Conceptual models developed in these early reports illustrated the transformation of extensive areas of hypersulfidic materials to sulfuric materials that was predicted to occur as they underwent drying (Figure 1).

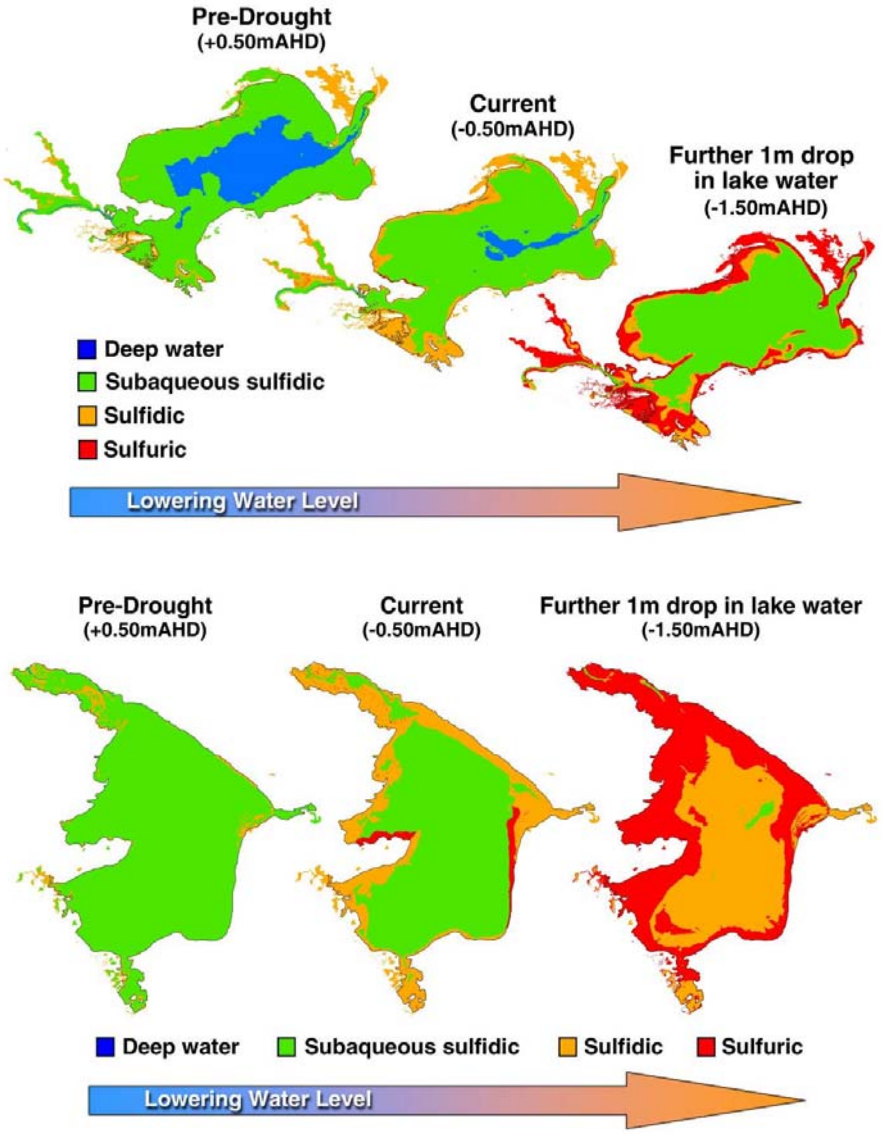


Figure 1. Predictive scenario maps depicting expected changes in acid sulfate soil materials at different water levels (0.5, -0.5 and -1.5 m AHD) in Lakes Alexandrina and Albert and the lower reaches of Finniss River and Currency Creek (Fitzpatrick*, et al.*, 2008c).

Subsequent laboratory investigations of the sulfuric materials showed there was a substantial risk that acidity, metals and other contaminants would be released from these soils into the surrounding ecosystem upon rewetting (Simpson*, et al.*, 2008, Sullivan*, et al.*, 2008). A risk assessment of the hazards posed by acid sulfate soils in the CLLMM region found that detrimental impacts to the aquatic ecosystem, domestic water supply, and stock and human health could be severe (Stauber*, et al.*, 2008).

Preliminary hydrogeochemical modelling was undertaken in an attempt to determine critical water levels in the Lower Lakes at which the risk of acidification of lake surface waters due to leaching from acid sulfate soil became too high (Hipsey and Salmon, 2008). Trigger levels, representing the minimum height that water levels in both lakes must be maintained above to prevent acidification, were adopted for Lakes Alexandrina and Albert. The reliability of many of the parameters used in these early modelling predictions was limited due to the lack of relevant available research to define these values.

Informed with the findings of these early research outputs, the requirement for further scientific research to address critical knowledge gaps relating to the protection of the CLLMM region's ecological character against acid sulfate soil impacts was acknowledged by the state and federal governments. As a result, the 'Research Priorities' Management Action was initiated.

1.4.1 Management actions relating to acid sulfate soils undertaken in the CLLMM region during the Millennium Drought

During the Millennium Drought the South Australian Government undertook several emergency management actions to protect the ecological health of the CLLMM region against impacts resulting from the oxidation and acidification of acid sulfate soils (DENR, 2010, DEWNR, 2010, DEWNR, 2014). A brief summary of the management actions undertaken are provided below in order to provide context for the ‘Research Priorities’ management action and this review. Emergency works and measures relating to the management of acid sulfate soils in the CLLMM region included:

- Purchase of environmental water to protect hot-spot locations within the CLLMM region (e.g. Finniss River and Currency Creek) from further acidification by keeping acid sulfate soils submerged and/or saturated;
- Implementation of broad-scale seeding and revegetation trials to stabilise exposed soils around the lake margins and provide a basis for the phytoremediation of acid sulfate soils;
- Installation of temporary water regulators in the Goolwa Channel and Currency Creek to pool water within the Finniss River and Currency Creek catchments and in the Goolwa Channel (via pumping from Lake Alexandrina) and limit acid sulfate soil exposure until sufficient freshwater flows returned;
- Installation of a temporary water regulator in the Narrung Narrows to maintain the water level in Lake Albert above -0.5 m AHD (via pumping from Lake Alexandrina) and prevent lake acidification until sufficient freshwater flows returned;
- Implementation of an adaptive soil and water quality monitoring program in a number of locations throughout the CLLMM region to provide an early warning system and identify areas of high risk where management actions, in the form of limestone dosing, were required to neutralise acidification and improve water quality; and
- Limestone applications including limestone barriers, aerial dosing and slurry dosing to treat surface water acidification at hot-spot areas such as Boggy Lake, Currency Creek and Finniss River.

2. Research program summary

This Section presents individual summaries of outputs (e.g. scientific reports) generated by the 'Research Priorities' Management Action. Outputs are categorised into the following key research themes;

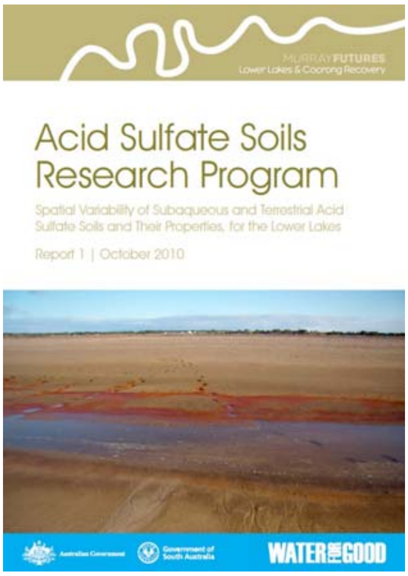
- Properties and spatial distribution of ASS materials in the CLLMM region
- Air quality impacts related to ASS
- Pyrite oxidation rates in the Lower Lake soils
- Contaminant mobilisation and transport
- Post reflooding recovery of sulfuric materials
- Benthic ecology and ecotoxicology impacts related to ASS
- Development of an integrated CLLMM water quality response model
- Conceptual models to aid the communication of complex ASS processes

2.1 Properties and spatial distribution of ASS materials in the CLLMM region

2.1.1 Spatial variability of subaqueous and terrestrial acid sulfate soils and their properties, for the Lower Lakes South Australia

Report details

Full details of the work undertaken and its findings are provided in the report:



MURRAYFUTURES
Lower Lakes & Coorong Recovery

Acid Sulfate Soils
Research Program

Spatial Variability of Subaqueous and Terrestrial Acid Sulfate Soils and Their Properties, for the Lower Lakes

Report 1 | October 2010

WATER FOR GOOD

Fitzpatrick, R., 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. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

Key research outcomes

- Identified the distribution of acid sulfate soil sub types and their properties in the Lower Lakes and Finniss River and Currency Creek tributaries;

- Sulfuric and hypersulfidic materials are widespread. 10% of the samples contained sulfuric material and a further 39% contained hypersulfidic materials that would acidify if water levels declined further;
- Database provided spatially resolved acid base accounting data that reduced uncertainty in model predictions (Section 2.7); and
- Although a 'snap shot' in time the database can be reinterpreted by considering the transformations likely to take place following changes in hydrological conditions.

Aim

Conduct a field soil survey to map the spatial extent of acid sulfate soils in Lake Alexandrina, Lake Albert and the tributaries of Finniss River and Currency Creek in order to:

- Ascertain the spatial distribution and heterogeneity of a number of acid sulfate soil physical and chemical properties such as; pH, acid generation potential, acid neutralising capacity and soil texture.
- Provide a spatially valid dataset to support the development of a hydrogeochemical model.

Approach

Field survey work undertaken in August 2009 resulted in the sampling and analysis of 330 soil profiles (and 706 discrete soil layers) distributed throughout the study area. Sample locations were initially selected using a grid based sampling strategy at a scale of 1:50 000 (with an average site density of 1 site per ha). However, the overall sampling density needed to be reduced due to time and budget constraints. The required reduction in sampling density was achieved without significant loss of mapping reliability by using existing knowledge (see Section 1.4) that established relationships between acid sulfate soil subtypes, bathymetry and vegetation. A non-uniform reduction in the number of sites was also used to ensure a greater proportion of sampling sites were located in areas where existing knowledge indicated greater variability was likely to occur. Namely, areas that were near the shoreline at the time of sampling.

Collected surface soil samples (0 to 10 cm depth) were analysed for a range of parameters including soil texture, pH, $\mathrm{pH_{incubation}}$, electrical conductivity, and full acid base accounting (e.g. net acid generation potential and acid neutralising capacity). Geostatistical techniques were then used to generate maps showing the distribution of the various soil physico-chemical properties.

Findings

The soil field survey produced a spatially reliable database of acid sulfate soil properties that allowed a variety of maps to be generated along with known confidence intervals. The maps produced provided a substantial increase in the spatial detail and reliability with respect to knowledge about acid sulfate soil subtype distribution and variability in the CLLMM region. Derived soil maps showing spatial patterns for soil pH (Figure 2) and net acidity (Figure 3) demonstrated the extensive acid sulfate soil hazard present in the CLLMM region.

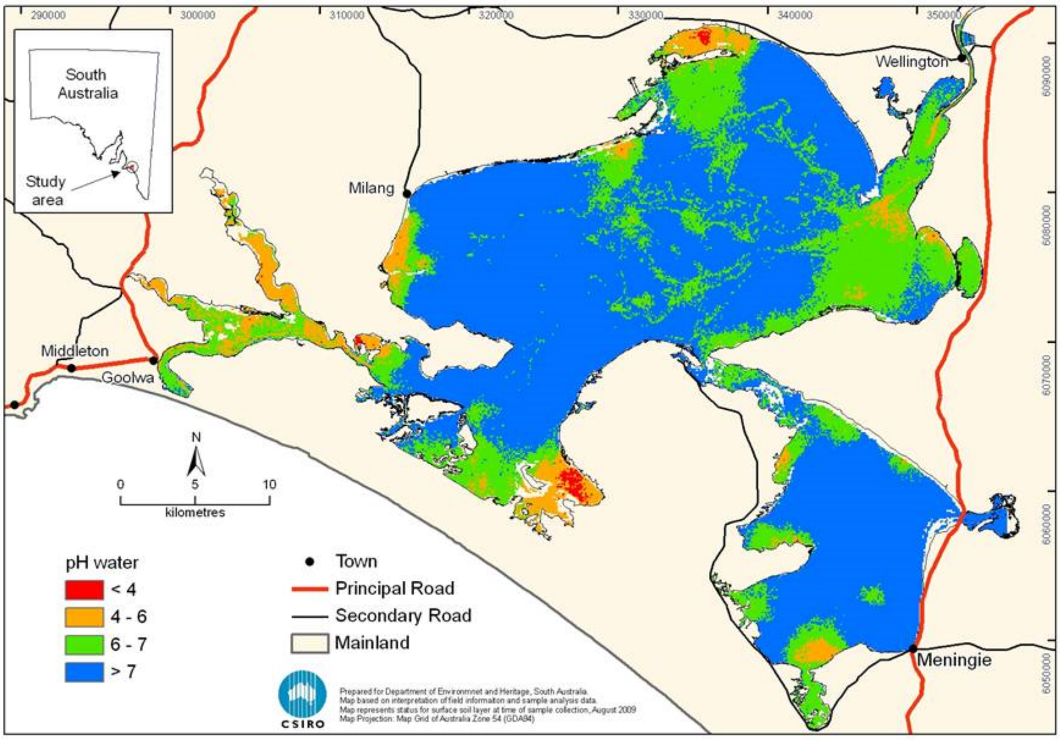


Figure 2. Soil pH map data grouped into four classes for the upper soil layer.

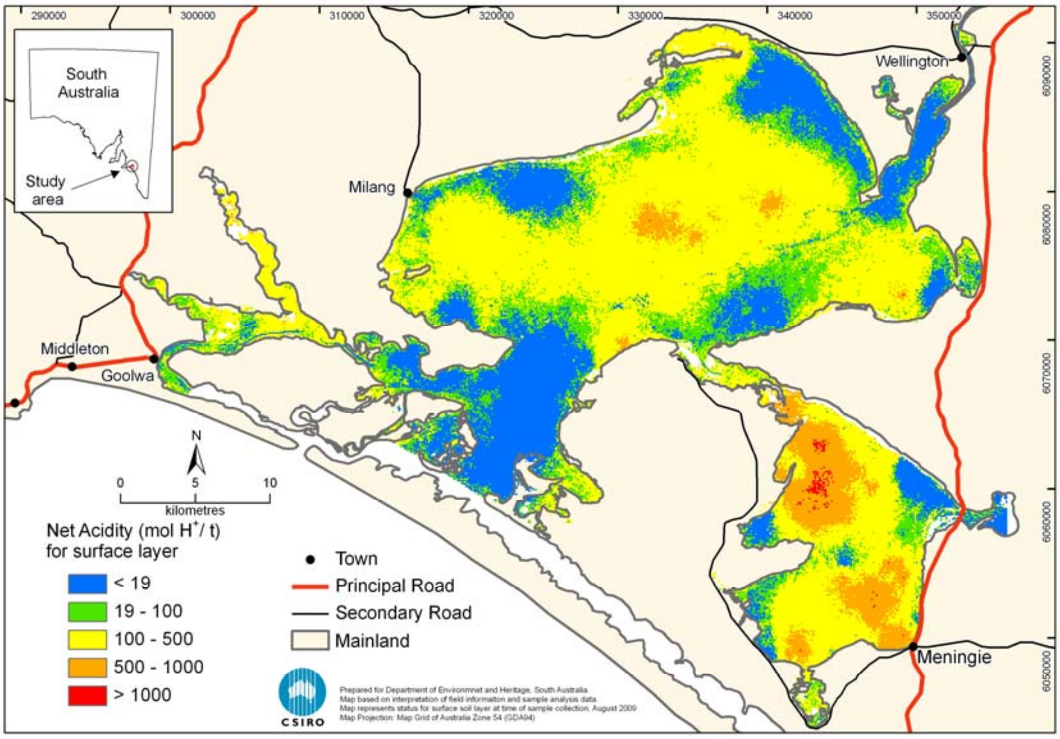


Figure 3. Net acidity map showing data grouped into five classes for the upper soil layer (0 to 10 cm).

At the time of sampling, approximately 20% (18,391 ha) of the total study area (89,219 ha) contained sulfuric materials (pH < 4.0) (Figure 4). Areas of concern included Loveday Bay (near the SE end of the barrages), Clayton (near the start of the Goolwa channel), Boggy Lake and Dog Lake (NE of Tolderol), Finniss River, Currency Creek, and isolated areas around the margins of Lake Albert. A further approximately 80% of the total area contained hypersulfidic materials, with associated hyposulfidic materials, at the time of sampling. These materials have the potential to acidify and form sulfuric materials if allowed to dry and oxidise (e.g. declining water levels). These areas of concern were identified throughout most of Lake Albert and in isolated locations in Lake Alexandrina.

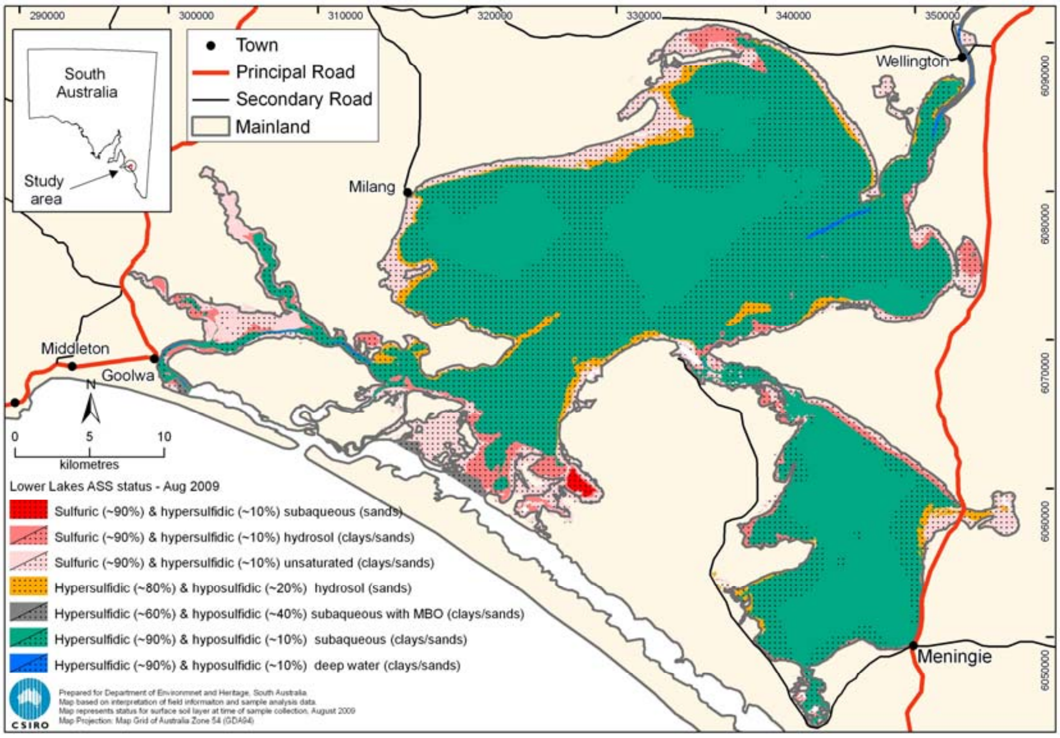


Figure 4. Soil classification map of the distribution of the wide range of acid sulfate soil subtypes. Map legend showing: i) acid sulfate soil materials with sulfuric (pH<4), hypersulfidic (pH<4 after incubation), hyposulfidic (pH>4 after incubation) and monosulfidic (MBO) materials; ii) depth of water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

Research limitations and future work

The maps produced from this research represent a ‘snap shot’ in time and are thus prone to becoming out of date due to the dynamic nature of acid sulfate soil material under changing climate conditions, such as a change in lake water levels. However, the database remains available for re-interpretation by a suitable expert that is able to consider the likely response of the various acid sulfate soil subtypes to a change in environmental conditions.

The collected dataset has considerable potential for further analysis, capitalising on the initial cost of a large scale field survey. Possibilities include:

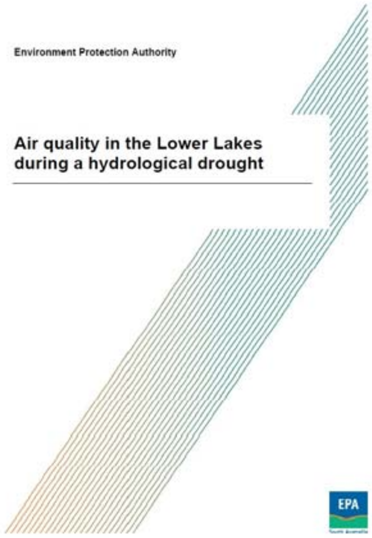
- Studying smaller localised area in greater detail to better identify salient trends in spatial acid sulfate soil subtype variation;
- Revisiting the geostatistical analysis approach to discover potential improvements to mapping reliability; and
- Conducting exploratory multivariate data analysis to understand the correlation between different parameters and improve the estimates of those parameters (e.g. pH).

2.2 Air quality impacts related to ASS

2.2.1 Air quality in the Lower Lakes during a hydrological drought

Report details

Full details of the work undertaken and its findings are provided in the report:



Environment Protection Authority

Air quality in the Lower Lakes during a hydrological drought

EPA

Palmer, D., Mitchell, R., Powell, C., Spencer, J., Mosley, L. (2011). Air quality in the Lower Lakes during a hydrological drought. Environmental Protection Authority, South Australia.

Key research outcomes

- Metals contained in dust blown off the dry acidified lake bed was not a public health risk; and
- Low lake levels resulted in an increased dust nuisance for communities around the Lower Lakes.

Aim

Assess possible human health risks and air quality impacts arising from the dust blown from exposed and acidified lake beds around the margins of the Lower Lakes.

Approach

High volume dust samplers were installed at the Goolwa and Meningie communities (March to May 2009) and at Meningie and Milang (November 2009 to May 2010) to collect fine dust particles (diameter of ≤ 10 µm) blown from the exposed lake beds. Photographs of a sampler and dust storm are shown in Figure 5. Dust collected on the air filters was analysed for dust concentration (number of particles), pH, metals and metalloids. Sub samples were also sent to compare the mineralogy of the dust particles to the mineralogy commonly associated with acid sulfate soils.

Figure 5. A high volume dust sampling unit (left) and dust storm (right) near Goolwa.

Water collected from 18 rainwater tanks in communities around the lower lakes was also analysed for pH, metals, alkalinity, sulfate, chlorite and nitrate. Sampling took place in April 2009 and again in May 2010. Control water samples were taken from two rainwater tanks in Strathalbyn.

Findings

Dust collected on the filters from high volume air samplers indicated that dust blown from the exposed lake beds does not represent a significant risk to public health in terms of acidity or heavy metals. Metal concentrations were compared against health reference guideline values for metals in air. Total chromium concentrations were found to exceed guideline values. However, chromium speciation testing showed the low toxicity form of chromium (Cr III) was the dominant species and the more toxic form of chromium (Cr VI) was only present in very low concentrations. Results for other metals analysed (i.e. aluminium, arsenic, cadmium, cobalt, copper, iron, manganese, nickel, lead, vanadium, and zinc) did not exceed guideline values. Overall particle concentrations were also relatively low (only 9 out of 32 filters collected over 20 µg/m^3) and below guideline values.

Mineralogy results showed that only minor concentrations of minerals commonly associated with acid sulfate soils were collected by the dust samplers. This is consistent with the low acidity and metal concentrations of collected dust samples. Halite (sodium chloride or common table salt) was found to be the dominant mineral present in collected dust samples.

Water collected from rainwater tanks had pH levels typical of rainwater (pH 6.4 to 7.7) and had metal and nutrient concentrations below the Australian Drinking Water Guidelines. Water samples were collected from the rainwater tanks following the first substantial rainfall event after the dry summer period. It is probable that samples collected represented the washing of several months of dust build-up from roof catchments into rainwater tanks. In a few circumstances zinc exceeded aesthetic (based on taste) guideline values (there is no health limit for zinc). These instances were associated with roof catchments, gutters or tanks that were constructed from zinc galvanised steel or zinc-aluminium alloy. South Australia Health, who examined the results, advised the EPA that the results obtained were of no concern and would have no implications to human health. No distinct differences in rainwater quality were observed between the control samples taken from Strathalbyn and samples taken from communities around the Lower Lakes.

Research limitations and future work

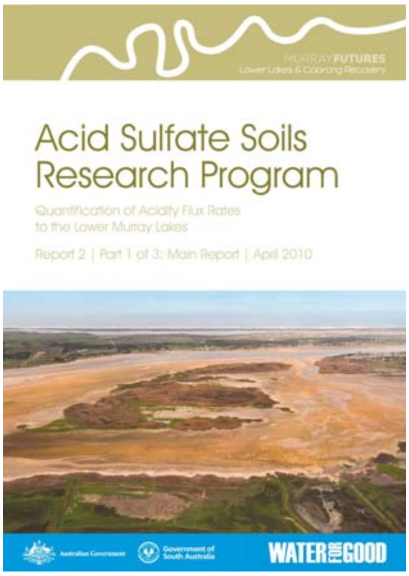
It was recognised that communities located in the Lower Lakes region experienced an increased dust nuisance during the Millennium Drought period, with increased complaints to SA Health during this period. The report recommends that future management strategies consider this issue.

2.3 Pyrite oxidation rates in the Lower Lake soils

2.3.1 Quantification of pyrite oxidation rates in the Lower Lakes

Report details

Full details of the work undertaken and its findings are provided in the report:



MURRAY FUTURES
Lower Lakes & Coorong Recovery

Acid Sulfate Soils
Research Program

Quantification of Acidity Flux Rates
to the Lower Murray Lakes

Report 2 | Part 1 of 3: Main Report | April 2010

Earth Systems. (2010). Quantification of acidity flux rates to the Lower Murray Lakes (and Supplementary Report). Prepared by Earth Systems Consulting Pty. Ltd. for the SA Department of Environment and Natural Resources, Adelaide

Key research outcomes

- Provides a range of pyrite oxidation rates specific to the Lower Lakes region for both sand and clay textured soils; and
- Highlights the dependence of the rate of pyrite oxidation on soil moisture content.

Aim

To determine pyrite oxidation rates for sulfidic acid sulfate soil materials in the Lower Lakes, as a function of soil texture (e.g. sands vs clays) and moisture content.

Approach

The OxCon (oxygen consumption) method developed by Earth Systems was used to determine sulfide oxidation rates by directly measuring the oxygen consumption as a function of time (Figure 6). Each OxCon test produces a result for the bulk oxygen consumption rate. This is attributed to both the oxidation of organic carbon and pyrite oxidation. By subtracting the oxidation consumption rate attributed to the oxidation of organic carbon from the bulk oxygen consumption rate, the oxidation consumption rate attributed pyrite oxidation can be determined. The pyrite oxidation rate was then calculated from the oxidation consumption rate attributed pyrite oxidation using the stoichiometry for the overall reaction of pyrite (FeS_2) with oxygen (O_2) shown below.

$$FeS_2 + {}^{15}/_{4}O_2 + {}^{7}/_{2}H_2O \rightarrow 2H_2SO_4 + Fe(OH)_3$$

Pyrite + oxygen + water → sulfuric acid + ferric hydroxide

This method of calculation assumes that all reduced sulfur present is in the form of pyrite and that the oxidation of pyrite proceeds to completion (i.e. both sulfur and iron is oxidised).

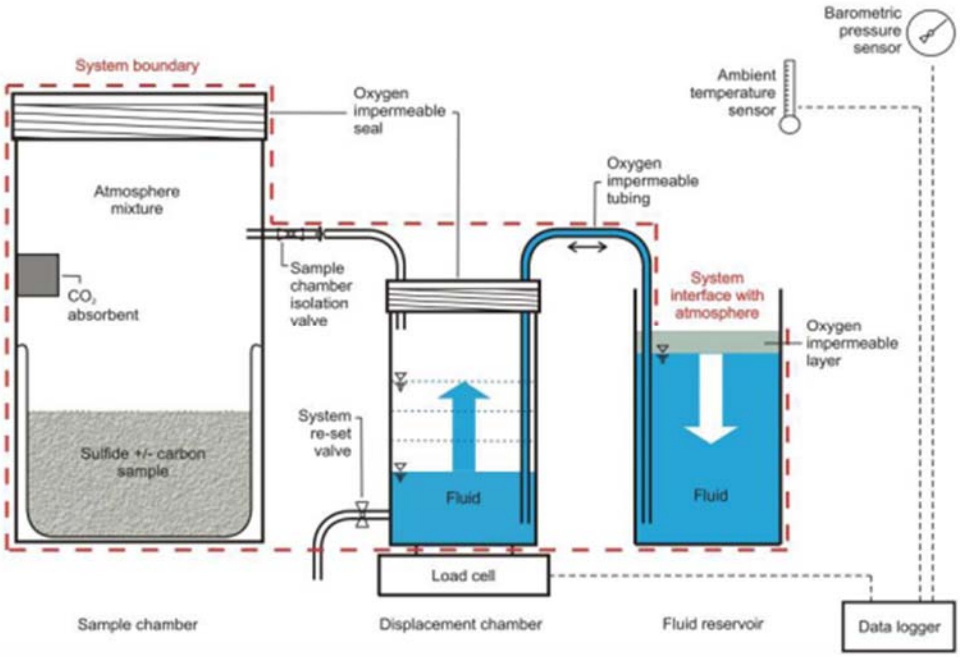


Figure 6. Schematic of the OxCon apparatus used to measure pyrite oxidation rates.

Bulk soil samples considered representative of sulfidic sands and sulfidic clays in the Lower Lakes region were collected from Campbell Park in Lake Albert. Sub-samples were prepared from the bulk soil samples and dried via vacuum desiccation to obtain a range of different moisture contents. Pyrite oxidation rates were determined for 8 sand sub-samples, with moisture contents between 0.00 wt% and 23.5 wt%, and 5 clay sub-samples, with moisture contents between 22.5 wt% and 47.9 wt%.

Findings

Calculated pyrite oxidation rates of the sand and clay samples at varying moisture contents are shown in Figure 7. Results show a complex relationship between the pyrite oxidation rate and moisture content in the sand. Pyrite oxidation rates were slower in the dry and highly saturated sands and faster in sands with intermediate moisture contents. For sand, a maximum pyrite oxidation rate of 1.24 wt% available pyrite per day was recorded at a moisture content of 14 wt%. Pyrite oxidation rates in clays showed an inverse linear relationship with increasing moisture content. Pyrite oxidation rates in clays increased from a minimum of 0.00 wt% available pyrite per day when saturated, to a maximum of 0.78 wt% available pyrite per day at a moisture content of 22.7 wt%. At maximum rates of pyrite oxidation, the time taken to oxidise all available pyrite was calculated to occur within 80 and 128 days (approximately 3 to 4 months), for sand and clay respectively. The general relationship between increasing moisture content and decreasing pyrite oxidation rates was attributed to a decrease in oxygen availability due to slower oxygen diffusion rates in water relative to air.

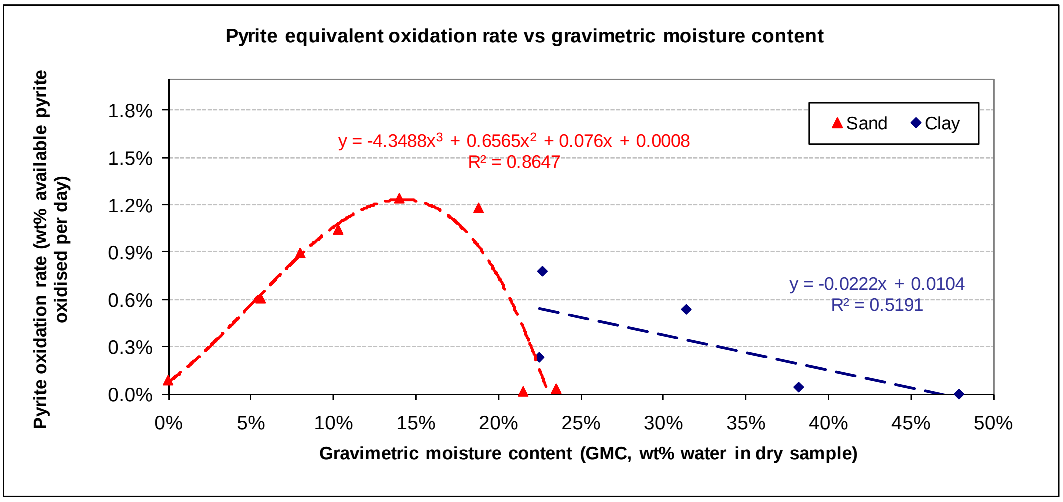


Figure 7. Pyrite oxidation rates vs moisture content for sand and clay sub-samples from Campbell Park, Lake Albert.

A wide range of pyrite oxidation rates have been reported in literature (from 0.00001 wt% to 10 wt% available pyrite per day) (Figure 8). Faster pyrite oxidation rates are predominately associated with unconsolidated soils and sediments such as acid sulfate soils, as opposed to consolidated sediments (i.e. rocks) associated with mine environments. This is because sulfidic materials, like those found in the Lower Lakes region, commonly contain pyrite minerals with very high surface area to volume ratios (i.e. frambiodal in nature), which make the minerals conducive to rapid oxidation. The relatively fast pyrite oxidation rates reported in this study are comparable to pyrite oxidation rates reported in literature for unconsolidated soils, and are consistent with field observations and pH incubation testing of acid sulfate soil materials in the Lower Lakes.

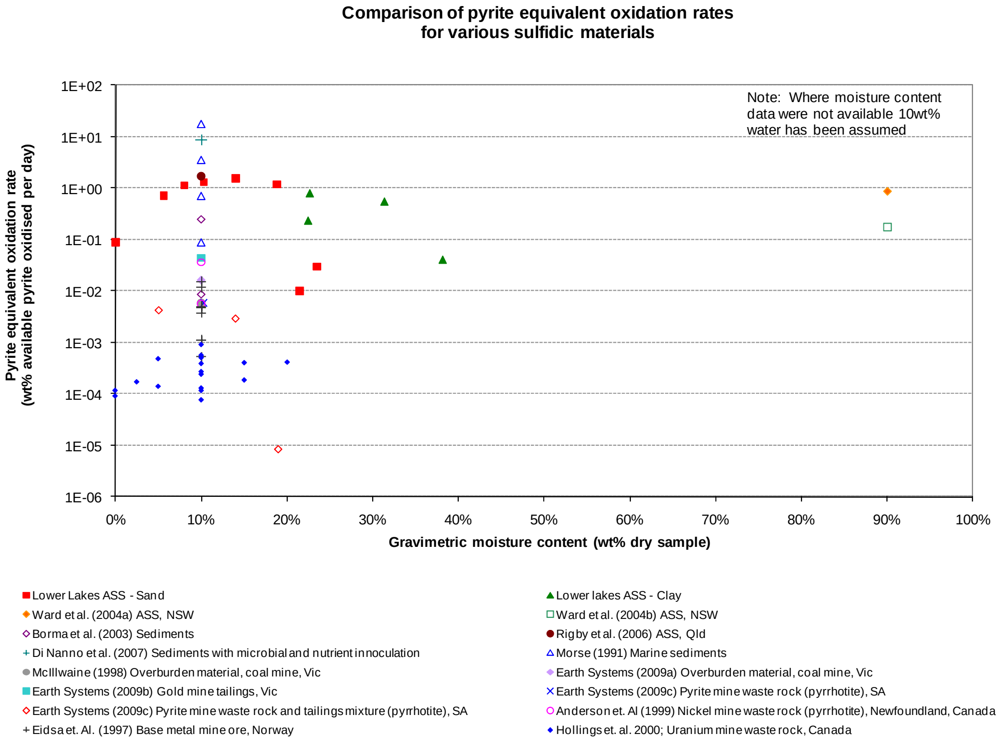


Figure 8. Comparison of reported pyrite oxidation rates for a variety of sulfidic materials including hard rock mine waste rock, tailings, coal mine overburden material and acid sulfate soils. Pyrite oxidation rate shown on log scale due to significant range in oxidation rate.

Research limitations and future work

The method used to calculate the rate of pyrite oxidation relies on the assumption that all sulfur in the sample exists as pyrite. Total sulfur (LECO combustion analysis) was used as a proxy measurement for reduced inorganic sulfur concentration, which was also assumed to represent the concentration of pyrite in the sample. There are known (and potentially significant) interferences associated with using total sulfur as a proxy for pyrite concentration. This is due to the fact that sulfur in forms other than pyrite-sulfur are commonly present in acid sulfate soils, for example organic sulfur and sulfate minerals (i.e. gypsum) and mono-sulfides (i.e. FeS). The validity of this assumption was not investigated for the samples analysed. The concentration of pyrite can be directly and reliably measured using the routine and well established chromium reducible sulfur method. Use of this method would have provided much greater assurance when calculating pyrite oxidation rates (and in turn acid generation rates). It is likely that the reported pyrite oxidation rates represent the upper or maximum rates of pyrite oxidation and may be an overestimation of the true in situ oxidation rates.

The pyrite oxidation rates calculated in this study represent a bulk measurement. Under in situ conditions pyrite oxidation rates are likely to change with depth as soil moisture, texture and pyrite contents vary and temporally as hydrological conditions, such as water table and capillary fringe height, change in response to rainfall, seiche events and evaporation.

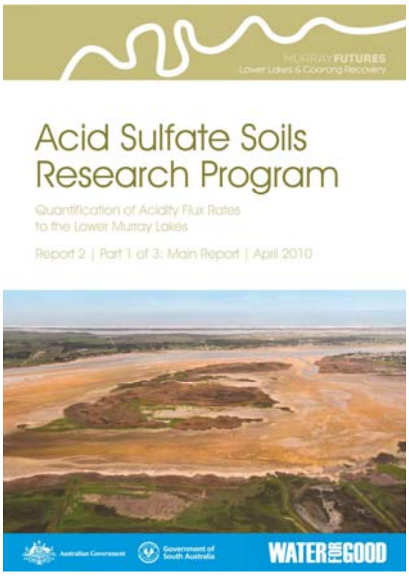
The report was limited to the investigation of pyrite oxidation rates in two different sulfidic materials. Acid sulfate soils in the Lower Lakes region are known to be highly heterogeneous. Hence, future work that includes a larger number of samples with varying physico-chemical properties would provide a better estimation of the potential range of pyrite oxidation rates possible in the Lower Lakes. Additionally, directly measuring pyrite-sulfur using the chromium reducible sulfur method in any future work would further improve the reliability and applicability of calculated pyrite oxidation rates.

2.4 Contaminant mobilisation and transport

2.4.1 Quantification of acidity flux rates to the Lower Lakes

Report details

Full details of the work undertaken and its findings are provided in the report:



MURRAY FUTURES
Lower Lakes & Coorong Recovery

Acid Sulfate Soils
Research Program

Quantification of Acidity Flux Rates
to the Lower Murray Lakes

Report 2 | Part 1 of 3: Main Report | April 2010

WATER FOR GOOD

Earth Systems. (2010). Quantification of acidity flux rates to the Lower Murray Lakes (and Supplementary Report). Prepared by Earth Systems Consulting Pty. Ltd. for the SA Department of Environment and Natural Resources, Adelaide

Key research outcomes

- Provided data and infrastructure to underpin the modelling of flux estimates to the Lower Lakes.

Aim

The aim of the study was to quantify acidity flux rates to proximal water bodies during wetting events, based on quantification of the hydrogeology and hydrogeochemistry of lake soils via a combination of laboratory and fieldwork programs.

Approach

The methodology for quantifying acidity flux rates to the Lower Lakes included (i) the design, establishment and implementation of a laboratory program, (ii) the design, establishment and implementation of a field monitoring program, (iii) an assessment of laboratory and field data in order to develop acidity generation and acidity flux models for the Lower Lakes, and (iv) determination of the management implications of acidity flux modelling for the Lower Lakes.

Findings

The dominant soil type on the low-lying margins of the Lower Lakes were sandy soils with high hydraulic conductivity. However, the very low hydraulic gradients of the water table mean that lateral transport of groundwater is limited.

Two-dimensional hydrogeological model outputs were used to convert modelled acidity generation rates (within the lake soils) to acidity flux rates (from the lake soils to the surface water bodies) for Lake Albert and Lake Alexandrina. A number of assumptions, in combination with field data, were used to model cumulative acidity generation in Currency Creek, Lake Alexandrina and in Lake Albert (Figure 9). The likely rate and duration of acidity release (flux) events in Lake Albert and Lake Alexandrina were estimated for a range of lake water levels, hydraulic conductivity and acidity concentration scenarios.

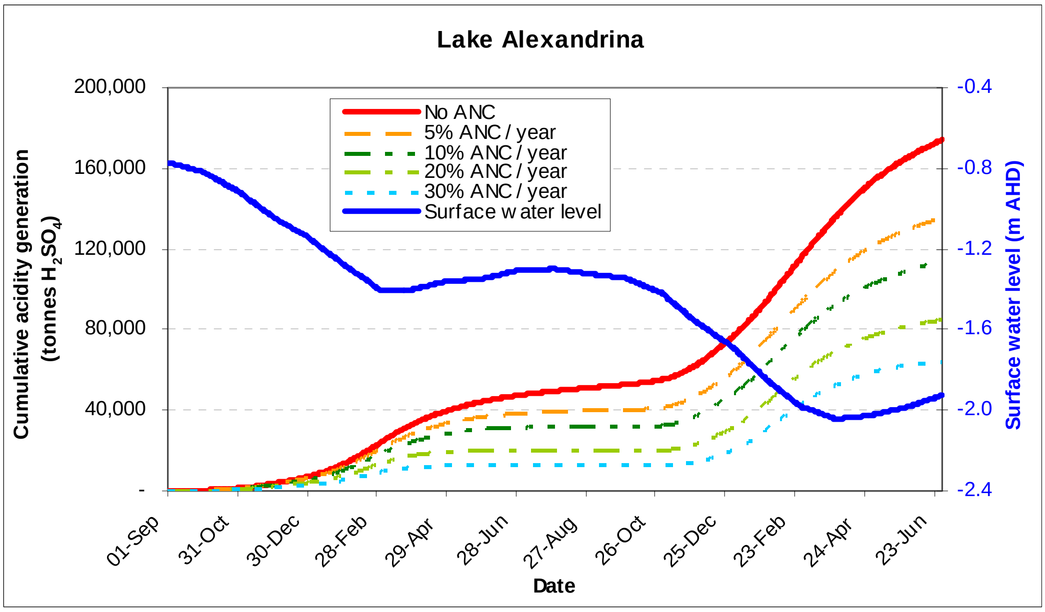


Figure 9. Preliminary estimates of cumulative acidity generation from Lake Alexandrina over 22 months from September 1st 2009.

It was noted that despite water levels decreasing to -0.45 m AHD in Lake Albert and -0.75 m AHD in Lake Alexandrina in late November 2009, there was no obvious impact on surface water quality (pH or alkalinity). This indicated that either little acidity had been generated, or little acidity had been released from exposed soils prior to November 2009, or that any acidity that had been released was neutralised within the lake soils or surface water.

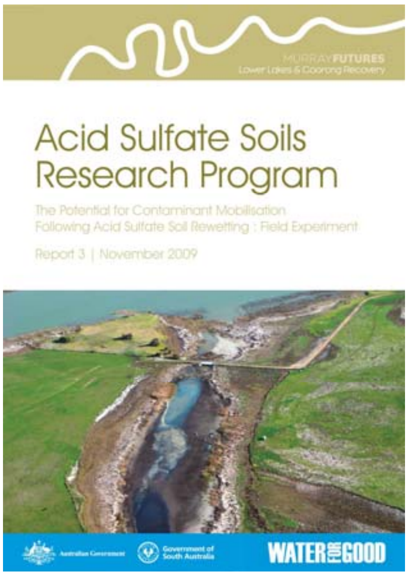
Research limitations and future work

Acidity fluxes were based on a model which contained a large number of assumptions rather than direct field measurements; in situ or laboratory flux measurements would be useful to validate the model. In addition, much of the acidity generated during drying in the Millennium Drought was stored in poorly soluble minerals such as natrojarosite, which are likely to control acidity fluxes. Their presence should be incorporated into future models.

2.4.2 The potential for contaminant mobilisation following acid sulfate soil rewetting: field experiment

Report details

Full details of the work undertaken and its findings are provided in the report:



MURRAY FUTURES
Lower Lakes & Coorong Recovery

Acid Sulfate Soils
Research Program

The Potential for Contaminant Mobilisation
Following Acid Sulfate Soil Rewetting : Field Experiment

Report 3 | November 2009

Hicks, W.S., Creeper, N., Hutson, J., Fitzpatrick, R.W., Grocke, S. and Shand. P. (2009). The potential for contaminant mobilisation following acid sulfate soil rewetting: field experiment. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

This research was supported by two additional studies; (i) 'The potential for contaminant mobilisation following acid sulfate soil rewetting: lab experiment' (Section 2.4.3) and (ii) 'Lower Lakes laboratory study of contaminant mobilisation under seawater and freshwater inundation' (Section 2.4.4).

Key research outcomes

- The mesocosm studies showed that seawater inundation at the time of the study was a much higher risk than freshwater inundation. This finding supported management decisions relating to seawater inundation through the barrages.

Aim

To assess the potential impacts of seawater and freshwater inundation on water and soil quality.

Approach

A Field based mesocosm was designed using large (5000 litre) modified water tanks installed into the exposed margins of Lake Alexandrina. Two sites with contrasting soil types representing the dominant soil types of the Lower Lakes were selected: a sandy soil on the southern side of Point Sturt Peninsula (Lake Alexandrina), and a clay soil at

Boggy Creek (Hindmarsh Island). The installation was duplicated at each site for both water treatments. The mesocosms (in duplicate) were filled with freshwater and seawater to compare and contrast changes due to the different water types. They were also designed to keep the volume of water in the tanks constant (0.5 m depth) for the duration of the experiments.

The sites were instrumented with piezometers, porewater samplers and monitoring equipment to assess the timing and extent of changes to water quality in both the water column and soil porewaters (Figure 10). The experimental design was set up to enable the measurement of solute and water fluxes between the soil and surface water for both soil materials, and to provide critical parameters for modelling studies.

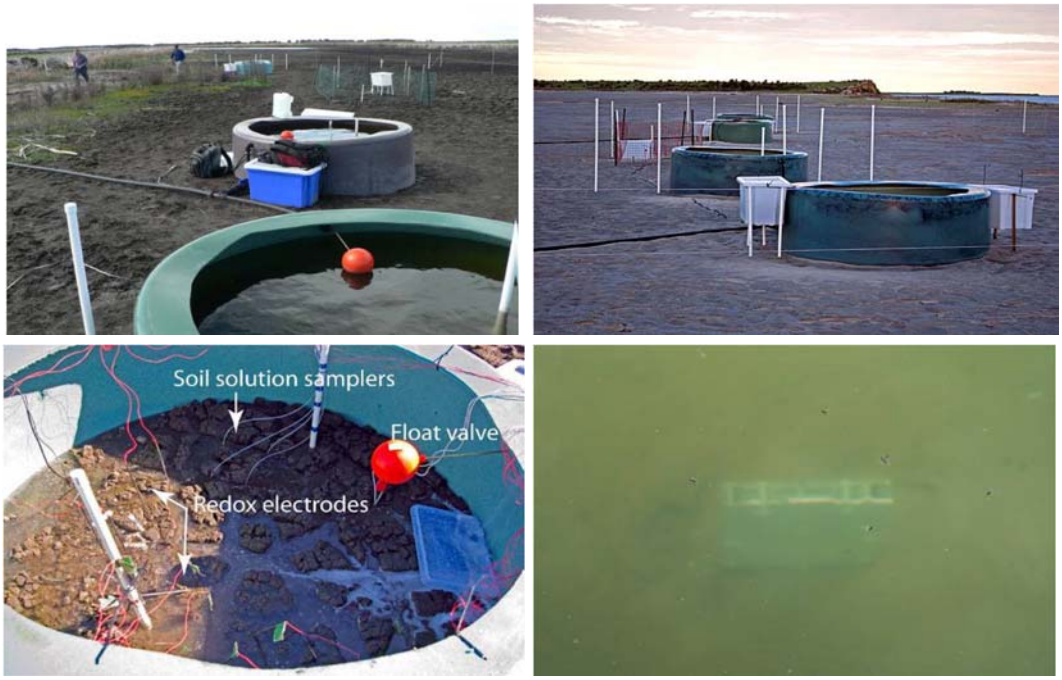


Figure 10. Mesocosm infrastructure at Boggy Creek (top left) and Point Sturt (top right). Instrumentation included piezometers and soil solution samplers (lower left) and peepers (lower right).

Findings

The study showed that seawater and freshwater produced very different results with respect to water quality. There was a greater initial mobilisation of acidity and pH decrease with seawater inundation, despite seawater having higher alkalinity than the freshwater. In the clay soil, the water column in one of the seawater tanks became very acidic (pH < 4) approximately 60 days after rewetting (Figure 11), while in the other seawater tank and both freshwater tanks the alkalinity continued to decrease and by 100 days was <0.25 mg/L (<12.5 mg $CaCO_3$/L).

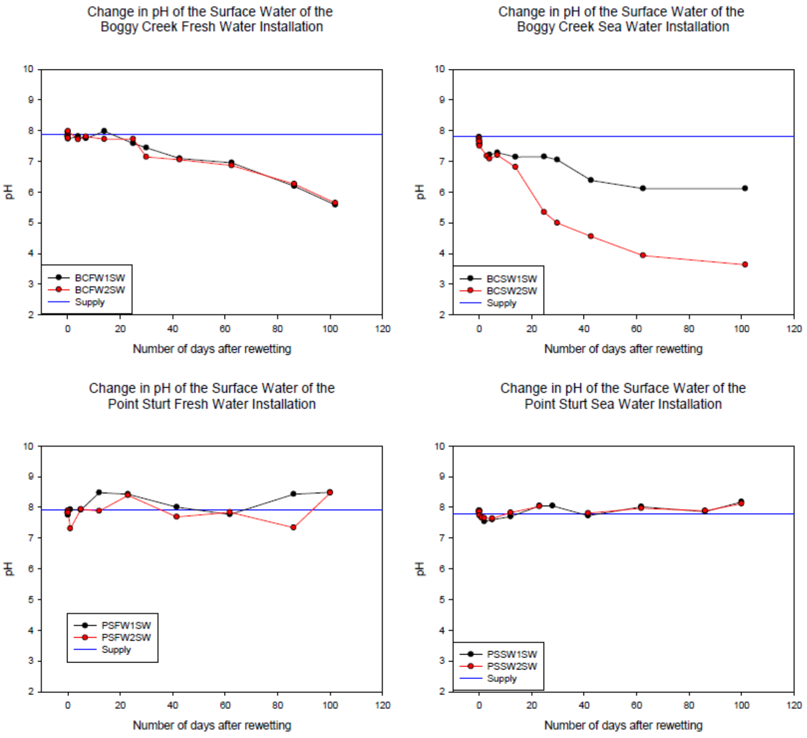


Figure 11. Changes in pH for Boggy Creek (top) and Point Sturt (right) surface waters.

The experimental design enabled the measurement of solute and water fluxes between the soil and surface water. For the clay soil, the seepage flux of water into the soil profile was low (<1 mm/day) and the stored acidity was higher, resulting in a net flux of solutes from the soil to the water column. In the case of the seawater treatment, this resulted in the acidification of the water column around 60 days after rewetting. In contrast, the sandy material had a much higher seepage flux (~10 mm/d), which displaced acid porewater deeper into the soil profile with potential for interaction with shallow ground water. However, this downward flux may not have occurred if the Lower Lakes were filled. Acidity fluxes to the surface waters were initially very high but decreased over time. Elevated concentrations of nutrients, particularly the release of ammonium and phosphorus were also noted in surface waters.

The shallow porewater beneath both soil types was of poor quality with a low pH of approximately 3 (Figure 12) and exceedances of ANZECC water quality guidelines (WQG) for a range of toxicants. Further changes following the planned monitoring were also reported which included dissolution of precipitates into the acidic water column in the case of the clay soil and a sharp drop in soil and water column redox potential for both soil materials.

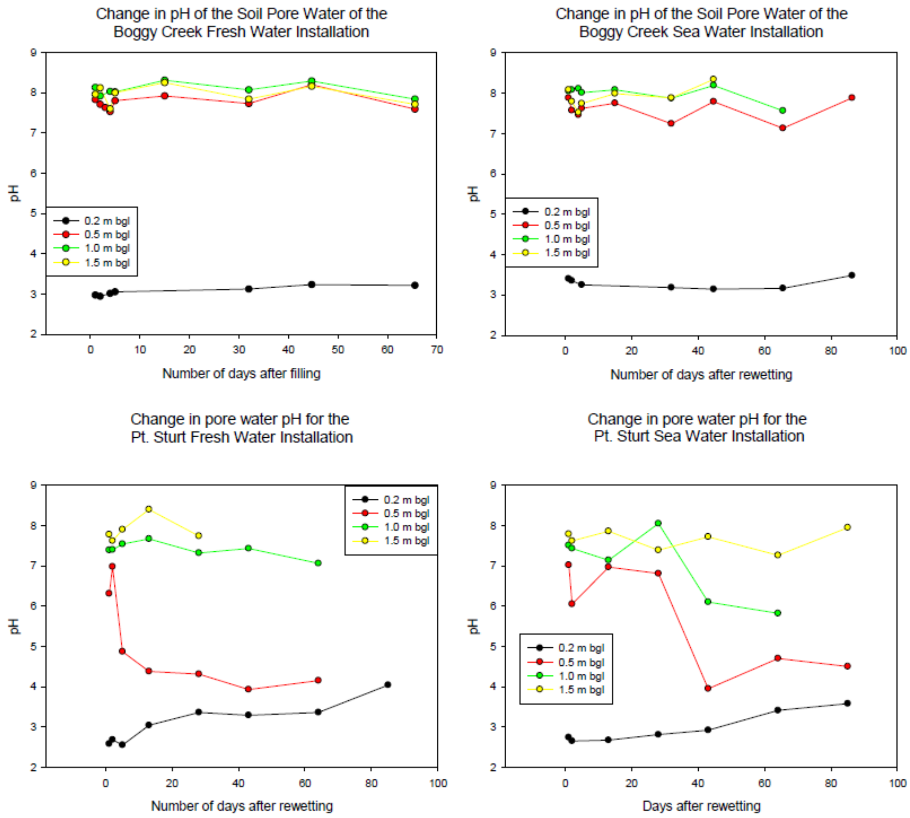


Figure 12. Monitored data for soil porewaters for Boggy Creek (top) and Point Sturt (bottom).

A mass balance of the acidity in the soil profiles showed that a single charge of water to any achievable depth was insufficient to neutralise stored soil acidity even for a site such as Point Sturt where the intensity of acidity was high (i.e. the pH was low) but the total quantity relatively low. This showed that several flushes of water would be required to neutralise and dilute soil acidity unless internal alkalinity is generated.

Research limitations and future work

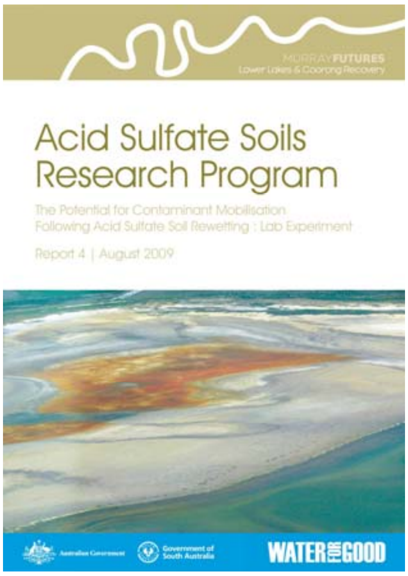
By their nature the design and size of the mesocosms could not fully replicate the actual processes on refilling of the Lower Lakes. This is largely due to the surrounding soils being dry, and a high head gradient being established between the filled tanks and local groundwater. This was most apparent in the sandy soils where infiltration was more prominent than in the less permeable clays. This may limit scaling of the data to larger areas.

The duration of the first phase experimentation was too short to capture the full range of geochemical conditions likely to be encountered, however they provided invaluable data for developing process-based models.

2.4.3 The potential for contaminant mobilisation following acid sulfate soil rewetting: lab experiment

Report details

Full details of the work undertaken and its findings are provided in the report:



Simpson, S., Jung, R., Jarolimek, C. and Hamilton, I. (2009). The potential for contaminant mobilisation following acid sulfate soil rewetting: lab experiment. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

This research was supported by two additional studies; (i) 'The potential for contaminant mobilisation following acid sulfate soil rewetting: field experiment' (see Section 2.4.2) and (ii) 'Lower Lakes laboratory study of contaminant mobilisation under seawater and freshwater inundation' (see Section 2.4.4).

Key research outcomes

- The conclusions largely validate the field mesocosm study with respect to seawater providing a higher degree of risk than freshwater inundation, and were used to support management decisions.

Aim

To quantify the potential for mobilisation of acid and metals from acid sulfate soils following inundation with seawater or freshwater and to support field studies outlined in Section 2.4.2.

Approach

Undisturbed cores were collected from Boggy Creek (clays) and Point Sturt (sands) and inundation experiments completed with River Murray water or seawater collected near the barrages. Custom designed corer-reactors (Figure 13) were used to collect the cores, which were used for subsequent experiments. A range of general water quality parameters and major and trace elements were monitored. Freshwater was added on selected days of the trials, and this was followed by experiments on soil resuspension.

Figure 13. Corer-reactors used to assess impacts of freshwater and seawater on contaminant mobilisation.

Porewater concentrations were analysed to quantify sub-surface compositions of the soil solution. Additional tests also investigated the influence of water type, soil:water ratio, leaching duration rates and sequential leaches on water quality. The potential ecological effects were considered with respect to water pH and concentrations of dissolved metals and metalloids released from the soils to the overlying water relative to the Australian ANZECC WQG. The 80% and 95% protection concentrations were used.

Findings

The pH of the overlying water remained above pH 7 during the water-renewal phase of the corer reactor experiments. For Point Sturt soils, alkalinity generally decreased for both freshwater and seawater addition, whilst for Boggy Creek there was a release of alkalinity. For both soil types, seawater inundation of the cores caused significantly greater releases of aluminium, manganese, cobalt and lead (and zinc for Boggy Creek cores), than the freshwater inundation. This was attributed to the higher ionic strength of seawater increasing the exchange of metals from soil particles.

The pH of surface waters fell by 0.3 to 0.8 pH units during the resuspension experiments. Alkalinity was removed from freshwater and seawater from the surface water for Point Sturt cores. In contrast, freshwater addition to the Boggy Lake resulted in a large increase in alkalinity from the soils to freshwater, and a small decrease for seawater. For both freshwater and seawater inundation experiments, the resuspension of the surface soils resulted in minor to moderate changes (increases or decreases) in the metals released from the sandy Point Sturt cores, but generally caused large increases in metals released for the clayey Boggy Creek cores.

Porewater metal concentrations were generally much greater in the seawater inundation tests than the freshwater inundation tests (Figure 14). They increased with increasing soil depth, consistent with the higher acidity (lower pH) of the deeper soils, which were generally pH ≤ 3 from 15 cm below the soil water interface to the base of the cores at -20 cm. The dissolved metal concentrations within the soil porewaters were much greater than the concentrations being released to the overlying water and the increased rate of release of metals from the soils during resuspension was therefore likely to be in part due to porewater-derived metals.

In the rapid-release tests, greater concentrations of metals were generally released from the soils by mixing with seawater than with freshwater. Repeated leaches of the same soil indicated that while acidity may be washed out of the soils, significant acidity carried through to the next cycle. With each successive leach of the soils, the concentrations of most metals (excluding vanadium) released from the soils generally decreased 2 to 10 fold compared to the previous leach cycle. This is consistent with there being a finite pool of metals available for release. During the resuspension phase, the pH dropped significantly, but generally remained above pH 5. Despite the pH remaining above pH 5, there were exceedances of WQG, and the exceedances were much greater for inundation with seawater than for freshwater. For seawater, the exceedances were (in order of magnitude) aluminium > manganese > cobalt > lead > copper > cadmium ~ zinc, and for freshwater inundation experiments there were minor exceedances for copper, cadmium and vanadium.

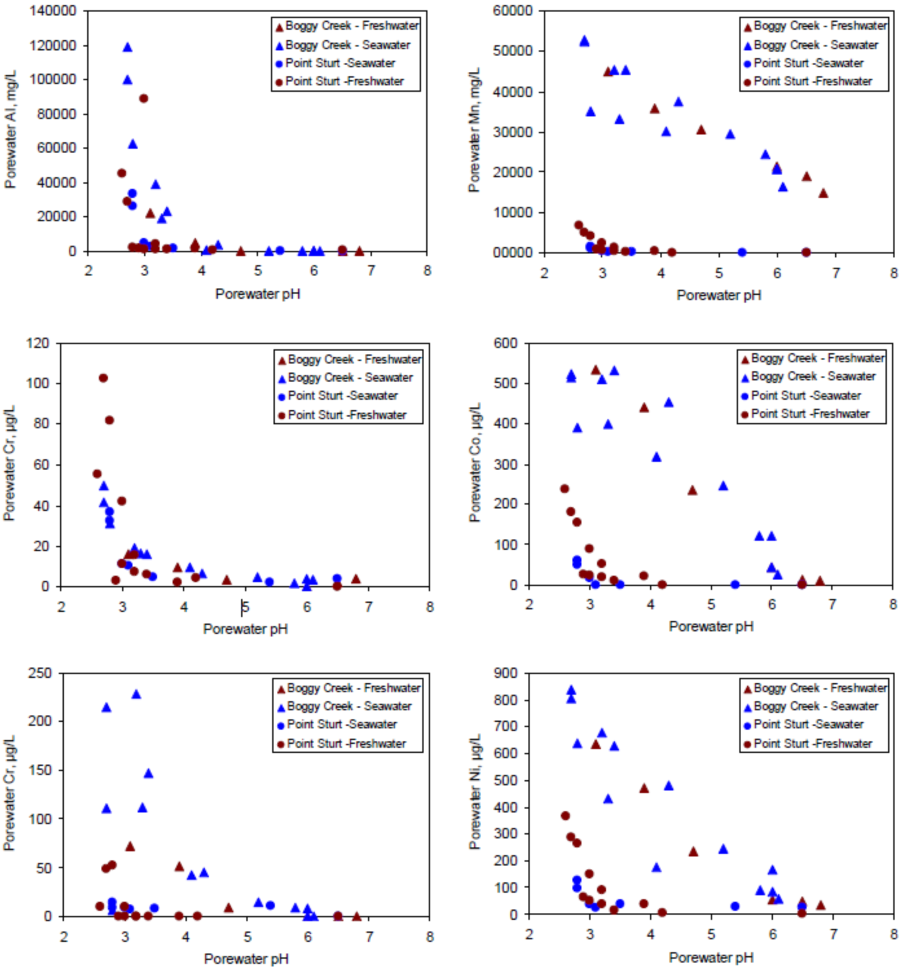


Figure 14. Relationship between porewater pH and porewater Al, Mn, Cr, Co, Cr and Ni concentrations: Point Sturt and Boggy Creek cores.

Overall, the study indicated that only short term exceedances to the WQG for metals would be expected to occur if the pH of the overlying water remained above pH 6. Moderate dilution of the waters overlying the inundated soils with surrounding waters is expected to result in both increased water pH and attenuation of dissolved metals released from the soils. Exceedances of WQG would be expected to be more frequent in shallow regions of the Lower Lakes where water exchange is restricted.

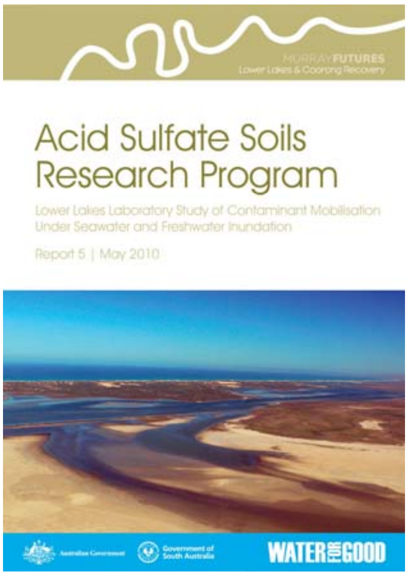
Research limitations and future work

This study provided detailed information on contaminants present and their potential mobility at only two key sites. It was recommended that rapid-release tests using seawater and freshwater be undertaken using soils collected from a greater range of sites in the Lower Lakes. These tests were considered as likely worst-case metal release from soils when inundated with different water types, and would thereby aid the risk assessment process. The impact on surface waters was different to that in the field mesocosm study. This may be due to the short duration of inundation (it took some time for the surface waters to become acidic in the field mesocosms) and the relatively shallow (≤ 20 cm) depth of sample.

2.4.4 Lower Lakes laboratory study of contaminant mobilisation under seawater and freshwater inundation

Report details

Full details of the work undertaken and its findings are provided in the report:



MURRAY FUTURES
Lower Lakes & Coorong Recovery

Acid Sulfate Soils
Research Program

Lower Lakes Laboratory Study of Contaminant Mobilisation
Under Seawater and Freshwater Inundation

Report 5 | May 2010

Australian Government
Government of South Australia
WATER FOR GOOD

Sullivan, L.A., Bush, R.T., Ward, N.J., Fyfe, D.M., Johnston, M., Burton, E.D., Cheeseman, P., Bush, M., Maher, C., Cheetham, M., Watling, K.M., Wong, V.N.L., Maher R. and Weber, E. (2010). Lower Lakes laboratory study of contaminant mobilisation under seawater and freshwater inundation. Prepared by Southern Cross GeoScience for the SA Department of Environment and Natural Resources, Adelaide.

This research was supported by two additional studies; (i) 'The potential for contaminant mobilisation following acid sulfate soil rewetting: field experiment' (Section 2.4.2) and (ii) The potential for contaminant mobilisation following acid sulfate soil rewetting: lab experiment' (Section 2.4.3).

Key research outcomes

- The conclusions largely validated the field mesocosm study with respect to seawater providing a higher degree of risk than freshwater inundation, and were used to support management decisions.

Aim

To provide data to assess the potential impact resulting from mobilisation of contaminants following rewetting of exposed soils around the Lower Lakes with seawater or River Murray water.

Approach

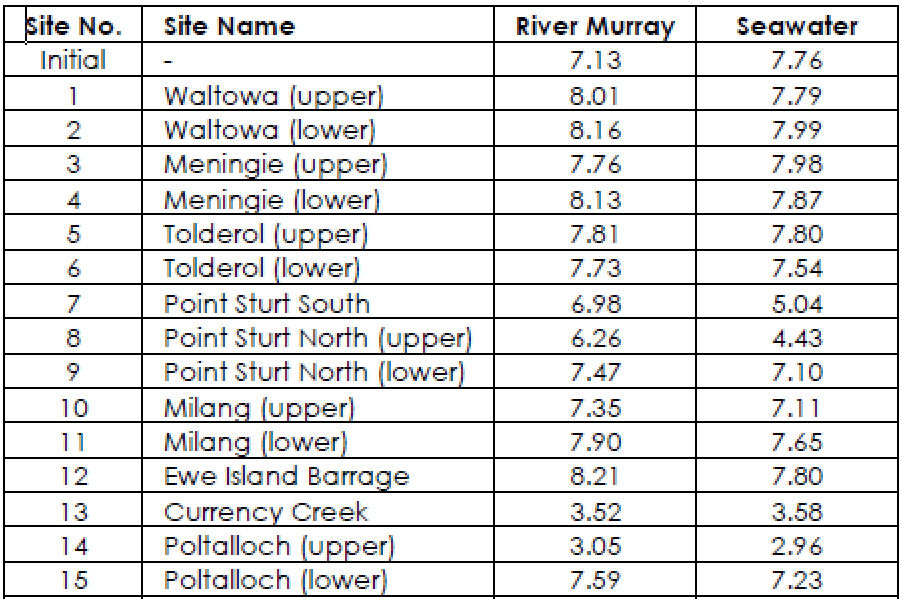
Shallow (0-15 cm depth) cores were collected at fifteen sites across the Lower Lakes. Laboratory experiments were conducted to determine the mobilisation of partially and fully oxidised acid sulfate soils from selected sites. The dynamics of contaminant release and neutralisation were determined using batch experiments, with an emphasis on the formation and cycling of sulfur species.

Findings

The results from this study supported the field and other laboratory studies and showed that the addition of seawater produced a greater acidifying effect on surface and porewaters.

Four of the fifteen soil materials studied showed a decrease in pH to < pH 5 (Table 1). Inundation of most sites did not appreciably acidify the inundating waters in the experiments. Seawater produced a more rapid initial acidification effect than freshwater, but the difference in effect decreased with time of inundation. The higher alkalinity of seawater was insufficient to overcome the additional exchange of acidity from the soils. The pH at some sites was decreasing after 135 days and a longer time frame was required to determine if this would have continued.

Table 1. Surface water pH after 136 days of inundation.



Site No.	Site Name	River Murray	Seawater
Initial	-	7.13	7.76
1	Waltowa (upper)	8.01	7.79
2	Waltowa (lower)	8.16	7.99
3	Meningie (upper)	7.76	7.98
4	Meningie (lower)	8.13	7.87
5	Tolderol (upper)	7.81	7.80
6	Tolderol (lower)	7.73	7.54
7	Point Sturt South	6.98	5.04
8	Point Sturt North (upper)	6.26	4.43
9	Point Sturt North (lower)	7.47	7.10
10	Milang (upper)	7.35	7.11
11	Milang (lower)	7.90	7.65
12	Ewe Island Barrage	8.21	7.80
13	Currency Creek	3.52	3.58
14	Poltalloch (upper)	3.05	2.96
15	Poltalloch (lower)	7.59	7.23

The lack of strong acidification was most likely due to the relatively low acidity stores in the sites selected e.g. it was noted that the acidities of the surficial (0 to 15 cm) soil materials were generally very low. Nevertheless, the study highlighted that mobilisation of several solute metals (e.g. copper, nickel and zinc) and nutrients (ammonium) occurred in addition to acidity, and that this increased for seawater inundation.

The data showed that the soil materials, excepting the few very acidic soil materials, were capable of producing substantial alkalinity during the 136 days of inundation. A decrease in dissolved sulfate in these soils suggested that this alkalinity was a consequence of sulfate reduction during organic matter decomposition.

The changes in flux of many soluble constituents from the soils to the inundating waters did not typically exhibit a simple linear trend. This was likely due to the range of slowly changing biogeochemical processes that resulted from the progression of geochemical regimes created by inundation. In addition, some soluble constituents that appear in increasing concentrations in the inundating waters during the initial inundation phase, decrease in concentration in later inundation phases. Consequently, the apparent net diffusion rates for most soluble constituents changed appreciably during the inundation.

Experiments on the capacity of the soils to undergo sulfate reduction showed that there was little difference in overall rates when seawater or freshwater was used (Figure 15). This finding appeared to be due to the organic carbon content in the soil being the limiting factor rather than the sulfate concentration in the overlying water (Figure 16).

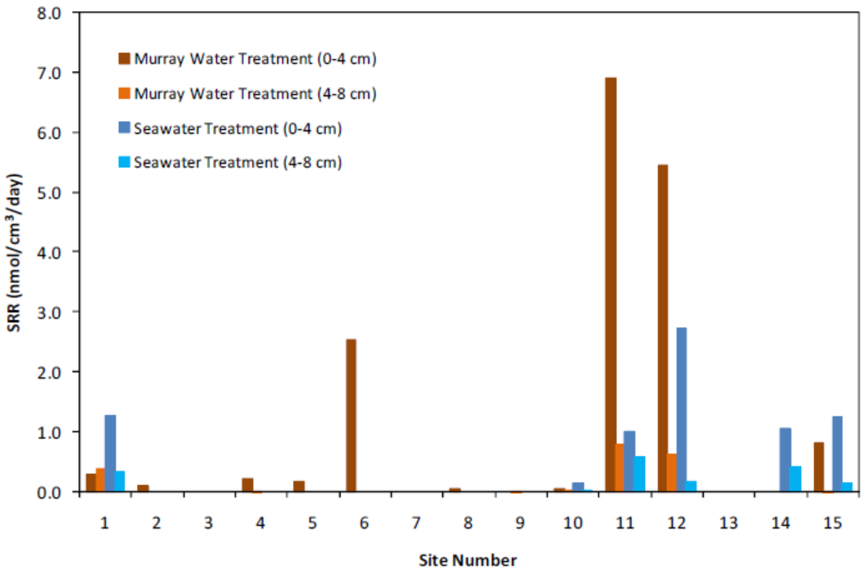


Figure 15. Comparison of the mean sulfate reduction rates following inundation using radiotracer methods.

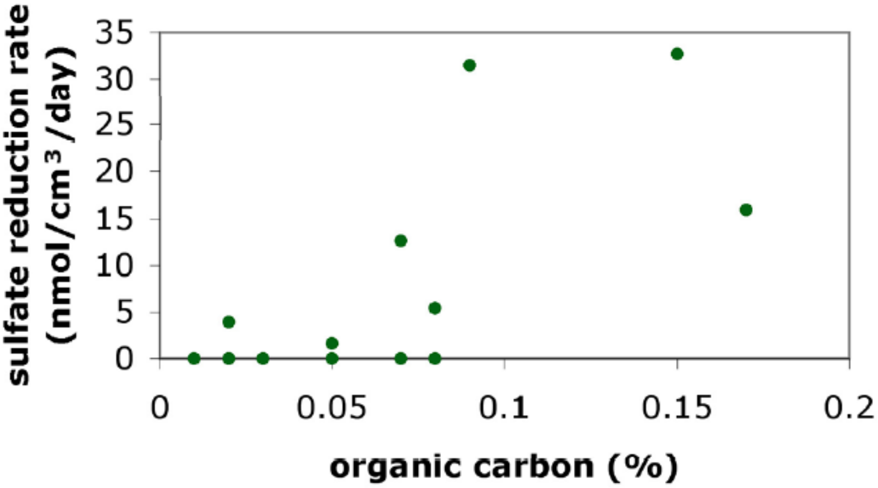


Figure 16. Comparison of the mean sulfate reduction rates in the 0-4 cm soil layer for freshwater inundation, using Cr-reducible method, with organic carbon in the 3-5 cm layer.

Research limitations and future work

The work was carried out with only freshwater and seawater. It is possible that waters of different salinity (e.g. mixtures of freshwater and seawater or hypersaline waters) may have produced different results in terms of fluxes of potential contaminants and acidity or alkalinity. It was possible that sampling was completed following a downward flushing of acidity in profiles, therefore, the data should be interpreted in this context and care taken when comparing results with other studies.

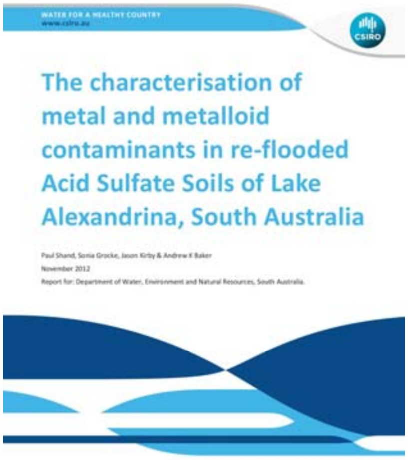
The experiments were carried out in a static environment and future work should assess actual fluxes in the Lower Lakes to determine if processes other than diffusion are important and if preferential flow paths are likely to provide preferred rapid pathways between the soil and surface water. Greater dilutions of seawater or greater exchanges of seawater should also be considered.

Further investigations aimed at examining ways to enhance the organic matter contents in these soils and the effects of such treatments on soil behaviour were also recommended due to organic matter being the likely limiting factor in sulfate reduction.

2.4.5 The characterisation of metal and metalloid contaminants in re-flooded acid sulfate soils of Lake Alexandrina, South Australia

Report details

Full details of the work undertaken and its findings are provided in the report:



WATER FOR A HEALTHY COUNTRY
www.csiro.au

The characterisation of metal and metalloid contaminants in re-flooded Acid Sulfate Soils of Lake Alexandrina, South Australia

Paul Shand, Sonia Grocke, Jason Kirby & Andrew K Baker
November 2012
Report for: Department of Water, Environment and Natural Resources, South Australia.

Shand, P., Grocke, S. Kirby, J., Baker, A.K. (2012). The characterisation of metal and metalloid contaminants in re-flooded Acid Sulfate Soils of Lake Alexandrina, South Australia. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

Key research outcomes

- The data showed that the distribution of contaminants is extremely complex and likely to evolve with time. This needs to be incorporated into any future models on contaminant impacts to achieve good outcomes.

Aim

To assess the range of contaminants and their solid phase associations in impacted acid sulfate soils following reflooding.

Approach

Soil cores were sampled from three contrasting impacted sites in Lake Alexandrina (Point Sturt (x2), Dog Lake and Boggy Lake). Porewaters were extracted from different depths based on observable changes in soil colour and texture down each profile. The porewaters were removed by centrifugation and filtered to determine colloidal (< 0.45 µm - 3 kDa) and dissolved (< 3 kDa) fractions. Following porewater extraction, sequential extractions were undertaken on the soils to determine solid phase associations in order to determine the likelihood of remobilisation under different environmental conditions. The extraction procedure is shown on Table 2, modified from previous studies of acid sulfate soils.

Table 2. Sequential extraction procedure used in study (modified from (Claff, *et al.*, 2010).

Sequential Fractionation Procedure	Metal Fraction	Treatment
1	Labile: readily soluble salts and exchangeable ions	1 M magnesium chloride
2	Weak acid soluble: includes carbonates and poorly ordered sulfides and oxides	1 M hydrochloric acid
3	Organic: reactive organic components	0.1 M sodium pyrophosphate (pH 10)
4	Reducible crystalline phases e.g. Fe and Mn oxides	0.35 M acetic acid/0.2M sodium citrate buffer with 50 g/L sodium dithionite (pH 4.8)
5	Sulfides, primarily pyrite	Concentrated nitric acid
6	Residual	EPA method 3052 (reverse aqua regia. microwave assisted extraction procedure)

Findings

This study showed that dissolved metals and metalloids remained of concern despite more than two years after the Lower Lakes refilled. In general, metal and metalloid concentrations were lowest in the upper parts of the profiles due to infiltration of fresh lake water, resulting in a downward flux of solutes and acidity. For all profiles, the concentrations of a number of contaminants exceeded ANZECC Guideline values, especially in the most acidic soil layers (soil pH varied from 3.9 to 8.7). The worst affected sites were Dog Lake and Boggy Lake, with one soil layer in Dog Lake having extremely high concentrations of some contaminants (Figure 17).

A comparison of different pore size filters showed that in general the metal and metalloids were present as dissolved species (< 3 kDa), although some deeper soil samples contained colloidal material (between 0.45 µm and 1kDa), and two soil layers contained very high colloidal manganese at shallow depth.

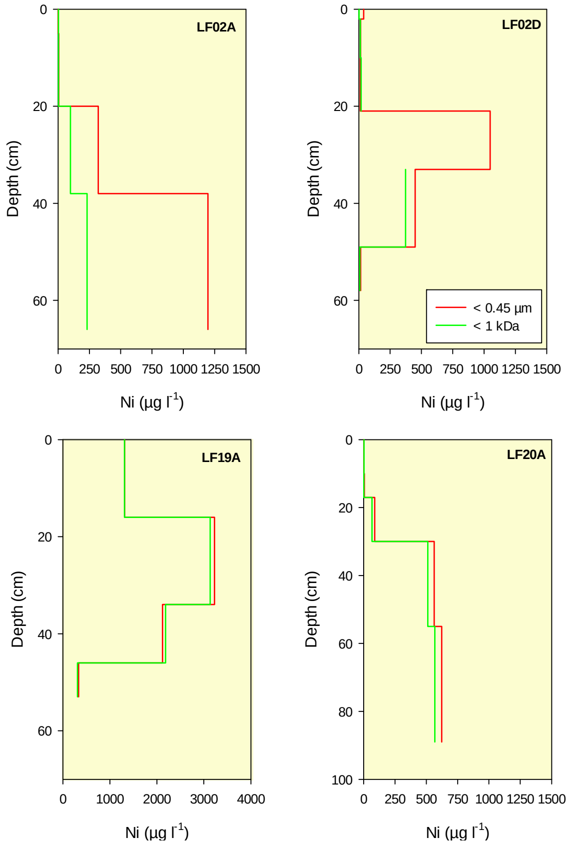


Figure 17. Porewater concentrations of nickel (Ni) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Ni is 11 µg l^{-1}. Note the different scales.

The sequential extraction data showed that a large number of trace metals and metalloids were present at high concentrations in different ‘soil fractions’. Although the exchangeable fraction formed a small part of the total, for some metals, concentrations were still high enough to be of concern in relation to water quality limits.

The sequential extraction data also showed that the potential contaminant availability was very heterogeneous. Individual contaminants were associated with a range of different fractions, from weakly-bound exchangeable to residual (Figure 18). The dominant solid phase speciation for contaminants often changed with depth e.g. Fe was largely present in the HCl extraction in shallow soil layers (suggesting it was present as a poorly crystalline oxide), with the nitric acid extraction (suggesting incorporation in pyrite) being more important at depth. This study also highlighted that the pyrophosphate extraction was very important in these soils, indicating that many contaminants are likely to be associated with organic matter. This was particularly true for iron, aluminium, nickel, arsenic, chromium, vanadium and beryllium.

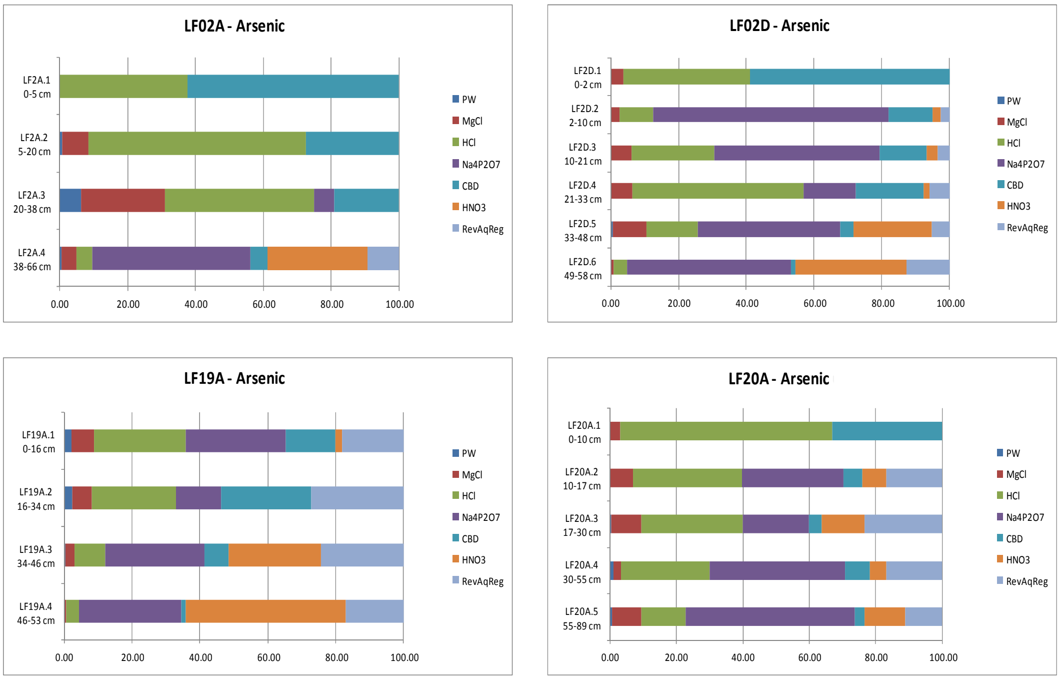


Figure 18. Sequential extraction data for arsenic (As) in the subaqueous soils, plotted as % of total concentration.

For some elements, there was a dominant element-extraction association e.g. zinc in the dithionite extraction, (more crystalline oxide phases), and uranium and lead in the HCl extraction (poorly crystalline oxide mineral phases). Although the exchangeable fraction formed a small part of the total of the solid phase, they were high enough to be of concern due to the low concentrations typical for water quality limits.

The stability of different mineral phases is likely to change with ageing of the soils and bioavailability will likewise be a function of time as well as geochemistry of the soil environment, particularly pH and Eh. The data also suggested that the soils were in a state of chemical disequilibrium, and likely to change with time; in agreement with other studies of soil recovery in reflooded wetlands (Shand*, et al.*, 2010). Acidity and contaminant mobilisation during a return to low water levels, may be more rapid due to the likely presence of poorly crystalline mineral phases which are known to be more reactive than aged more crystalline forms.

The relative mobility of contaminants is not necessarily related to the sequence of extractions, but will depend on the redox environment e.g. metals in the pyrite fraction (extraction 5) may become more rapidly available if oxygen is introduced than metals bound to oxidised Fe phases (extractions 2 and 4).

The dominant fractions associated with different metals and metalloids is summarised in Table 3. The data provide a good basis for making future predictions of metal mobilisation under different geochemical scenarios, and as a basis from which to ascertain in more detail the mineralogical phases present in the soils and their metal/metalloid associations. Although the data are a simple snapshot, they provide a much better basis for developing realistic predictive models of contaminant impacts.

Table 3. Typical fractionation of contaminants derived from sequential extraction procedure. Large tick and red box: generally a major fraction; small tick and orange box: often a moderate fraction or a major fraction in some profiles.

Extraction	1	2	3	4	5	6	7
Metal(loid)	Pore-water	$MgCl_2$	HCl	$Na_4P_2O_5$	CBD	HNO_3	Reverse Aqua Regia: residual
Al		🟧 √	🟧 √	🟥 √		🟧 √	🟥 √
Fe	🟧 √	🟧 √	🟥 √	🟥 √	🟧 √	🟧 √	🟥 √
Mn	🟥 √	🟥 √	🟧 √	🟧 √		🟥 √	🟥 √
Be			🟥 √	🟥 √	🟧 √	🟧 √	🟥 √
V		🟧 √	🟥 √	🟥 √	🟧 √	🟧 √	🟥 √
Cr			🟧 √	🟥 √		🟥 √	🟥 √
Ni	🟧 √	🟥 √	🟥 √	🟥 √	🟧 √	🟥 √	🟥 √
Zn		🟧 √	🟧 √	🟧 √	🟥 √		🟧 √
As		🟧 √	🟥 √	🟥 √	🟧 √	🟥 √	
Pb		🟧 √	🟥 √	🟧 √	🟧 √	🟥 √	🟧 √
U			🟥 √	🟥 √		🟧 √	🟥 √

Research limitations and future work

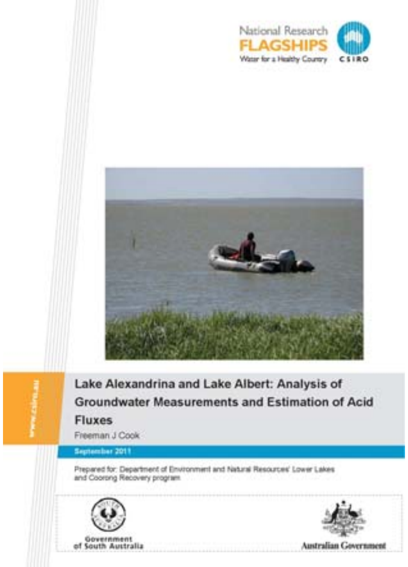
The study provided a detailed snapshot at one point in time of porewater and solid phase associations for contaminants and focused on severely impacted sites. Although colloidal transport appeared limited, it may play a much more important role in colloid transport as the acidic soils recover and pH increases.

The scope did not allow determination of changes in contaminant concentrations or associations over time and how their potential availability was modified by e.g. redox changes or mineralogical transformations in the soil, such as mineral ageing or precipitation/dissolution. More detailed studies on determining the actual solid-phase speciation should be considered as a basis for contaminant-association and any reaction-transport model.

2.4.6 Modelling of acidic solute fluxes from sediments to the water column in the Lower Lakes of South Australia

Report details

Full details of the work undertaken and its findings are provided in a series of three reports:



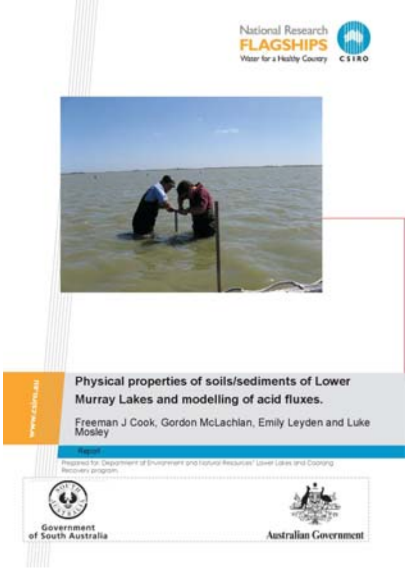
National Research FLAGSHIPS
Water for a Healthy Country
CSIRO

Lake Alexandrina and Lake Albert: Analysis of Groundwater Measurements and Estimation of Acid Fluxes
Freeman J Cook
September 2011
www.csiro.au

Prepared for: Department of Environment and Natural Resources' Lower Lakes and Coorong Recovery program

Government of South Australia
Australian Government

Cook, F.J. 2011. Lake Alexandrina and Lake Albert: Analysis of groundwater measurements and estimation of acid fluxes. CSIRO: Water for a Healthy Country National Research Flagship.



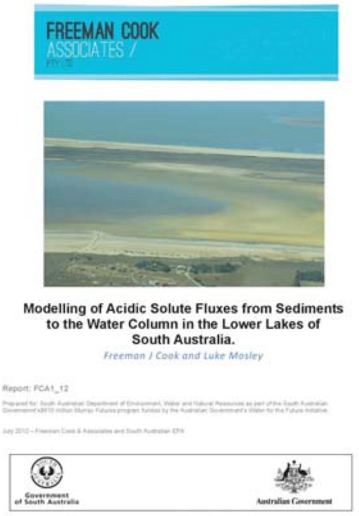
National Research FLAGSHIPS
Water for a Healthy Country
CSIRO

Physical properties of soils/sediments of Lower Murray Lakes and modelling of acid fluxes.
Freeman J Cook, Gordon McLachlan, Emily Leyden and Luke Mosley
Report
www.csiro.au

Prepared for: Department of Environment and Natural Resources' Lower Lakes and Coorong Recovery program.

Government of South Australia
Australian Government

Cook, F.J., McLachlan, G., Leyden, E. and 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.



FREEMAN COOK
ASSOCIATES /

Modelling of Acidic Solute Fluxes from Sediments to the Water Column in the Lower Lakes of South Australia.

Freeman J Cook and Luke Mosley

Report: FCA1_12

Government of South Australia

Australian Government

Cook, F.J., Mosley, L. (2012). Modelling of acidic solute fluxes from sediments to the water column in the Lower Lakes of South Australia. Report: FCA1_12.

Key research outcomes

- The modelling showed that transport of acid to the Lower Lakes via lateral groundwater flow was unlikely and that exfiltration (upward groundwater discharge) and runoff were more likely.
- The potential acidification effect on Lake Albert was considered much higher than Lake Alexandrina supporting management options undertaken.
- Seiche events, particularly in Lake Albert, were important in driving the exfiltration of acidity from the soil.
- Desiccation cracking in clayey soils was observed to enhance transport of acidity to the surrounding water by up to 30%.
- The fortuitous fast refilling of the Lower Lakes following the break of the Millennium Drought resulted in rapid inundation of acidified acid sulfate soils. The rapid inundation of the soils pushed acidity downwards away from the soil water interface and affected a considerable reduction in the flux of acidity from the soil to lake surface waters than what would have occurred if the water table rose slowly.
- Where lake refilling is predicted to occur slowly following a period of extended drought conditions similar to the Millennium Drought, storing water via temporary or existing regulatory structures to permit the rapid inundation of soils should be considered as a potential management option to reduce the risk of releasing acidity and contaminants from the soils into surface waters.

Aim

To estimate the flux of acidity to lake surface water, to review modelling of solute transport in benthic sediments and to review measurements in relation to the developed transport model.

Approach

A conceptual transport model was developed which considered four mechanisms of flux:

- Wash-off during rainfall or seiching events;
- Flow of acidic groundwater to the Lower Lakes;
- Exfiltration of acidic porewater; and

- Diffusion/mixing during seiching or upon reflooding.

In order to model fluxes, a number of physical properties were measured or estimated by collecting soil samples with contrasting soil types (i.e. sand and clay) from two sites within each Lake. Measured physical properties were used along with the HYDRUS model to estimate hydraulic conductivity of the different soils. The data were then used to simulate oxygen, water and solute movement into the soils. A model solution was developed for both diffusion-only transport and advection plus diffusion. The sensitivity of the model was tested using the likely range of model parameters. The model was evaluated by analysing existing water table data and water content monitoring at four sites (Section 2.4.1).

Findings

A number of conceptualisations were developed for the scenarios depicted in Figure 19. The lake shore was divided into different sections depending on the depth of water table and degree of soil saturation (capillary effects). The dominant transport processes were considered to be different in these regions.

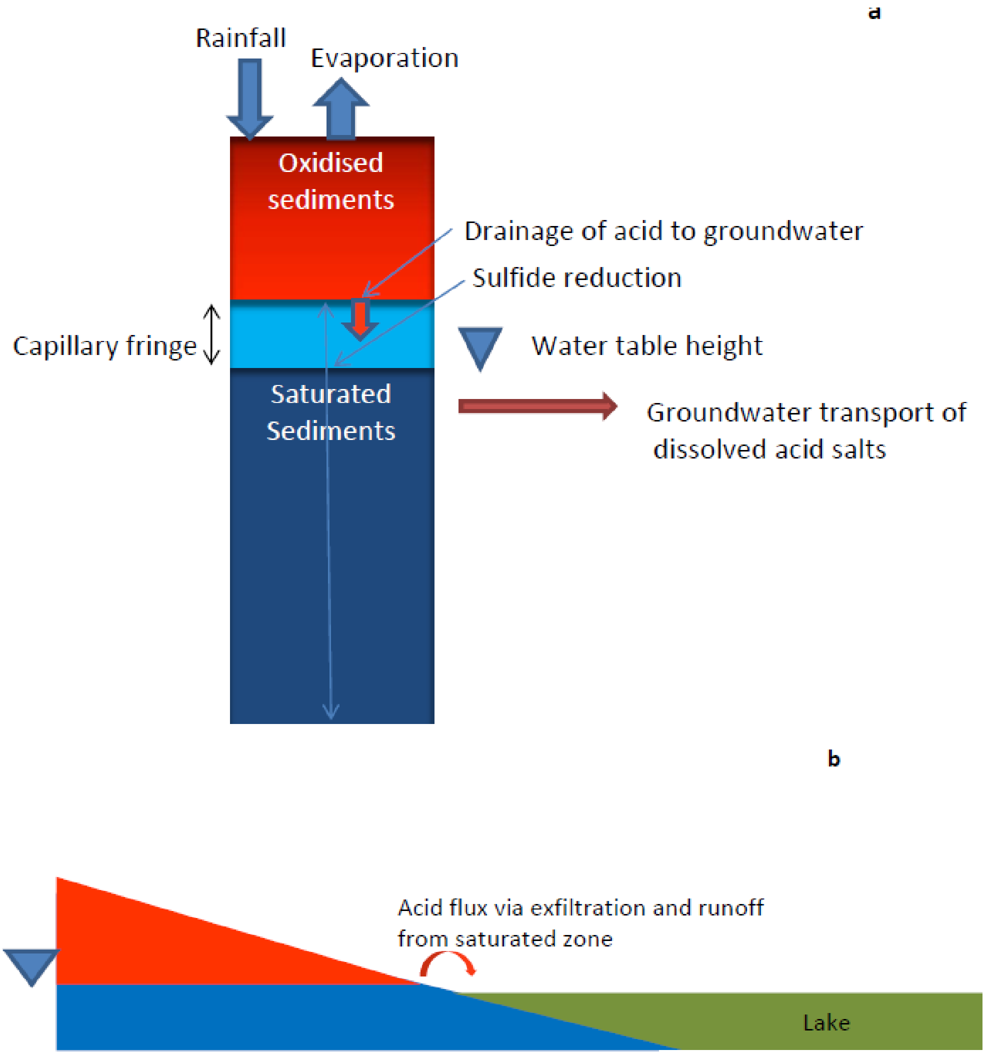


Figure 19. Flux of acidity to lake surface waters via groundwater (a) fluxes in the profile (b) exfiltration from a seepage.

Piezometer data showed that horizontal gradients in the water table were low, and the near shore region often sloped from the lake towards land during the study period. Modelling results indicated that hydraulic gradients sloping away from the shoreline, or in some cases towards the middle of the transects, was a result of the evaporation of water from saturated and near saturated soils near the shoreline. Therefore, movement towards the surface, due to evaporation, was a more likely direction for water than horizontally towards lake surface waters, due to the low slopes of groundwater in near shore regions.

Significant acid flux to the lake surface waters was considered more likely to result from runoff and exfiltration in these near shore areas. Exfiltration was also possible during seiching events or where lake refilling was slow, as the water pressure from the main lake water bodies could cause water to exfiltrate from the soils. In the case of seiching this was considered to be important although short lived. Worst case estimates of acid fluxes via exfiltration and runoff showed that during the time of monitoring, acid fluxes were unlikely to have had a significant impact on the alkalinity or pH of Lake Alexandrina. The same analysis for Lake Albert showed that for the worst case scenario the surface water alkalinity could be overwhelmed by the acid flux. This is because the amount of exposed soils at Lake Albert was much greater than for Lake Alexandrina and the volumes of surface water much lower.

Consistent with field observations, the drying and cracking of the clayey soils had considerable ability to change their density and porosity on drying. The results of modelling suggested that oxygen penetration would be controlled by crack and water table depth for small peds, but limited in the centre of peds as large as 30 cm. The cracking of soils (Figure 20) was calculated to enhance transport of acidity to the surrounding water by up to 30%. The simulations also indicated a rapid release of acidity upon rewetting with almost no further release from flat soils and a slow continued release from peds (Figure 21) Thus, the period of highest risk of surface water acidification and contamination was considered to be immediately after refilling. Subsequently, only clayey soils were predicted to continue to release acidity to the surrounding water. Overall, the results suggested that if the Lower Lakes had not turned acidic upon refilling they were unlikely to do so in the future, under a relatively stable water level scenario.

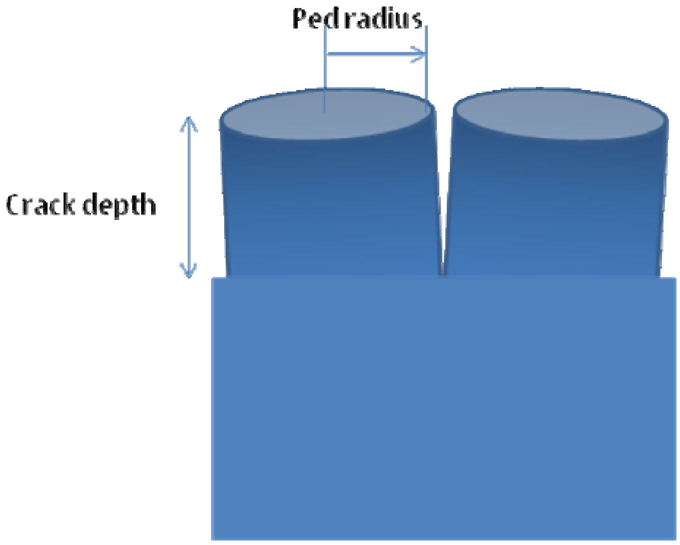


Figure 20. Conceptualisation of ped in cracking clay soil, with ped radius and crack depth indicated.

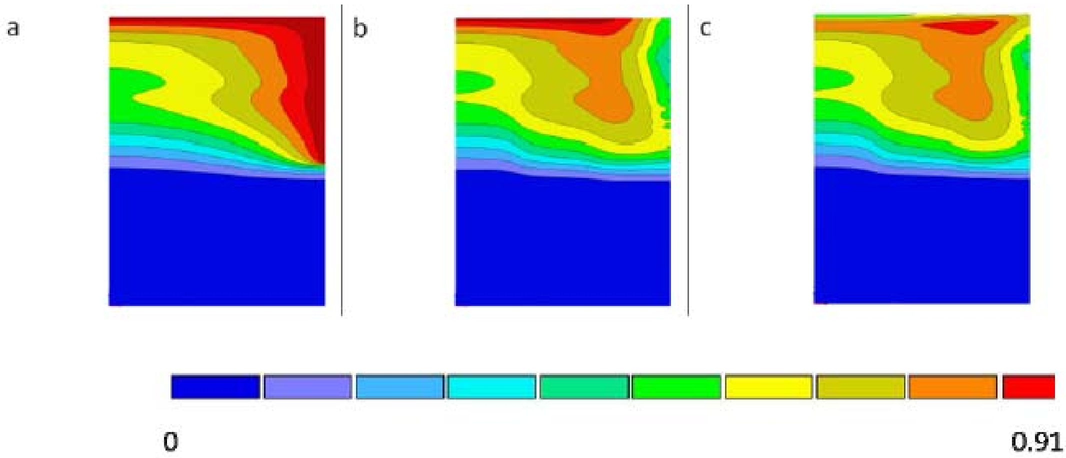


Figure 21. Simulations of solute transport in peds showing a) distribution of oxygen after 1000 days of drying, b) distribution of solute after 100 days of rewetting with water in crack, and c) distribution of solute after 100 days of rewetting with water in crack and on the surface. Relative scale is shown.

It was found that the initial flux of acidity upon rewetting was proportional to the dispersion coefficient for diffusion only processes. When advection was introduced, the time needed for diffusion into the Lower Lakes increased with time. Compared to the mesocosm studies summarised in Section 2.4.2, the model gave reasonable results. The diffusion-only model tended to overestimate the flux of acidity to the lake surface water while the advection plus diffusion scenario occasionally underestimated the flux. However, both scenarios were within one order of magnitude of the measured values, giving confidence in the modelling approach. The models showed that in the absence of significant advection into the soils, that acidity in the soils, and acid fluxes to the surface water will remain high for some time. The rates of recovery were likely to be very slow, of the order of years to decades.

The model for acid flux was run for worst case scenarios for 1000 days (Figure 22), and cumulative acidity was then compared to the alkalinity store in the Lower Lakes. It was concluded that, for Lake Alexandrina, whole lake acidification is unlikely, but there could be local impacts. In contrast, for Lake Albert, the worst case cumulative acid flux after 1000 days was greater than the lakes surface water alkalinity store. It was suggested that the use of smaller-scale wetting and drying cycles may be beneficial to reduce the build-up of pyrite in the soils.

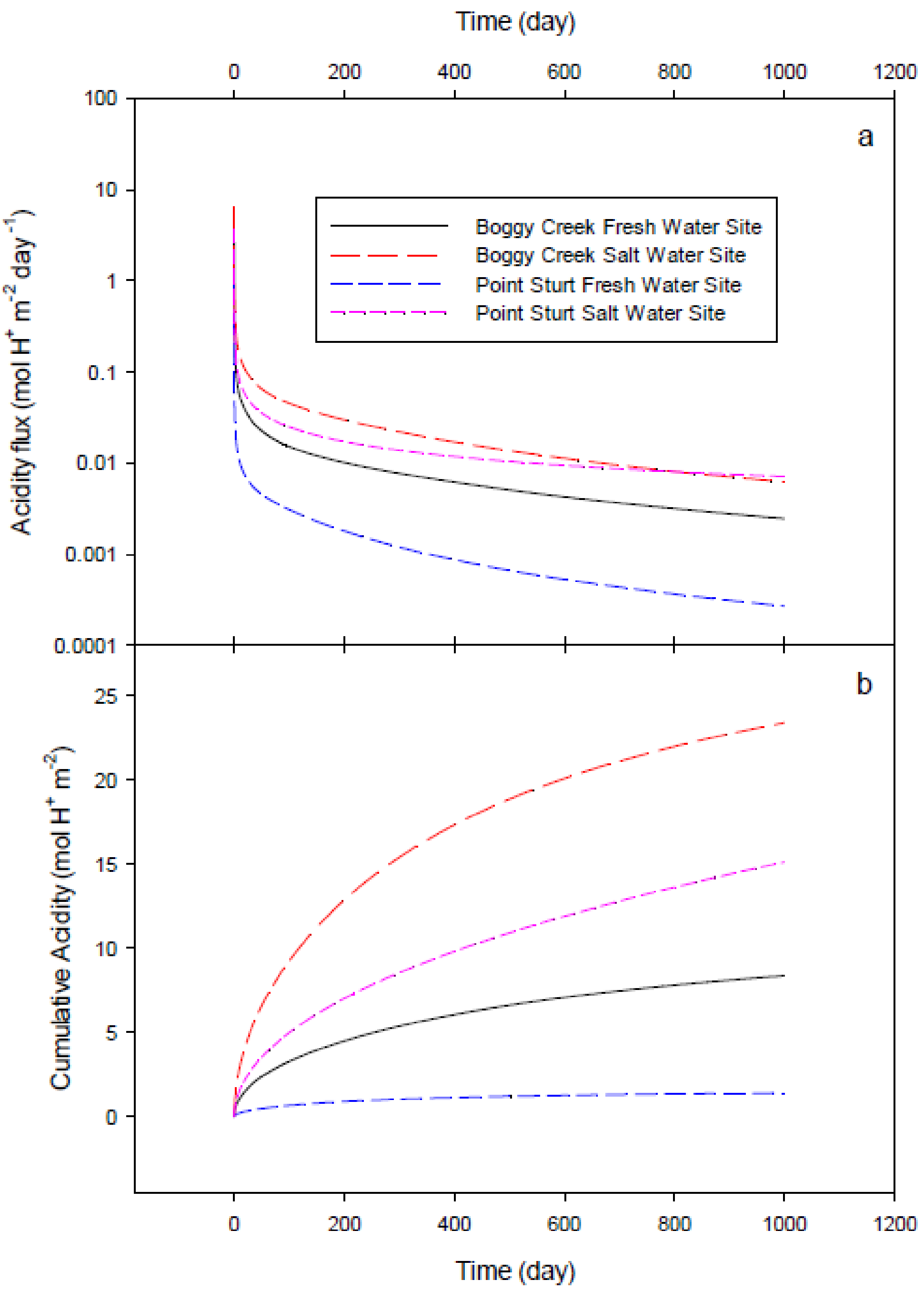


Figure 22. Long term modelling of worst case scenario at each of the four sites of Hicks et al. (2009) for a) flux of acidity, and b) cumulative acidity.

Research limitations and future work

A number of assumptions were needed in order to calculate exfiltration of groundwater, so estimates may be under or over estimated. Nevertheless, monitored data suggested that discharge occurred on a number of occasions and this is consistent with field observations at many sites (CSIRO, unpublished data). There was also some reliance on previous work using capacitance probes which were installed without an in situ calibration.

The transport of discharged groundwater from the mid-transect sites to lake surface waters via local surface flow was not considered. Some estimates of the depth that the soils became unsaturated appear inconsistent with actual data at the time (i.e. at one site the depth of oxidation observed in the field was much deeper than the depth used in modelling). It was also noted that this study was based on a limited number of transects. The model was also relatively simplistic in that it did not consider; the effects of alkalinity inputs to the soils from lake water, the range of likely biogeochemical processes such as sulfate reduction or iron and manganese oxidation, or hydrolysis reactions which provide acidity to the surface waters at the soil-water interface. For modelling aspects, the incorporation of key biogeochemical reactions would be worthwhile.

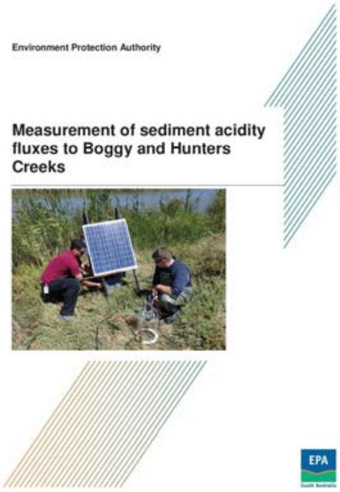
Soil cracking data was based on four transects and, therefore, scaling issues may be a problem in extrapolation across the Lower Lakes. Field observations suggest that peds vary in circumference and many contain abundant internal cracks which may enhance oxygen diffusion and contaminant mobilisation and transport. Due to the difficulty in sampling, the cores were of a relatively small radius.

Overall, a closer synergy between modelling and field activities in future work would help to develop a more robust model for the potential range of future scenarios possible in the Lower Lakes. This would include comparing data at the same time and location to support model assumptions and the measurements of flux at a broader range of sites and under different scenarios of water inflows.

2.4.7 Measurement of sediment acidity fluxes to Boggy and Hunters Creeks

Report details

Full details of the work undertaken and its findings are provided in the report:



Environment Protection Authority

Measurement of sediment acidity fluxes to Boggy and Hunters Creeks

EPA

Hamilton, B., Mosley, L., Stone, D., Zammit, B. (2013). Measurement of sediment acidity fluxes to Boggy and Hunters Creeks. Prepared by the South Australia Environment Protection Authority for the Department of environment, Water and Natural Resources.

Key research outcomes

- The in situ study provided the first direct measurements of acidity and metal fluxes from rewetted acid sulfate soils in the Lower Lakes.
- Findings suggested that the flux of acidity from the soil to the surface water was insufficient to consume surface water alkalinity and the risk of surface water acidification was low.

Aim

To determine the surface water:groundwater interactions at selected sites and the risk of re-acidification under low flow conditions.

Approach

Benthic chambers (Figure 23) were used to measure acidity fluxes from the soil to surface waters at two "hot-spot" locations (Boggy Creek and Hunters Creek on Hindmarsh Island) over a 6 week period.

Findings

Increases in the concentrations of acidity, soluble and total metals were measured inside the chambers, quantifying fluxes from the soil to the surface water. Despite these fluxes, none of the chambers went acidic (pH<6.5, zero alkalinity) over the six week experiment, due to a greater flux of alkalinity, although minor (<0.5 pH units) pH decreases were observed.

The experiment was considered to represent a near worst case condition in a water body with low water levels and stagnant conditions with little external alkalinity inputs (minor inputs during chamber sampling) from inflows. It was concluded that the data suggest a low risk of future water acidification under inundated low flow conditions. This was largely due to alkalinity fluxes from the soils due to sulfate reduction which were greater than acidity fluxes.

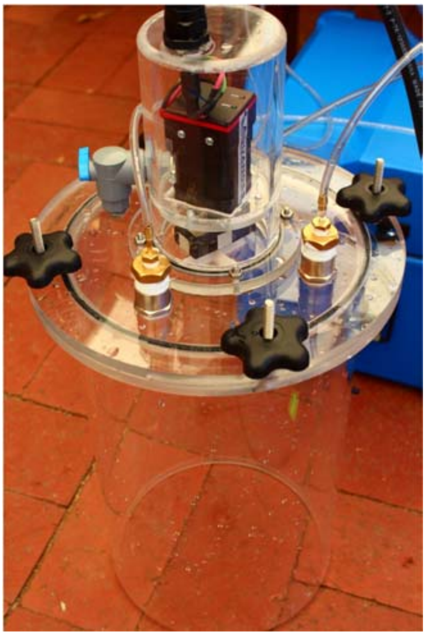


Figure 23. Benthic chamber used to measure fluxes to surface waters.

Ammonia and filterable reactive phosphorus also increased in the chambers, and oxygen and nitrate generally decreased inside the chamber. This was considered to be the result of organic matter mineralisation, nitrification and denitrification processes, although the increase in phosphorus could also have resulted from iron oxide dissolution in the soil.

Although the findings were very positive, the measured metal fluxes were considered to pose an ecological risk, and caution is required in interpreting the overall risk arising from re-submerged acid sulfate soils in the Lower Lakes. A conceptual model was developed to explaining the chemical changes from pre-drought conditions to post-drought (Figure 24).

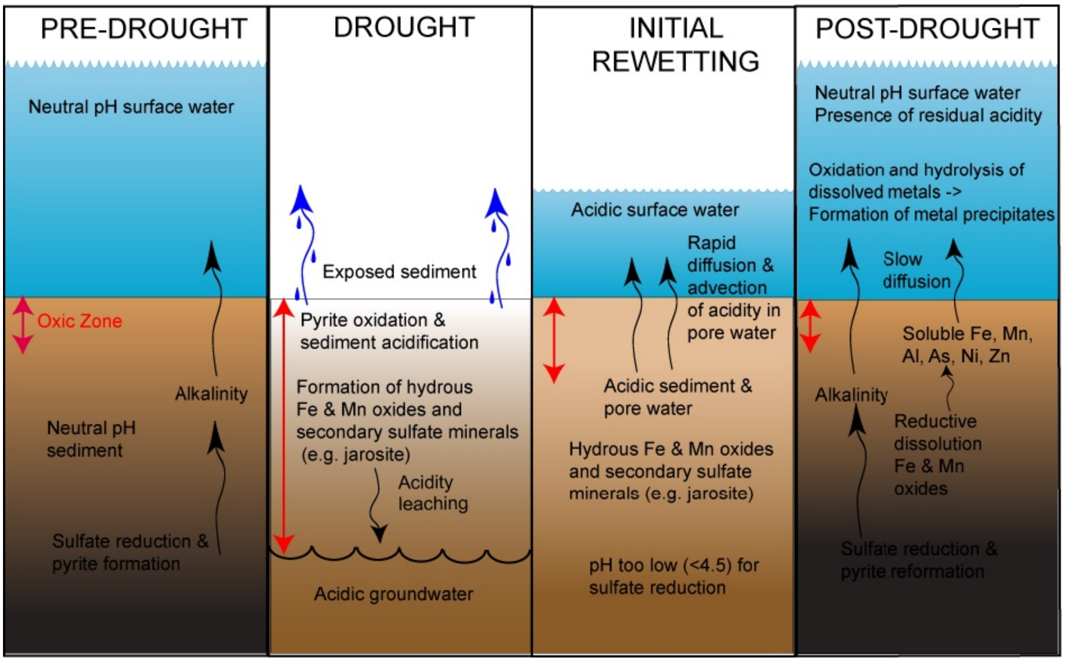


Figure 24. Conceptual model of acidification and metal flux processes in the Lower Lakes.

Research limitations and future work

Control chambers over non-acidic soils were not used to compare the results and this was a recommendation in the report for future studies along with assessing spatial and temporal (especially seasonal) variability. Nevertheless, the heterogeneity noted at these hot-spot sites, made extrapolation of the results to different areas difficult. A further limitation of using flux chambers in oxidising systems was that chambers are isolated from the oxygenated surface water when install (in this case a period of 6 days). This appears to have induced some changes such as oxygen consumption in the chamber (although they remained oxic-hypoxic) and may have imposed a change in redox condition particularly at the soil water interface. This could have altered the flux rate of metals from the soil to the water relative to undisturbed field conditions. Measurement of redox potential across the soil water interface, the porewater chemistry, and more detailed metal speciation measurements (e.g. colloidal and Fe2+ forms of iron) rather than just <0.4 µm filtered (termed "soluble", metals in the study) would be beneficial in future studies.

2.5 Post reflooding recovery of sulfuric materials

2.5.1 An overview of changes in soil acidity in reflooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia

Report details

Full details of the work undertaken and its findings are provided in a series of four chronological reports and a summary report:

National Research
FLAGSHIPS
Sustainable Agriculture
CSIRO

Temporal variations in representative Acid Sulfate Soil environments around Lakes Alexandrina and Albert, South Australia

A.K.M. Baker, R.W. Fitzpatrick, P. Shand, S.L. Simpson, R. H. Merry and M. Thomas

Report Number: R-00325-08-002

June 2010

Prepared For: Murray-Darling Basin Authority and
South Australian Murray Darling Basin Natural Resources Management Board

Baker, A.K.M., Fitzpatrick, R.W., Shand, P., Simpson, S.L., Merry, R.H., Thomas, M. (2010). Temporal variations in representative acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia.

CSIRO

March 2010

February 2011

Temporal variations in re-flooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia

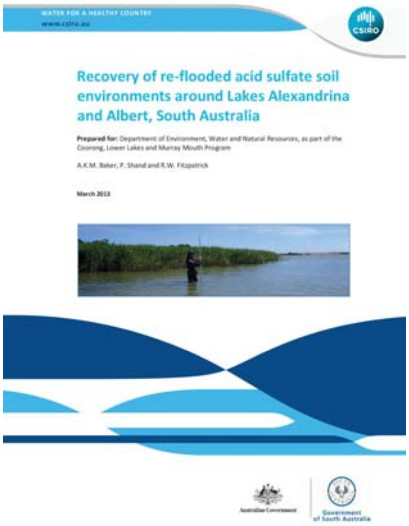
AKM Baker, RW Fitzpatrick, SL Simpson and RH Merry

CSIRO Land and Water Science Report 4/11

26 September 2011

Prepared for: Department of Environment and Natural Resources' Lower Lakes and Coorong Recovery program

Baker, A.K.M., Fitzpatrick, R.W., Simpson, S.L. and Merry, R.H. (2011). Temporal variations in re-flooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia. CSIRO Land and Water Science Report 4/11.


WATER FOR A HEALTHY COUNTRY
www.csiro.au

Recovery of re-flooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia

Prepared for: Department of Environment, Water and Natural Resources, as part of the Coorong, Lower Lakes and Murray Mouth Program

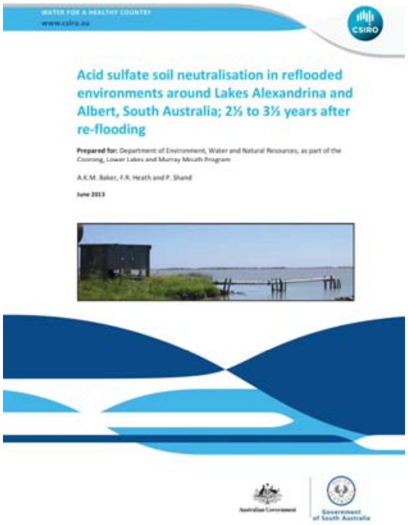
A.K.M. Baker, P. Shand and R.W. Fitzpatrick

March 2013

Australian Government

Government of South Australia

Baker, A.K.M., Shand, P. and Fitzpatrick, R.W. (2013). Recovery of re-flooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia. CSIRO Water for a Healthy Country National Research Flagship


WATER FOR A HEALTHY COUNTRY
www.csiro.au

Acid sulfate soil neutralisation in reflooded environments around Lakes Alexandrina and Albert, South Australia; 2½ to 3½ years after re-flooding

Prepared for: Department of Environment, Water and Natural Resources, as part of the Coorong, Lower Lakes and Murray Mouth Program

A.K.M. Baker, F.R. Heath and P. Shand

June 2013

Australian Government

Government of South Australia

Baker A.K.M., Heath, F.R. and Shand, P. (2013). Acid sulfate soil neutralisation in reflooded environments around Lakes Alexandrina and Albert, South Australia; 2.5 to 3.5 years after reflooding. CSIRO Water for a Healthy Country National Research Flagship.


WATER FOR A HEALTHY COUNTRY
www.csiro.au

An overview of changes in soil acidity in reflooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia

Prepared for: Department of Environment, Water and Natural Resources, as part of the Coorong, Lower Lakes and Murray Mouth Program

A.K.M. Baker and P. Shand

Australian Government

Government of South Australia

*Baker, A.K.M. and Shand, P. (2014). An overview of changes in soil acidity in reflooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia. CSIRO Water for a Healthy Country National Research Flagship.

*This summary report presents an overview of the findings from the above 4 reports.

Key research outcomes

- Overall, no change in net acidity was recorded and acidification hazards in the CLLMM region remain high.
- In areas where soil acid neutralising capacity has been lost, the onset of acidification may be more rapid in a future drought.
- The recovery or neutralisation of oxidised acid sulfate soils is complex. Under favourable conditions recovery in the surface layers can occur quickly. However, under less favourable conditions and for deeper soil layers, recovery can take several years.
- The long time-scales required for recovery highlighted that the best way to manage acid sulfate soils is to prevent them from being disturbed in the first place.
- The rapid rate of refilling of the Lower Lakes at the break of the Millennium Drought minimised the release of acidity from the soils to the surface water, particularly in the sandy soils. If the Lower Lakes refilled at a slower rate it is likely that the exfiltration of the acidity from the soils into surface water would have been much greater. This conclusion is supported by transport modelling results (Section 2.4.6 and 2.7)
- Under drying conditions sandy acid sulfate soils are considered more hazardous than clays as they lack buffering capacity. However, under rewetting conditions clayey textured soils were found to present the greatest hazard due to their larger quantities of acidity.
- Metal mobilisation tests demonstrated that ecologically hazardous concentrations of metal and metalloids could be rapidly mobilised when sulfuric materials were reflooded.

Aim

To monitor the recovery (e.g. neutralisation of acid) of drought-impacted acid sulfate soil materials following their inundation at the break of the Millennium Drought.

Approach

An ongoing field based monitoring program was established at 24 sites around the margins of Lakes Alexandrina and Albert and the Finniss River and Currency Creek tributaries. The selected monitoring sites were considered representative of the diverse environments encountered in the CLLMM region and had been used for acid sulfate soil investigations since 2007 (see Section 1.4). Soil profiles at monitoring sites were sampled on up to 7 occasions on an approximate bi-annual to annual schedule from November 2009 (sampling event ‘a’) to February 2013 (sampling event ‘g’) (Figure 25).

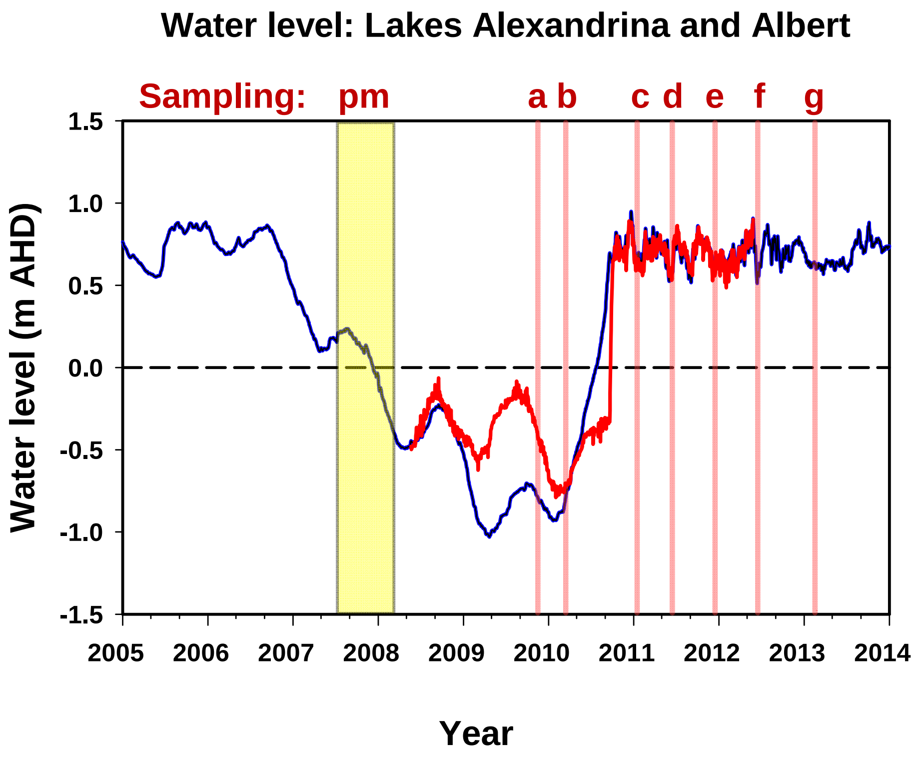


Figure 25. Plot of water levels in Lakes Alexandrina (blue line) and Albert (red line) showing when soil monitoring samples were collected. 'pm' indicates limited pre-monitoring sampling that was undertaken in 2007 and 2008. Generally, 'pm' samples were collected under subaqueous conditions and the data generated represents the best available pre-drought acid sulfate soil baseline conditions.

On each sampling occasion soil profiles were described in terms of physical properties (e.g. texture and colour), pH and EC measurements. The acidification potential of the soils was determined with 3 independent standard methods; pH peroxide testing, acid-base accounting and pH incubation testing. Results from each sampling occasion were compared to identify changes in soil conditions over time and determine rates of soil acid neutralisation following reflooding.

Metal release tests were also undertaken on a subset of samples to assess the potential for dried acid sulfate soil materials to release ecologically hazardous metals, metalloids, and nutrients into surface waters upon reflooding. The method involves suspending dry soil (50g) in deionised water (500ml) by gently agitating for 24 hours or longer. At the end of the test, samples are centrifuged allowing the water to be decanted for analysis. Contaminants made available following the weak extraction (i.e. deionised water) represent contaminants that are readily soluble and easily mobilised, and thus are potentially bioavailable. Initial reports investigated the rapid (24 hours) release of contaminants. In later reports longer time periods (up to 56 days) were also investigated in order to monitor the release or uptake of contaminants predicted to occur as the chemical environment in the soil changes from oxidising to reducing over time.

Findings

Soil neutralisation rates

The repeated monitoring of reflooded sites successfully highlighted a number of temporal changes and the rates of those changes, such as: the transformation from hypersulfidic subaqueous soils to sulfuric soils (due to falling water levels over samplings $h_{\#}$/a/b) to subaqueous sulfuric soils overlain by acidic water (due to reflooding over samplings c/d) to subaqueous hypersulfidic soils (due to prolonged inundation over samplings e/f) (Figure 25).

At the time of the final sampling ‘g’ in February 2013 monitoring sites in Lakes Albert and Alexandrina had been inundated for approximately 2.5 years and monitoring sites in the Finniss River and Currency Creek had been inundated for approximately 3.5 years (Figure 8). Generally, the pH and acidity of soils that did not acidify during the Millennium Drought were relatively unaffected by reflooding. Conversely, soils that did acidify during the Millennium Drought varied in their response to reflooding and either recovered to circumneutral conditions, partially neutralised (minor increases in pH), or showed no significant evidence of neutralisation after 2.5 to 3.5 years of inundation. The rates of soil neutralisation were complex, nonlinear and varied both spatially and with depth as a result of the highly heterogeneous nature of acid sulfate soils in the CLLMM region. Because of this, it is important to recognise that some sites may require individual consideration and tailored management (site specific findings can be found in the full reports).

Dominant factors controlling the rate and degree of soil neutralisation included the presence/absence of retained acidity and soil texture (Figure 26 and Figure 27). Minerals that are a form of retained acidity, such as jarosite, release acidity when dissolved. When soils contained retained acidity, the gradual release of acidity as the minerals slowly dissolved likely buffered soils at low pH for longer periods of time (than if retained acidity was not present). Soils with coarse textures such as the sandy soils around the Lower Lakes’ margins are more permeable to water than fine textured clayey soils. This meant acidity could be flushed more easily from sandy soils than from clayey soils. Additionally, sulfuric sandy soils commonly contained less acidity that needed to be neutralised than sulfuric clayey soils. Due to greater permeability and the smaller amount of soil acidity, sandy soils were generally observed to recover to circumneutral conditions more quickly and more frequently than clayey soils.

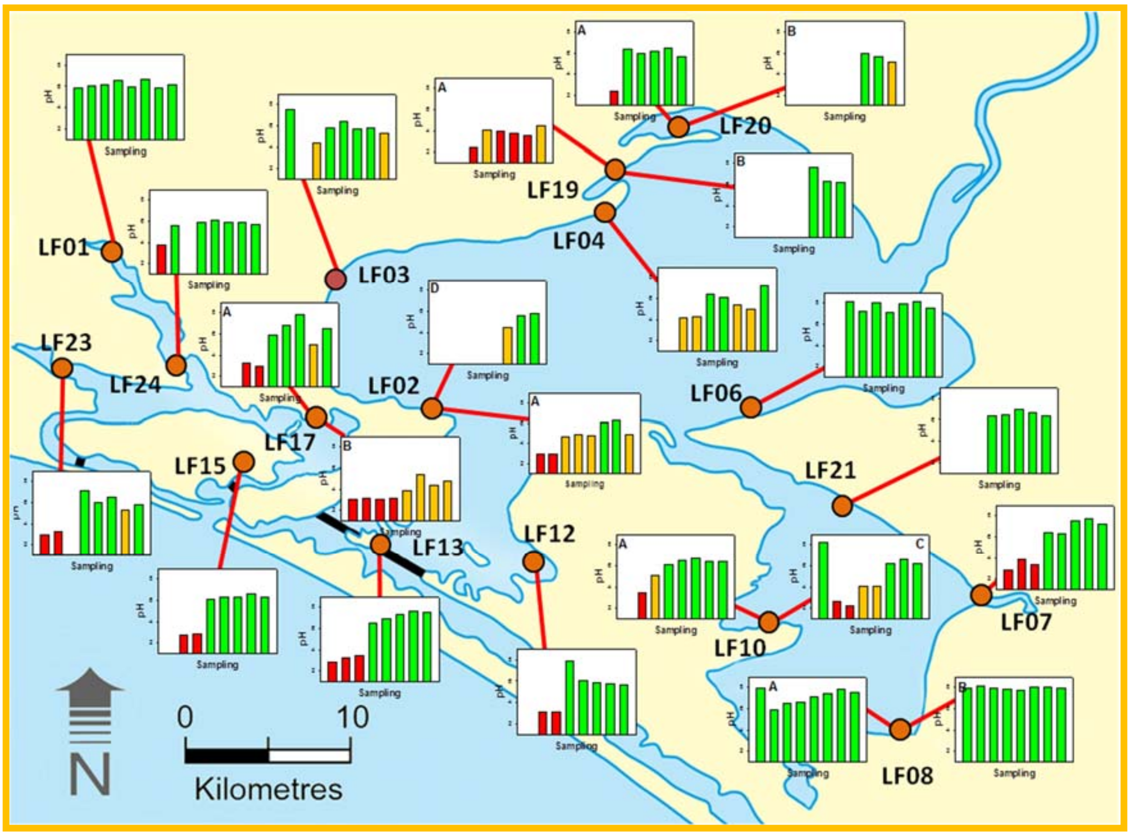


Figure 26. Surface (< 30 cm) soil pH as a function of time. Each plot comprises up to eight vertical bars (representing sampling events 'a' to 'g') illustrating changes in soil pH conditions (red: pH < 4, orange: pH 4 to 5.5, green: pH > 5.5).

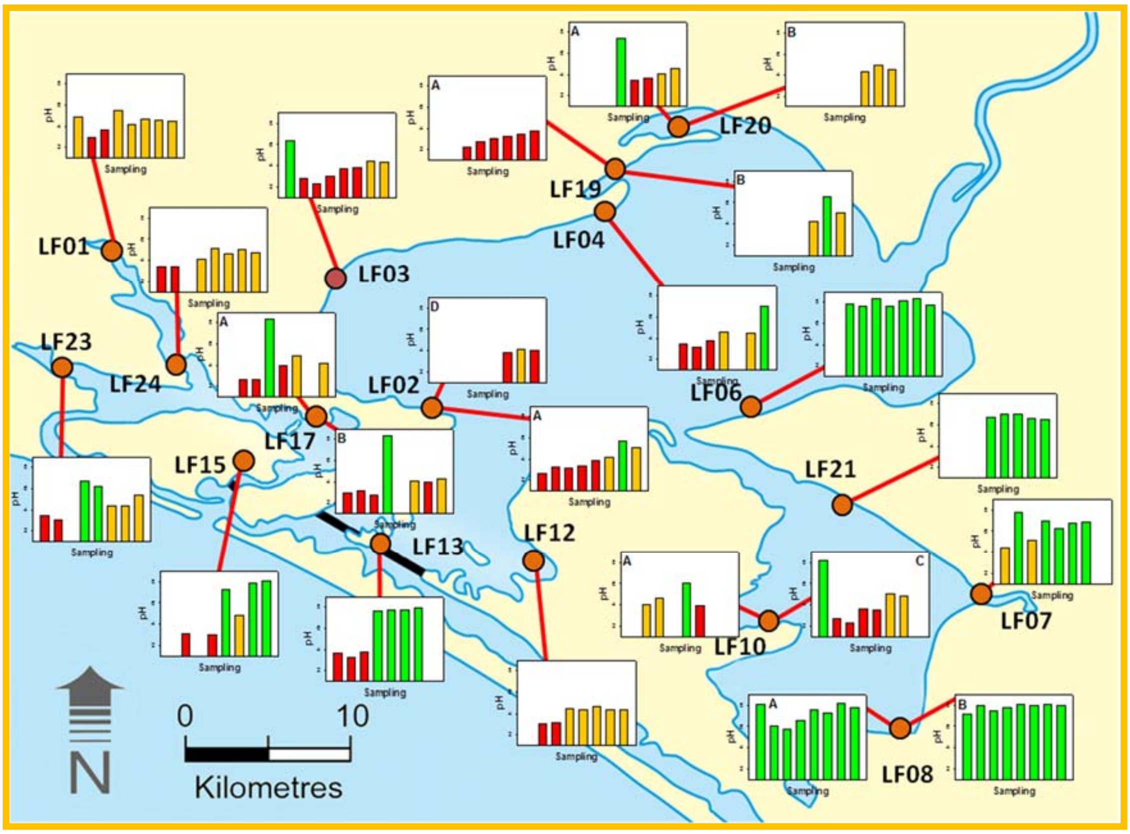


Figure 27. Mid-profile (30 to 50 cm) soil pH as a function of time. Each plot comprises up to eight vertical bars (representing sampling events 'a' to 'g') illustrating changes in soil pH conditions (red: pH < 4, orange: pH 4 to 5.5, green: pH > 5.5).

Often, where minor increases in soil pH occurred, it was restricted to the upper 20 to 40 cm of the soil profile. This can be seen in the contrast between Figure 26, showing the neutralisation of the surface layer, and Figure 27, showing the neutralisation of the sub-surface mid-profile layer. The reasons for this were observed to be several fold; surface soils were more commonly sandy, infiltration of fresh surface water in the permeable sandy surface layers pushing acidity downwards and higher organic carbon concentration in surface layers, which kick-started reduction processes that consume acidity. Circumneutral and reduced surface soils can act as a chemical barrier protecting surface water from the upward flux of acidity and metals from the acidic sub-surface layers. However, a potential side effect of this is the accumulation of precipitated metals and other contaminants in surface soil layers that are the habitat of benthic fauna.

Soil acidification hazard

Despite an apparent partial recovery of soil pH, the degree of acidification hazard remained high and largely unchanged during the pre-drought to drought to post-drought cycle. This means future droughts will likely see a rapid return to the acidified soil conditions of the Millennium Drought.

Although no net loss of acidity (actual + potential acidity) was observed during this hydrological cycle, the form of acidity changed over time. Data from the Milang monitoring site highlights how the conversion between different forms of acidity occurred over time (Figure 28). During prolonged subaqueous conditions, such as before the Millennium Drought, the dominant form of acidity was potential acidity stored as pyrite. When allowed to oxidise under the low water-height conditions during the Millennium Drought, potential acidity (CRS) was converted into actual acidity (TAA). As pH levels continued to drop, some of the potential acidity was also stored as retained acidity (RA). When these oxidised and acidified soils were reflooded at the break of the Millennium Drought, minerals such as jarosite slowly dissolved, converting retained acidity into actual acidity. Retained acidity continued to resist increases in pH until it was consumed. Once consumed any remaining actual acidity was then neutralised by the alkalinity contained in surface water (if able to infiltrate the soil) or by acidity consuming reducing reactions (if the onset of reducing conditions became favoured).

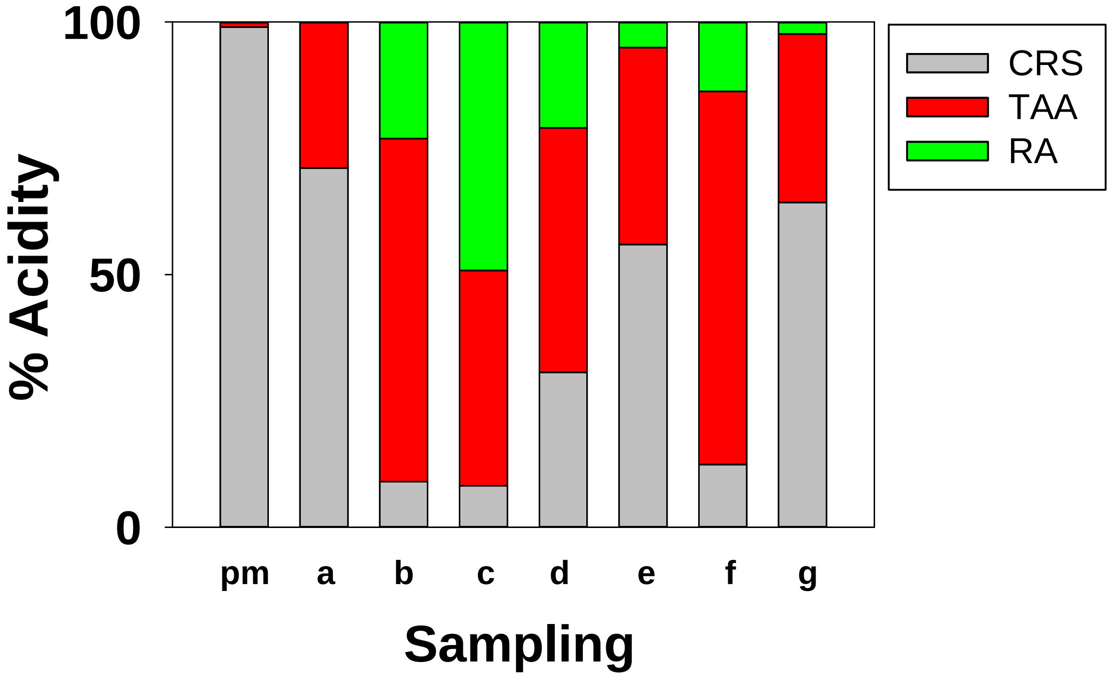


Figure 28. Proportion of acidity types (TAA = actual acidity, CRS = potential acidity (e.g. pyrite) and RA = retained acidity (e.g. jarosite)) for each sampling occasion between August 2007 and February 2013. Example is from middle-profile soil layer at Milang (LF03).

The above shows that acid sulfate soils have the ability to recover to pre-drought conditions given sufficient time. However, more importantly, this series of reports demonstrates that 2.5 to 3.5 years is not a sufficient amount of time and many of the acid sulfate soils in the CLLMM region have not yet recovered to a baseline pre-drought state. This timescale of recovery was much longer than previously anticipated by scientists and managers. Also of potential concern is the loss of inherent acid neutralising capacity (ANC) from soils that acidified during the Millennium Drought. The loss of ANC, which is the first line of defence in neutralising acid generated during the oxidation of sulfide minerals, may mean that future droughts result in acidification events that occur more rapidly and are more severe.

Metal release tests

Results of the metal release tests indicated that the potentially hazardous concentrations of major and trace metals would be rapidly (≤ 24 hours) released into reflooding waters when dry and acidified acid sulfate soil materials were rewet. It is important to recognise that metal mobilisation tests serve only as a guide to the potential availability of contaminants and are likely to represent a worst case scenario due to the high concentration of soil compared to deionised water. However, some trace metals were found to exceed WQG even when diluted by factors of 10x, 100x and 1000x. Overall, the release of Al was found to be of greatest concern, followed by the release of cobalt, chromium, copper, manganese, nickel and zinc. For recently reflooded soils there were observable relationships between the starting pH of the soils, the final pH of the deionised water and the concentrations of released metals. For soils with low starting pH values, the pH of the deionised water at the end of testing was also low, and metal concentrations were generally highest. This is due to the increased solubility of many metals at low pH (pH < 5.5). Also a consequence of increased Al and Fe solubility at low pH is the co-release of metals associated with these phases. This was demonstrated by the strong correlations observed between the concentrations of many of the metals. Results also indicated a high risk of sulfate release from reflooded acid sulfate soil, consistent with the ongoing oxidation of sulfide minerals and soil acidification in the dry soils. Conversely, the release of salts from rewetted acid sulfate soils contributing to increased saline conditions in the Lower Lakes was considered to be low risk. Particularly, when compared to the additions from seawater and saline groundwater intrusion and evapoconcentration. Rapid nutrient release (i.e. within 24hr) from rewetted acid sulfate soils was also considered to be low risk, however over longer timeframes (56 days) the release of ammonium and phosphate were a potential concern.

The relationship between pH and metal concentration was not as strong in soils that had already been inundated for a prolonged period of time (e.g. 1 to 3 years) before testing. This was attributed to the fact that considerable metal release may have already occurred prior to testing and that a range of chemical attenuation processes had been established in the soils following prolonged inundation. Overall, metal release tests conducted in this series of reports indicated that risk of exposure to ecologically hazardous concentrations of metals and metalloids is high and is likely to be greatest immediately following reflooding of sulfuric material. The risk of exposure is expected to decrease over time as the infiltration of surface water into the soil profiles dilutes solute concentrations and chemical attenuation processes are established. However, some soils will still contain high concentrations of metals and metalloids despite prolonged periods of inundation and present a longer term risk.

Conceptual models

Conceptual soil-regolith models for 6 of the monitoring sites were constructed from report findings and surveyor knowledge. The conceptual models were continuously improved upon throughout the series of reports for use as a visual communication aid to help explain the complex spatial and temporal transformations of acid sulfate soil materials that occurred as a consequence of drying and reflooding. For example conceptual models were used to demonstrate: (i) the behaviour and implications of acid sulfate soil materials (e.g. sulfuric, hypersulfidic, hyposulfidic and monosulfidic materials), and (ii) the degree of external and internal factors controlling pathways and processes of acid sulfate soil material evolution (e.g. sulfidization and sulfuricization). To inform management decisions, the conceptual models also incorporated a number of predictive scenarios that would likely result from the various management actions, such as pumping from Lake Alexandrina to Lake Albert, revegetation and the application of limestone. For example, Figure 29 is a conceptual soil-regolith model for Loveday Bay and shows the transformation between the various acid sulfate soil sub-types from 2007 to 2012.

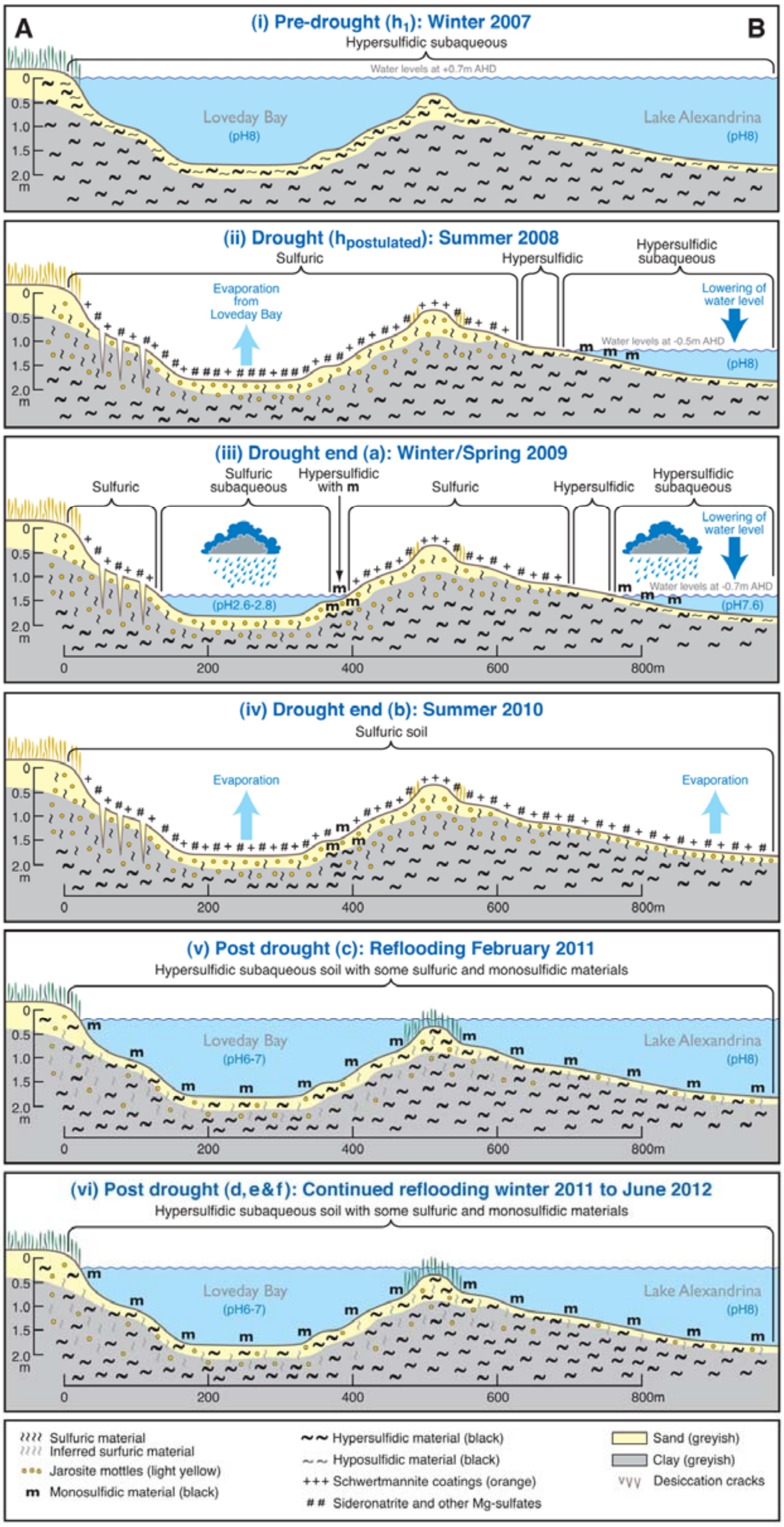


Figure 29. Predictive soil-regolith model for Loveday Bay.

Research limitations and future work

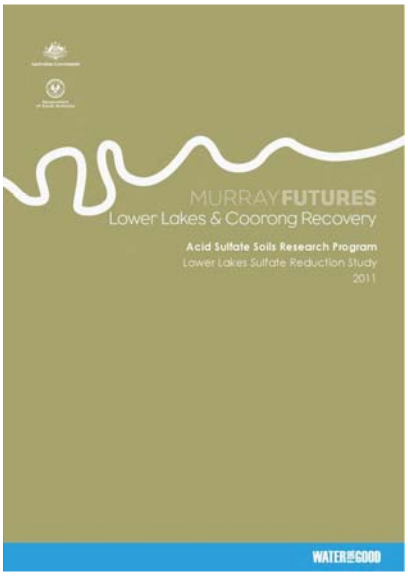
At the time of the final sampling occasion after 2.5 to 3.5 years of subaqueous conditions many soils had not yet fully recovered. It was recommended that yearly monitoring of sites that have persisting acidic soil layers be continued for ≥ 5 years or until the soils return to baseline conditions. It is unknown what physico-chemical changes may have occurred in the period from 2013 to current (2016).

Metal release tests were conducted under closed system conditions in the laboratory and serve only as a guide to the potential availability of contaminants. The upward flux of contaminants from the soil to the overlying surface water was not quantified in this study. Further investigation will help quantify the actual impacts of metal release from reflooded sulfuric materials on surface waters. Metal release results indicated that when metal-rich acidic waters released from the soil mixed with circumneutral surface waters aluminium, iron and manganese are likely to precipitate as solid phases (e.g. $Al(OH)_3$, FeOOH and MnOOH). Large amounts of metals are likely to become associated with these new precipitates through adsorption or co-precipitation. Although the removal of contaminants from the dissolved phase is a positive outcome, the precipitates that form may also be ecologically hazardous (e.g. aquatic organisms exposed to suspended solids through filter feeding or benthic organisms that reside near soil water interface). This effect also warrants investigation.

2.5.2 Lower Lakes sulfate reduction study

Report details

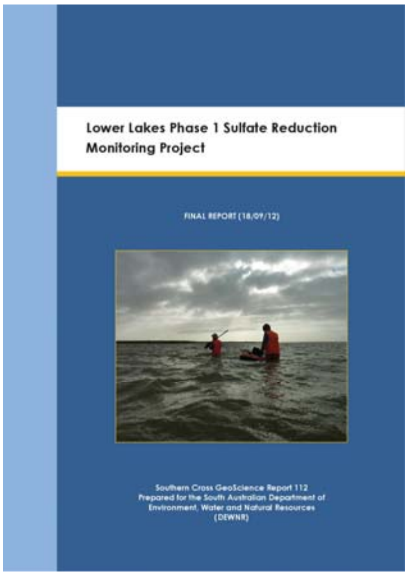
Full details of the work undertaken and its findings are provided in a series of three chronological reports:



MURRAY**FUTURES**
Lower Lakes & Coorong Recovery
Acid Sulfate Soils Research Program
Lower Lakes Sulfate Reduction Study
2011

WATER FOR GOOD

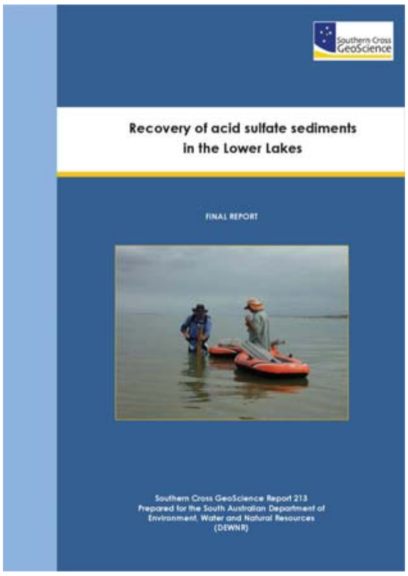
Sullivan, L.A., Burton, E.D., Ward, N.J., Bush, R.T., Coughran, J., Cheetham, M.D., Fyfe, D.M., Cheeseman, P.J. and McIntyre, T. (2011). Lower Lakes sulfate reduction study. Prepared for the SA Department of Environment and Natural Resources, Adelaide. Southern Cross GeoScience Technical Report No. 711.


Lower Lakes Phase 1 Sulfate Reduction Monitoring Project

FINAL REPORT (18/09/12)

Southern Cross GeoScience Report 112
Prepared for the South Australian Department of
Environment, Water and Natural Resources
(DEWNR)

Sullivan, L.A., Ward, N.J., Bush, R.T., Cheetham, M.D., Cheeseman, P.J., Fyfe, D.M., McIntyre, T., Bush, M. and Hagan, R. (2012). Lower Lakes Phase 1 Sulfate Reduction Monitoring Project. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide Southern Cross GeoScience Technical Report No. 112.


Southern Cross GeoScience

Recovery of acid sulfate sediments
in the Lower Lakes

FINAL REPORT

Southern Cross GeoScience Report 213
Prepared for the South Australian Department of
Environment, Water and Natural Resources
(DEWNR)

Sullivan, L.A., Ward, N.J., Rosicky, M.A., Li, S., Bush, R.T., Fyfe, D.M., Bush, M. and Toppler, N. (2013) Recovery of acid sulfate sediments in the Lower Lakes. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide. Southern Cross GeoScience Technical Report No. 213.

Key research outcomes

- The lack of organic matter in acidified lower lake soils was a chief factor limiting sulfate reduction following reflooding;
- Phytoremediation (via revegetation) was successful in providing a source of organic matter to drive sulfate reduction reactions;
- A continued increase in pH was observed at all sties following rewetting, some consequent of phytoremediation some not;
- Sub-surface soil layers that contained jarosite required a much longer period of inundation to restore the circumneutral pH conditions;
- Despite increases in pH no consistent decreases in soil net acidity were observed and, hence, soils remain vulnerable to re-acidification if low flows return;

- The use of inundation tolerant plant species (e.g. *Phragmites*) resulted in an increased acidification hazard due to the accumulation of pyrite than if left un-vegetated. *Phragmites* may also be a source of phosphate to the overlying lake waters;
- Increased acidification hazards were avoided almost completely when inundation intolerant vegetation was used; and
- Sandy surficial soil layers at unvegetated control sites were neutralised at approximately the same rate as revegetated sites.
- Revegetation substantially reduced the loss surface soil layers through wind and water erosion, preventing the highly acidic sub-surface soil layers from becoming exposed and making direct contact with the surface water following reflooding;

Aim

To examine the impacts of phytoremediation techniques (i.e. revegetation of exposed lake margins) on the recovery of reflooded acid sulfate soils that acidified during the Millennium Drought.

Approach

Four locations, two in Lake Alexandrina (Poltalloch and Tolderol) and two in Lake Albert (Waltowa and Campbell Park), were selected to monitor the recovery of drought-impacted acid sulfate soils after they had been reflooded for a total period of 2.5 years. The monitoring locations included bare sites (as controls) and a range of revegetated sites. Vegetation 'treatments' examined included common reeds (*Phragmites*), bulrush (*Typha*), cotula (*Cotula*), spiny rush (*Juncus*), saltmarsh grass (*Puccinellia*), and Bevy cereal rye (Figure 30). The experimental design allowed investigators to compare the recovery of soils under various revegetation treatments (i.e. phytoremediated sites) against each other, as well as against soils where no phytoremediation took place (i.e. unvegetated control sites). Recovery was mainly assessed in terms of the presence and rate of sulfate reduction, the types of reduced inorganic sulfur formed and their associated hazards, and increases in soil pH and alkalinity.

Figure 30. An example of the vegetation treatments investigated (clockwise from top left: unvegetated control, Bevy rye, *Cotula*, *Juncus* and *Phragmites*).

Field sampling of soil profiles took place prior to the Lower Lakes refilling in May 2010 and approximately 1, 3, 6, 19 and 24 months after refilling. The main parameters measured included pH, acid base accounting (including sequential extraction of elemental sulfur, monosulfides and pyrite), and total and hydrolysable carbon. Sulfate reduction rates were determined over a 24 hour incubation period using a $^{35}SO_4^{2-}$ radiotracer. Sulfate reduction rates were calculated from the sum of ^{35}S incorporated into reduced inorganic sulfur species (determined by liquid-scintillation counting) during the incubation period.

Two additional components of this project included preliminary scoping investigations for the uptake of metals into vegetation growing in acid sulfate soils and metagenomic investigations to characterise the microbial community structure in bioremediated acid sulfate soils. The uptake of metals into plant tissues (leaves, stems and flowers) was assessed by sampling a range of different vegetation types from 15 locations around the margins of Lakes Alexandrina and Albert. Vegetation samples were washed, dried and ground before digestion with nitric acid and analysis by ICP-MS. To examine the microbial soil communities, microbial DNA was extracted from surface (0 to 10 cm) and sub-surface (30 to 40 cm) soil samples at Tolderol in Lake Alexandrina and analysed using the GeoChip v4.0 approach. Investigations into microbial community structure did not continue beyond this preliminary scoping study.

Findings

Impacts of phytoremediation on sulfate reduction and soil recovery

Overall, the series of reports observed a continued improvement in soil pH and acidy values following rewetting over the 2.5 year monitoring period. The recovery of soil pH was most apparent in surface layers but was also observed in some sub-surface layers down to 60 cm (e.g. Figure 31). The continued recovery of the rewetted sulfuric soils was attributed to a number of processes, some related to phytoremediation, some not.

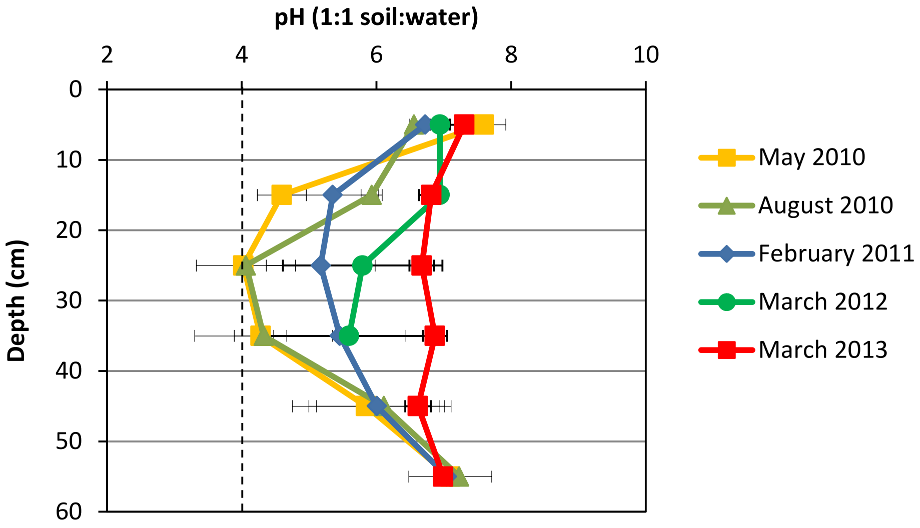


Figure 31. Poltalloch field pH dynamics at the Bevy rye site (May 2010 – March 2013).

The studies concluded that the phytoremediation (by revegetation) of acid sulfate soils resulted in a number of positive outcomes in terms of improving their recovery. The benefits provided through phytoremediation are a result of a combination of different processes. One revegetation related benefit was the provision of organic matter to stimulate alkalinity producing reduction reactions (Figure 32). The absence of sufficient organic matter to stimulate alkalinity producing reduction reactions can limit the rate of recovery of acid sulfate soils. As oxidised Lower Lake soils typically contained only small amounts of organic matter, this was identified as a chief limiting factor preventing rapid recovery.

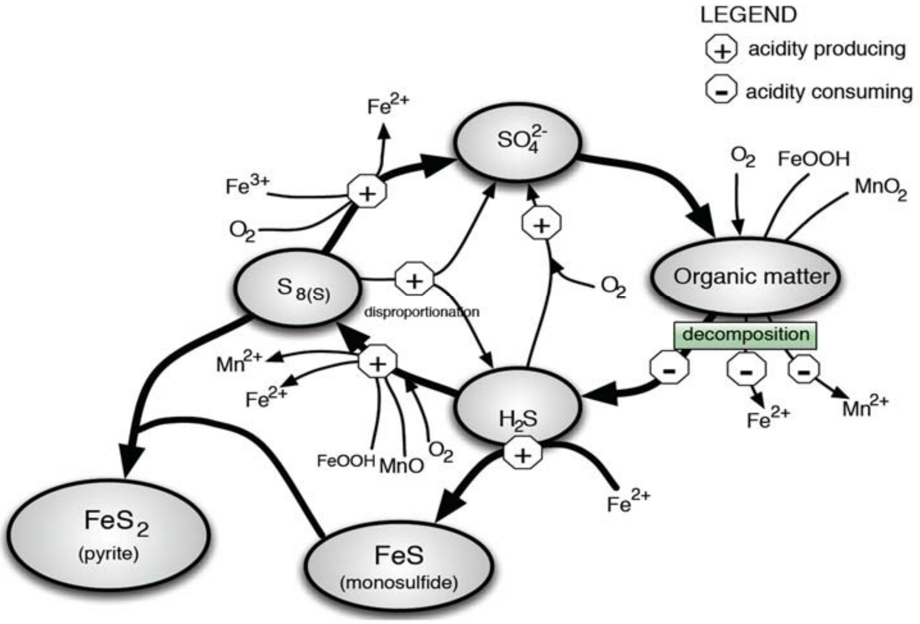


Figure 32. Conceptual diagram of sulfur cycle operating in the surface layers of the bioremediated inundated Lower Lake soils.

The establishment of vegetation on the previously exposed lake margins was successful in increasing the concentration of organic matter in the surface soil layers. When and how much organic matter was added was dependent on the type of vegetation. For example, Bevy rye, which was unable to survive inundation, supplied considerable amounts of organic matter in a short time frame but only on a single occasion. Whereas, perennial vegetation such as *Phragmites* which was able to tolerate inundation provided an ongoing supply of organic matter to the soil.

The organic matter provided by Bevy rye stimulated sulfate reduction in the surficial soil layers (0 to 5 cm) immediately after reflooding. However, available organic matter was rapidly depleted (within approximately 7 months) and sulfate reduction rates slowed. As Bevy rye was unable to survive lake refilling, it could not resupply organic matter to the soil once depleted. *Cotula* and *Juncus* were more tolerant of inundation and continued supply organic material and stimulate sulfate reduction in the surface soil layers for a longer period of time than Bevy rye, before eventually dying when water levels became too high. *Phragmites* was observed to survive prolonged periods

(≥ 19 months) and greater depths (approximately 1 m) of inundation in comparison to the other types of vegetation investigated. The ability of *Phragmites* to survive lake refilling allowed it to provide an ongoing supply of organic matter that continued to drive sulfate reduction over the 2.5 year monitoring period.

The nature of the sulfate reduction processes observed were also dependent on the supply of organic matter, which was in turn dependent on the type of vegetation used for phytoremediation. Under treatments where the vegetation type provided a short term supply of organic matter (e.g. Bevy rye) the most common product resulting from sulfate reduction was elemental sulfur, even when sulfate reduction rates were substantial. Elemental sulfur is a highly dynamic phase and was observed to oxidise back to sulfate soon after formation. This means the contribution of alkalinity to the soil through elemental sulfur production (via sulfate reduction) was both transient and minor. Under treatments where the vegetation type provided an supply of organic matter (e.g. *Phragmites*) over long time periods sulfur cycling processes resulted in the formation and accumulation of iron monosulfides (e.g. monosulfidic black ooze) and pyrite. The formation of these minerals (via sulfate reduction) provided greater amounts of alkalinity to the soil than the production of elemental sulfur and improved soil pH.

Although the production of iron monosulfides and pyrite increased soil pH in the *Phragmites* treatment it also resulted in the build-up of potential sulfidic acidity (Figure 33). The build-up of potential sulfidic acidity in the surface soils of the *Phragmites* treatment represents a potential acidification hazard should these soils become exposed in the future. Additionally, the accumulation of monosulfidic black ooze in the surface soils also represents acidity, deoxygenation and metal mobilisation hazards if disturbed.

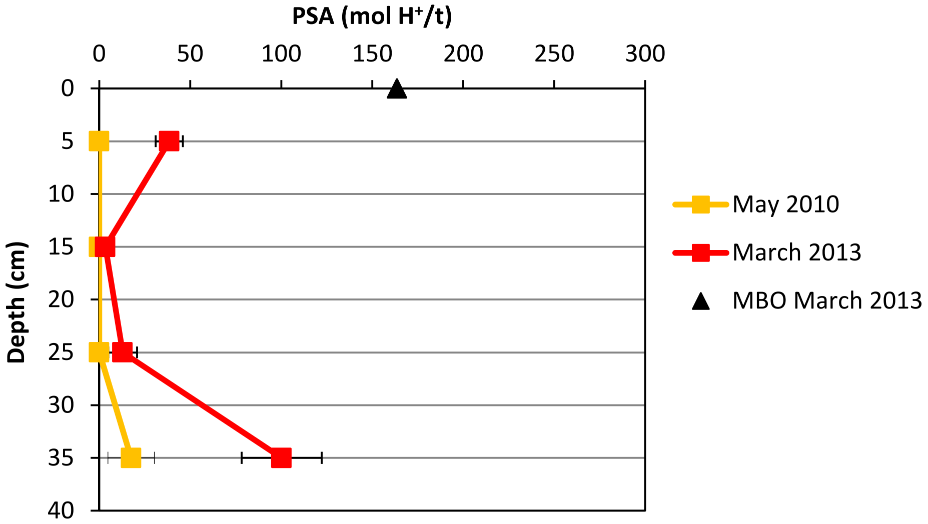


Figure 33. Waltowa Potential Sulfidic Acidity dynamics at the established *Phragmites* site (May 2010 and March 2013).

The pH of surface soil layers of unvegetated control sites were also observed to increase following rewetting. This is a result of alkalinity contained in surface waters entering the soil profile through advective or diffusive processes and neutralising soil acidity. The magnitude of this effect at the control sites, where other sources of alkalinity provided directly or indirectly by phytoremediation are negligible, is indicative of its significant contribution towards soil recovery. Results from the study indicated that, even left unvegetated, the movement of alkalinity from the surface water to the soil will slowly remediate the acidified surface soil layer. However, it was recognised that for soil layers containing jarosite much longer periods of inundation will be required to restore circumneutral pH conditions. This is due to jarosite being a store of retained acidity that is difficult to neutralise.

Another positive effect of revegetation was the stabilisation of exposed lake margin soils against erosion by wind and water (e.g. wave action and seiche events). Unvegetated control sites were observed to suffer considerable losses (i.e. approximately 9 cm) of soil from the surface during the Millennium Drought, when compared to revegetated sites. As well as minimising dust hazards (see Section 2.2.1), stabilising the surface soil layers through revegetation had a positive impact on acid sulfate soil recovery. Surface sulfuric layers were commonly found to have higher pH and contain less acidity than sub-surface sulfuric layers. The highly acidic sub-surface layers are also more likely to contain retained acidity (e.g. jarosite) and generally have a finer texture that is less permeable than the typically course sandy surface layers. These factors can make the sub-surface layers more difficult to neutralise than the surface layers. Thus, keeping the less acidic and more easily neutralised surface soil layers in place (via revegetation) prevents the direct contact between lake surface waters and the highly acidic and more difficult to neutralise sub-surface layers upon rewetting.

No consistent appreciable changes to soil net acidity were observed during the 2.5 year monitoring period. This indicated that processes apart from the external addition of alkalinity from lake surface waters have been important factors in the recovery of the soils at the unvegetated and vegetated sites. The dominate process that can increase soil pH without affecting soil net acidity is the reduction of sulfate to produce reduced inorganic sulfides (e.g. pyrite). The magnitude of changes to potential sulfidic acidity (i.e. pyrite generation) during the study period were not large enough to quantify this process. This was in part due to limitations of the acid base accounting method. Another factor that can increase soil pH without affecting soil net acidity is the transfer of acidity between different acidity pools. One example of this is the transfer of acidity from retained acidity in the form of jarosite to titratable actual acidy in the form of dissolved iron. This process was clearly observed in a number of soils.

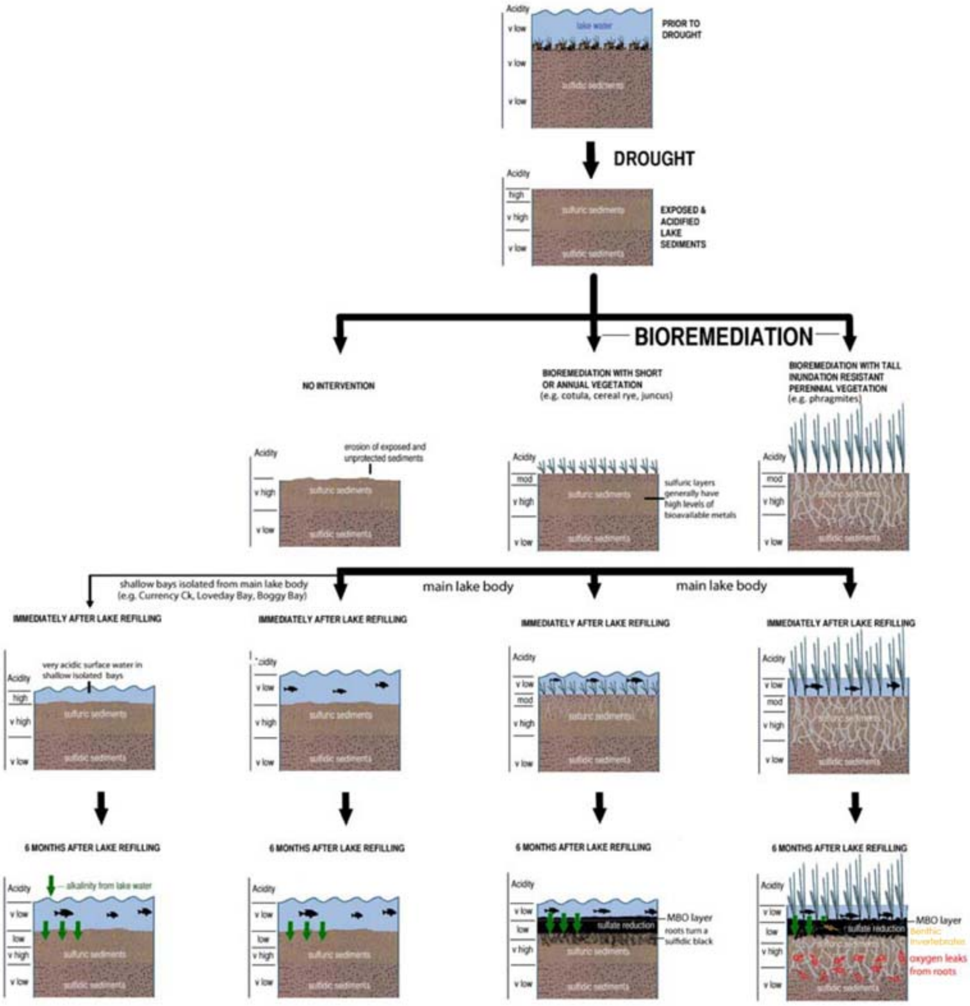


Figure 34. Conceptual diagram of sulfur cycling and acidity as affected by bioremediation. Note: has not been updated to include findings made after 6 months of inundation.

Metal uptake in emergent vegetation growing in acidified lake soils

It was recognised that universally accepted guidelines for metal concentrations in wetland vegetation is not available. However, high concentrations of metals, namely aluminium, iron, nickel and manganese, were found in the tissues of plants growing in acid sulfate soils that had acidified during the Millennium Drought. Concentrations of some metals were considered sufficiently elevated to pose a potential ecological hazard to both plant health as well as fauna health (as a food chain contaminant). However, the concentrations of many other metals (e.g. copper, cadmium, chromium, arsenic and lead) were low and often below detection limits.

Metal concentrations in the tissues of the same plant species that were unaffected by acid sulfate soils (e.g. growing in the fore dunes) were considerably lower (Figure 35). This indicates that the acidification and resultant mobilisation of metals of acid sulfate soils that oxidised during the Millennium Drought have affected the uptake of metals into plant tissues. Different vegetation species were found to uptake metals into different tissues (leaves, stems and flowers) and accumulate metals at different concentrations. For example, metals were generally more concentrated in the leaves rather than the stems of *Phragmites*. *Bolboschoenus caldwellii* species sampled had much lower concentrations of metals in its tissues than most of the other vegetation types sampled. On average, the highest metal concentrations were found in sedge (unidentified species) plant tissue samples collected near Meningie. It was also noted that vegetation growing in clayey surface soils, rather than sandy surface soils, tended to have lower metal concentrations. This was thought to be a result of metal adsorption onto the clay minerals (e.g. immobilisation) occurring in the clayey soils.

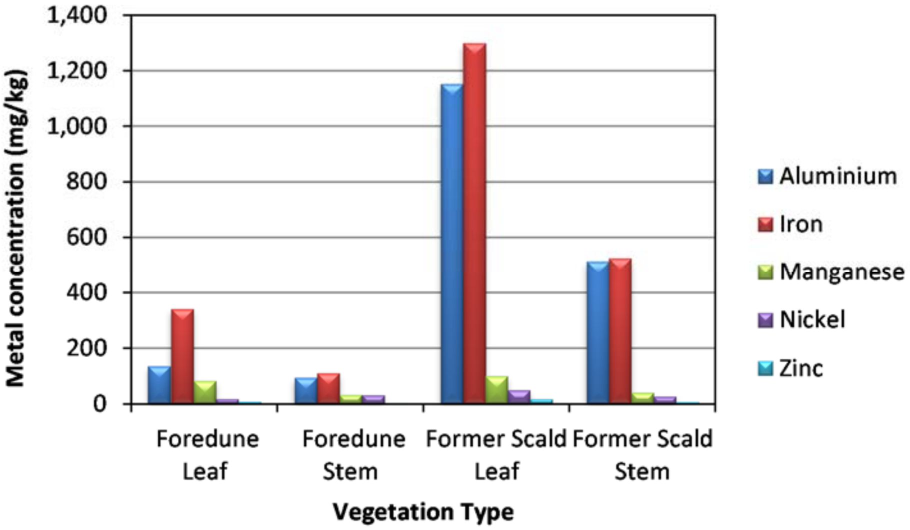


Figure 35. Metal concentrations in the leaves and stem of the *Phragmites australis* collected from the foredune and former scald at the Tolderol site.

Metagenomic pilot study

Results from the preliminary pilot study indicated the potential utility of metagenomic analyses to characterise and distinguish microbial community structures in different geochemical environments (e.g. vegetated and unvegetated soils). Microbial diversity was shown to be higher in the bioremediated surface soils, than in the unvegetated surface soils and both sub-soil materials. This was presumed to be due to the greater provision of organic materials to the surface soil from phytoremediation. Only a brief examination of the data was possible within the timelines of the study. There is considerable scope for further analysis of the data to identify how changes in microbial community, as a result of phytoremediation, may promote or suppress various biogeochemical processes.

Research limitations and future work

Phytoremediation of acid sulfate soils by revegetation was shown to promote soil neutralisation via sulfate reduction. However, there are a number limitations associated with phytoremediation that must also be considered.

- The benefits associated with the phytoremediation of acid sulfate soils by revegetation are limited to the uppermost surface soil layers.

- The phytoremediation of acid sulfate soils by revegetation may contribute further to acidification, deoxygenation and nutrient release hazards. Particularly if inundation tolerant vegetation is used (i.e. *Phragmites*).
- The revegetation of exposed lake bed soils is both logistically challenging and costly.
- Revegetation of exposed acid sulfate soil may lower local groundwater levels through evapotranspiration, exposing further acid sulfate soils originally below the groundwater table to atmospheric oxygen.

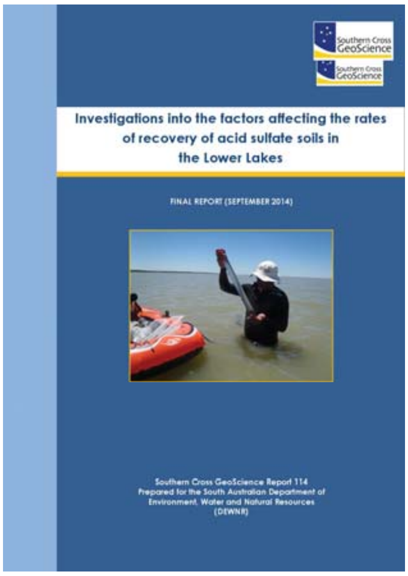
Considering these limitations and the fact that surface soil layers not assisted by phytoremediation were rapidly neutralised by alkalinity inputs from surface water at approximately the same rates, the use of revegetation for the purpose of phytoremediation needs to be considered carefully. Further research is required to better quantify the associated risks and benefits of the management technique.

The conceptual diagram illustrating the remediation of revegetated vs unvegetated rewetted acid sulfate soils was constructed from initial observations made after 6 months of monitoring. This conceptual diagram is an effective communication tool however, it requires updating to include the findings made between 6 months and 2.5 years after rewetting.

2.5.3 Investigations into the factors affecting the rates of recovery of acid sulfate soils in the Lower Lakes

Report details

Full details of the work undertaken and its findings are provided in the report:



Southern Cross GeoScience

Investigations into the factors affecting the rates of recovery of acid sulfate soils in the Lower Lakes

FINAL REPORT (SEPTEMBER 2014)

Southern Cross GeoScience Report 114
Prepared for the South Australian Department of Environment, Water and Natural Resources
(DEWNR)

Ward, N.J., Bush, R.T., Wang, Z., Sullivan, L.A., Fyfe, D.M., Choppala, G., Williams, L., Toppler, N. and Bush, M. (2014). Investigations into the factors affecting the rates of recovery of acid sulfate soils in the Lower Lakes. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide. Southern Cross GeoScience Technical Report No. 114.

Key research outcomes

- The addition of natural organic matter (i.e. *Phragmites australis* and *Schoenoplectus validus*) slowed the rate of recovery due to the release of organic acids from the vegetation.

- The addition of natural organic matter resulted in an increase in the mobilisation of metal(loid)s (e.g. cobalt, copper, manganese, nickel and zinc) and ammonia (consistent with field observations in Section 2.5.2). Concentrations often exceeded ANZECC guidelines. However, the risk to the surrounding ecosystem is dependent on the rate of metal(loid) flux from the soils and dilution.
- The hydrolysis of schwertmannite and jarosite led to acidification of the surface water and metal(loid) mobilisation. However, the reductive dissolution of these minerals in the presence of sufficient organic matter led to a rapid recovery.
- Elevated levels of some metals (i.e. manganese and aluminium) were observed in vegetation growing in the formerly acidified acid sulfate soils.

Aim

To determine the role of organic carbon in the recovery of inundated sulfuric materials and in the mobilisation of metal(loid) contaminants using laboratory techniques

Approach

This project builds on previous field based work (Section 2.5.2) to further quantify the role of organic matter in the recovery of drought-impacted soils.

Laboratory based incubation experiments were used to examine how the presence of different organic matter sources affected changes in soil pH and the mobilisation of metals under saturated reducing conditions (Figure 36). Incubation experiments consisted of a 50 ml test tube to which 8 g of soil, 0.4 g of organic material and 40 ml of distilled water was added. No organic material was added to un-modified control samples, however, organic matter was naturally present in low concentrations (approximately 0.2% C). The various prepared treatments were then incubated under reducing (oxygen free) conditions for up to 16 weeks before analysis.

Figure 36. Incubation experiments in the anaerobic chamber.

Surface (0-2.5 cm) and sub-surface (2.5-10 cm) soil samples used in the incubation experiments were collected from the same Tolderol and Waltowa monitoring sites used in the series of reports summarised in Section 2.5.2. Organic matter enriched samples were treated with dried and finely ground natural organic matter (e.g. plant material) from either *Phragmites australis* or *Schoenoplectus validus* or with simple organic compounds that commonly form during the microbial decomposition of plant material (i.e. glucose, acetate and humic acid). Laboratory synthesised jarosite and schwertmannite (0.4 g) was also added to a number of treatments to examine how these minerals affect soil pH and metal(loid) release.

A number of parameters were analysed to examine the changes during incubation of soil samples under anoxic conditions both in the presence (or absence) of different organic carbon sources and in the presence (or absence) of common acid sulfate soil minerals. Parameters analysed included general water quality, metal(loid) release and fractionation and changes to organic carbon and changes to redox sensitive species (i.e. Fe^{2+}, S^{2-}, Mn^{2+}).

An additional component of this project was to further examine the uptake of metal(loid)s by vegetation after preliminary scoping investigations identified elevated metal concentration in vegetation growing in formerly acidified acid sulfate soils (see Section 2.5.2). Plant materials) were collected from total of 18 sites near Tolderol on the fringes of Lake Alexandria and Waltowa on the fringes of Lake Albert. Samples included the leaves and stems from *Phragmites* and *Schoenoplectus*.

Findings

The addition of natural organic matter in the form of *Phragmites* resulted in similar behaviour to the addition of natural organic matter in the form of *Schoenoplectus* for the majority of parameters. An exception to this was that notably higher concentrations of ammonia were released from the *Phragmites* treatment than from the *Schoenoplectus* treatment and control samples. Ammonia concentrations in both natural organic matter treatments and control samples exceed ANZECC guidelines.

Data for pH showed improvement to circumneutral values within 8 weeks for the control samples and in samples enriched with natural organic matter (Figure 37). However, control samples were observed to recover more quickly (within 4-8 weeks). The addition of natural organic matter initially resulted in acidification. For some soils this acidification was temporary circumneutral pH was reached within 8 weeks, however, sub-surface soil samples near neutral pH was not achieved before the end of the incubation experiment (16 weeks). It is expected that the decrease in pH in the natural organic matter treated samples was a result of acidity produced through initial organic matter breakdown. The low pH observed during the temporary acidification was poorly buffered and therefore of minor concern, the small amount of acidity was easily consumed following further breakdown of the organic acids and reduction reactions. Glucose showed a similar recovery rate to natural organic matter, whereas acetate and humic acid had little to no effect on the pH recovery of soils.

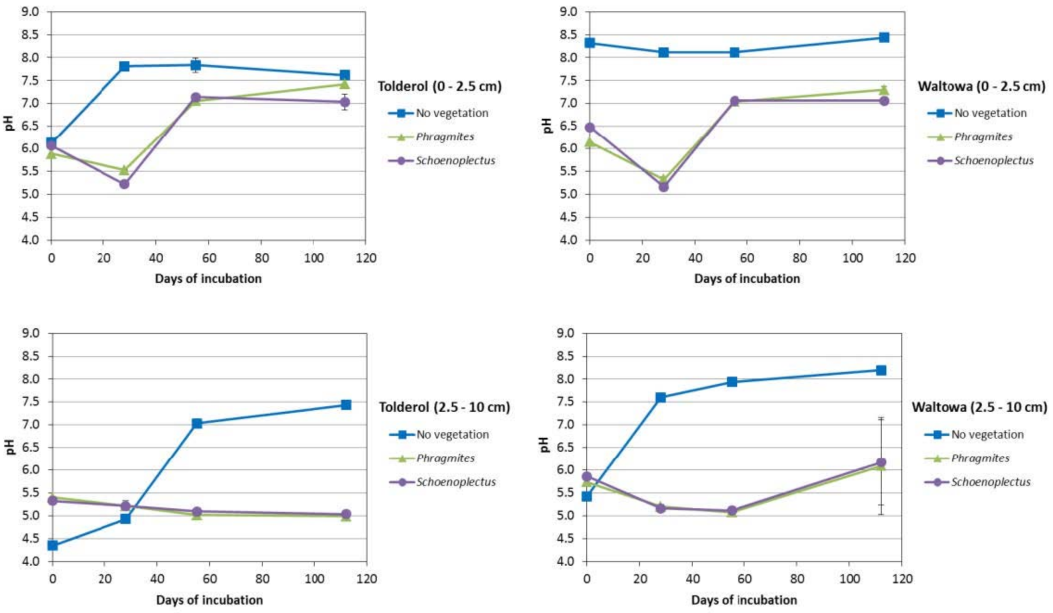
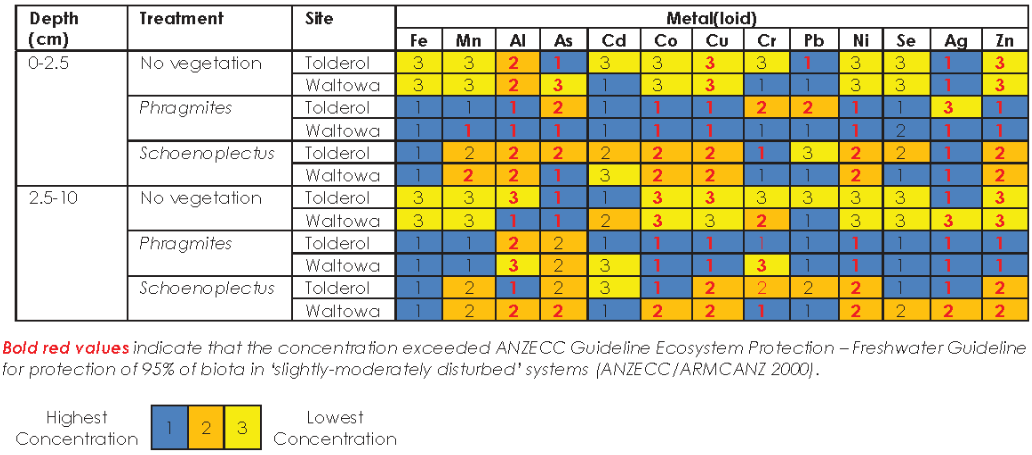


Figure 37. Tolderol and Waltowa surface water pH dynamics.

The addition of jarosite or schwertmannite to untreated soils and soil treatments enriched with natural organic matter or simple organic compounds usually resulted in substantially lower pH. This is likely due to the release of acidity when these minerals undergo hydrolysis. This is further evidenced by substantial increases in EC due to irons being released into solution following the hydrolysis and/or reductive dissolution of these minerals. Where schwertmannite was added to soil samples enriched with natural organic matter it was likely that iron monosulfide sulfide minerals began to form after 7 days of incubation. This is consistent with decreases in water soluble sulfur and iron concentrations and visual indication of a black mineral forming.

Metal(loid) concentrations were often elevated in treatments enriched with natural organic matter from *Phragmites* or *Schoenoplectus* compared to the control samples with no organic materials added (Figure 38). Metal(loid) concentrations (e.g. Cobalt, Copper, Chromium, Nickel, Manganese and Zinc) in *Phragmites* treated samples generally exceeded ANZECC guidelines by greater amounts than in *Schoenoplectus* treated samples.



Depth (cm)	Treatment	Site	Metal(loid)												
			Fe	Mn	Al	As	Cd	Co	Cu	Cr	Pb	Ni	Se	Ag	Zn
0-2.5	No vegetation	Tolderol	3	3	**2**	**1**	3	3	**3**	3	**1**	3	3	**1**	**3**
		Waltowa	3	3	**2**	**3**	1	3	**3**	1	1	3	3	**1**	**3**
	Phragmites	Tolderol	1	1	**1**	**2**	1	**1**	**1**	**2**	**2**	**1**	1	**3**	**1**
		Waltowa	1	**1**	**1**	**1**	1	**1**	**1**	1	1	**1**	2	**1**	**1**
	Schoenoplectus	Tolderol	1	2	**2**	**2**	2	**2**	**2**	**1**	3	**2**	2	**1**	**2**
		Waltowa	1	**2**	**2**	**1**	3	**2**	**2**	1	1	**2**	1	**1**	**2**
2.5-10	No vegetation	Tolderol	3	3	**3**	**1**	1	**3**	**3**	3	3	3	3	**1**	**3**
		Waltowa	3	3	**1**	**1**	2	**3**	3	**2**	1	3	3	**3**	**3**
	Phragmites	Tolderol	1	1	**2**	2	1	**1**	**1**	1	1	**1**	1	**1**	**1**
		Waltowa	1	1	**3**	2	3	**1**	**1**	**3**	1	**1**	1	**1**	**1**
	Schoenoplectus	Tolderol	1	2	**1**	2	3	**1**	**2**	2	2	**2**	1	**1**	**2**
		Waltowa	1	2	**2**	**2**	1	**2**	**2**	**1**	1	**2**	2	**2**	**2**

Bold red values *indicate that the concentration exceeded ANZECC Guideline Ecosystem Protection – Freshwater Guideline for protection of 95% of biota in 'slightly-moderately disturbed' systems (ANZECC/ARMCANZ 2000).*

Highest Concentration | 1 | 2 | 3 | Lowest Concentration

Figure 38. Summary of the rank of the maximum metal(loid) concentrations.

The addition of natural organic matter greatly increased the release of iron and manganese. This finding indicates that the addition of natural organic matter enhanced the mobilisation of these metals through the reduction of iron and manganese oxides or hydroxides present in the soils. Cobalt and nickel showed a similar behaviour to iron and manganese. Results indicate that these metals were associated with iron and manganese oxides or hydroxides and were released into solution when these minerals underwent reductive dissolution. Vegetation was the likely source of mobilised copper and zinc. These metals, initially released from the added natural organic matter, had become incorporated with the soil by the end of the incubation experiment. Both *Phragmites* and *Schoenoplectus* vegetation types have similar total metal concentrations, however, some released metal concentrations associated with the *Phragmites* treatments were slightly higher.

Metal(loid)s concentrations in the collected plant materials were generally low. However, some metal(liods) were found to be elevated. Aluminium and manganese concentrations were often well above the published criteria for the limit for most plants with mean concentrations of 473 mg/kg and 151 mg/kg, respectively. Findings summarised in Section 2.5.2 reported elevated nickel concentrations in some of the vegetation samples. In this study, maximum concentrations were found to be within published ranges for most natural vegetation. Differences were observed in the uptake and accumulation of metals by the two vegetation types. The *Phragmites* leaves at Tolderol were found to have higher concentrations of aluminium and manganese than those from Waltowa. The higher concentration of these metals in the *Phragmites* leaves at the Tolderol were thought to be a result of differences in the background concentration of these metals at the two sites.

Research limitations and future work

- The validity of using natural organic matter that had been finely ground for the incubation experiments was not discussed. It is unknown how the availability of natural organic matter derived from vegetation in natural systems (i.e. mix of fibric and/or hemic and/or sapric) compares to the availability of the finely ground fibric material used in the incubation experiment.
- The incubation experiments were limited to the testing of shallow surface layers with high starting pH (>4) values. Further work to compare the behaviour of deeper and more acidic soils is required before extrapolating the findings from the Tolderol and Waltowa sites to the CLLMM region.

It was recommended that the same experimental approach is repeated to further investigate:

- The effects of the organic carbon concentration on the rate of recovery and release of metal(loid)s;
- The role of sulfate reduction on metal immobilisation; and
- The effect of sulfate concentration on the formation of reduced organic sulfides.

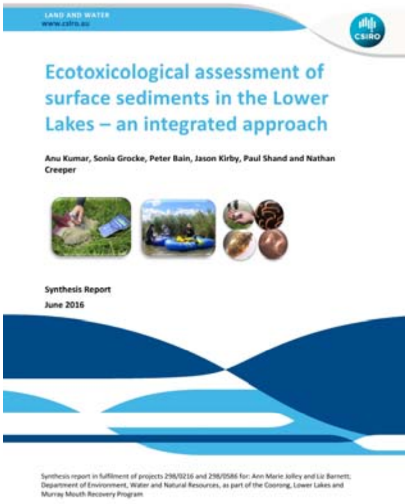
The release of nutrients from impacted acid sulfate soils associated with *Phragmites* could potentially result in algal blooms. It is recommended that the impact of *Phragmites* on the nutrient dynamics of soils around the Lower Lakes' margins is further examined.

2.6 Benthic ecology and ecotoxicology impacts related to ASS

This section presents brief summaries of each component of the three year 'Lower Lakes Ecotoxicology Project', namely:

- Lower Lakes benthic ecosystem toxicity assessment pilot study (Section 2.6.1).
- Sediment Quality Triad (SQT) assessment of surface soils in the Lower Lakes (Section 2.6.2).
- Ecotoxicological assessment of surface water, porewater and soil samples (Section 2.6.3).
- In situ assessment of bioavailability of contaminants released from acid sulfate soils (Section 2.6.4).
- Toxicity of selected metals and their binary mixtures to midge larvae, *Chironomus tepperi* and juvenile freshwater snail, *Physella acuta* (Section 2.6.5).

Full details of the work undertaken is provided in a series of six interim reports. A complete review of the 'Lower Lakes Ecotoxicology Project' and its findings are provided in a synthesis report entitled 'Ecotoxicological assessment of surface sediments in the Lower Lakes – an integrated approach'.



LAND AND WATER
www.csiro.au

Ecotoxicological assessment of surface sediments in the Lower Lakes – an integrated approach

Anu Kumar, Sonia Grocke, Peter Bain, Jason Kirby, Paul Shand and Nathan Creeper

Synthesis Report
June 2016

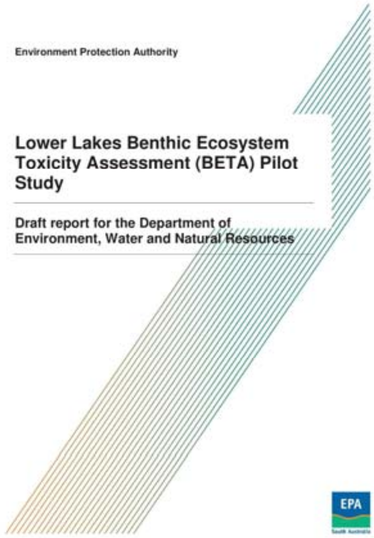
Synthesis report in fulfilment of projects 298/0216 and 298/0586 for: Ann Marie Jolley and Liz Barnett; Department of Environment, Water and Natural Resources, as part of the Coorong, Lower Lakes and Murray Mouth Recovery Program

Kumar, A., Grocke, S., Bain, P., Kirby, J., Shand, P. and Creeper, N. Ecotoxicological assessment of surface sediments in the Lower Lakes – an integrated approach. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide. CSIRO Technical report: Land and Water Flagship. *In preparation.*

2.6.1 Lower Lakes benthic ecosystem toxicity assessment pilot study

Report details

Details for this component of the 'Lower Lakes Ecotoxicology Project' are provided in the interim report;



Environment Protection Authority

Lower Lakes Benthic Ecosystem Toxicity Assessment (BETA) Pilot Study

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

Corbin, T., Mosley, L., Creeper, N., Hicks, W. (2012). Lower Lakes benthic ecosystem toxicity assessment (BETA) pilot study. Environmental Protection Authority, South Australia.

Key research outcomes

- Soil biota is spatially separated from potentially toxic concentrations of contaminants;
- pH and the concentrations of some nutrients were elevated sufficiently to be potentially harmful to biota;
- Overall, metal concentrations were sufficiently low to not be of concern to soil biota;
- Chironomid deformities were observed, however further research is required to elucidate if the rate of deformities observed were elevated or within natural range; and

- Lowered pH and increased acidity, originating from acid sulfate soil oxidation, may be impacting the recovery of mollusc communities due to exoskeleton dissolution. Note that these results were based on preliminary studies and should be treated with caution.

Aim

This study aimed to investigate the porewater chemistry in the lower reaches of the Finniss River and Currency Creek tributaries and determine if persisting acidification and general poor soil condition were negatively impacting soil dwelling biota. Specifically, the investigation included the assessment of:

- Soil porewater condition;
- The rate of chironomid deformities;
- Benthic community composition; and
- Mussel shell dissolution.

Approach

Soil porewater quality in the lower reaches of the Currency Creek and Finniss River tributaries was assessed using equilibrium dialysis samplers, commonly called peepers. Peepers are inserted directly into the soil and are used to collect soil porewater in order to determine the vertical distribution of contaminants in a soil profile at a high resolution (Figure 39; right hand side). Peepers were deployed at three sites of interest, two known to be impacted by acid sulfate soils and one reference site at a location not impacted by acid sulfate soils. Of the two impacted sites, one was in the Finniss River and the other in Currency Creek. The reference site was located upstream in the Finniss River, away from potential acid sulfate soil impacts. Soil porewater samples collected from the peepers were analysed for pH, EC, alkalinity or acidity, nutrients and major, minor and trace element concentrations with comparisons made against the ANZECC guideline trigger values.

Figure 39. Collecting a sweep net sample (left) and extracting soil porewater samples from the peeper chambers (right).

This study explored sub-lethal impacts on soil dwelling macroinvertebrates (i.e. chironomids). Together, chironomids and worms comprise the dominant types of soil dwelling fauna. Chironomids are commonly used as bioindicators of soil condition. Deformities in the mouthparts or antennae of chironomids are used as an indication of toxic effects resulting from poor soil condition (e.g. high concentrations of metals). Deformities are known to occur naturally at a low rate, however, much higher rates of deformities are often observed in contaminated soils. Sweep net samples were collected from the same three sites above (Figure 39). Samples collected in the sweep net were searched for live chironomids. Individuals found were collected and taken to the laboratory for analysis. In the laboratory, the head of each individual chironomid was removed and mounted on a microscope slide. Using a compound microscope, individuals were identified to the genus level and assessed for mouthpart and antennal deformities.

To assess the diversity, distribution and abundance of macroinvertebrates living in the soil, samples were taken from the soil profiles at the two acid sulfate soil impacted sites. Soil profile samples were divided into 0 to 2 cm, 2 to 5 cm and 5 to 10 cm sections and preserved with ethanol. In the laboratory, preserved soil sample sections were searched for fauna. All taxa found were identified to the lowest taxonomic level practicable.

Ecological monitoring in the region had previously highlighted that molluscs and some crustaceans present prior to the Millennium Drought were still missing in 2011. Mollusc and crustacean exoskeletons are constructed of calcium carbonate. Calcium carbonate is known to dissolve at low pH, making these taxa highly susceptible to ongoing acidic conditions. A novel approach was trialled to assess the potential dissolution of mollusc shells (e.g. freshwater mussel, *Velesunio ambiguous*) exposed to severely acidic soil conditions resulting from acid sulfate soil oxidation. Using a peeper, mussel shell pieces of known weight were placed directly into the soil at various depths in the soil profile from 3 cm above the soil surface to a depth of 21 cm below the soil surface. This peeper was deployed at an acid sulfate soil impacted site in the Finniss River for two weeks. Following retrieval of the peeper, mussel shell pieces were washed in distilled water and reweighed to determine the change of mass. A loss of mass was used to indicate potential dissolution due to soil porewater acidification.

Findings

Assessment of soil porewater conditions showed that acidity is still of concern in the impacted sites that had acidified during the Millennium Drought but were now reflooded. The pH of soil porewater dropped to potentially toxic values (i.e. pH < 6.5) at depths below approximately 8 cm at both of the impacted sites in Finniss River and Currency Creek. In contrast, porewater pH vales in 2009 were approximately 3. The pH of soil porewater at the non-impacted reference site was found to remain circumneutral over the entire sampling depth (27 cm). Surface water samples were also found to be circumneutral. While pH had improved by approximately 2 units at the acid sulfate soil impacted sites, alkalinity was still low (<0.2 mmol L^{-1}), and in many cases was less than the acidity (approximately 2 to 5 mmol L^{-1}). Nutrient concentrations (i.e. nitrate and nitrite, ammonia, and phosphate) were elevated in soil porewaters and commonly exceeded ANZECC trigger values below depths of approximately 5 to 10 cm at all sites. Elevated nutrient concentrations can favour algal blooms, which in turn can provide a source of organic carbon to drive the unwanted accumulation of monosulfidic materials. Metal and metalloid concentrations were elevated at the impacted sites in comparison to the reference site. However, ANZECC trigger values were generally not exceeded. A small number of exceedances for arsenic (speciation unknown), boron, chromium, and manganese were observed below a depth of approximately 10 to 15 cm at Currency Creek.

In total, chironomid deformities were observed in 0% and 4.3% of individuals collected from the impacted sites in Finniss River and Currency Creek, respectively. Deformities were observed in 4.1% of individuals collected from the non-impacted reference site. Deformities were observed in both the antennae and mouthparts of the chironomids (Figure 40). The deformity rate measured at the impacted Currency Creek site was only slightly higher than for the reference site. It is unknown if this small difference was significant, indicating that either soil biota were impacted by acid sulfate soil transformations, or the proportion of deformities were within the range of natural deformities. Elsewhere in the MDB chironomid deformities have been observed to occur at rates averaging 4 to 5%. The deformities seen at Currency Creek occurred on more major morphological structures. These more significant types of deformities are suggestive of impacts from soil pollution.

Figure 40. A deformed antenna (reduced number of antennal segments) of a chironomid individual.

Macroinvertebrates identified in soil profile samples comprised mostly of segmented worms, non-biting midges (chironomids) and round worms (nematodes). Many other taxa were also collected, including; microcrustaceans, the amphipod family Corophiidae, a larval specimen from the caddis-fly genus *Ecnomus*, a water mite, a springtail and a fly larva from the family Muscidae. Most of the biota were found to reside at a depth of 0 to 2 cm in the soil profile. At the impacted Finniss River site, considerable soil biota were also found at a depth of 2 to 5 cm. At the impacted Currency Creek site, only 5 individuals were observed at this depth. This was considered a legacy of the severe acid sulfate soils impacts this site received during the Millennium Drought. The observation that the majority of organisms living in the soil were observed within 5 cm of the soil surface is significant when compared to the soil porewater data, which shows most contaminants don't reach potentially toxic concentration until deeper in the soil profile.

All mussel shell pieces placed into the soil at the impacted Finniss River site showed a loss of mass (except for at 5 cm) after 2 weeks. Mussel shells were found to be coated in a black substance thought to be iron precipitate, potentially originating from the oxidation of reduced iron (Fe^{2+}) that had diffused upwards from deeper in the soil profile. The greatest decrease in mussel shell mass at 7 cm depth corresponded with a decrease in soil porewater pH and increase in acidity.

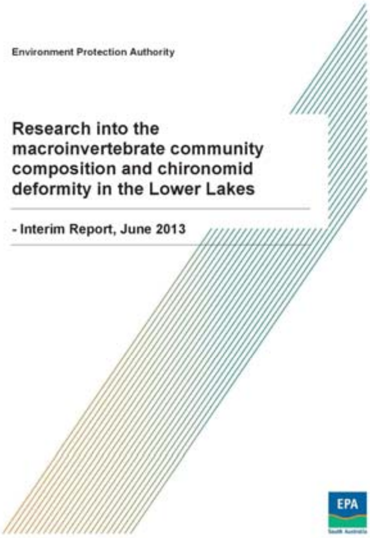
Research limitations and future work

- Although metal concentrations were found to be below trigger values, ecotoxicological impacts due to bioaccumulation may still occur in some biota.
- Biota were specially separated from the highest contaminant concentrations located deeper in the soil profile. However, the upwards diffusive flux of contaminants as a potential exposure pathway was not investigated.
- Further research is needed to confirm the natural rate of deformities in chironomids in the River Murray and Lower Lakes region and if they are suitable for use as an indicator of environmental impacts.
- Only a single mussel shell dissolution trail was conducted, hence, results in this study should be treated with caution.
- The importance of baseline data was highlighted when the lack of Lower Lakes pre-drought background data available for comparison made the interpretations of some findings difficult.

2.6.2 SQT assessment of surface soils in the Lower Lakes

Report details

Details for this component of the 'Lower Lakes Ecotoxicology Project' are provided in a series of three interim reports:



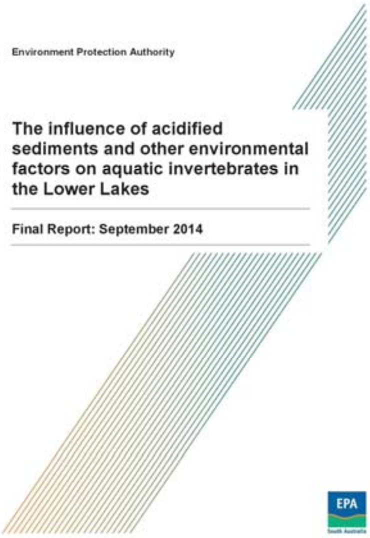
Environment Protection Authority

Research into the macroinvertebrate community composition and chironomid deformity in the Lower Lakes

- Interim Report, June 2013

*Corbin, T., Cummings, C. (2013). Research into the macroinvertebrate community composition and chironomid deformity in the Lower Lakes. Environmental Protection Authority, South Australia.

*Interim report



Environment Protection Authority

The influence of acidified sediments and other environmental factors on aquatic invertebrates in the Lower Lakes

Final Report: September 2014

Corbin, T., Cummings, C., Mosley, L. (2013). The influence of acidified sediments and other environmental factors on aquatic invertebrates in the Lower Lakes. Environmental Protection Authority, South Australia.

LAND AND WATER FLAGSHIP
www.csiro.au

Sediment Quality Triad (SQT) assessment of surface sediments in the Lower Lakes

Anu Kumar, Tracy Corbin, Hai Doan, Sonia Grocke, Deb Gonzago, Jason Kirby, Luke Mosley and Paul Shand

January 2015
Interim Report-Commercial in confidence

Interim report Interim report in fulfilment of project milestones 1.3 and 2.3 of project 298/0586 for:

Ann Marie Jolley and Liz Barnett; Department of Environment, Water and Natural Resources, as part of the Coorong, Lower Lakes and Murray Mouth Recovery Program

*Kumar, A., Corbin, T., Doan, H., Grocke, S., Gonzago, D., Kirby, J., Mosley, L. and Shand, P. (2015). Sediment Quality Triad (SQT) assessment of surface sediments in the Lower Lakes. CSIRO Technical report: Land and Water Flagship.

*Commercial in confidence

Key research outcomes

- The SQT approach was a useful tool to assess the ecotoxicological impacts of acid sulfate soil acidification.
- The SQT approach found most surface soils were likely unaffected by acidification. However, two sites, Boggy Creek and Boggy Lake were of concern.
- Observed changes in the benthic community assemblage were a result of natural seasonal changes and unlikely to be a reflection of impacts due to acid sulfate soils.
- Metal concentrations in soil porewaters (the most bioavailable fraction) may still be present at concentrations that could impact the health of aquatic organisms.
- Lake water is neutralising the top layer of soil. As the top layer of soil (top 2 cm) is where the majority of taxa were found, this neutralising effect could be important in maintaining the invertebrate community of the Lower Lakes post a drought related acidification event.

Aim

Investigate the extent and significance of ecotoxicological effects resulting from acid sulfate soil acidification during the Millennium Drought in lake soils that are transitioning through recovery.

Approach

The SQT approach used in this investigation provided a method for the integrated assessment of ecosystem health. By integrating multiple lines of evidence, the SQT approach is able to generate 'weight of evidence' and separate natural variability from variability due to the toxic effects of contaminants. Three lines of evidence were used, namely:

- Soil chemistry;
- Soil ecotoxicity; and
- Benthic community assemblage.

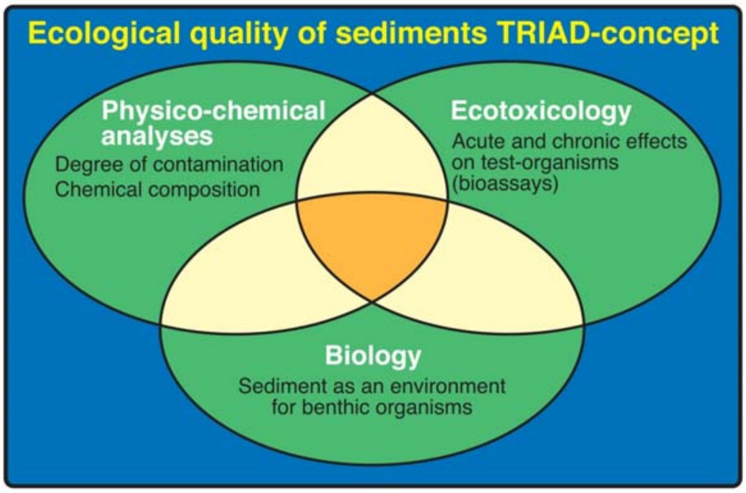


Figure 41. Sediment Quality Triad approach based on multiple lines of evidence.

The combination of potential cause (i.e. chemistry and ecotoxicity) and effect (e.g. benthic community) makes the SQT approach a powerful tool to investigate the potential impacts of drought induced acidification of acid sulfate soils.

Seventeen study sites located in Lakes Alexandrina and Albert and the lower reaches of the Currency Creek and Finniss River were selected for assessment. Study sites coincided with those used by CSIRO to monitor the post-drought recovery of acid sulfate soils (Section 2.5.1). Required samples were collected from the study sites in March and November 2013, three years after the break of the Millennium Drought and refilling of the Lower Lakes. The approach used for each line of inquiry is summarised below.

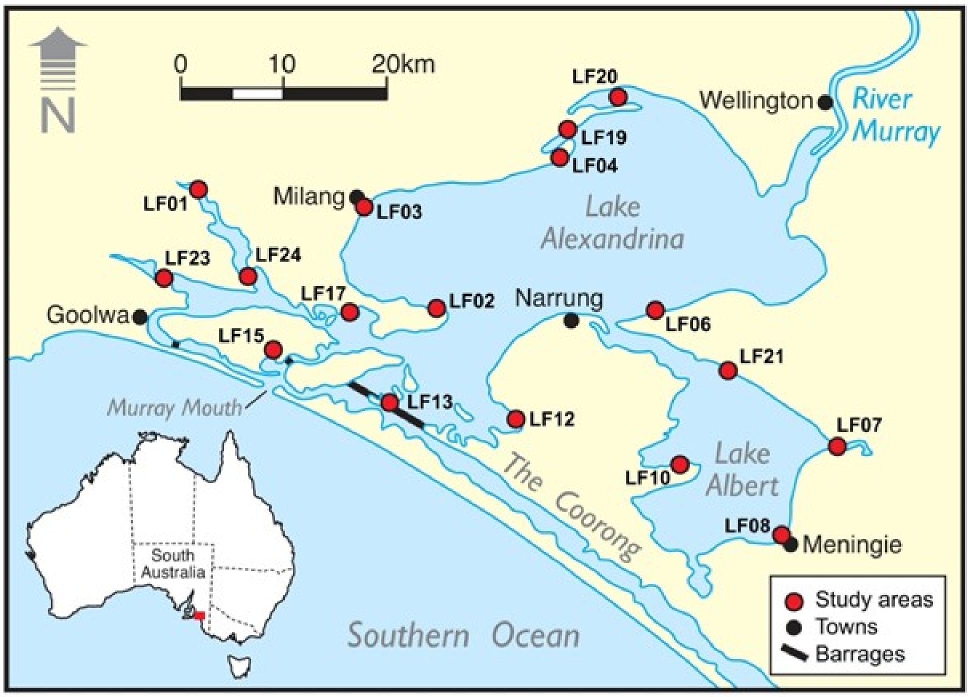


Figure 42. Lower Lakes' soil sampling locations for March and November 2013. LF01- Wallys Landing; LF02- Point Sturt North; LF03- Milang; LF04- Tolderol; LF06- Poltalloch; LF07- Waltowa; LF08- Meningie; LF10- Campbell Park; LF12- Loveday Bay; LF13- Tauwitchere; LF15- Boggy Creek; LF17- Point Sturt South; LF19- Dog Lake; LF20- Boggy Lake; LF21- Windmill Site; LF23- Lower Currency; LF24- Lower Finniss.

Chemistry

Soil chemistry was assessed to determine potential exposure of benthic organisms to contaminants. Porewater was collected from soil samples (0 to 2 cm depth) by centrifugation and analysed for alkalinity or acidity, total organic carbon, major cations and anions and trace elements. Metal concentrations were also assessed following a weak acid extraction and strong acid digestion. Metals in soil porewater are the most bioavailable. Metals released following weak acid extraction are readily mobilised and therefore potentially bioavailable. Metals released following strong acid extraction are not generally bioavailable and represent the total pool of elements in the soil. Parameters were assessed against ANZECC guideline trigger values. The hazard quotient (HQ) from individual parameters was calculated by dividing the observed concentration by its corresponding guideline value. Thus, a HQ greater than 1 indicated the guideline trigger value had been exceeded, and concentrations were a potential hazard. Cumulative HQs were calculated from the sum of individual parameter HQ divided by the total number of parameters. Again, a cumulative HQ greater than 1 indicated a potential hazard.

Ecotoxicity

Laboratory ecotoxicity tests were used to determine the response of benthic fauna to available contaminants. Acute toxicity was assessed by determining survival rates of midge larvae (*Chironomus tepperi*) after 5 to 12 days of exposure to acid sulfate soils samples in the laboratory. The bioassay test involved combining 10 midge larvae, 140 g of field collected soil sample and 200 ml of water in a beaker. For a complete description of the bioassay test methods refer to Table 2 in the full report. Sub-lethal chronic effects such as growth inhibition (midge larvae length), emergence success (% larvae emerged as adult) skewed sex ratio (sex of emerged adult) were also investigated using the same bioassay test method.

Benthic community

The South Australian EPA investigated the biological component of the larger SQT study. The types, abundance and distribution of invertebrate species living in the lake bed soils were investigated to assess potential impacts of acid sulfate soils on the invertebrate community. Surface soil samples and sweep net samples were collected from study sites and analysed for macroinvertebrates and microcrustacea. Individuals found were counted and identified to the lowest taxonomic level possible. Resemblance matrices and hierarchical cluster analyses were produced from the biological data to determine which samples had high similarities in benthic community composition and grouped together. The influence of physical and chemical variables of interest (e.g. pH, soil texture and location) on benthic community structure was also explored. The abundance of taxa considered tolerant to acidity [acid tolerant taxa (ATT)] and those considered sensitive to acidity [acid sensitive taxa (AST)] identified from each site were recorded for use in the SQT approach.

SQT Methodology

The possible scenarios resulting from the SQT approach are outlined in Table 4. The chemical, ecotoxicological and benthic community variables used in the SQT approach were categorised and assigned a value between 0 and 3 to indicate the likelihood of potential acid sulfate soil impacts (Table 5). For a single variable, a score of 0 indicated a low likelihood of potential impacts for that variable, and a score of 3 indicated a high likelihood of potential impacts. A total score for each line of evidence (chemistry, toxicity and biota) was calculated from the sum of the scores for each individual variable. To account for the unequal number of variables that were used in each line of evidence (chemistry, toxicity and biota) standardised scores were calculated for each site.

Table 4. Possible scenarios from SQT approach using three lines of evidence.

Situation	***Chemistry***	***Toxicity***	***Community***	***Biomagnification***	***Conclusion*** ***(Note + different to reference, - equivalent to reference)***
1	+	+	+	+	Strong evidence for sediment contamination
2	-	-	-	-	Strong evidence for no contamination
3	+	-	-	-	Contaminants unavailable
4	-	+	-	-	Unmeasured chemicals or conditions exist with potential to cause contamination and resistance may have developed
5	-	-	+	-	Alteration not due to chemical contamination
6	+	+	-	-	Toxic chemicals stressing system but resistance has developed
7	-	+	+	-	Unmeasured toxic chemicals causing contamination
8	+	-	+	-	Chemicals are not bioavailable or alteration is not due to toxic chemicals

Table 5. Table of variables used in the assessment and the scores given to each category.

	SCORE			
	0	**1**	**2**	**3**
Chemistry				
Sediment metals	No metals exceed trigger values[a]	ND	ND	ND
Porewater analytes	No analytes exceed trigger values[b]	1 analyte exceed trigger values[b]	2 or 3 analytes exceed trigger value[b]	ND
Sediment pH (pH units)	>6.5	6.0-6.5	ND	ND
TAA (mol H^+/tonne)	0	1 to 2	3 to 5	>5
AVS (mol H^+/tonne DW)[c]	<18	18-62	>62	ND
Toxicity to midge larvae				
% survival	>80	60 to79	45 to 59	<45
% growth inhibition	<10	10 to 24	25 to 34	>35
% emergence	>80	60 to 79	45 to 59	<45
Sex ratio	No skewed ratio	ND	Skewed ratio	ND
Biota				
ATT/AST	No ATT	AST>ATT	ATT>AST	ND

ND = Not determined as scores not required for data collected. ATT = abundance of acid tolerant taxa in benthic community, AST = abundance of acid tolerant taxa in benthic community

[a] = trigger values provided in the ANZECC/ARMCANZ (2000) Sediment Quality Guidelines

[b] = trigger values set for the protection of 95% of species in freshwater systems (ANZECC/ARMCANZ 2000), which were adjusted for hardness of Lake Alexandrina and Lake Albert.

[c] =AVS only measured in November survey

Findings

Chemistry

The surface soil pH ranged from approximately 6 to 8, with most sites found to be circumneutral and within the pH range considered not to cause significant impacts on ecosystems. However, surface soil layers were found to be acidic (6.0 < pH < 6.5) at seven sites in March and five sites in November. Three sites (Milang, Poltalloch and Dog Lake) had a pH of less than 6.5 in both March and November (Figure 43).

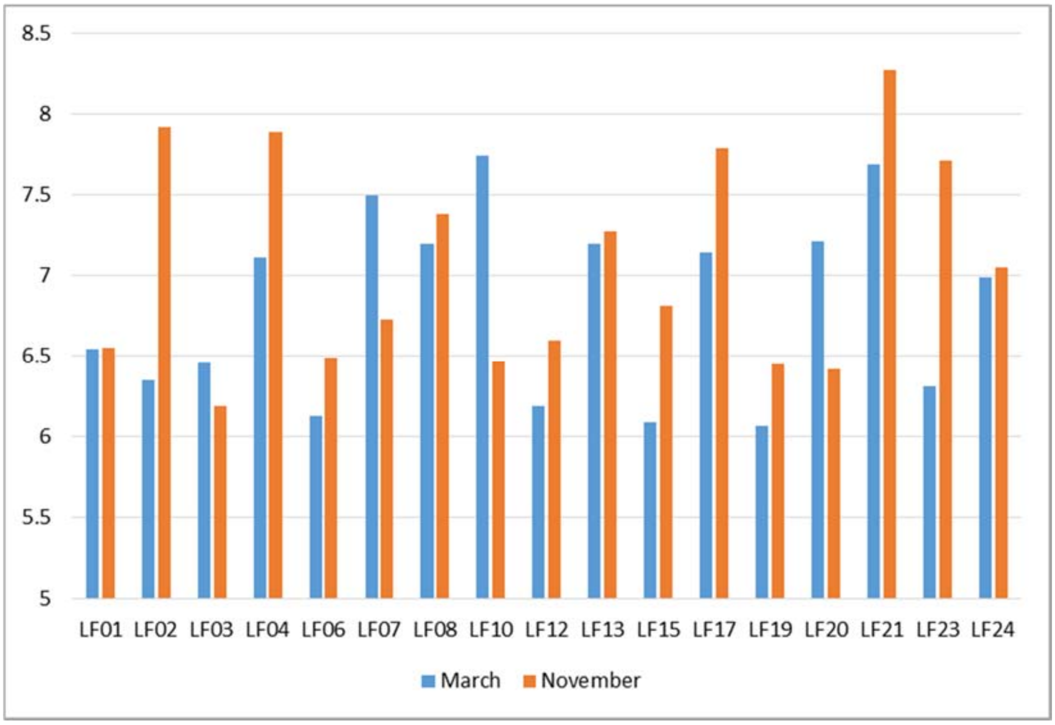


Figure 43. Surface soil pH values recorded at each of the 17 sampling sites in March and November 2013. See Figure 42 for site names.

The porewater concentrations for aluminium and copper were above ANZECC guideline trigger values at most sites sampled in March 2013. Arsenic concentrations were high at Dog Lake, Campbell Park and Boggy Lake sites in March 2013 and at Tauwitchere site in November 2013. The porewater concentrations of other metals such as manganese, zinc, cobalt and chromium were reported to be above guideline levels at some sites. Based on the HQ calculations, Wally's Landing and Point Sturt South were the most contaminated sites in March 2013, with cumulative HQ greater than 10. Dog Lake, Boggy Lake, Boggy Creek and Lower Finniss were considered moderately contaminated. In November 2013 Wally’s Landing was the most contaminated site (HQ 11.92) and Point Sturt South was moderately contaminated (HQ 7.77). Element concentrations in whole soils and 0.1M HCl extracts were generally low and were below concentrations considered to impact environmental health.

Ecotoxicity

No acute toxic effects were observed in either sampling occasion, with ≥90% survival of midge larvae exposed to soils. However, sub-lethal effects were seen in the form of growth inhibition, emergence success and skewed sex ratio of the adults (Figure 44 and Figure 45).

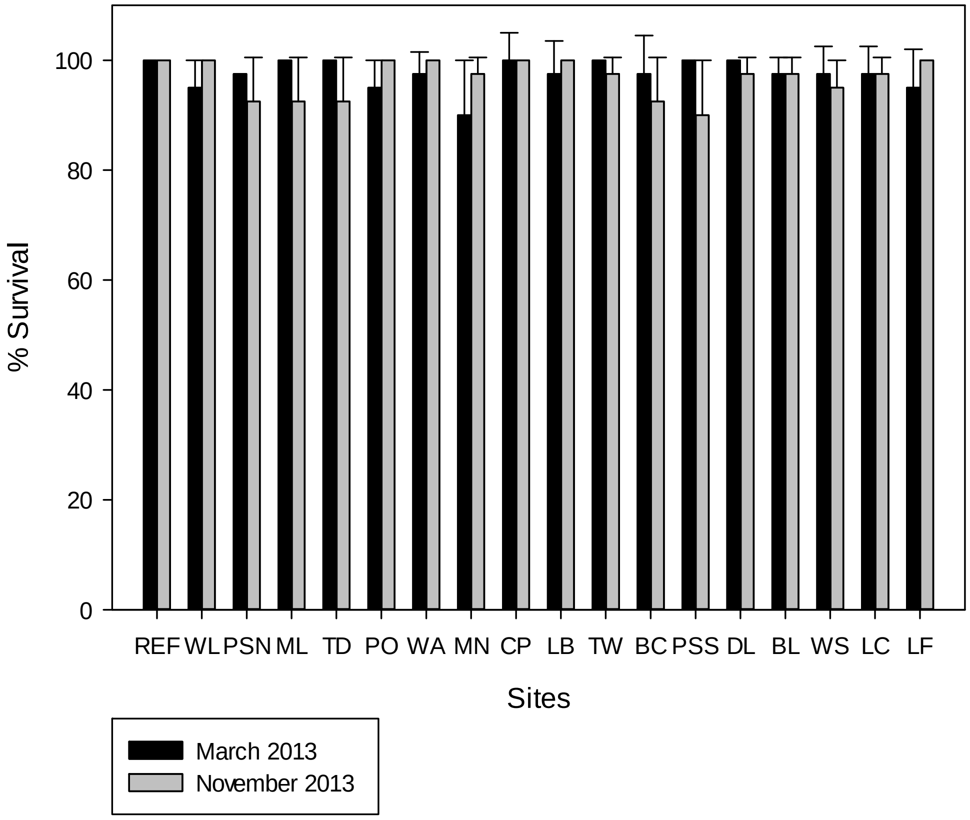


Figure 44. Survival of midge larvae exposed to soils collected from 17 sites in March and November 2013. Error bars represent one standard deviation. REF- Reference site; WL- Wallys Landing; PSN- Point Sturt North; ML- Milang; TD- Tolderol; PO- Poltalloch; WA- Waltowa; MN- Meningie; CP- Campbell Park; LB- Loveday Bay; TW- Tauwitchere; BC- Boggy Creek; PSS- Point Sturt South; DL- Dog Lake; BL- Boggy Lake; WS- Windmill Site; LC- Lower Currency; LF- Lower Finniss.

In 2013, inhibition to midge growth was evident at five sites (Point Sturt North, Milang, Tolderol, Poltalloch and Lower Finniss) in March but no sites had statistically significant differences from the reference site in November. Emergence success was significantly reduced at three sites (Meningie, Lower Finniss, and Windmill Site) in March and five sites (Wally's Landing, Boggy Lake, Meningie, Campbell Park and Point Sturt South) in November. A skewed sex ratio (<40% or >60% of one sex) occurred at only two sites (Loveday Bay and Lower Finniss) in March but six sites (Waltowa, Campbell Park, Boggy Lake, Point Sturt South, Dog Lake and Lower Currency Creek) in November. All three chronic endpoints showed differences between the March and November sampling events, indicating that there were temporal differences in soil toxicity, potentially resulting from temporal changes in soil chemistry (i.e. pH and metals).

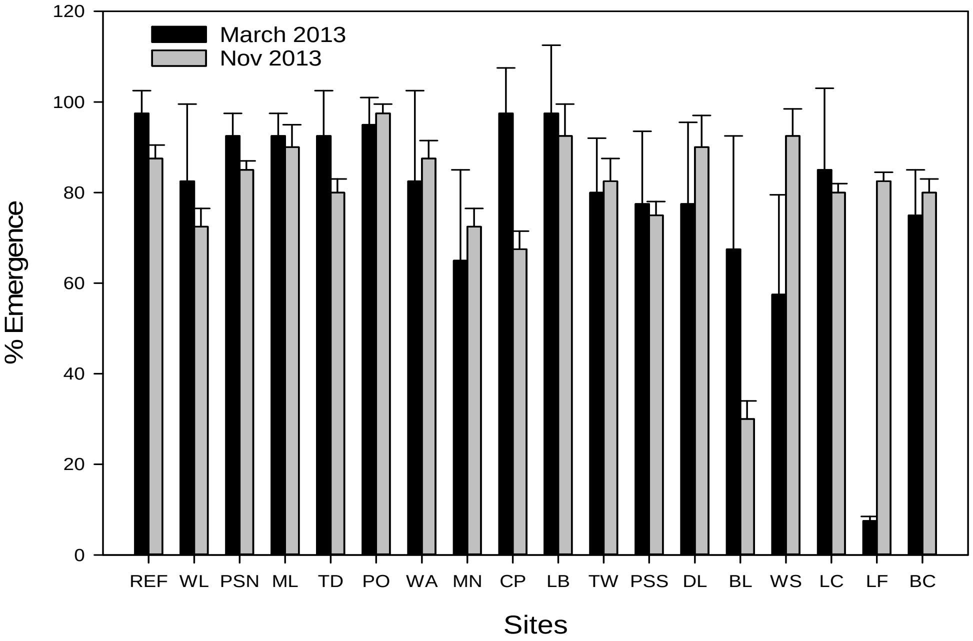


Figure 45. Emergence of midge larvae exposed to soils collected from 17 sites in March and November 2013. Error bars represent one standard deviation. REF-Reference site; WL- Wallys Landing; PSN- Point Sturt North; ML- Milang; TD- Tolderol; PO- Poltalloch; WA- Waltowa; MN- Meningie; CP- Campbell Park; LB- Loveday Bay; TW- Tauwitchere; BC- Boggy Creek; PSS- Point Sturt South; DL- Dog Lake; BL- Boggy Lake; WS- Windmill Site; LC- Lower Currency; LF- Lower Finniss.

Benthic community

Invertebrate richness (number of different species present) and abundance (total number of individuals) was highest in the top 2 cm of the soil profile. Invertebrate richness and abundance was significantly lower in deeper soil layers (i.e. 2 to 5 cm and 5 to 10 cm) and was consistent with previous studies in this region (Figure 46). Neither soil pH, nor texture (i.e. fine, medium or coarse) was observed to influence the species richness in these deeper soil layers. Hence, the reduced abundance of invertebrates in these deeper layers was likely a result of a less-favourable habitat and not a result of acid sulfate soil impacts.

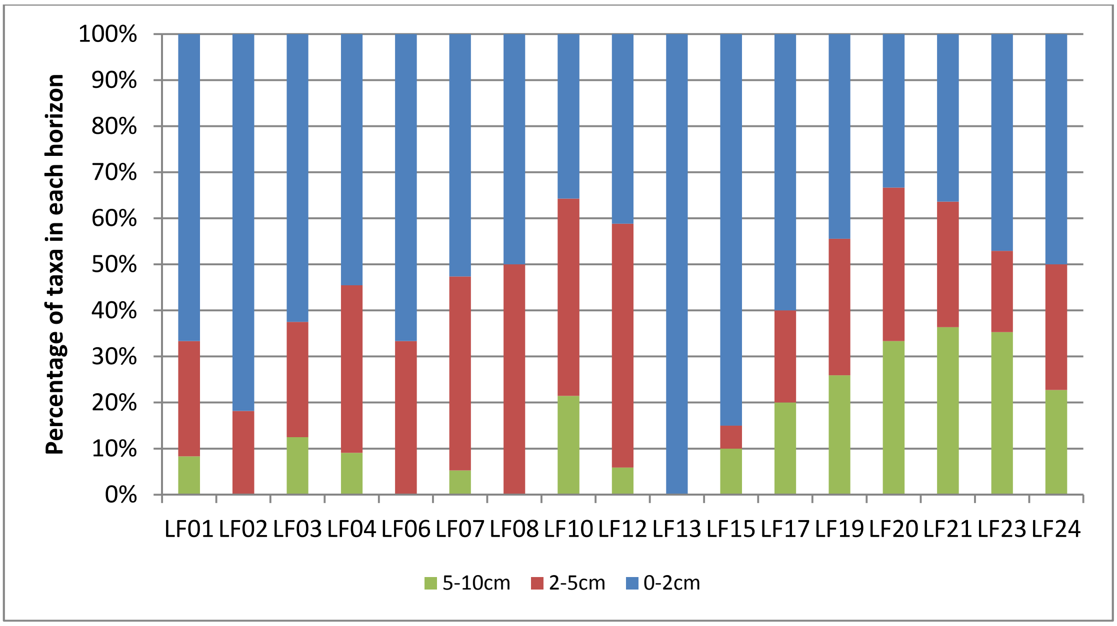


Figure 46. Vertical distribution of invertebrate abundance in the soil profile. See Figure 42 for site names.

Soil pH was observed to influence the species composition of benthic communities in March (Figure 47), but not in November. How soil pH changed between the two sampling occasions is unknown, however, the inconsistent relationship between invertebrate community and pH was probably due to the lack of prolonged acidic conditions (i.e. less than 8 months between March and November). In other studies, marked changes in community structure, where communities shifted from one dominated by acid-sensitive taxa to one dominated by acid-tolerant taxa, has been observed as a result of low pH. If acidic conditions in the Lower Lakes were to worsen it is likely that a shift towards a community dominated by acid tolerant taxa would be observed. This trend, along with data for the abundance of acid tolerant and acid sensitive taxa collected from the soil samples, was used in the SQT approach below to assess the impact of acidity on the invertebrate community. In this study, the shift in the invertebrate community structure seen between March and November was likely a result of seasonal differences and was attributed to acid sulfate soil impacts. For example, more invertebrates are pushed downstream when winter rainfall causes higher flows. This often results in more diverse invertebrate communities occurring in spring, following the winter rains.

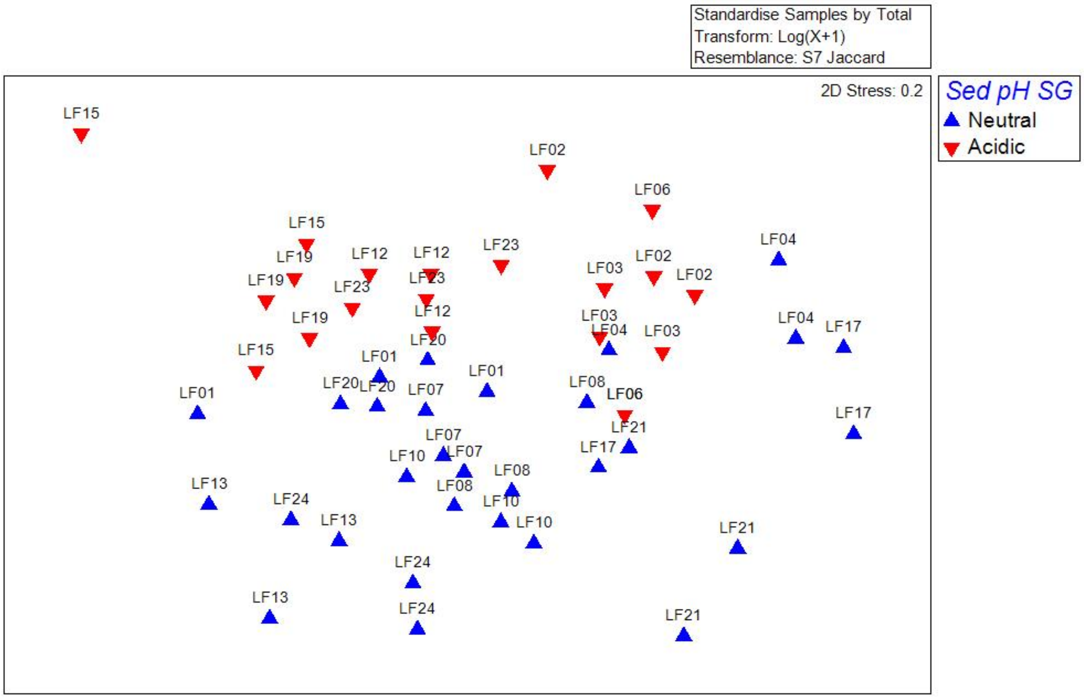


Figure 47. Resemblance matrices of March core samples showing influence of soil pH on invertebrate community similarity in March. Blue (neutral) = 6.5 ≤ pH < 9. Red (acidic) = pH < 6.5. See Figure 42 for site names.

Many of the taxa that were 'missing' in a survey of the Lower Lakes in 2011 were observed in this study. This included taxa with calcium carbonate exoskeletons. Previously, concerns were raised about these species due to their sensitivity to low pH (Section 2.6.1).

Soil texture had considerable influence on the benthic invertebrate community. Fine textured soils typically had higher species and coarse textured soils had low species richness but high abundance (i.e. nematodes). Soil texture was found to be associated with the degree of sheltering in the different regions. Open water areas in Lake Alexandrina comprises mainly coarse textured soils whereas more sheltered areas, such as Finniss River and Currency Creek, consisted of fine substrate types such as silts and clays. As a result, significant differences in invertebrate communities were apparent between the three regions of the Finniss River, Lake Alexandrina and Lake Albert. Chemical as well as physical differences between the regions also influenced benthic community composition. For example, the invertebrate community in Lake Albert is likely to continue to be different from communities in other Lower Lakes regions due to higher salinity levels continuing to persist post-drought.

SQT Results

The SQT approach enabled researchers to compare the sites and categorise them according to the severity of the impact. The majority of sites had low scores and were considered to be either 'unimpacted' or 'possibly unimpacted' by the acidification of acid sulfate soils during the Millennium Drought. However, two locations, Boggy Creek (LF15) on Hindmarsh Island and Boggy Lake (LF20) on the north-western margin of Lake Alexandrina received higher scores of 3.83 and 4.45 over both March and November sampling occasions, respectively (Figure 48). These sites were considered 'possibly impacted', suggesting recovery in these areas had not occurred three years after the soils were rewet. The SQT approach was found to be a useful tool capable of detecting acid sulfate soil impacts, despite some of the legacy effects from acidification being only minor at the time of the study.

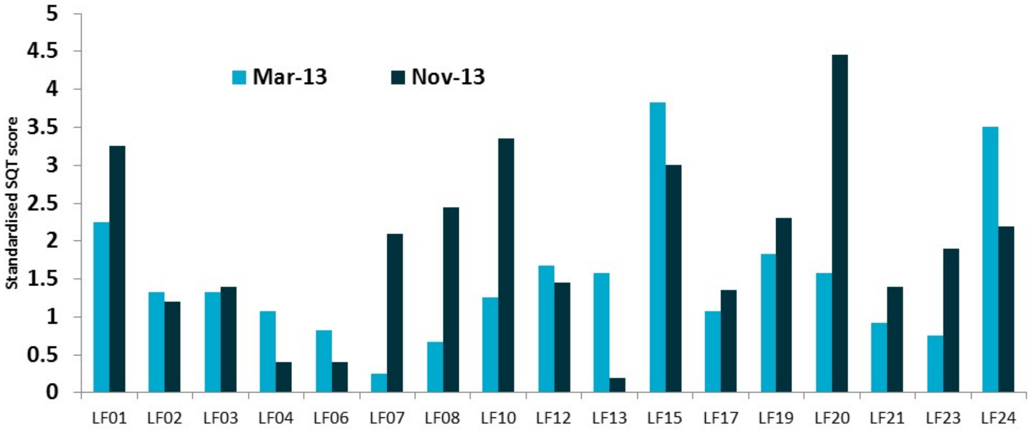


Figure 48. SQT results for March and November 2013. See Figure 42 for site names.

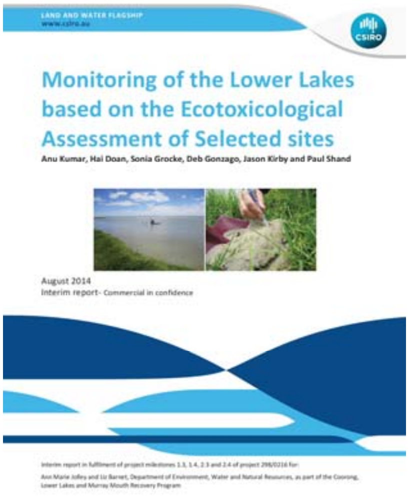
Research limitations and future work

- Surface soils at most sites had recovered to circumneutral pH Lakes three years after rewetting. However, deeper soil layer may still be acidic. The impact of contaminant fluxes from deeper acidified layers has not been quantified. If the SQT assessment was undertaken during or straight after the reflooding, toxicity effects relating to acid sulfate soil impacts may have been more easily observed.
- In the present study, a mixture of metals were above ANZECC guideline values in soil porewaters. With potential for multiple chemical exposure future research is required to assess the toxicity of mixtures of chemicals is toxicity additive or synergistic (Section 2.6.5).
- Although aluminium is identified as a significant hazard associated with acid sulfate soils currently, there is a shortage of information on the speciation, bioavailability and toxicity of aluminium in acid sulfate soil systems.
- It was recommended that development of rapid monitoring tools and modelling approaches is considered. These rapid monitoring tools would allow further ecotoxicological monitoring to be completed to better capture heterogeneity of the soils and seasonal changes (i.e. spatial and temporal variation).
- Subsequent sampling of the invertebrate community at selected sites after an additional 3 to 5 years (2016 to 2018) would provide additional information about the recovery of the Lower Lakes from drought conditions and provide more baseline information about the natural state of the system.

2.6.3 Ecotoxicological assessment of surface water, porewater and soil samples

Report details

Details for this component of the 'Lower Lakes Ecotoxicology Project' are provided in the interim report:



LAND AND WATER FLAGSHIP
www.csiro.au

Monitoring of the Lower Lakes based on the Ecotoxicological Assessment of Selected sites

Anu Kumar, Hai Doan, Sonia Grocke, Deb Gonzago, Jason Kirby and Paul Shand

August 2014
Interim report- Commercial in confidence

*Kumar, A., Doan, H., Grocke, S., Gonzago, D., Kirby, J. and Shand, P. (2014). Monitoring of the Lower Lakes based on the ecotoxicological assessment of selected sites. CSIRO Technical report: Land and Water Flagship.

*Commercial in confidence

Key research outcomes

- The ecotoxicological assessment of porewaters confirmed that contaminants generated at by acid sulfate soil acidification and still present in deeper soil layers four years after rewetting, are bioavailable and potentially severely toxic to aquatic organisms. If ecotoxicological assessments were undertaken during or straight after the water had returned, the surface soils may also have posed a similar risk to aquatic organisms.
- Surface water samples generally exhibited no acute or chronic toxicity to biota. However, the upward flux of contaminants from toxic sub-surface soil layers may pose a moderate to high level risk to the biota inhabiting the surface soil layers where acid sulfate soils are present.
- The cause of toxicity was attributed to a combination of stressors such as pH, salinity and high metal concentrations.

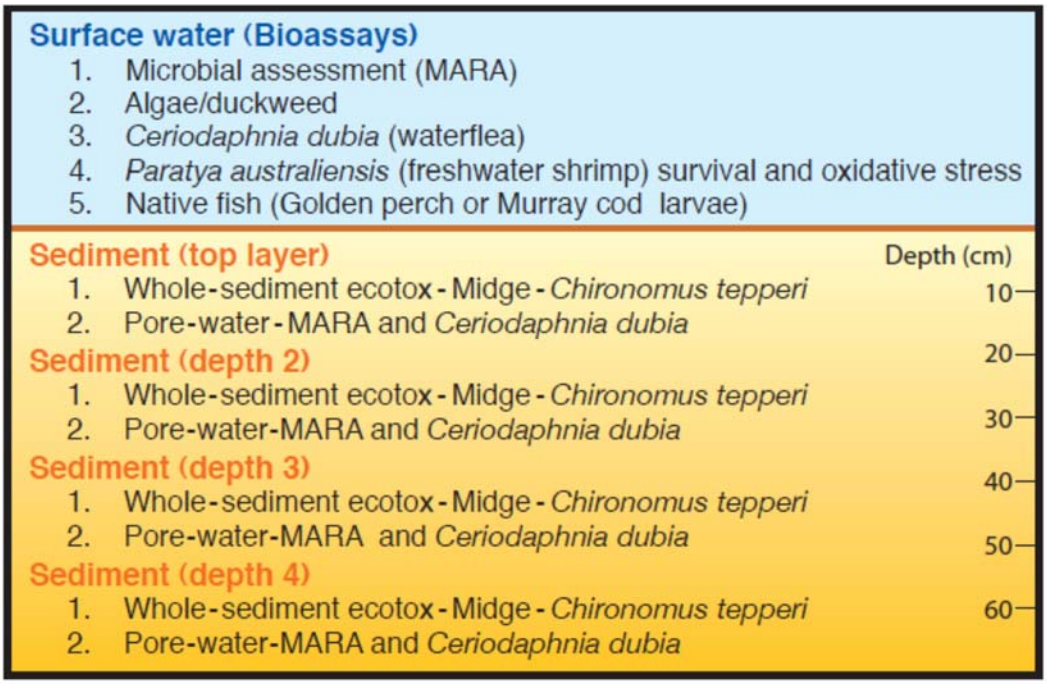
Aim

Undertake chemical and biological characterisation of surface water, porewater and soils at sites impacted by acid sulfate soils to determine the ecotoxicological risk posed to benthic organisms and the cause(s) for any observed toxicity.

Approach

Three study areas were selected: Point Sturt North (sampled in 2013 and 2014), Dog Lake (sampled in 2013), and Boggy Creek (sampled in 2014). Selected study area had been impacted by severe acidification during the Millennium Drought but following rewetting 3 to 4 years earlier were either recovering or recovered at the time sampling. Study areas were positioned nearby established sampling sites used in monitoring (Section 2.5.1) and other 'Lower Lakes Ecotoxicology Project' studies.

Surface water, porewater and bulk soil samples were collected from each study area. An overview of the suite of bioassays that were conducted is provided in Figure 49. Survival, growth, emergence, sex ratio and fertility were used as acute and chronic endpoints for the bioassays.



Surface water (Bioassays)

1. Microbial assessment (MARA)
2. Algae/duckweed
3. *Ceriodaphnia dubia* (waterflea)
4. *Paratya australiensis* (freshwater shrimp) survival and oxidative stress
5. Native fish (Golden perch or Murray cod larvae)

Sediment (top layer)

1. Whole-sediment ecotox - Midge - *Chironomus tepperi*
2. Pore-water - MARA and *Ceriodaphnia dubia*

Sediment (depth 2)

1. Whole-sediment ecotox - Midge - *Chironomus tepperi*
2. Pore-water-MARA and *Ceriodaphnia dubia*

Sediment (depth 3)

1. Whole-sediment ecotox - Midge - *Chironomus tepperi*
2. Pore-water-MARA and *Ceriodaphnia dubia*

Sediment (depth 4)

1. Whole-sediment ecotox - Midge - *Chironomus tepperi*
2. Pore-water-MARA and *Ceriodaphnia dubia*

Figure 49. Overview of ecotoxicological assessment.

In addition to the bioassays a number of analyses were conducted to characterise the chemical properties of surface water, porewater and bulk soil samples. This included measurements of pH, salinity, dissolved oxygen, alkalinity or acidity, total organic carbon, major cations and anions and trace metals.

Findings

Surface water

Surface water samples generally exhibited no acute or chronic toxicity to biota (no toxicity) apart from in undiluted surface water samples from Boggy Creek and Point Sturt North, where chronic effects (low toxicity) were observed in shrimp and fish larvae bioassays (toxicity was removed completely at 50% dilution) (Table 6). Low toxicity and moderate-to-high toxicity was observed for duckweed (*Lemna* sp.) at Boggy Creek and Point Sturt North (2014), respectively (Table 6). In general, elemental concentrations in surface water samples were below those considered to be of concern to aquatic organisms.

Table 6. Summary of ecotoxicological assessment of surface water samples.

Dates sampled	**Sites**	**Microbial**	***Lemna***	**Water flea**	**Shrimp**	**Fish larvae**
March, 2013	**Dog Lake**	**LT**	**NT**	**LT**[b]	**NT**	**NT**
March, 2013	**Point Sturt North**	**LT**	**NT**	**LT**[b]	**NT**	**LT**[d]
February, 2014	**Point Sturt North**	**NT**	**T**[a]	**NT**	**LT**[c]	**LT**[d]
February, 2014	**Boggy Creek**	**NT**	**LT**[a]	**NT**	**LT**[c]	**LT**[d]
2013 and 2014	**Synthetic water**	**NT**	**NT**	**NT**	**NT**	**NT**

NT: No toxicity	**LT: Low toxicity**	**T: Moderate to high toxicity**	**HT- very high toxicity**
NOEC 100-90%	**NOEC 89-49%**	**NOEC 50-10%**	**NOEC <10%**

No Observed Effect Concentration (NOEC)

[a] frond numbers reduced during 7 d exposure.

[b] number of neonates over three broods reduced for 100% surface water sample.

[c] oxidative stress enzymes reduced in shrimp exposed to 100% surface water sample.

[d] fish larval growth reduced when exposed to 100% surface water sample.

Porewater

Porewater samples collected from surface soil layers generally showed no acute toxicity to water fleas, however chronic (sub-lethal) effects ranged between low and moderate-to-high toxicity (Table 7). Porewater samples collected from deeper in the soil profile were more toxic to biota than surface layers. Acute (lethal) effects on water fleas, indicating moderate-to-high toxicity or very high toxicity, were observed at all sampling areas and for most of the depths analysed. Many metal concentrations in porewaters from deeper soil layers were above their ANZECC guideline trigger values and it is likely that low pH, high salinity and combination of high metal concentrations contributed to the toxicity observed.

Table 7. Summary of ecotoxicological assessment of porewater samples collected from surface and sub-surface soil layers.

Water Samples	**Microbial**	**Water flea Acute**	**Water flea Chronic**
Point Sturt North (March 2013)			
0-22 cm	**LT**	**LT**	**T**
22-37 cm	**LT**	**HT**	**HT**
37-55 cm	**LT**	**HT**	**HT**
55-78 cm	**LT**	**T**	**HT**
Point Sturt North (February 2014)			
0-12 cm	**NT**	**NT**	**LT**
12-25 cm	**LT**	**T**	**HT**
25-42 cm	**T**	**HT**	**HT**
42-67 cm	**T**	**NT**	**LT**
Boggy Creek (February 2014)			
0-3 cm	**T**	**NT**	**LT**
3-13 cm	**T**	**T**	**HT**
13-27 cm	**LT**	**T**	**HT**
27-47 cm	**T**	**T**	**HT**
Dog Lake (March 2013)			
0-5cm	**LT**	**NT**	**LT**
5-30cm	**LT**	**HT**	**HT**
30-42cm	**LT**	**HT**	**HT**
River water			
na	**NT**	**NT**	**NT**
NT: No toxicity **NOEC >100-90%**	**LT: Low toxicity** **NOEC 89-49%**	**T: Moderate to high toxicity** **NOEC 50-10%**	**HT- very high toxicity** **NOEC <10%**

No Observed Effect Concentration (NOEC)

Soil

Soils generally comprised sub-aqueous (underwater) hypersulfidic materials with high net acidities (100 to 613 moles H+/tonne). Therefore, these soils are likely to re-acidify if disturbed in the future. Soil layers below approximately 40 cm had negative net acidities and likely remained below the water table during the Millennium Drought.

At Boggy Creek and Point Sturt North midge larvae survival was not affected. Both the growth and emergence of midge larvae were impacted when exposed to surface and mid-profile soil layers (approximately 0 to 40 cm) but not in the lowest soil layers (approximately below 40 cm). Skewed sex ratios of midge larvae exposed to the surface and mid-profile soil layers were also observed at Boggy Creek.

Research limitations and future work

- Although surface soil layers were generally found to have no or low toxicity to biota, the sub-surface sample was observed have very high toxicity. The upward flux of contaminants from these toxic sub-surface layers may pose a moderate to high level risk to the biota inhabiting the surface soil layer in the future.
- Recommendations from this study were consistent with those given in the SQT component of the 'Lower Lakes Ecotoxicology Project' (Section 2.6.2).

2.6.4 In situ assessment of bioavailability of contaminants released from acid sulfate soils

Report details

Details for this component of the 'Lower Lakes Ecotoxicology Project' are provided in the ecotoxicological synthesis report 'Ecotoxicological assessment of surface sediments in the Lower Lakes – an integrated approach' (a separate report for this component of the Lower Lakes Ecotoxicology Project is not available).

Key research outcomes

- An upward flux of contaminants from sub-surface acid sulfate soil layers were bioavailable to benthic organisms and resulted in adverse effects (growth and hatching success) in the exposed organisms.
- The hatching success of snail egg masses was significantly reduced following a four-week in situ deployment of adult snails at all of the acid sulfate soil impacted sites.
- Shell thinning in mussels exposed to acid sulfate soil impacted sites for an 8 week period was observed at all sites.
- Metals were bioavailable and accumulated in the yabby and mussel tissues during the 8 week deployment period.

Aim

To assess the bioavailability and ecotoxicological impacts of contaminants mobilised from deeper sub-surface acid sulfate soil layers using in situ techniques.

Approach

Yabbies, mussels and adult snails were deployed in cages at four acid sulfate soil impacted sites around the Lower lakes (e.g. Figure 50). Namely, Dog Lake, Point Sturt North, Poltalloch and Wally's Landing (Figure 42). For adult snails, egg masses were collected weekly over a period of 4 weeks. The egg masses were then reared in the laboratory using surface water collected from the respective site. After 10 days length and hatching success of the snail larvae were determined and compared against laboratory controls. For yabby and mussel tests, samples were collected from the deployed cages after a period of 4 weeks and 8 weeks. Collected samples were assessed for survival, mussel shell thickness (Figure 50), oxidative stress in mussel gills and uptake of metals into yabby and mussel tissue.

Figure 50. In situ cages (left), the deployment location of the cages at Point Sturt North site (centre) and mussel shell thickness tests (red stars denote the location of the thickness measurements).

Findings

Snail larvae

Over the four week in situ deployment of the adult snails at acid sulfate soil impacted sites, the hatching success of snail egg masses was significantly reduced (Figure 51). After 1 week of deployment, the adult snails deployed at Pt Sturt North and Poltalloch sites exhibited significantly lower hatching success than in comparison to the adult snails deployed at Dog Lake and Wally's Landing sites. The snail hatching success was reduced by 75-85% at Pt Sturt North, Dog Lake and Wally's Landing and 95% at Poltalloch over 4 week deployment.

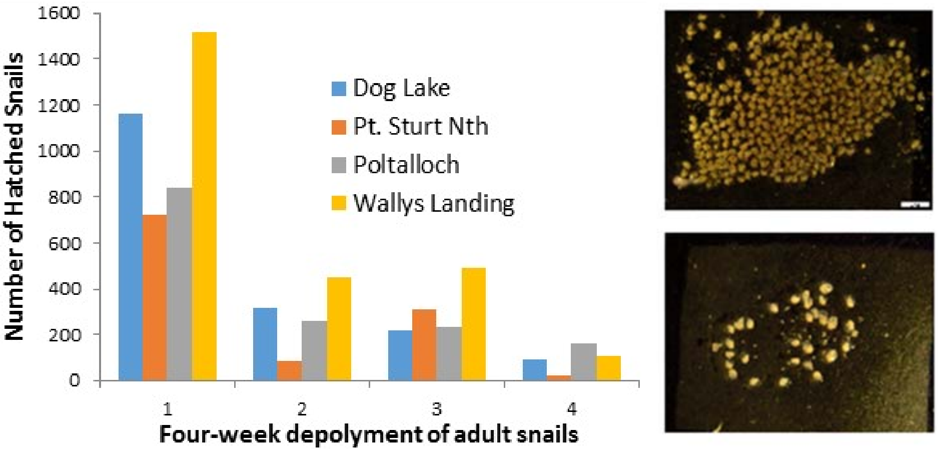


Figure 51. Hatching of snail egg masses under laboratory conditions

The average length of hatched snail larvae, following exposure of adults to acid sulfate soil impacted sites, was shorter than the control (raised under laboratory conditions), indicating the presence of potential sub-lethal chronic effects (Figure 52). As previous tests, summarised in Section 2.6.3, indicated that surficial soil layers and surface waters had no or low toxicity, it was likely that these chronic effects (snail larvae hatching success and growth) were a result of exposure to bioavailable contaminants that were transported upwards from the severely toxic sub surface layers during the 4 week in situ deployment period.

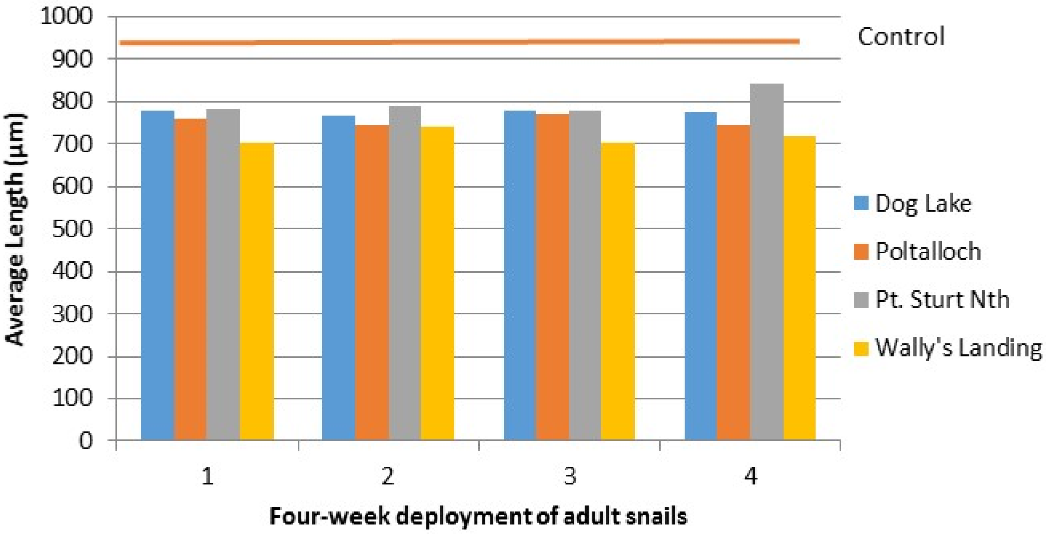


Figure 52. Average length of hatched snail larvae following the exposure of adults to acid sulfate soil impacted sites versus control samples raised under laboratory conditions.

Mussel shell thickness

A notable decrease of shell thickness in mussels deployed above acid sulfate soil impacted soils, compared to control samples, was observed at all sites (Figure 53). This was consistent with the results from the preliminary study summarised in Section 2.6.1, and indicates that acid fluxes from persisting acidity in sub-surface layers may be impacting on benthic biota with carbonate exoskeletons.

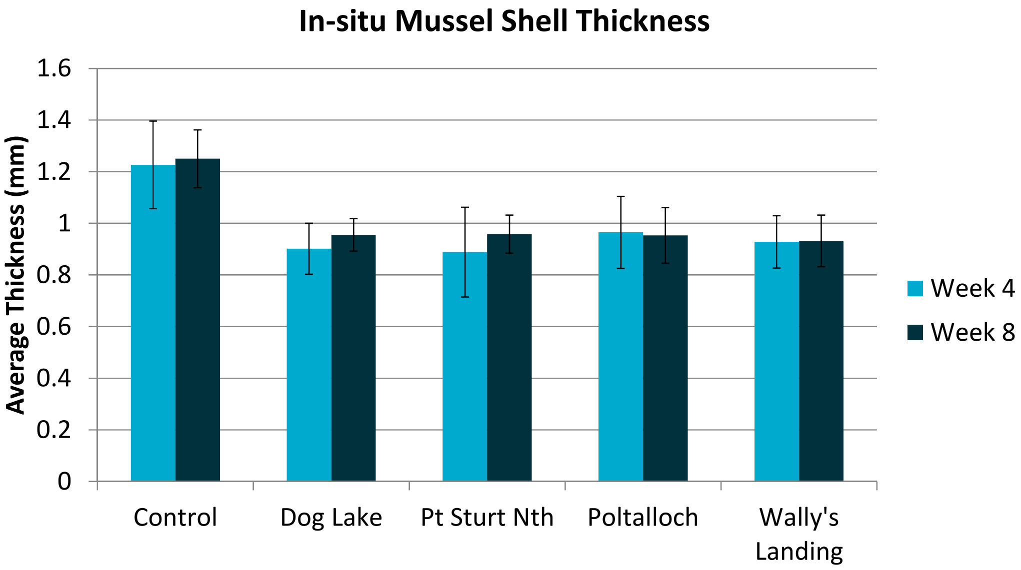


Figure 53. Average mussel shell thickness after 4 and 8 weeks deployment at Dog Lake, Point Sturt North, Poltalloch and Wally’s Landing verses laboratory control samples.

There was no significant mortality of mussels and snails recorded during their deployment at the 4 acid sulfate soil impacted sites. Over the 8 week deployment, accumulation of metals was higher in yabby tissue than in the mussel tissue samples (Figure 54 Figure 55). Mussels may have modified their behaviour (e.g. closed or reduced the rate of opening) following exposure to acid sulfate soil impacted sites to prevent or decrease the uptake of metal laden acidic waters and potential adverse effects.

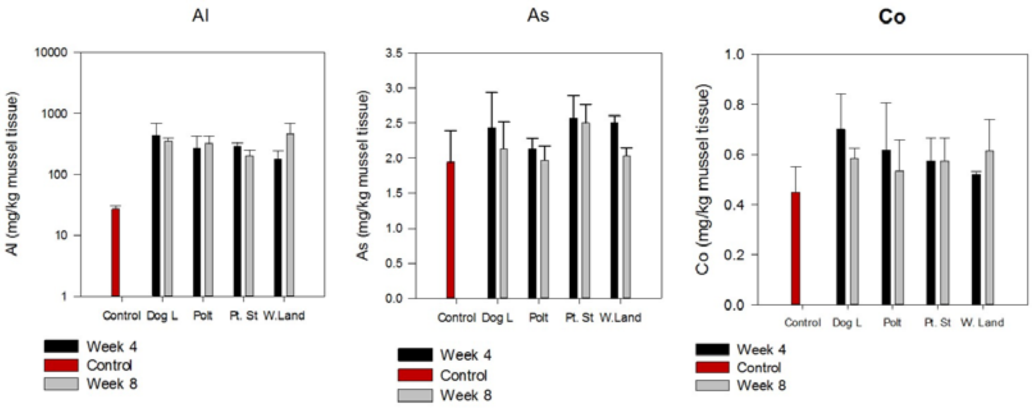


Figure 54. Concentration of aluminium (left), arsenic (middle) and cobalt (right) in mussel tissue following exposure to acid sulfate soil impacted sites versus laboratory control.

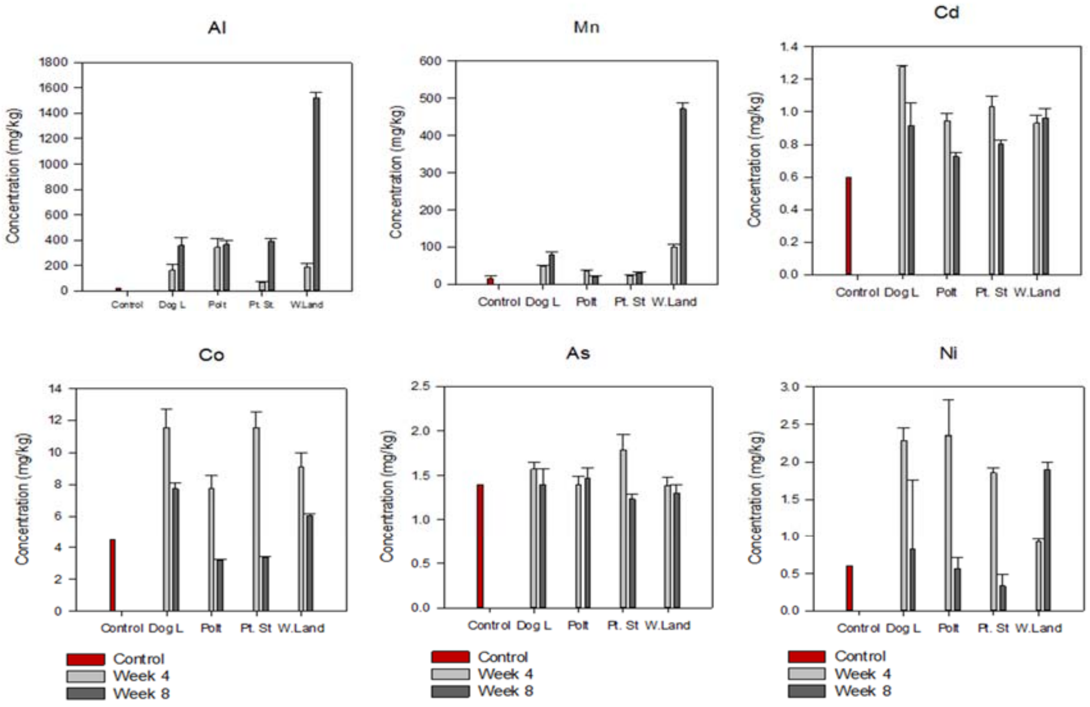


Figure 55. Concentration of aluminium, manganese, cadmium, cobalt, arsenic, nickel, in yabby tissue following exposure to acid sulfate soil impacted sites versus laboratory control.

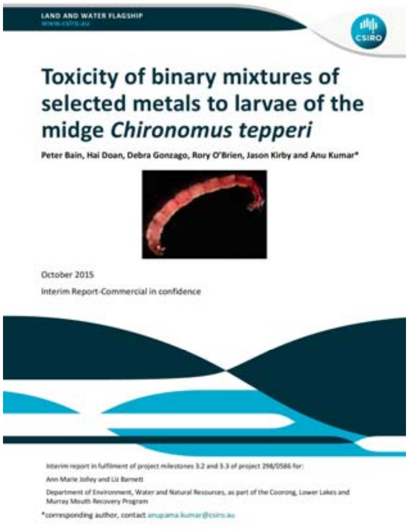
Research limitations and future work

- Due to difficulties in selecting a field site un-impacted from acid sulfate soil oxidation and acidification laboratory controls were used to determine the presence of adverse effects to benthic biota. The use of a suitable field control site is preferable to a laboratory control. It was recommended that a field control be used in future work, assuming a suitable site can be found.
- Recommendations from this study were consistent with those given in the SQT component of the 'Lower Lakes Ecotoxicology Project' (Section 2.6.2).
- It is recommended that future in situ investigations assesses the influence of liming (see Section 1.4.1) on the toxicity of discharged waters and precipitates.

2.6.5 Toxicity of selected metals and their binary mixtures to midge larvae, *Chironomus tepperi* and juvenile freshwater snail, *Physella acuta*

Report details

Details for this component of the 'Lower Lakes Ecotoxicology Project' are provided in a series of two interim reports:



LAND AND WATER FLAGSHIP
www.csiro.au

CSIRO

Toxicity of binary mixtures of selected metals to larvae of the midge *Chironomus tepperi*

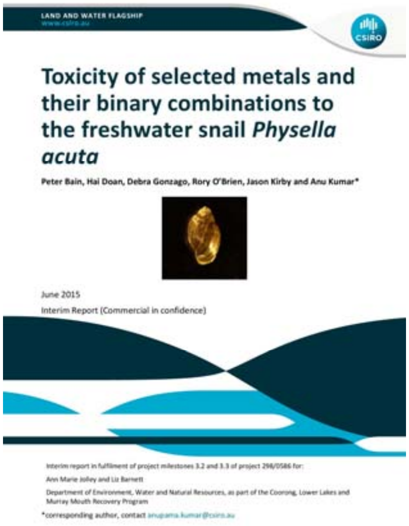
Peter Bain, Hai Doan, Debra Gonzago, Rory O'Brien, Jason Kirby and Anu Kumar*

October 2015
Interim Report-Commercial in confidence

Interim report in fulfilment of project milestones 3.2 and 3.3 of project 298/0586 for:
Ann Marie Jolley and Liz Barnett
Department of Environment, Water and Natural Resources, as part of the Coorong, Lower Lakes and Murray Mouth Recovery Program
*corresponding author, contact anupama.kumar@csiro.au

*Bain, P.A., Doan, H., Gonzago, D., O'Brien, R., Kirby, J. and Kumar, A. (2015). Toxicity of binary mixtures of selected metals to larvae of the midge *Chironomus tepperi*. CSIRO Technical report: Land and Water Flagship.

*Commercial in confidence



LAND AND WATER FLAGSHIP
www.csiro.au

CSIRO

Toxicity of selected metals and their binary combinations to the freshwater snail *Physella acuta*

Peter Bain, Hai Doan, Debra Gonzago, Rory O'Brien, Jason Kirby and Anu Kumar*

June 2015
Interim Report (Commercial in confidence)

Interim report in fulfilment of project milestones 3.2 and 3.3 of project 298/0586 for:
Ann Marie Jolley and Liz Barnett
Department of Environment, Water and Natural Resources, as part of the Coorong, Lower Lakes and Murray Mouth Recovery Program
*corresponding author, contact anupama.kumar@csiro.au

*Bain, P.A., Doan, H., Gonzago, D., O'Brien, R., Kirby, J. and Kumar. A. (2015). Toxicity of selected metals and their binary combinations to freshwater snail *Physella acuta*. CSIRO Technical report: Land and Water Flagship.

*Commercial in confidence

Key research outcomes

- Binary metal mixtures dominantly exhibited less-than-additive (antagonistic) toxicity to midge larvae.
- Binary metal mixtures dominantly exhibited greater-than-additive (synergistic) toxicity to freshwater snail.
- The significant differences in test species sensitivity highlighted the importance of using more than one organism for metal toxicity testing.
- Biological processes (i.e. species dependant) may be important factors driving the observed deviations from additive (predicted) metal toxicity.

Aim

Investigate the potential for ecosystem-level effects of high concentrations of dissolved metals and their binary combinations in aquatic environments associated with acid sulfate soils, using the juvenile freshwater snail (*Physella acuta*) and midge larvae (*Chironomus tepperi*) as test species.

Approach

Previous studies have showed that metals mobilised by low pH condition in acid sulfate soils often exceeded ANZECC guideline trigger values. As high metal concentration rarely occur in isolation, it is more appropriate to test toxicity effects of mixtures of dissolved metals rather than the toxicity of individual metals to better understand the likely response of aquatic organisms in situ

The combined toxicity effects of mixtures of dissolved metals are not easily predicted. In this study modelling approaches were used to predict the concentration-response curves for binary mixtures of metals based on the toxicity of each metal applied individually. The toxicity of binary combinations of metals were then determined by bioassay in the laboratory. By comparing laboratory results with predicted concentration-response curves it could be determined if the toxicity of the binary mixture is additive, greater than additive (i.e. synergistic), or less than additive (i.e. antagonistic) (Figure 56).

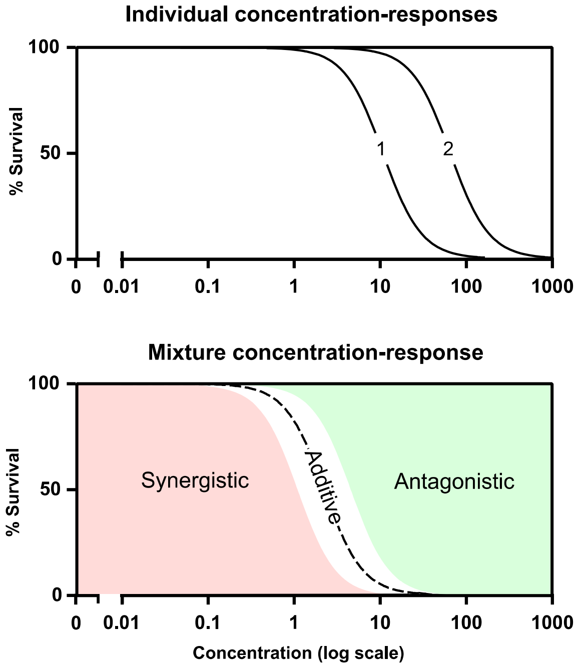


Figure 56. Conceptual diagram of mixture toxicity assessment. The lower plot indicates how the effects of a combination of the two individual toxicants can, comparatively, be additive, greater than additive (i.e. synergistic) or less than additive (antagonistic).

The toxicity of aluminium (Al), copper (Cu), cobalt (Co), manganese (Mn), nickel (Ni), zinc (Zn) and their binary combinations to the two test species was determined in water only exposures at pH 7 and pH 5 (Table 8). In exposure bioassays, test species were exposed to ranges of dissolved metal concentration based on EC50 values (EC50 represents the concentration where adverse effects are observed in 50% of the test organisms) for a period of 48 hours. The midge larvae (*Chironomus tepperi*) is widely distributed in Australia and has been used extensively in aquatic toxicology studies and as bio-indicators of metal contamination in Australian environments. Although an introduced species, the freshwater snail (*Physella acuta*) is well established in the Coorong, Lower Lakes and Murray Mouth (CLLMM) region. Therefore, these two test species were considered suitable for ecotoxicological studies relevant to the region.

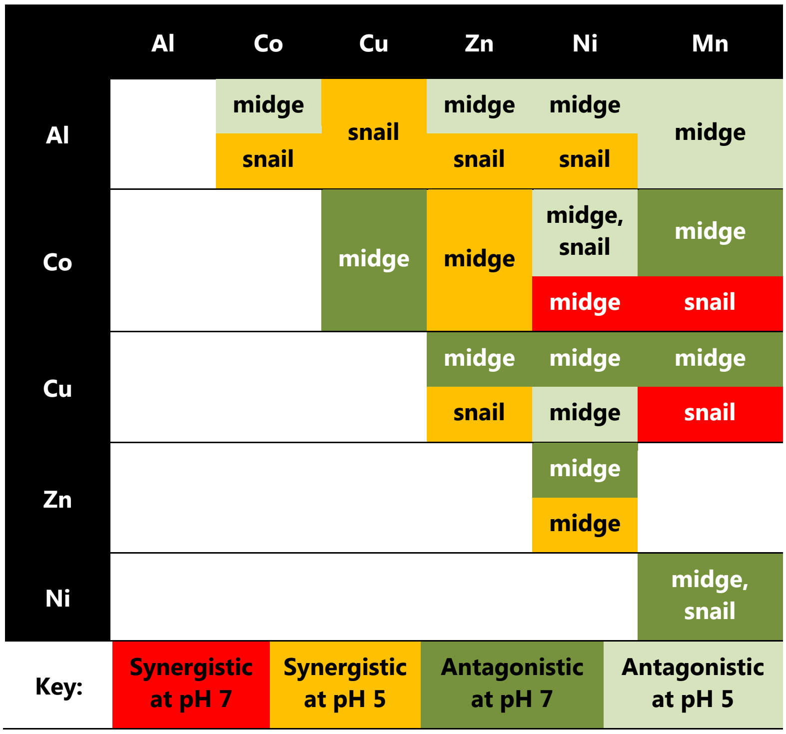
Table 8. Binary combinations of metals tested in this study.

	Al	Co	Cu	Zn	Ni	Mn
Al		Al + Co	Al + Cu	Al + Zn	Al + Ni	Al + Mn
Co			Co + Cu	Co + Zn	Co + Ni	Co + Mn
Cu				Cu + Zn	Cu + Ni	Cu + Mn
Zn					Zn + Ni	Zn + Mn
Ni						Ni + Mn

Findings

The majority of binary metal combination exhibited additive toxicity to the freshwater snail and midge larvae. However a number of significant deviations from the additive model were observed. These observations are summarised in Table 9. For the freshwater snail, metal mixtures that were less toxic than what was predicted for and additive mixture included nickel and cobalt (pH 5) and nickel and manganese (pH 7). Mixtures that had greater toxicity than the predicted additive effect of the individual metal included copper and manganese (pH 7) and copper and zinc (pH 5).

Table 9. Summary of mixture toxicity interactions after exposure to binary combinations of metals in juvenile freshwater snail and midge larvae.



	Al	**Co**	**Cu**	**Zn**	**Ni**	**Mn**
Al		▨ **midge** 🟨 **snail**	🟨 **snail**	▨ **midge** 🟨 **snail**	▨ **midge** 🟨 **snail**	▨ **midge**
Co			🟩 **midge**	🟨 **midge**	▨ **midge, snail** 🟥 **midge**	🟩 **midge** 🟥 **snail**
Cu				🟩 **midge** 🟨 **snail**	🟩 **midge** ▨ **midge**	🟩 **midge** 🟥 **snail**
Zn					🟩 **midge** 🟨 **midge**	
Ni						🟩 **midge, snail**

Key:	🟥 **Synergistic at pH 7**	🟨 **Synergistic at pH 5**	🟩 **Antagonistic at pH 7**	▨ **Antagonistic at pH 5**

Metal mixtures containing aluminium at pH 5 were found to exhibit synergistic toxicity to the freshwater snail and antagonistic toxicity to the midge larvae (Figure 57). The lower pH of tests containing aluminium (due to acidity contributions from dissolved aluminium) may have had a confounding influence on the observed toxicity and further study to confirm the synergistic effect is needed. For this reason, the toxicity of aluminium containing mixtures could not be investigated at neutral pH.

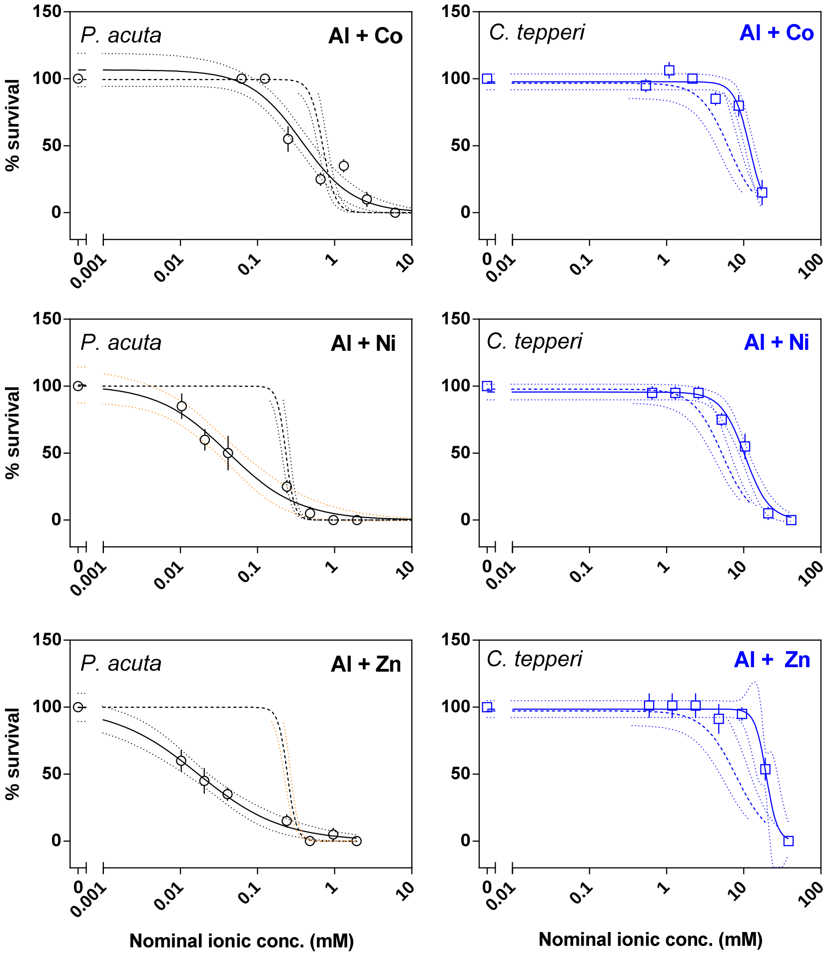


Figure 57. Aluminium containing mixtures (pH 5) exhibiting significant deviations from additive toxicity. The direction of deviation of experimental bioassay data (solid line) from the additive model (dashed line) was opposite for the freshwater snail (to the left = synergistic) and the midge larvae (to the right = antagonistic).

At pH 7 most metal combinations tested exhibited significantly less-than-additive (antagonistic) toxicity to midge larvae. The limited mixtures that exhibited synergistic interactions with midge larvae included: nickel and zinc (pH 5), zinc and cobalt (pH 5) and nickel cobalt (pH 7). In many cases marked differences in sensitivity between the snail and midge larvae were observed, indicating differences in species sensitivity to the individual metals. Midge larvae were almost always less sensitive than juvenile snails to the toxic effects of most of the metals tested, for example, zinc was approximately 200 times more toxic to snails at pH 7 and 400 times more toxic at pH 5 compared to midge larvae.

The observation of opposite toxic interactions (synergistic vs antagonistic) in snail and midge larvae suggests that the mechanisms underlying deviation from additive toxicity may be due to biological responses rather than physico-chemical factors. Mixtures that produced consistently antagonistic results between test species (e.g. nickel and manganese) may be attributable to changes in chemical speciation that result in reduced bioavailability.

Research limitations and future work

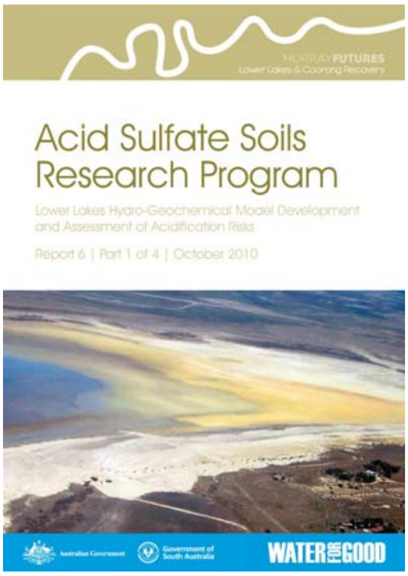
- Binary metal combinations identified as synergistic warrant further targeted research to clarify if deviations from additive behaviour are due to changes in bioavailability resulting from differing metal speciation or related to synergistic biological effects within the organism. This research would help inform ecotoxicological risk assessments for metal mixtures under varying pH conditions.
- Mixture toxicity under laboratory conditions may not accuracy represent toxicity in real world scenarios. For example, physico-chemical parameters (e.g. dissolved organic matter, water hardness and salinity) are known to affect metal speciation and bioavailability and may vary between conditions used in laboratory bioassay experiments and the natural aquatic environment. This study has identified a number of metal combinations that should be targeted in future studies that investigate metal mixture toxicity under a range of conditions relevant to the Lower Lakes' aquatic environments.

2.7 Development of an integrated CLLMM water quality response model

2.7.1 Lower Lakes hydrogeochemical model development and assessment of acidification risks

Report details

Full details of the work undertaken and its findings are provided in the report:



MURRAY FUTURES
Lower Lakes & Coorong Recovery

Acid Sulfate Soils
Research Program

Lower Lakes Hydro-Geochemical Model Development
and Assessment of Acidification Risks

Report 6 | Part 1 of 4 | October 2010

Hipsey, M.R., Bursch, B.D., Coletti, J. and Salmon, S.U. (2010). Lower Lakes hydrogeochemical model development and assessment of acidification risks. Prepared by University of Western Australia for SA Water, Adelaide.

Key research outcomes

- Adequately modelled location, severity and duration of acidification events in hindcast simulations for the period January 2008 to September 2009;
- Model parameterisation successfully utilised findings from concurrent field and laboratory experiments associated directly with the Lower Lakes region;
- Model was used to set 'trigger levels' for Lakes Alexandrina and Albert – water height levels below which the risk of acidification was too high;
    - For Lake Albert the 'trigger level' was set at - 0.5 m AHD;
    - For Lake Alexandrina the 'trigger level ' was set at – 1.5 m AHD; and
- The model should be used as a predictive tool within an adaptive monitoring framework, and not used in isolation.

Aim

Develop a spatially resolved hydrogeochemical model to:

- Better understand the impacts of acid sulfate soils on lake water quality on a regional scale; and
- Forecast Lake and acid sulfate soil conditions following multiple year management scenarios including water level stabilisation with freshwater and/or seawater inputs.

Approach

Following a review of the suitability of various existing models the ELCOM–CAEDYM (Estuary, Lake and Coastal Ocean Model – Computational Aquatic Ecosystem Dynamics Model) model was considered best able to meet the aims of the research project. In its existing form there were a number of limitations (e.g. the diffusion of oxygen in to unsaturated soil layers) of the ELCOM-CAEDYM model which required development to adequately simulate acid sulfate soil processes. These limitations were addressed through the development of a standalone acid sulfate soils module. The module adopted a simplified vertical representation of acid sulfate soil hydrogeochemical properties and was computationally efficient. Therefore, the module could be applied spatially, by coupling with the 3D ELCOM-CAEDYM model, and was suitable for simulating multiple year management scenarios, without computational run-times becoming unmanageable. Horizontal transport processes were also modelled by adopting a simplified conceptual model built from the results of a more detailed two dimensional Richard's equation model (HYDRUS-2D). For example, this included simulating the transport of acidity contained in surficial groundwater from the soil profile to lake surface waters under various hydrological conditions, such as lake water level fluctuations and rainfall events.

Model parameterisations and justifications were based on findings made in associated concurrent Lower Lakes' research projects or literature values where available. These parameterisations are summarised in Table 5.2 of the full report. This included information on the spatial variability of soil physical properties, spatial variability of actual and potential acidity, pyrite oxidation rates, acidity generation and neutralisation processes and acidity and contaminant transport (e.g. Sections 2.1, 2.3, and 2.4).

The coupled ELCOM-CAEDYM-ASS model (Figure 58) was configured on a range of model subdomains, representing i) Lake Alexandrina, ii) Lake Albert and iii) a high-resolution domain for the Currency Creek, Finniss River and Goolwa Channel region. Simulated variables included velocity, temperature, salinity, nutrients, algae, major ions, pH and alkalinity and solid phase precipitates. The model was validated against a large variety of parameters from extensive field collected water quality and hydrological monitoring data sets, and more limited soil condition data for the period January 2008 to September 2009. This included, for example, hindcast simulations of pH values in the high resolution Currency-Finniss subdomain, where large-scale acid impacts had occurred.

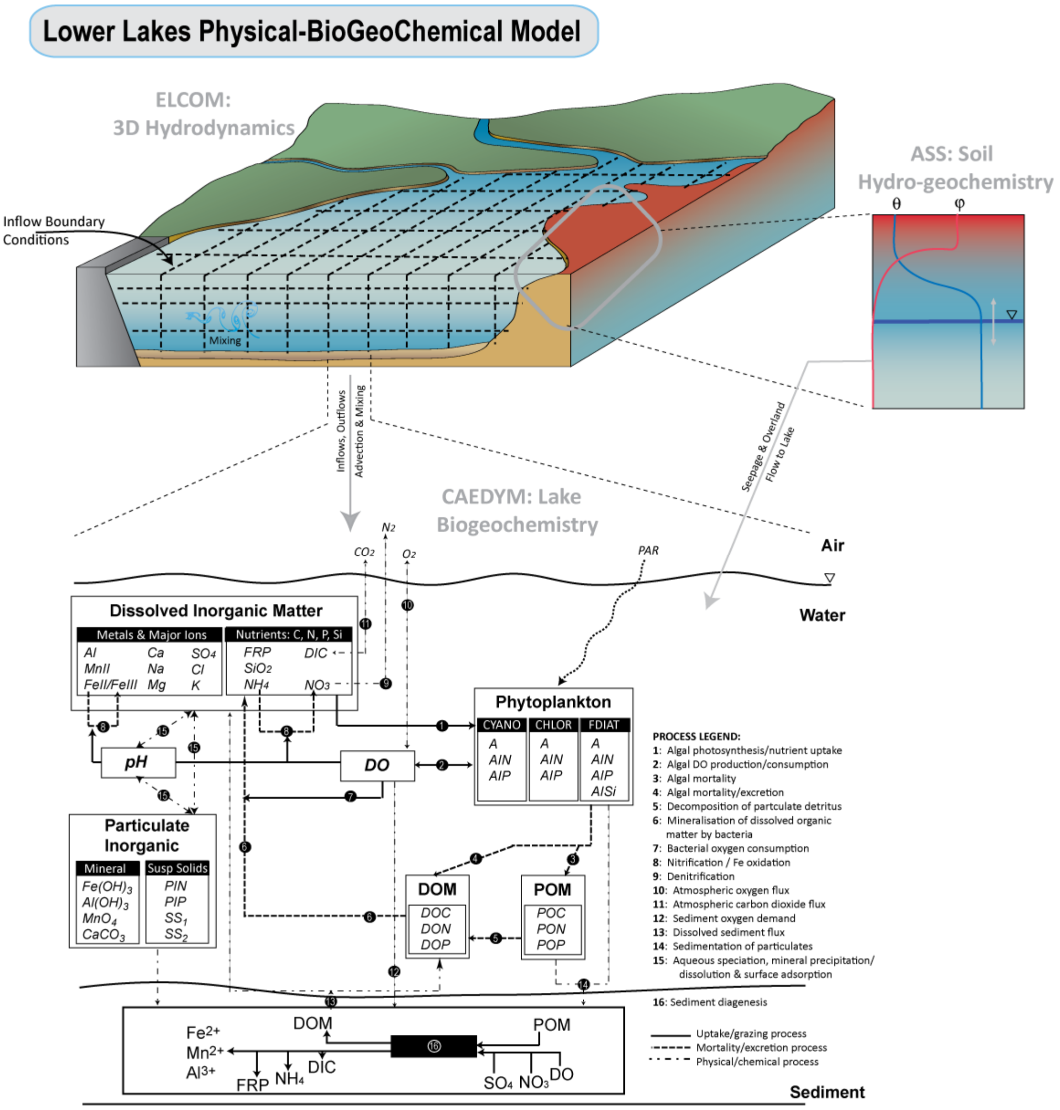


Figure 58. Conceptual outline of the coupled ELCOM-CAEDYM-ASS model showing hydrodynamic-biogeochemical-acid sulfate soil model linkages as configured to the Lower Lakes.

The model was then used to forecast lake conditions for the period October 2009 to January 2013. Various water level management scenarios were run including augmentation of lake volumes with additional freshwater allocations or with seawater through the barrages. Results of the model forecast simulations were used to inform water management target levels for both Lake Alexandrina and Lake Albert to prevent lake surface water acidification.

Findings

Following its development and calibration the ELCOM-CAEDYM-ASS model was unique in its ability to model:

- Three dimensional hydrodynamics, including prediction of circulation patterns, inflows (including pumping and seawater entrance), wetting and drying, temperature, salinity, surface thermodynamics and evaporation;
- Two dimensional spatially variable specification of soil texture and geochemistry, which allows for heterogeneity in soil hydraulic properties, pyrite content, and acid neutralising capacity at high-resolution (100 to 250 m grid spacing);
- Vertically resolved pyrite oxidation reaction kinetics in exposed cells based on dynamically predicted moisture content profiles, and subsequent neutralisation kinetics;
- Acidity flux to the surface water following re-wetting of exposed cells, and also from overland flow and seepage processes; and
- Buffering of water pH by lake and river alkalinity, and approximation of alkalinity generation by organic matter decomposition in submerged soils.

The calibrated model performed well in hindcast simulations of lake physical properties (water level, temperature and salinity). Alkalinity and pH dynamics were also well predicted in cases where no acidification was reported. In areas where acidification was reported, the model was competent in predicting when and where pH would fall. In particular the timing, severity and recovery from the acidification event that occurred in Currency Creek tributary in 2009 was adequately modelled in hindcast simulations (Figure 59). However, there were some areas predicted to acidify in hindcast simulations that were not observed to acidify in reality. This highlights that uncertainty in model predictions remain and that the model should be used as a predictive tool within an adaptive monitoring framework, and not used in isolation.

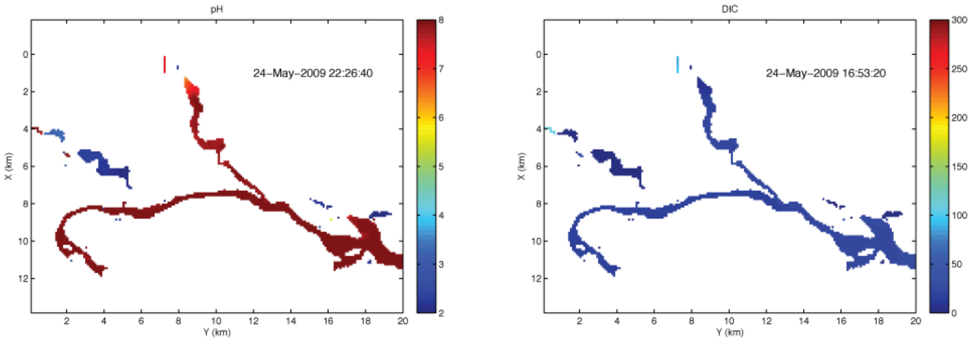


Figure 59. Plot of surface water pH and dissolved carbonate alkalinity (DIC, mg C L-1) showing hindcast simulation of Currency Creek acidification event.

Model outputs confirmed that a substantial risk of acidification of surface water in both Lakes Alexandrina and Albert existed that required active management. The amount of potential acidity stored in pyrite in exposed soils that is able to oxidise was found to be orders of magnitude larger than that needed to cause water body acidification. The rate of pyrite oxidation was found sufficiently fast as to be non-limiting (i.e. able to release ample acidity to create management concerns). Conversely, the dominance of vertical transport processes and the typically slow moving groundwater (i.e. horizontal transport) were found to limit the flux of acidity into lake surface waters. As a result soil hydrology dynamics were found to be of critical importance in determining the predicted outcome. A dominant mechanism controlling the flux of acidity to lake surface waters was found to be large threshold rain events. These large rainfall events were observed to deliver large loads of acidity to the Lower Lakes by:

- Overwhelming the vertical percolation rate, generating temporary acidic surface ponding events that are subsequently incorporated into lake surface water through surface runoff or raising water levels (e.g. lake filling or seiche events); and
- Inducing vertical transport of acidity from the oxidised unsaturated zone to shallow groundwater which is subsequently incorporated into lake surface water through lateral transport driven by the temporarily increased hydraulic gradient.

The diffusion of acidity out of rewetted acidified clay textured soils (e.g. Lake Albert) following lake refilling was also observed as a potential mechanism delivering large loads of acidity to lake surface waters. Therefore, there is potential for lake surface water acidification during drawdown and also during refilling.

Various forecast simulations investigated potential future conditions in the Lower Lakes for a range of potential future flow scenarios and management regimes. The chief aim of the forecast simulations was to determine critical water height levels (termed 'trigger levels') for Lake Albert and Lake Alexandrina at which the risk of lake acidification became too high. This risk was defined as the lowest lake water height prior to pH dropping below 6, even if this occurred at some time in the future (i.e. at a delayed time after lake refilling).

For Lake Albert, the lake surface water was observed to acidify for all simulations where lake water levels were allowed to fall below a height of -1.0 m AHD (Figure 60). The alkalinity, and subsequently pH, were predicted to first become unstable near the Narrung Narrows, and then on the north-western edge near Campbell Park. Salinity was also predicted to increase to values around 50,000 μScm^{-1} (e.g. approximately seawater) over summer 2010/2011 if pumping from Lake Alexandrina was not maintained and Lake levels were allowed to drop. Total nutrient concentrations were also predicted to reach very high concentrations. Sensitivity testing of the model did not change this outcome. Stabilisation of lake levels at a height of either -0.75 or -0.5 m AHD was predicted to prevent any large scale deterioration in pH or alkalinity until the end of 2012. However, pH instabilities at the lake's 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 in Lake Albert is to maintain water levels above -0.5 m AHD. Seawater scenarios were not modelled for Lake Albert in this report.

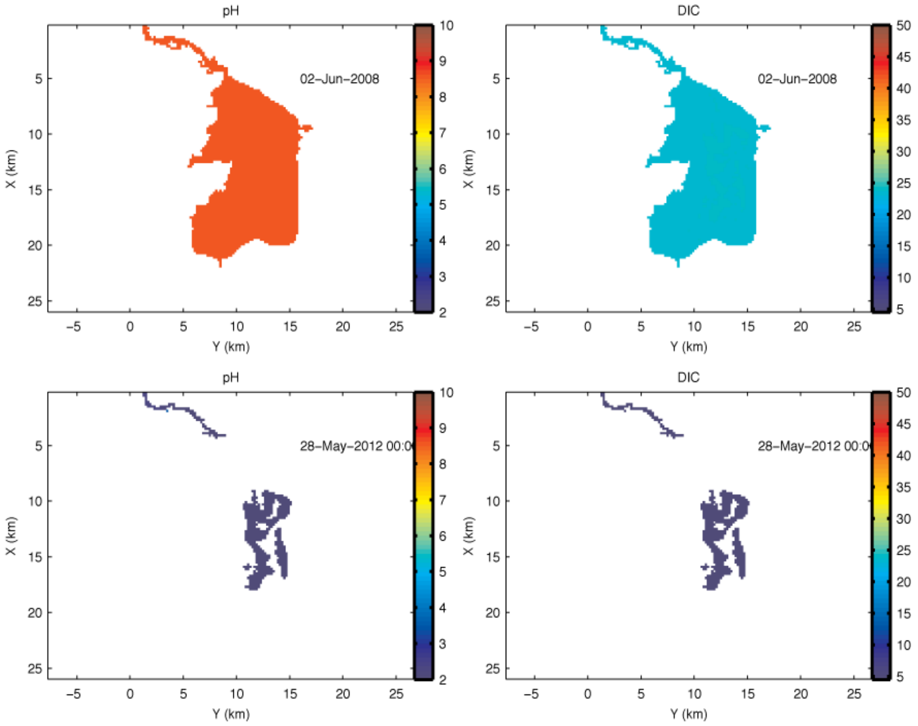


Figure 60. Plots of predicted pH and dissolved carbonate alkalinity (DIC mg C L^{-1}) for Lake Albert on June 2008 and May 2012.

For all simulations conducted, the area of sulfuric soils is large and continued to expand in both Lakes Alexandrina and Albert until lake water levels were stabilised. Figure 61 highlights that acidity levels in the soil were predicted to remain high despite fluxes to lake surface water. Figure 61 also illustrates predicted changes to key acidity pools, for example, the store of acidity available for mobilisation was predicted to increase from approximately 49,000 to approximately 113,000 tonnes of sulfuric acid over the period 2010-2012 (assuming lake level stabilisation at a height of -1.0 m AHD until 2012).

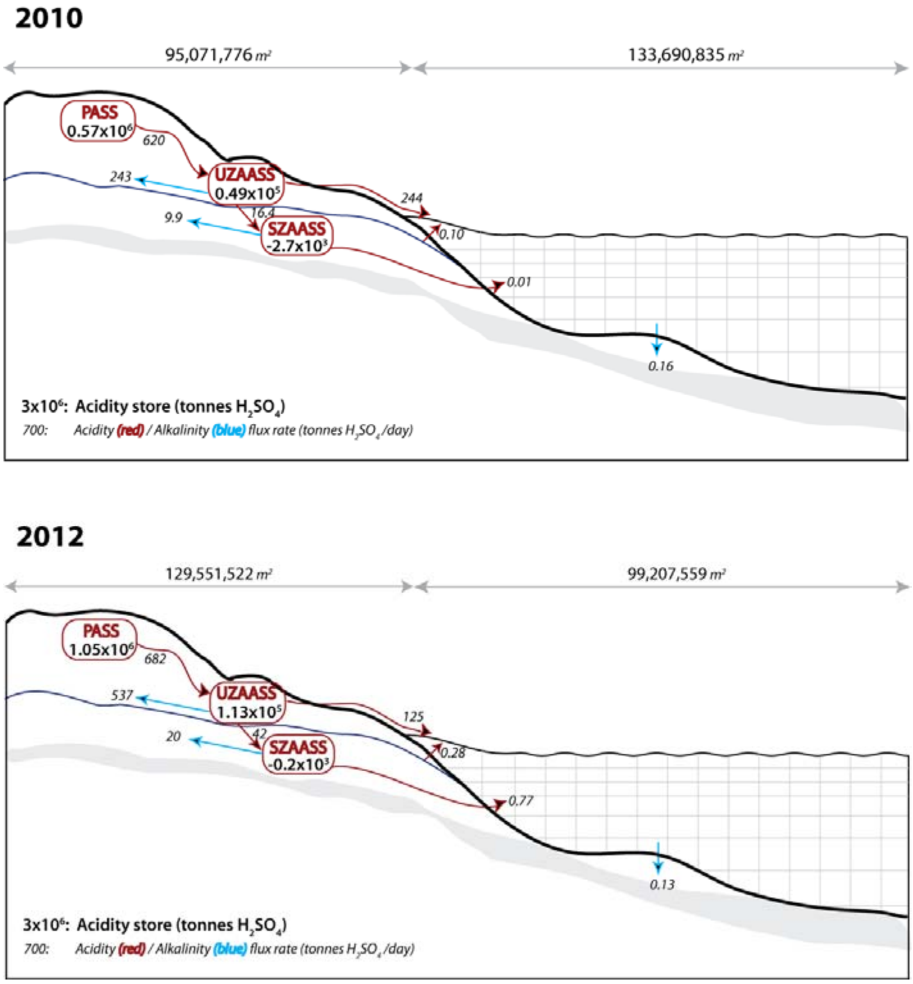


Figure 61. Changes in annual average budgets of acidity stores and fluxes for Lake Albert over the period from 2010 to 2012. Data from the -1.0m AHD stabilisation forecast simulation. PASS = potential acid sulfate soils. UZAASS = unsaturated zone actual acid sulfate soil. SZAASS = saturated zone actual acid sulfate soil.

For Lake Alexandrina, forecast simulations of potential management scenarios included draw down (i.e. ‘do nothing’), partial freshwater refill (additional 500 GL allocation in 2009-2010), and stabilisation at -1.0 m AHD with freshwater or seawater. For all refill or stabilisation and drawdown scenarios, the main lake body surface water maintained satisfactory pH and alkalinity up until the end of 2012 (Figure 62). However, at lake water height levels below -1.5 m AHD, the volume of acidity stored in the soil is considerable compared to the alkalinity stores of the surface water.

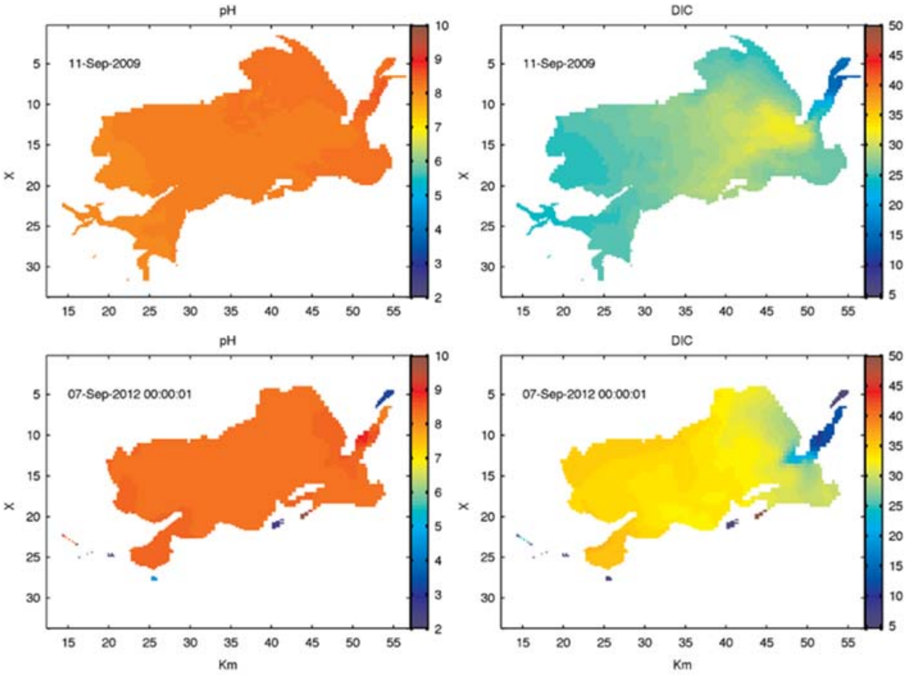


Figure 62. Plots of predicted pH and dissolved carbonate alkalinity (DIC mg C L^{-1}) for Lake Alexandrina in September 2009 and September 2012 for the -1.0m AHD water level stabilisation scenario.

The model indicated several potential management issues:

- The north western region showed temporary acidification during lake drawdown and then seasonal rewetting (this was later confirmed with field observations of surface water acidification in Boggy Lake);
- For the forecast simulation, 'water level stabilisation at -1.0 m AHD by seawater', acidification was predicted to occur in the southern reach of the lake around Pt Sturt. Alkalinity was also observed to decline over the whole lake area and salinity values across the whole lake area rapidly reached seawater or higher concentrations. Seawater simulations also indicated that seawater was more efficient at mobilising acidity (the ELCOM-CAEDYM-ASS model accounts for how variations in salinity affect acidity flux) and hence was less able to prolong pH neutral conditions when compared to freshwater; and
- Large accumulations of available acidity in the unsaturated soil combined with increasing cumulative loadings of acid reaching lake surface waters by shallow groundwater flow were evident over the modelled period (Figure 63). This indicated that in longer simulations run beyond 2012 lake surface water and alkalinity values could eventually deteriorate if levels were maintained below -1.5 m AHD.

Based on these issues, the key management recommendation to prevent lake acidification was to maintain water levels above -1.75 m AHD in Lake Alexandrina and that stabilisation of lake levels above -1.5 m AHD would significantly reduce acidification risk. Although the stabilisation of lake levels at these recommended water heights were predicted to prevent lake surface water acidification, it was noted that even at these levels, large areas of sulfuric soils with poor quality porewater would be exposed and fringing waterbody regions with poor connection to the main lake water body would continue to acidify in response to rainfall events.

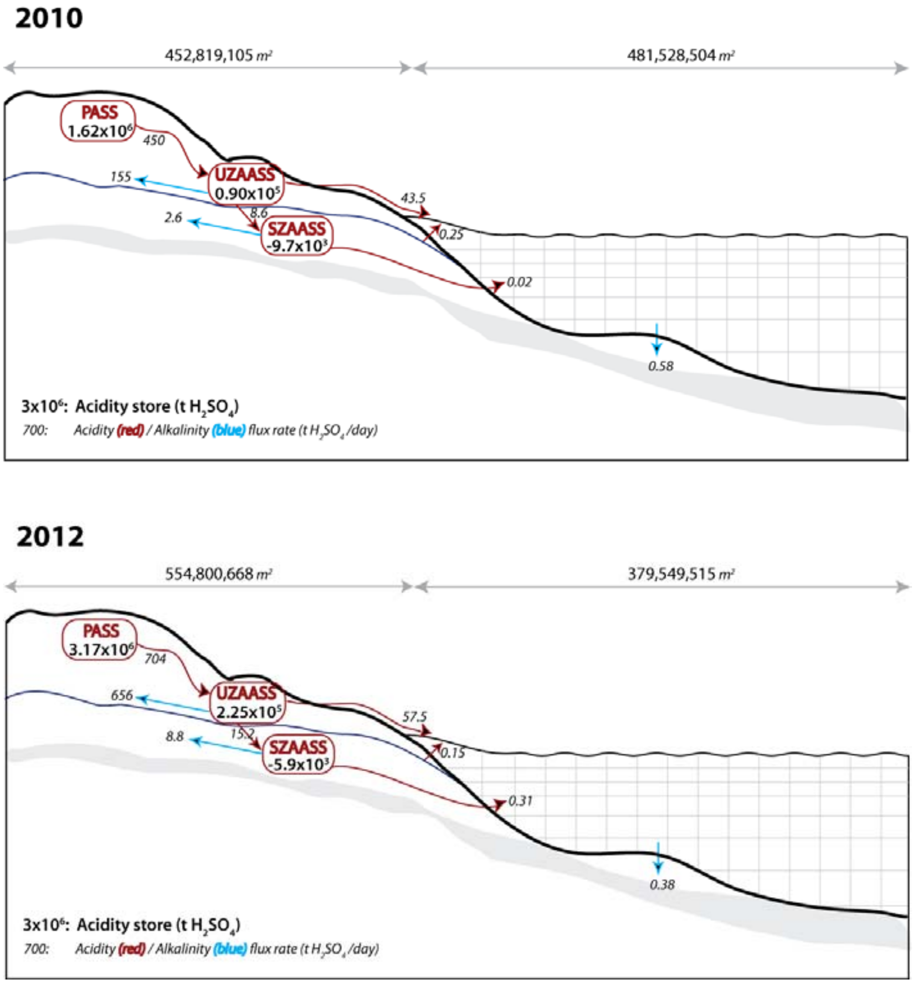


Figure 63. Changes in annual average budgets of acidity stores and fluxes for Lake Alexandrina over the period from 2010 to 2012. Data from the continued draw down (i.e. 'do nothing') forecast simulation. PASS = potential acid sulfate soils. UZAASS = unsaturated zone actual acid sulfate soil. SZAASS = saturated zone actual acid sulfate soil.

Research limitations and future work

It was recommended that further research would provide significant opportunities to improve model predictions. For example:

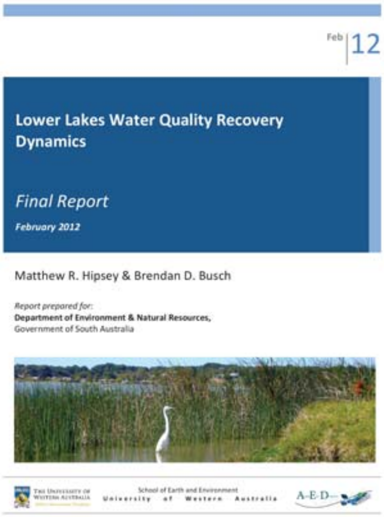
- Further calibration of the model as more monitoring data became available would improve model predictions;
- The use of a vertically resolved Richard's equation for simulations was avoided due to computational limitations. However, simulations of less than 1 year in the Currency Creek sub-domain is computationally achievable and would help gain a better understanding of the key controls on acidification dynamics; and
- An improved two-dimensional transport model would better predict lateral flows and help develop a better understanding of ponding and through flow dynamics following high rainfall events. 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.

The model was highly sensitive to the spatial input data with respect to the physical and chemical properties of the soils. Significant error resulting from input uncertainty, or simplification of these properties, needs to be considered when interpreting simulated results. 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.

2.7.2 Lower Lakes water quality recovery dynamics

Report details

Full details of the work undertaken and its findings are provided in the report:



Feb 12

Lower Lakes Water Quality Recovery Dynamics

Final Report

February 2012

Matthew R. Hipsey & Brendan D. Busch

Report prepared for:
Department of Environment & Natural Resources,
Government of South Australia

The University of Western Australia
School of Earth and Environment
University of Western Australia
A-E-D

Hipsey, M.R., Bursch, B.D. (2012). Lower Lakes water quality recovery dynamics. Prepared by University of Western Australia for the Department of Environment & Natural Resources, Adelaide.

Key research outcomes

- In hindcast simulations the model accurately predicted:
    - The acidification of Loveday Bay, Boggy Creek and Currency Creek; and
    - The stability of pH in Lake Albert and other areas in Lake Alexandrina.
- Model simulations demonstrated that the rapid rate of lake refilling prevented localised manifestations of acidification;
- The dominant flux of acidity to lake surface waters occurred following pulses of rain. Rainfall events collect surficial acidity in exposed marginal soils and drives its transport to the lake edge via lateral and overland flow;
- Acidification of groundwater and subsequent baseflow and the diffusive flux of acidity following rewetting were less significant acidity delivery mechanisms;
- The updated model supports the threshold ‘trigger levels’ for minimum water levels in Lake Alexandrina and Albert set in the previous report. To prevent widespread acidification it was recommended that water levels are kept above -1.5 m AHD and -0.5 m AHD, for Lake Alexandrina and Lake Albert respectively; and

- The model highlighted the importance of flushing and dilution by the main lake water body in preventing acidification hot-spots. Acidification hot-spots were observed in isolated regions where lake bathymetry prevented connection with the main lake water body.

Aim

To further develop and validate the spatially resolved hydrodynamic-biogeochemical ELCOM-CAEDYM-ASS model, outlined in Section 2.7.1 of this report, to improve its predictive ability and reduce uncertainty so that it can better support decision making and management outcomes. Using the improved model, investigate the potential for a renewed acid sulfate soil acidification hazard if low flow conditions returned in the future.

Approach

A conceptual description of the ELCOM-CAEDYM-ASS model and its components is provided in Section 2.7.1 of this report. Herein, the 2010 report summarised in Section 2.7.1 is referred to as the ‘previous report’. In this Section details of the approaches used to further develop the model are provided.

In the previous report the Lower Lakes region was separated into three sub-domains; Lake Alexandrina, Lake Albert and a high resolution Finniss-Currency domain). Connections between sub-domains were modelled by pumping transfers at Clayton and Narrung. Following the removal of temporary structures in September 2010, and the overflow of the Lower Lakes into the Coorong following Lake refilling, the Lower Lakes region became reconnected. As a result, it became necessary to model the region as a single combined domain (replacing the 3 separate sub-domains). In order to achieve this, a high resolution ‘CLLMM full domain’ was developed. The development of the CLLMM full domain allowed the model to simulate conditions in the Lower Lakes from January 2008 to April 2011 for validation (hindcast) and beyond for assessment of future lake conditions (forecast) (Figure 64)

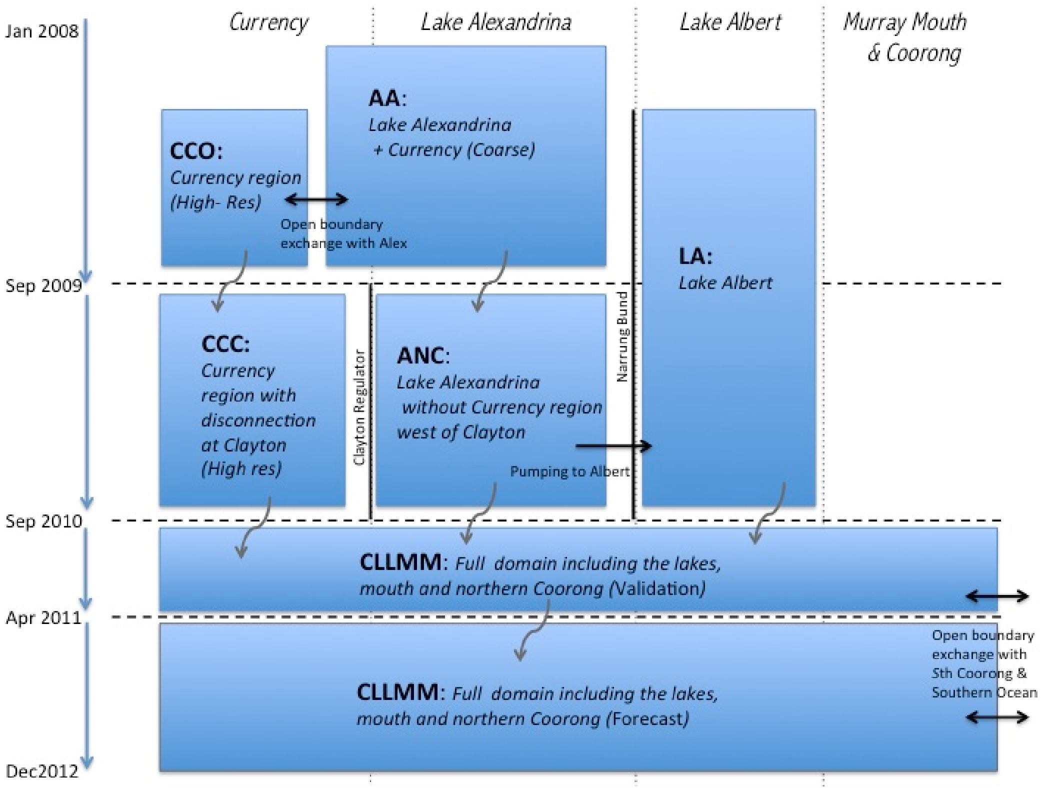


Figure 64. Schematic of model system outlining how the different hindcast validation simulations are configured to cover the reconnection of sub-domains to a CLLMM full domain in September 2010. Also shows the use of the CLLMM full domain for forecast simulations past April 2011.

A substantial quantity of new field-based monitoring data had been generated since the previous report. The increase in monitoring data available for model validation provided an opportunity to rigorously test the performance of the model, and guide calibration of model parameter sets. Modelled parameters for nutrients, Chl-a, EC, turbidity, pH, alkalinity, major ions, sulfate, chloride, aluminium and iron were tested against monitoring data equivalents for the period January 2008 to April 2011. Monitoring data was compiled into a flexible framework that allowed new data to be rapidly incorporated (i.e. semi-automated) as it was generated and thus kept validation plots up-to-date.

The opportunity to further develop the model was also used to reconfigure various model components, namely the acid sulfate soils module and the CAEDYM surface water quality components. The revision of these components was based on discussions that followed the previous modelling initiative. Improvements to the acid sulfate soils module included the addition of iron and sulfate to acid sulfate soil leachate and the inclusion of fictional conservative leachate 'tracer' (termed 'COL') to follow the fate of material leached from acid sulfate soils as is enters lake surface waters and give a qualitative indication of potential trace and heavy metal hot-spots. Updates to CAEDYM included the addition of turbidity (and its effects on light attenuation) and refinements to nutrient cycles.

Forecast simulations were used to assess the risk of a renewed acidification hazard should a further period of rapid water level drawdown occur in the future. Two different forecast simulations, termed 'depleted' and 'regenerated', were used to explore the hypothetical range of acidification risk between a 'best' case and 'worst' case scenario. The depleted simulation assumed all acidity generated via pyrite oxidation by the end of May 2011 was removed/flushed from the system and represents the best case scenario. The regenerated simulation assumed all acidity generated via pyrite oxidation by the end of May 2011 was re-accumulated as pyrite and represents the worst case scenario (e.g. starting point is the same as the Millennium Drought).

Findings

The model received extensive testing during validation exercises. In total more than 1,200 validation plots were constructed, comparing simulated parameters against field based monitoring data for the period 2008 to 2011. Hindcast predictions of general parameters, such as water level and salinity, adequately captured the spatial and temporal trends observed in field based monitoring data. For example, the rapid increase in water level in Lake Albert following the removal of the bund in the Narrung Narrows was simulated well. However, a tendency for the model to over predict the decline in water levels during drawdown over summer (by up to 0.25 m) was observed.

The updated acid sulfate soils module was validated against the greater amount of available water quality monitoring data Currency Creek-Finniss River region (Figure 65). Since the previous report the currency acidification event area had been inundated (behind currency regulator) and further acidification events in Boggy Creek, Loveday Bay and other lake margin areas had been observed. Model validation demonstrated that the model was able to capture acidification events (such as those listed above) in high-risk areas during hindcast simulations. The stability of pH in the main water bodes was also captured well during hindcast simulations. Alkalinity and EC showed good performance against monitoring data in the Currency Creek-Finniss River region but was occasionally over-predicted, particularly during the 2009-2010 summer period. This was associated with either inaccuracies for the Currency Creek inflow or an under prediction of the continued acidity flux from acid sulfate soils to the surface water following rewetting.

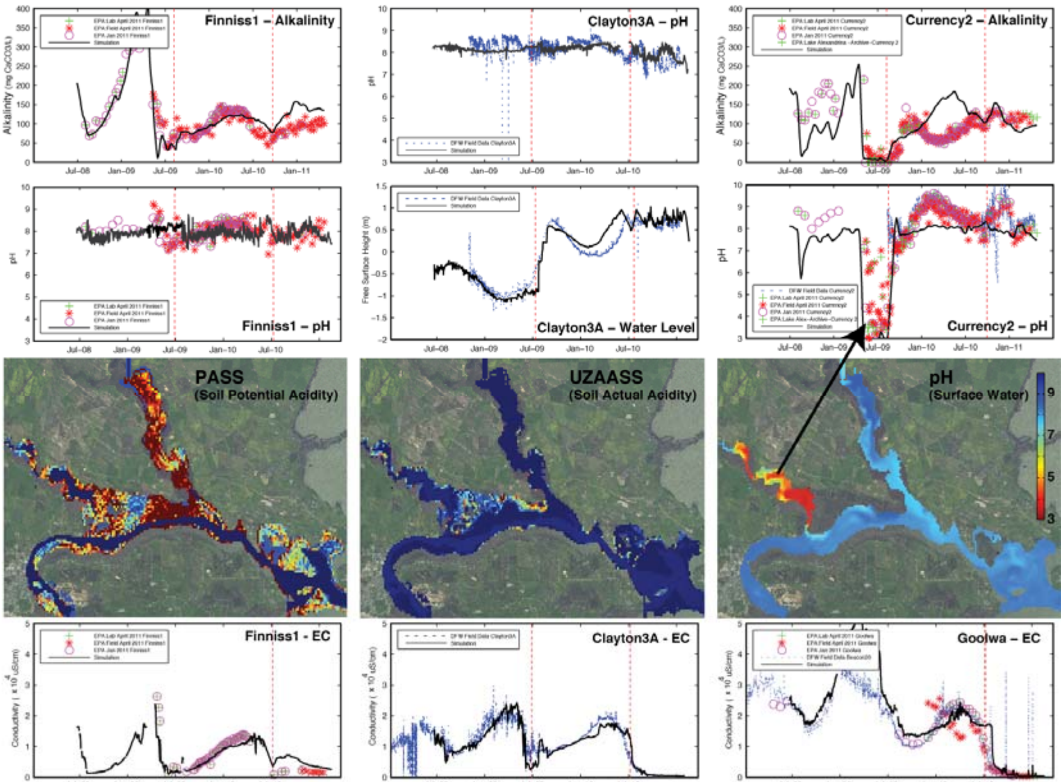


Figure 65. Spatial distribution of PASS, AASS and water pH in the Currency Creek-Finniss River region (July 2009) with time-series model validation plots comparing water level, EC, alkalinity and pH at key points.

The inclusion of the COL tracer in the acid sulfate soils module allowed researches to investigate the magnitude and spatial and temporal distribution of acid sulfate soil leachate loading in surface waters following refilling events. The COL 'tracer' was used as an indicator of metal contaminant loading originating from acid sulfate soils. However, model outputs provide a qualitative indication only. This is because contaminant reactions and/or transformations, such as the removal of Al^{3+} from solution by precipitation as gibbsite, were not accounted for (i.e. conservative behaviour was assumed). The COL tracer was successfully used to highlight the build-up and persistence (i.e. still apparent after 12 months) of contaminants behind the Currency Creek regulator relative to the high level of dilution in the Finniss River and Goolwa Channel (Figure 66). The simulation demonstrated the effectiveness of the Clayton regulator in isolating poor water quality until water levels had better recovered.

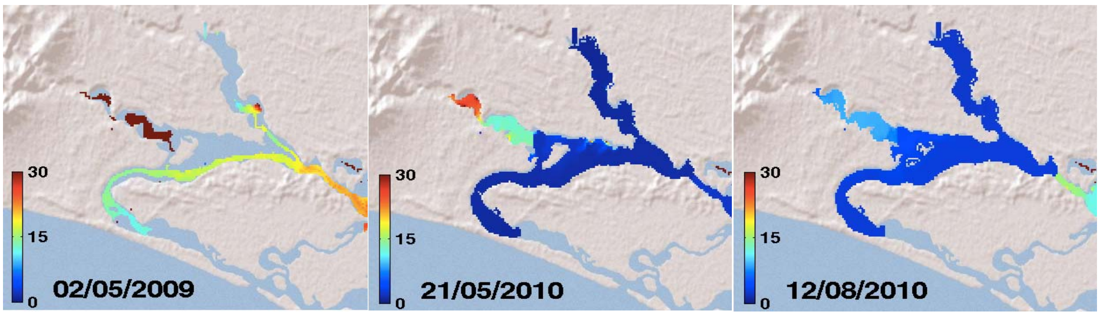


Figure 66. Distribution and relative concentration (arbitrary units) of acid sulfate soil leachate in the surface water of Currency Creek during acidification (left panel), the period following initial rewetting (middle panel) and continued inundation (right panel). Simulating the areas of accumulation and the transport and dilution of potential contaminants released from acid sulfate soils.

An annual average budget of key acidity stores and fluxes compiled for the September 2008 to September 2009 period showed that, of the various flux mechanisms that transport stored acidity to surface waters, surface flow processes (i.e. overland flow and shallow flow through the unsaturated zone) were the most important. An annual average of approximately 12 tonnes of sulfuric acid per day was transported to the lake, however, the flux was significantly higher following periods of high rainfall. In contrast, acidity fluxes to the lake surface water via lateral flow in the saturated zone and via diffusive flux following inundation were relatively small, approximately 0.01 and 0.003 tonnes sulfuric acid per day respectively. Approximately 22% of the 60,000 tonnes of acidity produced was transported to lake surface waters. A further 30% was neutralised by soil and/or surface water alkalinity or by alkalinity produced via sulfate reduction following rewetting.

The above results for the Finniss-Currency region highlight the significance of lake bathymetry on acidification hot-spot occurrence. Where a region is isolated due to lake bathymetry, acidity can accumulate unabated without any neutralisation, dilution and/or flushing from the main lake body. Under these conditions the occurrence of an acidification hot-spot is more likely (e.g. disconnected pools in Currency Creek, Boggy Lake and Loveday Bay).

A specific aim of this report was also to investigate the potential reason for the decline in alkalinity in lake surface waters observed following the arrival of floodwaters in 2010. While some areas were predicted to have a high flux of acidity from the surface soil layers to lake surface waters following rewetting, no local manifestation of high acidity loading was observed in hindcast simulations. The alkalinity decline in lake surface waters was attributed to the alkalinity decline in floodwaters entering the Lower Lakes, consistent with monitoring data from Tailem Bend. Overall, the rapid rate of refilling was observed to prevent localised acidification due to the replenishment of lost alkalinity through continued inflows and the high degree of mixing/exchange and dilution with the main lake water body (i.e. large inflow volume).

Forecast simulations were used to investigate if the risk of acidification would return if drought conditions were to be encountered in the future. In the hypothetical simulations water levels in Lake Alexandrina lowered to minimum -1.0 m AHD. Hence, the simulation did not have as large or as fast a decline in lake water levels as in the Millennium

Drought. Nevertheless, acidification events in isolated areas (e.g. Boggy Lake, Currency Creek, Loveday bay) were observed to occur within one year. Main lake water bodies generally maintained a stable pH. However, without the Clayton regulator in place to contain acidified surface water, the Goolwa channel received a pulse of acidification from the acidified Currency Creek tributary.

A similar response in surface water pH was observed between the 'regenerated' and 'depleted' scenarios. The insensitivity to the differences of the two scenarios demonstrated that even if all of the acidification potential realised during the Millennium Drought was removed from the system, sufficient pyrite still remains in the soil to present an acidification hazard. The similarity between the scenarios also indicated that water level trigger values for Lakes Alexandrina and Albert set in the previous report remain valid.

Research limitations and future work

It was recognised that the difficulties in answering questions relating to the reoccurrence of acidification hazards under potential future drought conditions were due to the lack of updated spatial soil data. In particular, how acid sulfate soils materials (i.e. pyrite content and acid neutralising capacity) had evolved since the original survey in 2010 (see Section 2.1.1).

A project to assess the change in acid sulfate soil materials (e.g. the level of depletion of pyrite following oxidation) would:

- Allowing a rigorous validation of the model's soil module. To date module validation has been based on the manifestation (i.e. acidity and pH) of acid sulfate soils; and
- Provide an improved confidence of starting conditions for forecast predictions (i.e. are starting condition the same, better or worse than for the Millennium Drought).

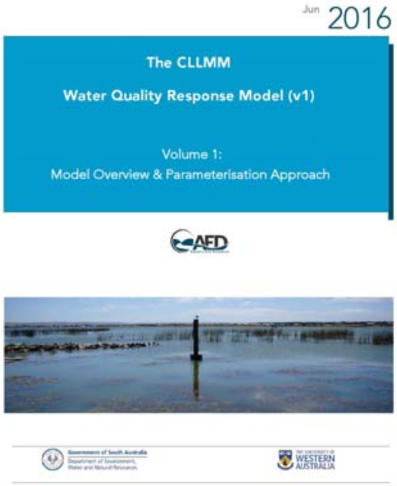
Further field research is recommended to characterise the dominant controls on hydrological pathways in the exposed soil. Currently many of the hydrological module parameters are assumed and could be further refined by field investigations that measure soil physical properties such as texture and hydraulic properties.

Alkalinity was over-predicted on a number of occasions during the summer periods when evapoconcentration was highest. Further investigation to understand the geochemical controls on alkalinity, such as calcite/aragonite solubility, would unravel the reasons for over-prediction.

2.7.3 CLLMM water quality response model (v1)

Report details

Full details of the work undertaken and its findings are provided in the report (in two volumes);



Jun 2016

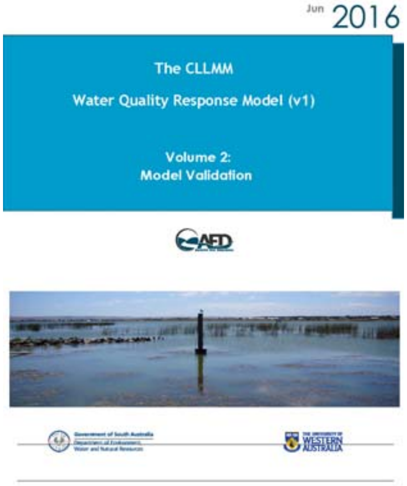
The CLLMM

Water Quality Response Model (v1)

Volume 1:

Model Overview & Parameterisation Approach

Hipsey, M.R., Busch, B.D. and Katumba, G. (2016). The CLLMM Water Quality Response Model (v1) – Volume 1: Model Overview & Parameterisation Approach. AED Report #R31, The University of Western Australia, Perth, Australia.



Jun 2016

The CLLMM

Water Quality Response Model (v1)

Volume 2:

Model Validation

Hipsey, M.R. and Busch, B.D. (2016). The CLLMM Water Quality Response Model (v1) – Volume 2: Model Validation. AED Report #R32, The University of Western Australia, Perth, Australia.

Key research outcomes

- An integrated modelling platform, able to simulate the hydrodynamics and biogeochemistry of the system from 2008-2015, was developed and validated for the CLLMM region.
- Model predictions were consistent with empirical data and conceptual models for the region, with the advantage of being able to interpolate in space and extrapolate in time.
- ‘Trigger levels’ of -1.5 m AHD for Lake Alexandrina and -0.5 m AHD for Lake Albert that were established in previous modelling efforts are supported, with greater confidence, by the present model development. It is critical that water heights are managed above these ‘trigger levels’ to prevent surface water acidification in Lake Alexandrina and Lake Albert.

- The dynamic factors that influence surface water acidification and the spatial heterogeneity in its occurrence (i.e. hot-spot locations) were the result of a coalescence of favourable hydrologic conditions and geomorphological setting. For example, where the rainfall threshold (rate) for overland flow is exceeded (following critical antecedent conditions) and alkalinity and/or volume of ponded water is below critical thresholds.
- Therefore due to the above, hot-spot locations of surface water acidification are unlikely to change in a future drought.
- The time scale for sulfide accumulation was estimated by diagenesis modelling to take approximately ≥ 8 to 10 years

Aim

To develop the Coorong, Lower Lakes and Murray Mouth Water Quality Response Model (CLLMM-WQRM) that incorporates relevant information from monitoring and research studies into an updated comprehensive model. The CLLMM-WQRM will be used to understand and simulate water quality (including acid sulfate soil dynamics) that can be used to characterise the ongoing and potential ecological risks to the region. The CLLMM-WQRM builds on from previous ELCOM-CAEDYM-ASS modelling efforts (Sections 2.7.1 and 2.7.2).

Approach

The approaches used in the model are outlined in detail in Volume 1 of the full report. Below, a brief summary of improvements or notable changes to approaches used in the model, compared to previous efforts, is presented.

Following the application of the ELCOM-CAEDYM model in the CLLMM system (Sections 2.7.1 and 2.7.2), the flexible mesh model TUFLOW-FV was developed for the CLLMM system (Figure 67) (BMTWBM Pty Ltd, 2010). The flexible coordinate system used by TUFLOW-FV allowed the use of differing levels of resolution to capture regions of vaying morphological complexity. This flexible mesh approach offered several advantages over the fixed grid of the ELCOM-CAEDYM model in terms of allowing hydrodynamics in a complex system (i.e. lakes, rivers, esturaries, barrages etc.) to be resolved in computationally efficient way, thus allowing longer term simulations of the region to be undertaken in its entirity.

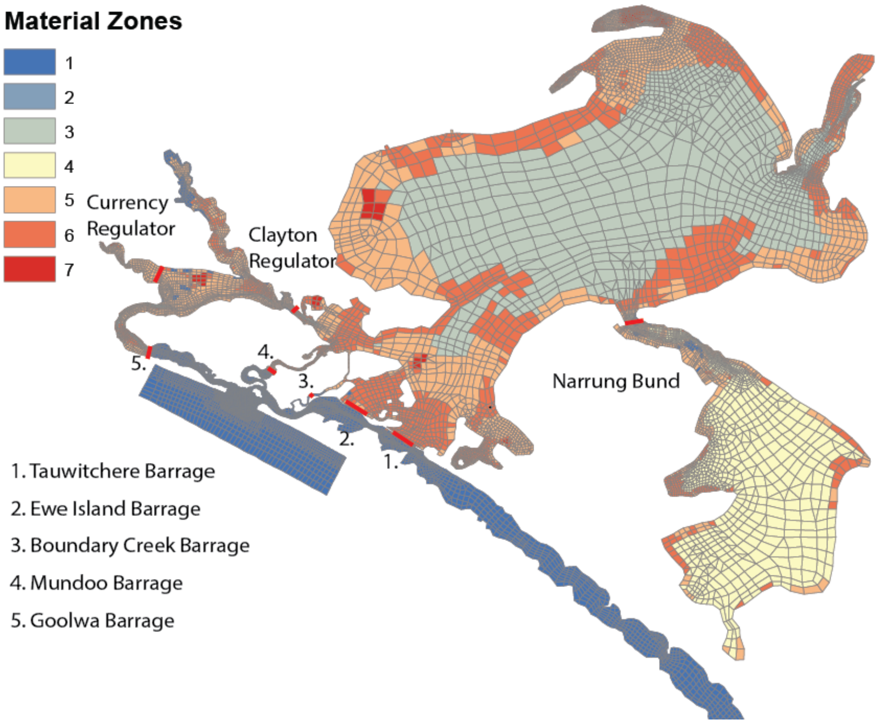


Figure 67. Updated TUFLOW-FV flexible grid mesh applied to the CLLMM region. Increased mesh resolution was adapted to better capture the hydrological dynamics in acid sulfate soil areas of interest (i.e. Campbell Park, Boggy Lake, Dog Lake, Loveday Bay and Currency Creek). Material zones categories are based on spatial soil data (Section 2.2.1).

The CLLMM-WQRM uses the TUFLOW-FV hydrodynamic model to drive the AED2 biogeochemical model. The AED2 model comprised a number of biogeochemical and ecological modules that have the ability to simulate the full range of physical, chemical and biological processes relevant to the system, by adopting a simple modular approach. For example, the 'aed_ass' module predicted pyrite oxidation and acidity accumulation and neutralization and the 'aed_land' module predicted drying of exposed soil, seepage and runoff. Using these modules the coupled TUFLOW-FV and AED2 model was used to simulate turbidity, oxygen, organic matter and nutrient cycling, soil biogeochemistry, acid sulfate soils, metals and phytoplankton.

The modelling was supported by a comprehensive set of field monitoring and experimental data specifically related to the CLLMM region. This data was used for model parameterisation or aggregated for model validation, thus integrating data from over 300 sites into the modelling assessment (Figure 66).

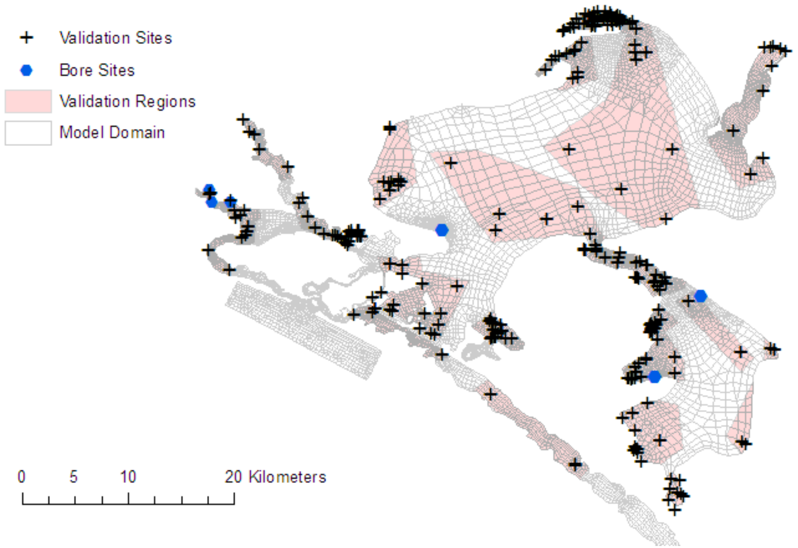


Figure 68. Overview of available monitoring data and aggregation of monitoring data into 22 regions for the purposes of comparison with the model.

The CAEDYM acid sulfate soil module that was used in previous efforts to simulate soil hydrochemistry as the Lower Lakes dried and then reflooded was updated to take advantage of the flexible TUFLOW-FV mesh system and further developed to better resolve rainfall-runoff dynamics, seepage and the effect of lake seiching on acid mobilisation. By taking advantage of the flexible resolution, the updated module increased the resolution of riparian zone bathymetry and hydrogeochemical dynamics in critical areas to better simulate acidity generation and the mobilisation of acidity to the Lower Lake in these key areas. Overall the coupled TUFLOW-FV AED2 model approach can simulate several pathways of acid fluxes including seepage, overland flow and diffusion from rewetted soil following refilling or from temporary lake seiching (Figure 67).

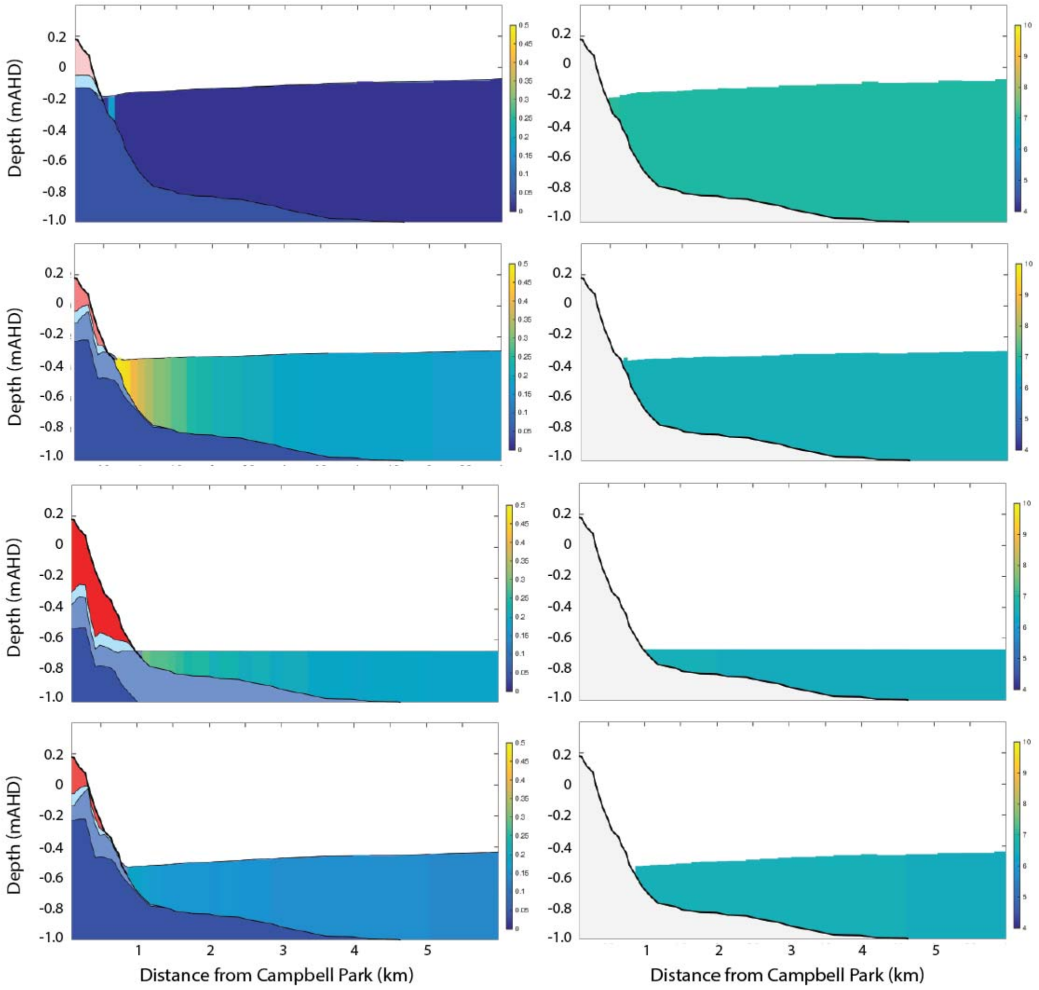


Figure 69. Snap shots of a Lake Albert shoreline simulation from TUFLOW-FV–AED2, showing lake level drawdown (first three rows) and partial refilling (bottom row). The left indicates predictions of the soil exposure and acidification (red indicates the degree of acidification) and water table position relative to the lake level. The water colour indicates the contribution of surface runoff or groundwater seepage form the soil contributing to the lake volume (0-1 arbitrary units). Predictions on the right show lake pH, in this case indicating the lake alkalinity was able to buffer the received acidity load.

Findings

The model competently reproduced the dynamics of conservative or slow-reacting species. Species subject to high turnover rates (e.g., the dissolved nutrients) and general water quality attributes were also reproduced well. Parameters that require further calibration included soil biogeochemistry, soil acidity and lake water pH and alkalinity. Overall, the model predictions were consistent with empirical data and conceptual models for the region, with the advantage of being able to interpolate in space and extrapolate in time.

Several key findings were evident from analysis of the model predictions. Groundwater seepage was found to be a low overall contributor to acid transport. Surface runoff over previously acidified soil was a much more significant pathway for acid transported to lake surface waters. Exposed soil near the lake shore were rarely high contributors of acidity, due to shallow depth of oxidation. However large seiche events, particularly in Lake Albert, could reach acidified soils with deep oxidative fronts at relatively large distances away from average lake levels.

Whilst acidification risk was prevalent across the Lower Lakes, emergence of acidification (hazard) was the result of highly nonlinear threshold behaviour (e.g. rainfall threshold exceeded following critical antecedent conditions, with ponded water sitting below critical volume thresholds). Therefore, a coalescence of favourable hydrologic conditions and geomorphological settings are required for surface water acidification. As a result, hot-spot locations was unlikely to change between drought cycles (Figure 70). Furthermore, whilst the main body of Lake Alexandrina is unlikely to go acidic if water levels are kept above -1.5 m AHD, Lake Albert was at greater risk of acidifying at low water levels. The use of the Narrung Bund to maintain the level in Lake Albert above -0.5 m AHD was considered an appropriate and successful management strategy to prevent surface water acidification in Lake Albert during the Millennium Drought. The critical water levels to prevent surface water acidification established in previous modelling efforts were supported, with greater confidence, by the present model development. The 'trigger levels' for Lake Alexandrina and Lake Albert are -1.5 and -0.5 m AHD respectively.

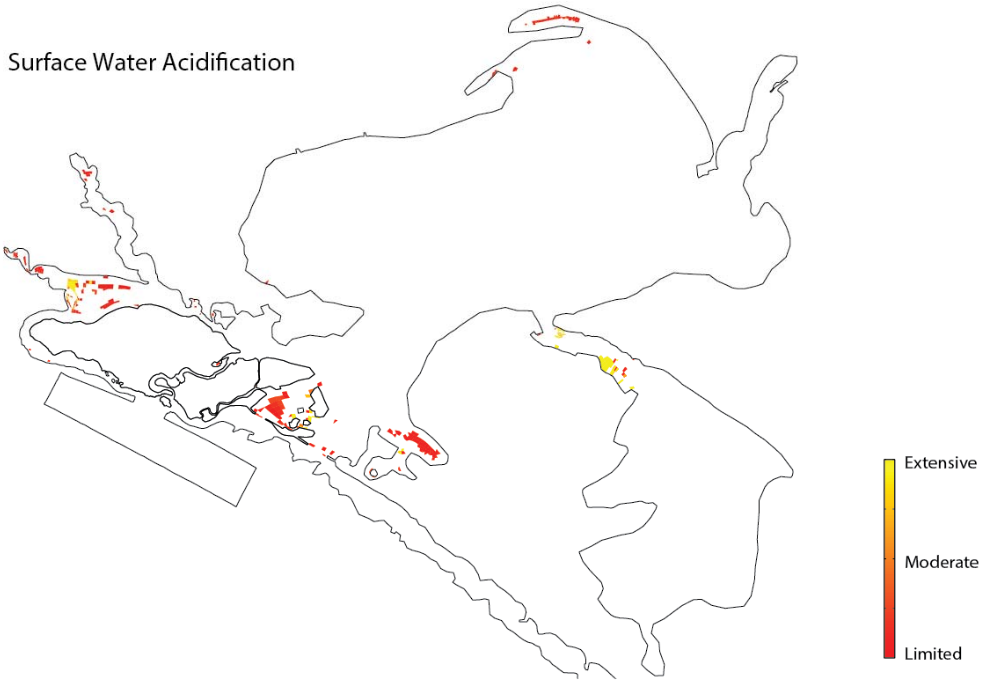


Figure 70. Summary map indicating locations of surface water that experienced a pH <4.0 during the 2009-2010 period as simulated by the model.

The re-filling of the Lower Lakes at rates experienced during 2010 did not lead to acidification, as the pulse of acidify following re-wetting, and the subsequent diffusive flux, was not significant enough to cause a substantial drop in the alkalinity or pH of the main Lake water bodies. In contrast, slow re-filling of the Lower Lakes may result in larger fluxes of acidity and metals into lake surface water and represent an increased risk of acidification.

Whilst not directly assessed with the full 3D model, soil diagenesis predictions run with an initial concentration of zero sulfides, suggested the time-scale for sulfide accumulation was ≥ 10 years (Figure 71). Given that the majority of previously accumulated sulfides were not exhausted during the Millennium Drought, it is likely that a renewed drought cycle, even just a few years after rewetting, would lead to a repeat of acidification of the margins.

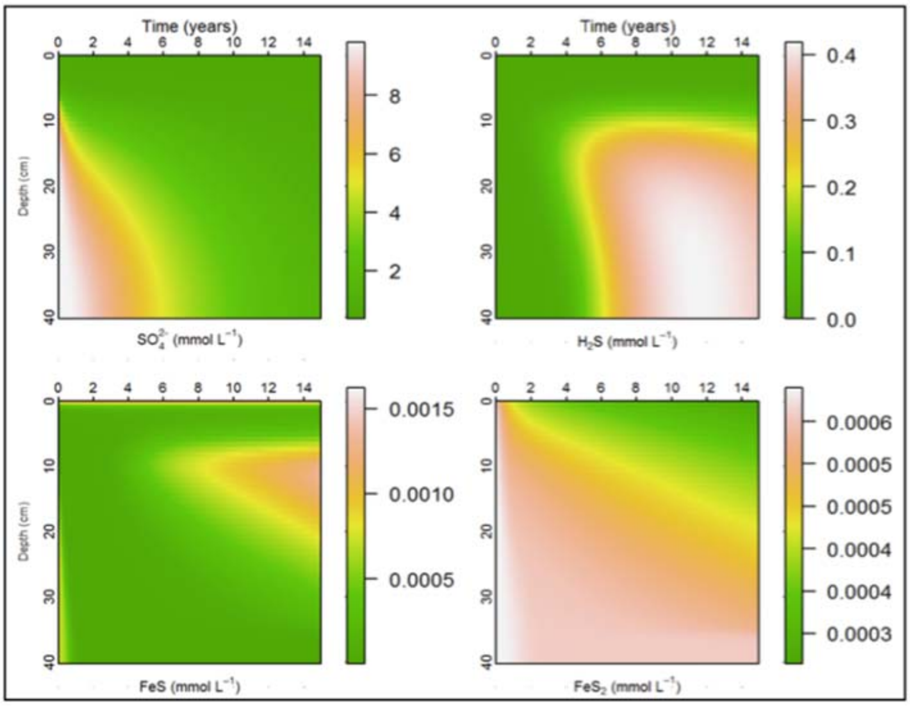


Figure 71. Soil diagenesis showing temporal trends for the consumption of sulfate and accumulation of sulfides over a 15 year period.

Model variables, including water depth, soil and/or water acidification and associated metal release, were used to assess areas of reduced habitat quality for foraging by wading birds during the Millennium Drought. Modelling results demonstrated large differences in habitat quality and total area, in response to water level variability, from 2008 to 2011. The model has shown potential to extend habitat predictions to include metal toxicity to benthic biota and *Ruppia* germination probability based on a similar approach (outlined in the Volume 1 of the full report) used to simulate habitat quality for wading birds.

Research limitations and future work

The model was observed to perform well against monitoring data for major parameters including physico-chemical properties, nutrients and turbidity. However, some elements of the model predictions remain uncertain, such as those related to soil dynamics, geochemistry and algal productivity, and future work has been identified to collect data to improve these aspects of the model. For example:

- Improved soil model parameter calibration across various sites within the domain is required to better predict spatial heterogeneity in water infiltration, recharge and seepage;
- Improved alkalinity, organic matter, nutrient and soil acid-base accounting budgets;

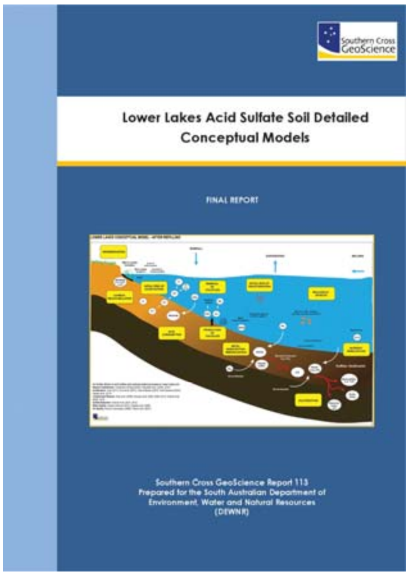
- Improved benthic metabolism parameterisation and validation and calibration of calcite precipitation and settling;
- Soil diagenesis (e.g. reformation of sulfides) dynamics in response to organic matter deposition in different regions of the domain; and
- Refinement of the habitat quality metrics and assessment approach.

2.8 Conceptual models to aid in the communication of complex ASS processes

2.8.1 Lower Lakes acid sulfate soil detailed conceptual models

Report details

Full details of the work undertaken and its findings are provided in the report:



Southern Cross GeoScience

Lower Lakes Acid Sulfate Soil Detailed Conceptual Models

FINAL REPORT

Southern Cross GeoScience Report 113
Prepared for the South Australian Department of Environment, Water and Natural Resources (DEWNR)

Ward, N.J., Sullivan, L.A., Bush, R.T. (2013). Lower Lakes acid sulfate soil detailed conceptual models. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide. Southern Cross GeoScience Technical Report No. 113.

Key research outcomes

- Conceptual models developed during this study highlighted the complex and dynamic interrelationships between acid sulfate soil and ecological processes operating in the Lower Lakes during periods of hydrological change

Aim

To develop conceptual models of the biogeochemical, hydrological and physical processes associated with acid sulfate soils in the CLLMM region.

Approach

A review of existing conceptual models covering various acid sulfate soil processes was undertaken. The concepts illustrated in the reviewed conceptual models were adapted and integrated with up-to-date knowledge of acid sulfate soil processes in the CLLMM region and where appropriate, the broader acid sulfate soil literature. This allowed the development of three conceptual models that best describe the acid sulfate soils process applicable to or operating in the CLLMM region under three different water regimes, namely:

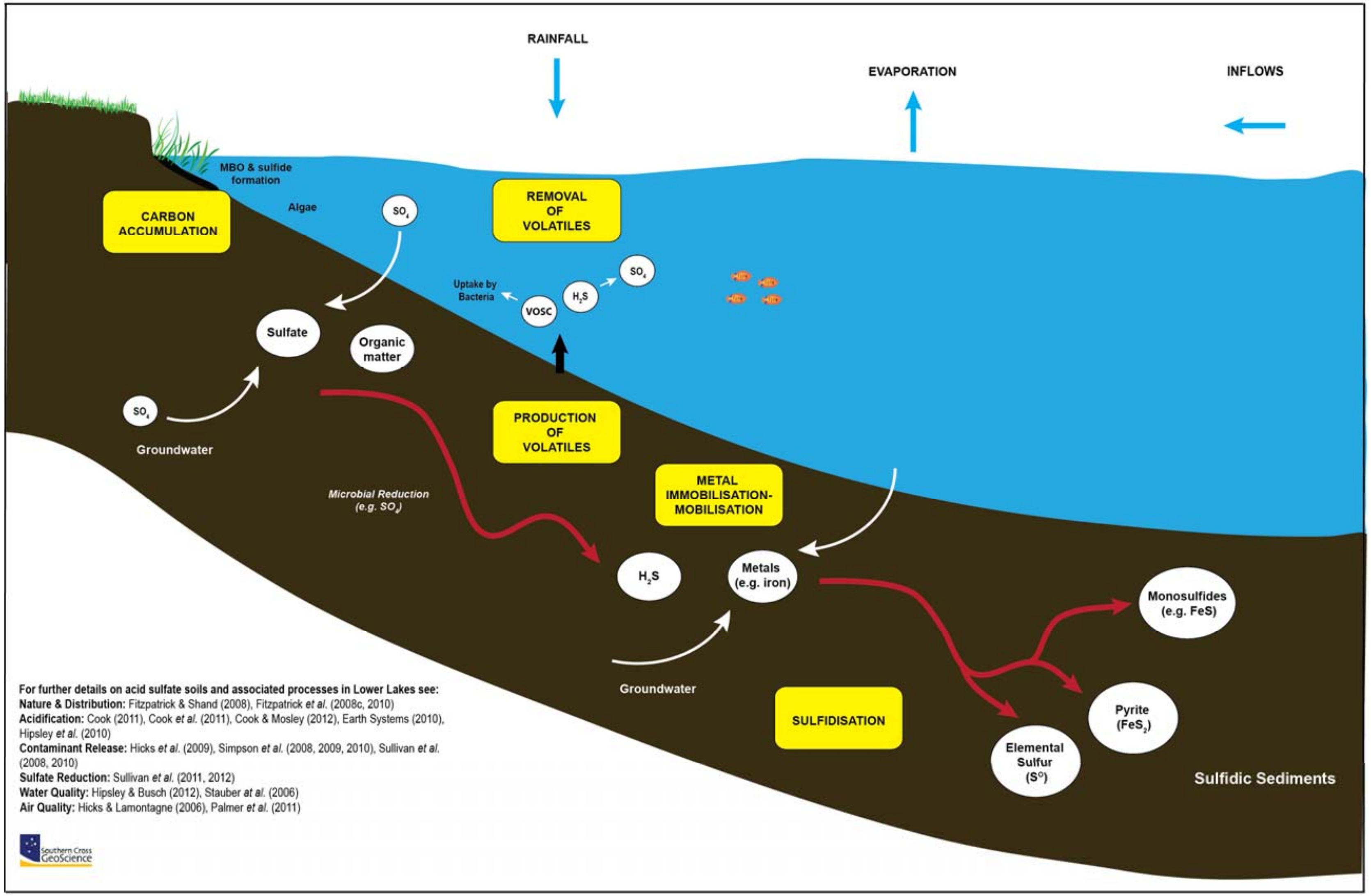
- Prior to the Millennium Drought, following an extended multiple decade period of high lake levels;
- During the Millennium Drought, after lake drawdown and the exposure of large areas of acid sulfate soils; and
- After the break of the Millennium Drought, following rapid refilling of the Lower Lakes.

The large number of acid sulfate soil processes operating in the CLLMM region, their complexity and the interrelationships between different processes precluded their incorporation into the main conceptual model. This issue was addressed through the development of individual 'flow chart' diagrams that illustrated the main processes operating in detail. These supporting figures were developed for the following processes, which are shown as 'yellow boxes' in the main conceptual models:

- Sulfidization;
- Acidification;
- Acid consumption;
- Metal immobilisation-mobilisation;
- Deoxygenation;
- Production of volatiles;
- Bioremediation;
- Carbon production and accumulation;
- Nutrient mobilisation; and
- Biological effects.

Findings

The conceptual models developed during this study highlighted how different acid sulfate soils processes operate under different hydrological conditions. They contribute to our overall understanding and communication of the complex acid sulfate soil processes operating in the Lower Lakes. Here the three main conceptual models are presented. Supporting diagrams that illustrate a number of acid sulfate soil processes (shown as 'yellow boxes' below) in further detail, can be found in the full report.

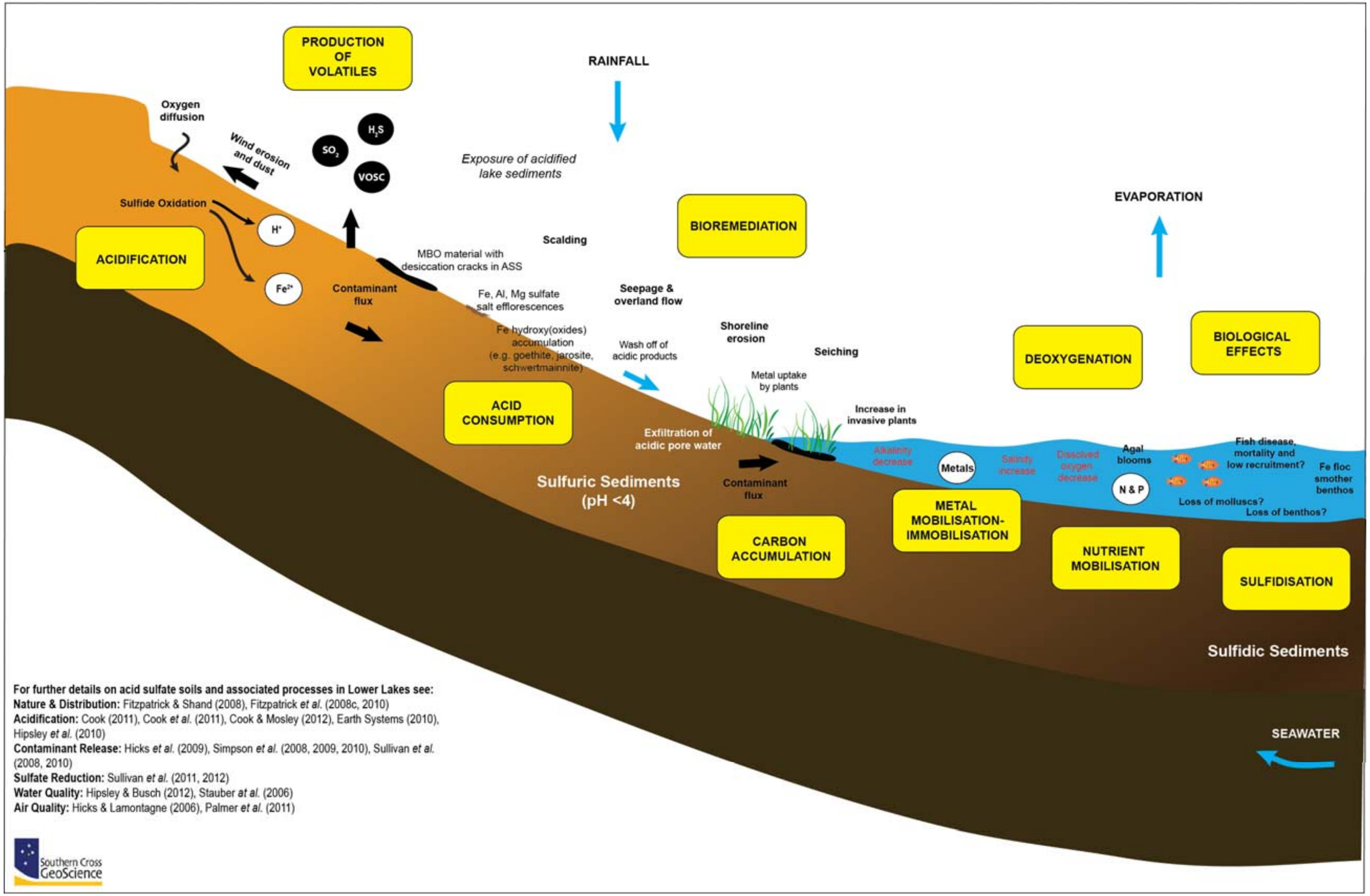


LOWER LAKES CONCEPTUAL MODEL - UNDER STABLE CONDITIONS

For further details on acid sulfate soils and associated processes in Lower Lakes see:
Nature & Distribution: Fitzpatrick & Shand (2008), Fitzpatrick *et al*. (2008c, 2010)
Acidification: Cook (2011), Cook *et al*. (2011), Cook & Mosley (2012), Earth Systems (2010), Hipsley *et al*. (2010)
Contaminant Release: Hicks *et al*. (2009), Simpson *et al*. (2008, 2009, 2010), Sullivan *et al*. (2008, 2010)
Sulfate Reduction: Sullivan *et al*. (2011, 2012)
Water Quality: Hipsley & Busch (2012), Stauber *at al*. (2006)
Air Quality: Hicks & Lamontagne (2006), Palmer *et al*. (2011)

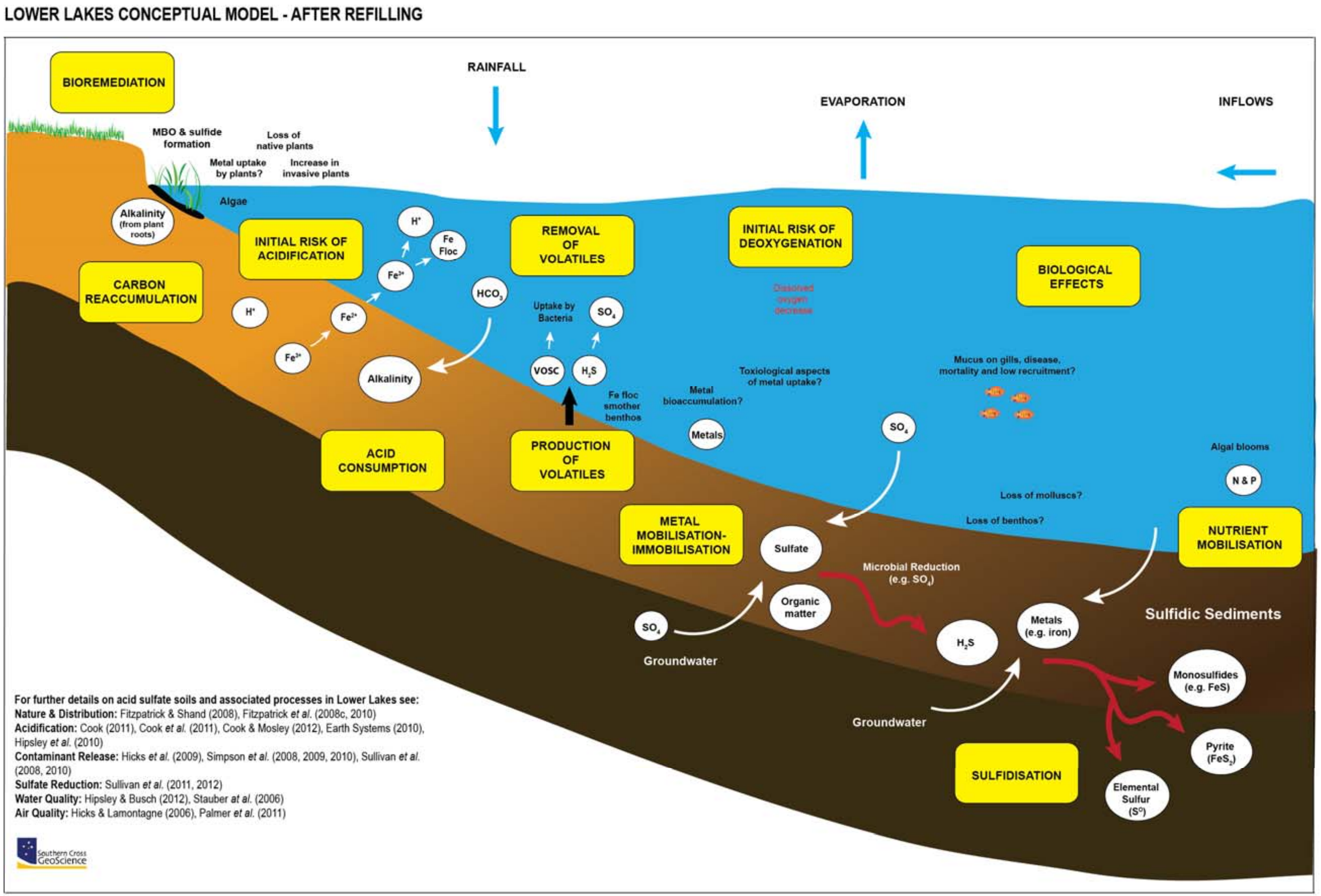
Figure 72. Conceptual model of the main acid sulfate soil related processes in the Lower Lakes under stable conditions.

LOWER LAKES CONCEPTUAL MODEL - DROUGHT CONDITIONS



For further details on acid sulfate soils and associated processes in Lower Lakes see:
Nature & Distribution: Fitzpatrick & Shand (2008), Fitzpatrick *et al.* (2008c, 2010)
Acidification: Cook (2011), Cook *et al.* (2011), Cook & Mosley (2012), Earth Systems (2010), Hipsley *et al.* (2010)
Contaminant Release: Hicks *et al.* (2009), Simpson *et al.* (2008, 2009, 2010), Sullivan *et al.* (2008, 2010)
Sulfate Reduction: Sullivan *et al.* (2011, 2012)
Water Quality: Hipsley & Busch (2012), Stauber *at al.* (2006)
Air Quality: Hicks & Lamontagne (2006), Palmer *et al.* (2011)

Figure 73. Conceptual model of the main acid sulfate soil related processes in the Lower Lakes under drought conditions.


LOWER LAKES CONCEPTUAL MODEL - AFTER REFILLING

For further details on acid sulfate soils and associated processes in Lower Lakes see:
Nature & Distribution: Fitzpatrick & Shand (2008), Fitzpatrick *et al.* (2008c, 2010)
Acidification: Cook (2011), Cook *et al.* (2011), Cook & Mosley (2012), Earth Systems (2010), Hipsley *et al.* (2010)
Contaminant Release: Hicks *et al.* (2009), Simpson *et al.* (2008, 2009, 2010), Sullivan *et al.* (2008, 2010)
Sulfate Reduction: Sullivan *et al.* (2011, 2012)
Water Quality: Hipsley & Busch (2012), Stauber *at al.* (2006)
Air Quality: Hicks & Lamontagne (2006), Palmer *et al.* (2011)

Figure 74. Conceptual model of the main acid sulfate soil related processes in the Lower Lakes following lake refilling.

Research limitations and future work

The development of these conceptual models occurred in 2013 and thus do not include findings made after this date. For example, while key processes controlling the release of metals from acid sulfate soils are included in these conceptual models the ecotoxicological impacts of the released metals on the surrounding aquatic environment are not included. In addition to the above, a number of other processes operating in the Lower Lakes including contaminant transport, bioremediation and carbon sequestration and reaction kinetics were not fully explained due to knowledge gaps. Some of these knowledge gaps have been answered partially or in full since these conceptual models were developed, however others remain unanswered. It was recommended that the conceptual models developed in this project were regarded as frameworks that should undergo periodic revision as new knowledge and understanding became available. The conceptual models also have significant potential to better illustrate the hydrological, ecological and physico-chemical properties unique to the CLLMM region. An update of the conceptual models presented above would further enhance their utility and relevance to the CLLMM region.

3. Key research theme summaries

3.1 Properties and spatial distribution of ASS materials in the CLLMM region

This key research theme extends from a single project that commenced at the beginning of the 'Research Priorities' Management Action in 2010. The aim of the project was to map the spatial extent of acid sulfate soils and their properties in the CLLMM region. Prior to this, the distribution of acid sulfate soil sub-types in the CLLMM region was not well known and had been estimated from a small number of representative sites around the Lower Lake margins. Therefore a spatially reliable database was needed that accurately mapped the distribution and variability of a number of acid sulfate soil physical and chemical parameters. These included pH, acid generation potential, acid neutralising capacity and soil texture. A total of 330 soil profiles were collected, resulting in a substantial increase in the resolution and reliability with respect to knowledge about acid sulfate soil subtype. A key outcome of this project was the provision of quantitative three dimensional acid base accounting data that was successfully incorporated into future modelling efforts. The database significantly reduced the uncertainty in model predictions and has continued to support modellings efforts throughout the Management Action.

At the time of sampling, approximately 20% (18,391 ha) of the total study area (89,219 ha) contained sulfuric materials ($pH < 4.0$). Areas of concern identified through the study included Loveday bay, Clayton, Boggy Lake, Dog Lake, Finniss River and Currency Creek. A further approximately 80% of the total area contained hypersulfidic materials at the time of sampling. These materials have the potential to acidify and form sulfuric material. Identifying the location and depth of these materials and quantifying their net acidity potentials was important. At the time of the study, levels in Lake Alexandrina and Lake Albert were -0.8m AHD and -0.2 m AHD respectively. Drought conditions continued following the survey and as lake levels lowered the acidification potential of some of the hypersulfidic material identified in this study was realised.

Although a 'snap shot' in time, data from the soil survey can be reinterpreted by considering the transformations likely to take place following changes in hydrological conditions. Predictive modelling efforts to simulate the post-drought recovery of oxidised acid sulfate soil material and subsequent low water events have been hindered by a lack of knowledge regarding post-drought net acidity data. It is not known if acidity generated during the Millennium Drought was removed from the system when sulfuric materials were rewet in late 2010, or if acidity remains. Monitoring of rewetted acid sulfate soils (Section 2.5) highlighted that in many cases there were no changes to net acidity between drought and post-drought periods, suggesting acidity has remained in the system. Further work to update the spatial soil database, through a combination of expert reinterpretation of the existing data and new field soil surveying, will increase the confidence of predictive modelling outputs

3.2 Air quality impacts related to ASS

This key research theme consists of a single project. Low water levels in the CLLMM region exposed large areas of lake bed soils, resulting in more frequent dust storm events. Many of the exposed lake bed soils contained acid sulfate soil materials that had become severely acidified (pH < 4). In addition, acid minerals had accumulated as salt efflorescence on the surface of the soils as a result of evapoconcentration. There were government and community concerns of potential human health risks and air quality impacts arising from exposure to the dust blown of the acidic soils. Extensive sampling and analysis of dust and drinking water samples from household rainwater tanks in communities around the lower lakes found that the windblown dust did not present a public health risk. However, it was noted that communities around the Lower Lake had to contend with an increased dust nuisance during the Millennium Drought period, with increased complaints to SA Health reordered during this period. The report recommended that future management strategies that may result in increased frequency of dust storm event consider this issue.

3.3 Pyrite oxidation rates in the Lower Lake soils

The need to better determine the rate of pyrite oxidation (and in turn acidity generation) in acid sulfate soils typical of the CLLMM region was identified as a critical knowledge gap needed to inform management decision making. In part, this was due to the high sensitivity of predictive modelling results to the rate of pyrite oxidation. In early modelling efforts these parameters were not known and literature values had to be used. The wide range of pyrite oxidation rates reported in literature (from 0.00001 wt% to 10 wt% available pyrite per day) made the selection of an appropriate rate difficult. In this study, the pyrite oxidation rates specific to the CLLMM region were determined as a function of soil texture (e.g. sands vs clays) and moisture content. Pyrite oxidation rates were found to be highly dependent on soil moisture, with pyrite oxidation rates decreasing as moisture content increased. This was attributed to decreases in oxygen availability as soils became saturated. Also notable was an observable decrease in pyrite oxidation rates when sands were extremely dry. Maximum pyrite oxidation rates of 0.78 wt% and 1.24 wt% available pyrite per day were recorded for clays and sands, respectively. At maximum rates of pyrite oxidation, the time taken to oxidise all available pyrite was calculated to occur within 80 and 128 days (approximately 3 to 4 months), for sand and clay respectively. The relatively fast pyrite oxidation rates recorded in this study were consistent with field observations and pH incubation tests and were comparable to pyrite oxidation rates reported in literature for unconsolidated soils.

The method used to calculate the rate of pyrite oxidation relied on the assumption that all sulfur in the sample existed as pyrite. There are known (and potentially significant) interferences associated with using total sulfur as a proxy for pyrite concentration. Therefore, it is likely that the reported pyrite oxidation rates represent the upper or maximum rates of pyrite oxidation and may be an overestimation of the true in situ oxidation rates. A repeat of the experiment using the routine and accurate chromium reducible sulfur method would more precisely determine rates of pyrite oxidation. The report was limited to the investigation of pyrite oxidation rates in two different sulfidic materials. Acid sulfate soils in the Lower Lakes region are known to be highly heterogeneous. Hence, future work that includes a larger number of samples would also help to refine rates of pyrite oxidation in the CLLMM region.

3.4 Contaminant mobilisation and transport

The main aims of this key research theme were to determine the impacts of acidification on soils, and the potential for contaminant mobilisation and transport to tributaries and the Lower Lakes. A specific aim was also to assess the relative impacts of seawater vs. freshwater inundation of the Lower Lakes. A number of studies were completed between 2009 and 2013, continuously building on identified data gaps to allow improvements in the modelling of acidic and solute fluxes to the water column.

The strategy was to focus on key sites where detailed field studies could support the development of conceptual models which were subsequently incorporated into a solute transport model of acidity to the water column of the Lower Lakes.

Early attempts at assessing acidity and contaminant fluxes highlighted key data gaps. Some of these were determined by laboratory (Sections 2.4.3 and 2.4.4) and in situ field mesocosms experiments (Section 2.4.2) using seawater and freshwater inundation for the dominant soil types around the Lower Lakes (sandy and clayey soils). The field mesocosm study showed that seawater and freshwater produced very different results in regard to water quality. There was a greater initial mobilisation of acidity and decrease in pH with seawater inundation, despite seawater having higher alkalinity than the freshwater. This was due to the higher ionic strength of seawater and displacement of acidity and contaminants into the water. There were also large differences between clayey and sandy soils, for example, the surface water became acidic only above the clayey soils. The reason why the surface water didn’t become acidic above the more permeable sandy soils may in part be due to a loss of water through advective downward flow. The study concluded that a single charge of water was insufficient to neutralise stored soil acidity even for the sandy soil where the quantity of acidity was relatively low. This showed that several flushes of water are required to neutralise and dilute soil acidity unless internal alkalinity is generated through reduction reactions. The field study provided critical parameters for incorporation into later transport models (Section 2.4.6) as well field measurements of in situ flux (albeit under conditions different from reality).

Experimental studies on undisturbed soil cores from the same sites were also completed in corer-reactor apparatus in the laboratory, but over a much shorter timescale. Although the pH of surface waters in these studies remained circumneutral, there was a much greater release of contaminants from the seawater inundation. It was also observed that many of the porewaters at both sites were very acidic and contained high concentrations of metal contaminants, much more so in those inundated with seawater compared to freshwater. Resuspension experiments also showed that pH decreased, although typically remained above pH 5. It was concluded that only short term exceedances to the WQG for metals would be expected to occur if the pH of the overlying water remained above pH 6. Dilution of the waters overlying the inundated soils with surrounding waters would be expected to result in both increased water pH and attenuation of dissolved metals released from the soils. Exceedances of water quality guidelines would only be expected in shallow regions of the Lower Lakes where exchange with the main lake body is restricted. Other studies focused only on shallow (<15 cm) samples, but from a larger number of sites (15 locations in the Lower Lakes). Although the sites mainly had low acidity (probably due to previous downward flushing), the conclusions were in agreement that seawater posed a much higher risk of acidification than freshwater in the short term. This study also found little difference in the rates of sulfate reduction on the water salinity, instead noting that organic carbon appears to be the limiting factor in this and other reactions that generate internal alkalinity and therefore acid neutralisation. Changes in the flux of solutes to inundated waters did not exhibit a simple linear trend, and it was concluded that there are likely to be changes in hydrochemistry and biogeochemical processes with time following inundation.

The range and chemical forms of contaminants in acid sulfate soils was characterised in a study of soil cores from selected impacted sites (Section 2.4.5). Porewater extractions and a sequence of solid-phase extractions showed that the distribution of contaminants varied enormously with depth as well as between sites. At the time of sampling, different contaminants were associated with different mineral or organic phases (operationally defined) and these in turn are controlled by the ambient geochemical conditions in the soil which varied with depth. The soil profiles at the time of sampling were acidic, two years after inundation, and were still in a state of continued change as the soils have not returned to pre-drought conditions. It was concluded that the rates of contaminant release may be more rapid in near future droughts because newly formed minerals tend to be more reactive than aged minerals.

The data from some of the previous studies in the Lower Lakes were used as a basis to develop models for acidity flux to lake surface waters. The earliest work focussed on estimating flux based on water table and soil water content data monitored during the Millennium Drought period. This showed that lateral sub-surface flow was likely to be insignificant, and that groundwater movement would at times be from the lake shore inland. This would in effect minimise any direct acidic groundwater flow to the Lower Lakes. Significant acid flux to the Lower Lakes was considered more likely to come from runoff and exfiltration. Estimates of worst case acid fluxes via exfiltration (i.e. transport out of the soil) and runoff were estimated and showed that during the time of monitoring, acid fluxes were unlikely to have had a significant impact on the alkalinity of Lake Alexandrina at the water levels encountered during this time. The same analysis for Lake Albert showed that for the worst case scenario the alkalinity in the lake could be overwhelmed by the acid fluxes out of the soils. Calculated fluxes were much lower in this study than suggested in earlier studies.

A later modelling study focused on investigating the physical properties of the soils, data which until this study had been estimated, limiting the development of more realistic models (Section 2.4.6). The data were incorporated in the HYDRUS model to estimate hydraulic conductivity, and to simulate oxygen, water and solute movement into the soils. The cracking of clays was found to have a big influence on water quality by enhancing the transport of acidity to the water column. Simulations for sandy and clayey soil suggested that the most dangerous period was immediately following refilling, and that subsequently only clayey soils were likely to continue to release acidity to the surrounding water. Overall, the results suggest that if the Lower Lakes have not turned acidic upon refilling they are unlikely to do so in the future under a relatively stable water level scenario.

Further models were developed for both diffusion-only and advection plus diffusion processes to determine the effect of reflooding of the Lower Lake margins. The calculated flux results were similar to those measured in the field mesocosm study giving some confidence to the model application. The transport models showed that in the absence of significant advection into the soils, that acidity in the soils, and acid fluxes to the surface water will remain high for some time. The rates of recovery are likely to be very slow, of the order of years to decades. The conclusions agreed with earlier work suggesting that for worst case scenarios whole lake acidification was unlikely for Lake Alexandrina, except locally. However, the acid leeched from soil in Lake Albert could be greater than the alkalinity store for Lake Albert and could result in whole lake acidification.

Following reflooding, a preliminary study was undertaken to quantify actual contaminant fluxes at selected impacted sites using benthic chambers (Section 2.4.7). Although increases in acidity were measured inside the chambers, this was outweighed by alkalinity increases. This was considered a ‘worst-case scenario’. However, this was an early study and it was not clear if the changes were an artefact of the methodology used.

This research theme has contributed significantly to modelling and understanding acidity transport to the Lower Lakes. Although there are significant differences in the quantification of acidity fluxes in different studies, the conclusions are similar and pointed to a much higher risk to Lake Albert than Lake Alexandrina under Millennium Drought conditions. The incorporation of biogeochemical processes was considered an area of future research, and this would require a much closer and better synergy between laboratory, field and modelling activities. This would then allow a much better basis on which to link acid and contaminant fluxes, and biogeochemical processes to ecological impacts throughout the food chain.

3.5 Post reflooding recovery of sulfuric materials

The main aims of this key research theme were to determine the time-scales required for severely acidified acid sulfate soils to recover to pre-drought conditions following rewetting, and determine the factors affecting the rates of recovery. A number of projects representing this key research theme were conducted from 2010 to 2014, providing approximately 2.5 to 3.5 years of monitoring and research into the post- reflooding recovery of sulfuric materials.

The recovery and neutralisation of oxidised and acidified acid sulfate soils is complex and depends upon a number of factors including; whether it is a surface or sub-surface soil layer, the degree of acidification, the presence (or absence) of jarosite, the presence (or absence) of organic matter, and soil texture and soil cracking.

Under favourable conditions, recovery and neutralisation in the surface layers can occur quickly. Results from the projects showed that the pH of many of the surface soils recovered to circum-neutral conditions within approximately 12 months. This was attributed to a range of assisting factors. Sandy soils with coarse textures are more permeable than fine textured clayey soils, allowing acidity to be neutralised and/or flushed out more easily. The common occurrence of sandy textured surface layers around the margins of the Lower Lakes was one reason surface layers recovered quickly. Sulfuric sandy soils commonly contained less acidity than sulfuric clayey soils. The lower amount of acidity requiring neutralisation in sandy soils was another factor assisting the recovery of surface layers. Finally, surface layers typically had higher concentrations of organic carbon that were able to fuel reduction processes that consume acidity, again assisting in the recovery and neutralisation of surface layers. The influence of organic carbon concentration on recovery rates is discussed further below.

Under less favourable conditions, such as deeper clayey soils, recovery can take several years. Historically, sandy acid sulfate soils are considered more hazardous than clayey soils as they lack buffering capacity and can rapidly acidify under drying conditions. However, it was shown that clayey textured soils often present the greatest hazard, as once oxidised they contained more acidity and took longer to recover when rewetted.

A dominant factor slowing the rate of soil neutralisation was the presence of retained acidity (e.g. jarosite). When a soil contained retained acidity in the form of jarosite, the gradual release of acidity as the jarosite slowly dissolved buffered the soil at a low pH for longer periods of time, reducing the rate of recovery. As a consequence of persisting low pH, the presence of jarosite also prevented or delayed alkalinity producing reduction processes that are inhibited at low pH values.

The rapid rates of acidification combined with the potentially long time-scales required for recovery, highlights that the best management option for acid sulfate soils is to prevent them from being disturbed in the first place.

The low concentrations of organic carbon in acidified lower lake soils was identified as a chief factor limiting sulfate reduction following reflooding. Sulfate reduction is an important process that generates alkalinity, or in other words consumes acidity. If sulfate reduction is limited, the development of alkalinity to neutralise acidity will also be limited, and recovery may be slowed. Phytoremediation, via revegetation of the exposed lake bed, aimed to increase the availability of organic carbon in order to facilitate sulfate reduction and aid recovery. The impacts of phytoremediation techniques on the recovery of reflooded acid sulfate soils that acidified during the Millennium Drought were investigated in a series of studies over a 2.5 year period.

Overall, the series of reports observed a continued improvement in soil pH and acidy values following rewetting over the 2.5 year monitoring period. The recovery of rewetted sulfuric soils was attributed to a number of processes, some related to phytoremediation, some not. Phytoremediation (via revegetation) was successful in providing a source of organic matter to drive sulfate reduction reactions and aid recovery. When and how much organic matter was added to the soils was dependent on the type of vegetation used for phytoremediation. Trialled revegetation species including Bevy Rye, *Cotula*, and *Juncus*, were unable to survive inundation. These vegetation types initially supplied considerable amounts of organic matter to the soil, but were not able to replenish organic matter once the initial supply was depleted. Conversely, *Phragmites* was able to survive inundation and provided an ongoing supply of organic matter. The ongoing supply of organic matter continued to drive sulfate reduction over the 2.5 year monitoring period and resulting in the production of iron monosulfides (e.g. monosulfidic black ooze) and pyrite. The formation of these minerals (via sulfate reduction) generated alkalinity in the soil and improved pH but also resulted in a build-up of potential sulfidic acidity.

Hence, the use of inundation tolerant plant species (e.g. *Phragmites*) may result in an increased acidification hazard due to the accumulation of pyrite. Acidification hazards were avoided almost completely when inundation intolerant vegetation was used for phytoremediation.

A positive effect of revegetation was the stabilisation of exposed lake margin soils against erosion by wind and water. By substantially reducing the loss of surface soil layers revegetation prevented the highly acidic sub-surface soil layers from becoming exposed and making direct contact with the surface water upon reflooding.

It is important to note that there are a number of limitations associated with phytoremediation (Section 2.5.2). These limitations, combined with the observation that surface soils not assisted by phytoremediation were rapidly neutralised at approximately the same rates as revegetated sites, mean the use of revegetation for the purpose of phytoremediation needs to be considered carefully. Further research is required to better quantify the associated acid sulfate soil related risks and benefits of this management technique before it can be considered as a panacea for the remediation of acid sulfate soils without caveats.

In both monitoring and phytoremediation investigations, no consistent appreciable changes to soil net acidity were observed. Therefore, despite an apparent partial recovery of soil pH, the degree of acidification hazard in the Lower Lakes remains high and is largely unchanged from the pre-drought to drought to post-drought cycle. This means future droughts will likely see a rapid return to the acidified soil conditions of the Millennium Drought.

3.6 Benthic ecology and ecotoxicology impacts related to ASS

This key research theme comprises the 'Lower Lakes Ecotoxicology Project' and represents three years of research and monitoring. Acid sulfate soil research conducted prior to the 'Lower Lakes Ecotoxicology Project' focused mainly on the physico-chemical properties of these soils in the Lower lakes. Findings from these research projects consistently demonstrated that a wide range of contaminants, including metals, acidity and nutrients, are released when acid sulfate soils are rewet. Many of these contaminants were at elevated concentrations potentially toxic to aquatic and benthic biota (Section 2.4). Hence, it became necessary to determine the extent and significance of ecotoxicological effects resulting from acid sulfate soil acidification as they transitioned through recovery following rewetting. The 'Lower Lakes Ecotoxicology Project' aimed to address the following objectives:

- Assessment of spatial and temporal variation of ecotoxicological effects of drought-induced acidification in the soils of the Lower Lakes that are transitioning through recovery;
- Identification of hot-spots in the Lower Lakes region based on the SQT approach;
- Assessment of contaminant bioavailability in acid sulfate soils under in situ conditions; and
- Evaluation of toxic and synergistic effects of key contaminants to selected key aquatic organisms.

To assess the bioavailability of contaminants and, in turn, the toxicity of recovering acid sulfate soils that had severely acidified in the Millennium Drought, the surface waters and porewaters of four sites were characterised. The ecotoxicological assessment of porewaters confirmed that contaminants generated through acid sulfate soil acidification and were still present in deeper soil layers four years after rewetting, were severely toxic to aquatic organisms. Surface water generally exhibited no acute or chronic toxicity to biota. However, the upward flux of contaminants from severely toxic sub-surface soil layers poses a moderate to high level risk to the biota inhabiting surface waters and the surficial soil layers. The cause of toxicity was attributed to a combination of stressors including low pH, elevated salinities and high metal concentrations.

The SQT approach was used to more confidently assess the ecotoxicological effects resulting from acid sulfate soil acidification. The SQT approach provided a method for the integrated assessment of ecosystem health. By integrating multiple lines of evidence, the SQT approach was able to generate 'weight of evidence' and provide greater certainty of the toxic effects of contaminants released from acid sulfate soils. Three lines of evidence were used, namely soil chemistry, soil ecotoxicity and benthic community assemblage. Through the SQT approach it was found that most surface waters were likely not impacted from acidification. However, two hot-spot sites, Boggy Creek and Boggy Lake, remain impacted from acid sulfate soils acidification and have the potential for detrimental ecological issues.

During the above studies, it was recognised that aquatic biota were being exposed to mixtures of contaminants with concentrations above those considered potentially toxic. It became necessary to investigate the toxicity of mixtures of dissolved metals, rather than the toxicity of individual metals in isolation, to better understand the likely response of aquatic organisms in situ. The combined toxicity effects of mixtures of dissolved metals are not easily predicted and can be additive, greater than additive (i.e. synergistic), or less than additive (i.e. antagonistic). The freshwater snail (*Physella acuta*) and midge larvae (*Chironomus tepperi*) were used as test species in bioassays to assess the toxicity of high concentrations of dissolved metals and their binary combinations. Binary metal mixtures dominantly exhibited less-than-additive (antagonistic) toxicity to midge larvae. In contrast, binary metal mixtures dominantly exhibited greater-than-additive (synergistic) toxicity to the freshwater snail. The significant difference in test species sensitivity highlighted the importance of using more than one organism for metal toxicity testing.

The significant deviations from additive binary metal toxicity may be a result of differences in biological processes (i.e. species dependant).

Binary metal combinations identified as having synergistic toxicity in this study should receive priority in future investigations. Research to clarify if deviations from additive behaviour are related to synergistic biological effects within the organism or due to changes in bioavailability resulting from differing metal speciation would help inform ecotoxicological risk assessments for metal mixtures under varying pH conditions.

3.7 Development of an integrated CLLMM water quality response model

The main aim of this key research theme was to develop an integrated hydrodynamic-geochemical model for the CLLMM region capable of simulating lake and acid sulfate soil conditions following multiple year management scenarios and that could be used to support decision making and management. Initial modelling efforts occurred prior to the 'Research Priorities' Management Action (Section 1.4). As the 'Research Priorities' Management Action progressed, more knowledge gaps in other key research themes became filled and greater amounts of field monitoring data became available. Research findings from each of the key research themes were used to further develop or parameterise the model. The growing databases of monitoring data were then used to better validate the results of modelling simulations. Improvements to the integrated hydrodynamic-geochemical model were made on three occasions, corresponding with the commencement, midpoint and conclusion of the 'Research Priorities' Management Action.

Following its development and calibration the CLLMM-WQRM model was unique in its ability to model CLLMM hydrodynamics, water quality, pyrite oxidation (including acid generation and neutralisation kinetics) and acidity transport processes.

The calibrated model performed well in hindcast simulations. The model is currently capable of simulating the complex hydrodynamics and biogeochemistry of the system from 2008 to 2015, covering the drought to post-drought period. In particular the timing, severity and recovery from the hot spot acidification events (e.g. the acidification of the Currency Creek tributary in 2009) was adequately modelled in hindcast simulations. However, some areas predicted to acidify in hindcast simulations were not observed to acidify in reality. This highlights that there is uncertainty associated with model predictions and that models should only be used as a predictive tool within an adaptive monitoring framework and not in isolation.

Various forecast simulations investigated potential future conditions in the Lower Lakes for a range of potential future flow scenarios and management regimes. The chief aim of the forecast simulations were to determine critical water height levels (termed ‘trigger levels’) for Lake Albert and Lake Alexandrina at which the risk of lake acidification became too high. This risk was defined as lake's lowest level prior to pH dropping below 6, even if this occurred at some time in the future (i.e. at a delayed time after lake refilling). Based on modelling, the key management recommendation to prevent lake acidification in Lake Albert is to maintain water levels above -0.5 m

AHD. Similarly, the ‘trigger level’ for Lake Alexandrina was set at – 1.5 m AHD. These threshold ‘trigger levels’ for minimum water levels in Lakes Alexandrina and Albert set in this fist modelling effort continued to be supported following subsequent model refinements in 2012 and 2016. Whilst the main body of Lake Alexandrina is more resilient against surface water acidification. Lake Albert is at greater risk of acidifying at low water levels. The use of Narrung Bund to maintain the level in Lake Albert above -0.5 m AHD was considered an appropriate management strategy and successfully prevented Lake Albert from acidification during the Millennium Drought.

In 2012, a number of improvements were made to the original ELCOM-CAEDYM-ASS model. Improvements included the revision of the acid sulfate soils module, the addition of turbidity and refinements to nutrient cycles. In the two years since previous modelling efforts, a substantial quantity of new field-based monitoring data had been generated. This data was used to rigorously test the performance of the model over the period 2008 to 2011, and guide calibration of model parameter sets. Where available, model parameterisations and justifications were based on findings made in associated concurrent Lower Lakes’ research projects. Again, the model performed well in hindcast simulations and was able to capture acidification events observed in Loveday Bay, Boggy Creek and Currency Creek. The stability of pH in Lake Albert and other areas in Lake Alexandrina was also accurately simulated. This was in part due to the fast rate of refilling of Lakes Albert and Alexandrina following the break of the Millennium Drought. In contrast, if the Lower Lakes were refiled more slowly at the break of the drought it is likely that larger fluxes of acidity and metals into lake surface water would have occurred, representing an increased risk of acidification. This conclusion is also supported by reports summarised in Section 2.4.6.

The improved model was used to investigate the potential for a renewed acid sulfate soil acidification hazard if low flow conditions returned in the future. In forecast simulations, water levels in Lake Alexandrina were lowered to a minimum -1.0 m AHD. Hence, the simulation did not have as large or as fast a decline in lake water levels as in the Millennium Drought. Nevertheless, acidification events in isolated areas (e.g. Boggy Lake, Currency Creek, Loveday bay) were observed to occur within one year. The rapid acidification of the isolated areas highlights the significance of lake bathymetry on acidification 'hot-spot' occurrence. In all modelling efforts, the dominant flux of acidity to lake surface waters was observed to occur following pulses of rain. Large rainfall events collect surficial acidity in exposed marginal soils and drive its transport towards the lake edge via lateral and overland flow. In contrast, the acidification of groundwater and subsequent base flow and diffusive flux of acidity following rewetting were less significant acidity delivery mechanisms. Hence, whilst acidification risk is prevalent across the Lower Lakes, emergence of surface water acidification is the result of highly nonlinear threshold behaviour. Therefore, a coalescence of critical antecedent conditions, favourable hydrologic conditions and favourable geomorphological setting are required for surface water acidification. As a result, hot-spot locations are unlikely to change between drought cycles. Main lake water bodies generally maintained a stable pH. However, without the Clayton regulator in place to contain acidified surface water, the Goolwa channel would have received a pulse of acidification from the acidified Currency Creek tributary. This simulation demonstrated the effectiveness of the Clayton regulator in isolating poor water quality until water levels had better recovered.

Whilst not directly assessed with the full 3D model, soil diagenesis predictions run with an initial concentration of zero sulfides, suggest the time-scale for sulfide accumulation is approximately ≥ 10 years. A forecast simulation of a future drought that assumed a 'best case' scenario, demonstrated that even if all of the acidification potential realised during the Millennium Drought was removed from the system, sufficient pyrite still remained in the soil to present an acidification hazard. Given that majority of previously accumulated sulfides were not exhausted during the Millennium Drought indicated by reports summarised in Section 2.5, it is likely that a renewed drought cycle, even just a few years after rewetting, would lead to a repeat of acidification of the margins.

3.8 Conceptual models to aid the communication of complex ASS process

Conceptual models specific to the CLLMM region and the pre-drought, drought and post drought hydrological cycle were developed to aid the communication of complex aid acid sulfate soils process. The conceptual models contribute to our overall understanding of the acid sulfate soils in the Lower Lakes, and of their management requirements especially in relation to wetting and drying cycles of decadal frequency. By illustrating interrelationships between the findings from each key research theme that comprised the overall 'Research Priorities' Management Action the conceptual models will assist managers to protect the ecological character of the CLLMM region. As well as the 'Lower Lakes Acid Sulfate Soil Detailed Conceptual Models' a variety of other site or process specific conceptual models are used in a number of reports throughout the research program, highlighting their utility.

4. Conclusions and future research priorities

Overall, research activities undertaken as part of the 'Research Priorities' Management Action contributed significantly to our understanding of a wide range of acid sulfate soil processes and impacts operating in the CLLMM region. Research outputs in the key research themes represent a considerable expansion to the knowledge base, from relatively little knowledge to a sound conceptual and empirical understanding, within the relatively short timeframe of 6 years.

Of course, knowledge gaps and uncertainties remain. Future acid sulfate soil research in the CLLMM region should prioritise post-drought legacy impacts and continue to monitor the recovery of acid sulfate soil materials. Uncertain inter-drought periods mean that knowledge of acid sulfate soil status must be well established and ready to inform the appropriate management responses head of time. Otherwise, researchers and managers will again have to contend with a rapidly evolving system and managers will be forced to follow the precautionary principle. A better synergy between laboratory, field and modelling activities would further substantiate linkages between acid and contaminant fluxes, coupled biogeochemical cycles and ecological impacts throughout the food chain. In particular, microbiological controls operating in acid sulfate soils and the impacts of acid sulfate soils on the base of the food web is poorly understood and worthy of greater attention in future studies.

A number of specific research priorities were identified at the acid sulfate soils Expert Workshop held in Adelaide in June 2016 (Section 7.2; Appendix B). These research priorities are outlined below:

- The identification of 'early warning' antecedent conditions and an up-to-date knowledge of acid sulfate soil recovery status is critical to successfully responding to a future drought in the CLLMM region. This information could be readily obtained through annual or bi-annual monitoring projects. Monitoring efforts could be augmented with citizen science. It may also be possible to reuse existing soil monitoring data and the spatial acid sulfate soil database (both data and the original soil samples) in conjunction with expert reinterpretation to ascertain the likely current state of acid sulfate soils in the CLLMM region.
- Initial ecotoxicological investigations showed that contaminants released from acid sulfate soils are bioavailable to benthic organisms. Further research is required to determine if acid sulfate soils are also impacting (or have the potential to impact) higher tropic level species such as fish.
- Aluminium was frequently found to be a dominant contributor to toxicity. The speciation and in turn bioavailability of aluminium in the dynamic acid sulfate soils system is poorly understood and requires further research to better quantify associated hazards.
- Cracking in clayey soils can increase the flux of acidity to surface waters upon rewetting. Considerable heterogeneity in the spatial occurrence, abundance and type of cracking exists in the CLLMM region. Further research to investigate how these factors influence contaminant flux would help to better define potential ecotoxicological hazards posed by long term diffusive fluxes. In the same manner, it would be useful to determine the contribution of benthic bioturbation to contaminant fluxes.
- The developed conceptual models are critical in communicating the complex and extensive findings generated by the 'Research Priorities' Management Action to a wider audience. Currently, a number of processes operating in the Lower Lakes including; ecotoxicological impacts, contaminant transport, and bioremediation are not adequately communicated in the developed conceptual models. An update of the conceptual models would further enhance their utility and relevance to the CLLMM region.

5. Management implications

In a difficult environment, where researchers were challenged by rapidly evolving acid sulfate soil properties and hydrological conditions, the 'Research Priorities' Management Action successfully addressed essential information needs to underpin the effective management of the threat posed to the ecological character of the CLLMM region by acid sulfate soils.

In general, the findings of research activities conducted as part of the 'Research Priorities' Management Action supported management actions undertaken during the Millennium Drought. This included:

- The use of temporary structures to keep acid sulfate soils saturated, if not inundated, and minimise further acidification. This is because pyrite oxidation rates slow considerably when soils became more saturated (Section 2.3);

- The use of a temporary structure at Narrung to maintain water levels in Lake Albert (via pumping from Lake Alexandrina) was crucial in preventing whole lake acidification in Lake Albert. Overall, modelling pointed to a much higher risk of whole lake acidification for Lake Albert than for Lake Alexandrina (Section 2.7);
- A positive management outcome from using temporary water control structures was the ability to contain areas of poor water quality until sufficient volumes of freshwater were available to dilute and neutralise acidity. For example, the Currency Creek regulator successfully isolated poor water quality until water levels had better recovered (Section 2.7);
- Isolated acid sulfate soil hot-spots can be managed or treated locally with the addition of lime. Hot spot represent areas where antecedent condition coalesce Hot-spot locations of surface water acidification observed in the Millennium Drought are unlikely to change in a future drought (Sections 2.4 and 2.7).

The findings of the 'Research Priorities' Management Action carry a number of implications in regards to the best practice management of acid sulfate soils in the CLLMM region, some of which were previously identified in DENR, 2010. Management implications resulting from the ‘Research Priorities’ management action include:

- The rewetting of severely acidified soils with seawater carries a higher risk of surface water acidification and contamination as opposed to freshwater (Section 2.4). The use of seawater as a management option to prevent acid sulfate soils from oxidising results in the rapid development of hypersaline conditions (salinities above that of seawater) throughout the CLLMM region (Section 2.7);
- The fortuitous rapid rate of lake refilling at the end of the Millennium Drought minimised localised manifestations of acidification (Section 2.4). Where lake refilling is predicted to occur slowly, storing water to permit the rapid inundation of soils should be considered as a potential management option to reduce the risk of surface water acidification;
- The rapid rate of acidification and the potentially long time-scales required for recovery highlight that the best way to manage acid sulfate soils is to prevent them from being disturbed in the first place (Sections 2.4 and 2.5).

6. References

Bain, P.A., H. Doan, D. Gonzago, R. O’Brien, J. Kirby and A. Kumar. 2015a. Toxicity of binary mixtures of selected metals to larvae of the midge *Chironomus tepperi*. CSIRO Technical report: Land and Water Flagship.

Bain, P.A., H. Doan, D. Gonzago, R. O’Brien, J. Kirby and A. Kumar. 2015b. Toxicity of selected metals and their binary combinations to freshwater snail *Physella acuta.* CSIRO Technical report: Land and Water Flagship.

Baker, A. and P. Shand. 2014. An overview of changes in soil acidity in reflooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia. CSIRO Water for a Healthy Country National Research Flagship. Adelaide. 177.

Baker, A.K.M., R.W. Fitzpatrick, P. Shand, S.L. Simpson, R.H. Merry and M. Thomas. 2010. Temporal variations in representative Acid Sulfate Soil environments around Lakes Alexandrina and Albert, South Australia. CSIRO Sustainable Agriculture Research Flagship. Adelaide. Client Report R-325-8-2. 250.

Baker, A.K.M., R.W. Fitzpatrick, S.L. Simpson and R.H. Merry. 2011. Temporal variations in re-flooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia. Adelaide. CSIRO Land and Water Science Report 4/11. 480.

Baker, A.K.M., P. Shand and R.W. Fitzpatrick. 2013. Recovery of re-flooded acid sulfate soil environments around Lakes Alexandrina and Albert, South Australia. CSIRO: Water for a Healthy Country National Research Flagship.

BMTWBM Pty Ltd. 2010. Barrages Environmental Impact Statement (EIS): Modelling Report (Coorong, Murray Mouth, Barrages, Lower Lakes). BMTWBM Pty Ltd. Technical Report prepared for SA Water Corporation, 160pp.

Claff, S.R., L.A. Sullivan, E.D. Burton and R.T. Bush. 2010. A sequential extraction procedure for acid sulfate soils: Partitioning of iron. Geoderma. 155: 224-230. doi:DOI 10.1016/j.geoderma.2009.12.002.

Cook, F.J. 2011. Lake Alexandrina and Lake Albert: Analysis of groundwater measurements and estimation of acid fluxes. CSIRO: Water for a Healthy Country National Research Flagship.

Cook, F.J., G. McLachlan, E. Leyden and L. Mosley. 2011. Physical Properties of Soils/Sediments of Lower Murray Lakes and Modelling of Acid Fluxes. CSIRO: Water for a Healthy Country National Research Flagship.

Cook, F.J. and L. Mosley. 2012. Modelling of acidic solute fluxes from sediments to the water column in the Lower Lakes of South Australia. Report: FCA1_12.

Corbin, T., L. Mosley, N. Creeper and W.S. Hicks. 2012. Benthic Ecosystem Toxicity Assessment (BETA) Pilot Study. Draft report for the Department of Environment, Water and Natural Resources.

Corbin, T. and C. Cummings. 2013. Research into the macroinvertebrate community composition and chironomid deformity in the Lower Lakes. Environmental Protection Authority, South Australia.

Corbin, T., C. Cummings and L. Mosley. 2013. The influence of acidified sediments and other environmental factors on aquatic invertebrates in the Lower Lakes. Environmental Protection Authority, South Australia.

DEH. 2009. Securing the Future: A Long-Term Plan for the Coorong, Lower Lakes and Murray Mouth. Department for Environment and Heritage, Adelaide, South Australia.

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.

DEWNR. 2010. Limestone dosing Boggy Lake to manage acidification (Fact Sheet). Retreived from http://www.naturalresources.sa.gov.au/files/sharedassets/public/cllmm/cons-gen-cllmm-limestonedosingfactsheet.pdf.

DEWNR. 2014. Managing acid sulfate soils (Fact sheet). Retrieved from http://www.naturalresources.sa.gov.au/files/sharedassets/public/cllmm/cllmm-managing-acid-sulfate-soils-fact.pdf.

Earth Systems. 2010. Quantification of acidity flux rates to the Lower Murray Lakes. Prepared by Earth Systems Consulting Pty. Ltd. for the SA Department of Environment and Natural Resources. Adelaide.

Fitzpatrick, R.W., B. Powell and S. Marvanek. 2008a. Atlas of Australian Acid Sulfate Soils. In: R. W. Fitzpatrick and P. Shand, editors, Inland Acid Sulfate Soil Systems Across Australia. CRC LEME Open File Report No. 249. CRC LEME, Perth, Australia. p. 75-89.

Fitzpatrick, R.W. and P. Shand. 2008a. Inland Acid Sulfate Soil Systems Across Australia. CRC LEME open file report No. 249. CRC LEME, Perth, Australia. p. 304. http://www.clw.csiro.au/publications/acid-sulfate-soils/ass-book/Inland-ASS-book-print.pdf.

Fitzpatrick, R.W. and P. Shand. 2008b. Inland Acid Sulfate Soil in Australia: Overview and Conceptual Models. In: R. W. Fitzpatrick and P. Shand, editors, Inland Acid Sulfate Soil Systems Across Australia. CRC LEME, Perth, Australia. p. 6-74.

Fitzpatrick, R.W., P. Shand, S. Marvanek, R.H. Merry, M. Thomas, S.L. Simpson, et al. 2008b. Acid Sulfate Soils in subaqueous, waterelogged and drained soil environments in Lake Albert, Lake Alexandrina and River Murray below Blanchetown (Lock 1): properties, distribution, genesis, risks and management. CSIRO Land and Water. Adelaide. Science Report 46/08. 167.

Fitzpatrick, R.W., P. Shand, R.H. Merry, B. Thomas, S. Marvanek, N.L. Creeper, et al. 2008c. Acid sulfate soils in the Coorong, Lake Alexandrina and Lake Albert: properties, distribution, genesis, risks and management of subaqueous, waterlogged and drained soil environments. CSIRO Land and Water Adelaide. Science Report 52/08. 177.

Fitzpatrick, R.W., G. Grealish, P. Shand, S.L. Simpson, R.H. Merry and M.D. Raven. 2009a. Acid Sulfate Soil Assessment in Finniss River, Currency Creek, Black Swamp, and Goolwa Channel, South Australia. CSIRO Land and Water. Adelaide. Science Report 26/09. 213.

Fitzpatrick, R.W., G. Grealish, P. Shand, B.P. Thomas, R.H. Merry, N.L. Creeper, et al. 2009b. Preliminary Risk Assessment of Acid Sulfate Soil Materials in the Currency Creek, Finniss River, Tookayerta Creek and Black Swamp region, South Australia. CSIRO Land and Water. Adelaide. Science Report 01/09. 45.

Fitzpatrick, R.W., G. Grealish, S. Chappell, S. Marvanek and P. Shand. 2010. Spatial variability of subaqueous and terrestrial acid sulfate soils and their properties for the Lower Lakes South Australia. CSIRO Sustainable Agriculture National Research Flagship. Adelaide. Client Report R-689-1-15. 122.

Fitzpatrick, R.W., G.J. Grealish, P. Shand and N.L. Creeper. 2011. Monitoring and assessment of reflooded Acid Sulfate Soil materials in Currency Creek and Finniss River Region, South Australia. CSIRO Sustainable Agriculture National Research Flagship. Adelaide. Client Report R-325-8-6. 103.

Hamilton, B.E., L. Mosley, D. Stone and B. Zammit. 2014. Measurement of sediment acidity fluxes to Boggy and Hunters Creeks. Environment Protection Authority, South Australia.

Hicks, W.S., N.L. Creeper, J. Hutson, R.W. Fitzpatrick, S. Grocke and P. Shand. 2009. The potential for contaminant mobilisation following acid sulfate soil rewetting: field experiment. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide. . CSIRO, Adelaide. 113.

Hipsey, M.R. and S.U. Salmon. 2008. Numerical assessment of acid-sulfate soil impact on the River Murray Lower Lakes during water level decline. Centre for Water Research, The University of Western Australia.

Hipsey, M.R., B.D. Bursch, J. Coletti and S.U. Salmon. 2010. Lower Lakes hydrogeochemical model development and assessment of acidification risks. Prepared by University of Western Australia for SA Water, Adelaide.

Hipsey, M.R. and B.D. Bursch. 2012. Lower Lakes water quality recovery dynamics. Prepared by University of Western Australia for the Department of Environment & Natural Resources, Adelaide.

Hipsey, M.R. and B.D. Busch. 2016. The CLLMM Water Quality Response Model (v1) – Volume 2: Model Validation. AED Report #R32, The University of Western Australia, Perth, Australia.

Hipsey, M.R., B.D. Busch and G. Katumba. 2016. The CLLMM Water Quality Response Model (v1) – Volume 1: Model Overview & Parameterisation Approach. AED Report #R31, The University of Western Australia, Perth, Australia.

Kumar, A., H. Doan, S. Grocke, D. Gonzago, J. Kirby and P. Shand. 2014. Monitoring of the Lower Lakes based on the ecotoxicological assessment of selected sites. CSIRO Technical report: Land and Water Flagship.

Kumar, A., T. Corbin, H. Doan, S. Grocke, D. Gonzago, J. Kirby, et al. 2015. Sediment Quality Triad (SQT) assessment of surface sediments in the Lower Lakes. CSIRO Technical report: Land and Water Flagship.

Palmer, D., R. Mitchell, C. Powell, J. Spencer and L. Mosley. 2011. Air quality in the Lower Lakes during a hydrological drought. Environmental Protection Authority, South Australia.

Shand, P., R.H. Merry, S. Grocke, M. Thomas, R.W. Fitzpatrick, B. Thomas, et al. 2010. Water and soil quality impacts during reflooding of Nelwart Lagoon. CSIRO: Water for a Healthy Country National Research Flagship. Adelaide, Australia. 171.

Shand, P., S. Grocke, J. Kirby and A.K. Baker. 2012. The characterisation of metal and metalloid contaminants in re-flooded Acid Sulfate Soils of Lake Alexandrina, South Australia. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

Simpson, S., R. Jung, C. Jarolimek and I. Hamilton. 2009. The potential for contaminant mobilisation following acid sulfate soil rewetting: lab experiment. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

Simpson, S.L., R.W. Fitzpatrick, P. Shand, B.M. Angel, D.A. Spadaro, R.H. Merry, et al. 2008. Acid, Metal and Nutrient Mobilisation Following Rewetting of Acid Sulfate Soils in the Lower Murray. CSIRO, Adelaide. CSIRO land and Water Science Report CLW27/08. 192.

Stauber, J.L., A.A. Chariton, M.T. Binet, S.L. Simpson, G.E. Batley, M. Durr, et al. 2008. Water quality screening risk assessment of acid sulfate soil impacts in the Lower Murray. CSIRO. Lucas Heights. CSIRO land and Water Science Report 45/08. 156.

Sullivan, L., E. Burton, R. Bush, K. Watling and M.A. Bush. 2008. Acid, metal and nutrient mobilisation dynamics in response to suspension of MBOs in freshwater and to freshwater inundation of dried MBO and sulfuric soil materials. Prepared for the South Australian Environmental Protection Agency. Southern Cross GeoScience, Southern Cross University, Lismore, NSW.

Sullivan, L.A., R.T. Bush, N.J. Ward, D.M. Fyfe, M. Johnston, E.D. Burton, et al. 2010. Lower Lakes laboratory study of contaminant mobilisation under seawater and freshwater inundation. Prepared by Southern Cross GeoScience for the SA Department of Environment and Natural Resources, Adelaide.

Sullivan, L.A., E.D. Burton, N.J. Ward, R.T. Bush, J. Coughran, M.D. Cheetham, et al. 2011. Lower Lakes sulfate reduction study. Southern CrossGeoScience. Prepared for the SA Department of Environment and Natural Resources, Adelaide. Technical Report No. 711.

Sullivan, L.A., N.J. Ward, R.T. Bush, M.D. Cheetham, P.J. Cheeseman, D.M. Fyfe, et al. 2012. Lower Lakes Phase 1 Sulfate Reduction Monitoring Project. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide Southern Cross GeoScience Technical Report No. 112.

Sullivan, L.A., N.J. Ward, M.A. Rosicky, S. Li, R.T. Bush, D.M. Fyfe, et al. 2013. Recovery of acid sulfate sediments in the Lower Lakes. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide. Southern Cross GeoScience Technical Report No. 213.

Ward, N.J., L.A. Sullivan and R.T. Bush. 2013. Lower Lakes acid sulfate soil detailed conceptual models. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide. Southern Cross GeoScience Technical Report No. 113.

Ward, N.J., R.T. Bush, Z. Wang, L.A. Sullivan, D.M. Fyfe, G. Choppala, et al. 2014. Investigations into the factors affecting the rates of recovery of acid sulfate soils in the Lower Lakes. Prepared for the SA Department of Environment, Water and Natural Resources, Adelaide. Southern Cross GeoScience Technical Report No. 114.

7. Appendices

7.1 Appendix A: Shortened forms and acronyms

AASS	Actual acid sulfate soil (i.e. sulfuric material)
AED2	Aquatic Ecodynamics modelling library
AHD	Australian Height Datum
ANC	Acid neutralising capacity
ANZECC	Australian and New Zealand Environmental Conservation Council
ASS	Acid sulfate soil
AST	Acid sensitive taxa
ATT	Acid tolerant taxa
CLLMM	Coorong, Lower Lakes and Murray Mouth
CLLMM-WQRM	Coorong Lower Lakes Murray Mouth - Water Quality Response Model
COL	Conservative leachate ‘tracer’
CRS	Chromium reducible sulfide
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DEH	Department of Environment and Heritage
DENR	Department of Environment and Natural Resources
DEWNR	Department of Environment, Water and Natural Resources
DIC	Dissolved organic carbon

EC	Electrical Conductivity
EIS	Environmental Impact Statement
ELCOM–CAEDYM–ASS	Estuary, Lake and Coastal Ocean Model - Computational Aquatic Ecosystem Dynamics Model – Acid Sulfate Soils
EPA	Environment Protection Agency
EPBC	Environment Protection and Biodiversity Conservation (Act)
HQ	Hazard Quotient
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
MBO	Monosulfidic black ooze
MDB	Murray-Darling Basin
PASS	Potential acid sulfate soil (i.e. hypersulfidic material)
RA	Retained acidity
SARDI	South Australian Research and Development Institute
SQT	Sediment Quality Triad
TAA	Titratable actual acidity
WQG	Water quality Guidelines

7.2 Appendix B: Workshop minutes key discussion points

Key Theme	Discussion topic	Discussion outcomes
Properties and spatial distribution of ASS materials in the CLLMM region	Re-survey of acid sulfate soil properties	The current status (June 2016) of acid sulfate soils in the CLLMM region is not well known. Monitoring by CSIRO ceased in 2013. For a relatively low cost it would be possible to update the spatial acid sulfate soil database using a combination of expert re-interpretation, ground truthing, and repurposing site monitoring data. Updating the spatial acid sulfate soil database would allow a higher confidence to be applied to results generated by process models when investigating the behaviour of acid sulfate soils in the CLLMM region during a future low water event.
	Soil sample archive	Due to the high cost involved in conducting field based soil surveys the soil samples collected represent a valuable resource. The possibility of archiving these samples to allow future work and analysis should be considered.
Air quality impacts related to ASS	Nil	Nil

Key Theme	Discussion topic	Discussion outcomes
Pyrite oxidation rates in the Lower Lake soils	Concerns regarding OxCon methodology	Pyrite oxidation rates calculated in this study have contributed greatly to improving the certainty of acid sulfate soil related process modelling. However, a number of concerns were raised regarding the reliability of the methodology used, that if addressed would greatly improve our understanding of the range of pyrite oxidation rates possible in the heterogeneous CLLMM region and the kinetics of this initial step. Further research into pyrite oxidation rates in the CLLMM region should prioritise the analysis of a larger number of soils with different physico-chemical properties. The use of an alternative or variety of alternative approaches to measure pyrite oxidation rates would also increase confidence. Particularly if the approach(es) accounted for in-profile heterogeneity.
Contaminant mobilisation and transport	Aluminium	See key theme 'Benthic ecology and ecotoxicology impacts related to ASS'
	Seiche event	Seiche events, particularly in Lake Albert, are a significant driver for transport of acidity to lake surface waters. This needs to be highlighted in the summary report.
	Rate of lake refilling	The fortuitous rapid refilling of the Lower Lakes at the break of the Millennium Drought minimised the release of acidity from the soil into surface waters. This effect was highlighted in multiple reports throughout the research program. Where the rate of refill is unlikely to result in the rapid inundation of desiccated and acidified acid sulfate soils, the use of permanent or temporary structures to prevent gradual rewetting should be considered as a management option to reduce the risk of surface water acidification.

Key Theme	Discussion topic	Discussion outcomes
	Soil cracking	Research has shown that acid sulfate soils with desiccation cracking can increase the flux of acidity to surface waters upon rewetting compared to a non-cracked surface. There is considerable heterogeneity of cracking depth, ped size and abundance of intra-ped cracking/macropores. Further research to investigate how these factors influence contaminant flux would help to better define potential hazards posed by long term diffusive fluxes. In the same manner it would also be useful to determine the contribution of benthic bioturbation to contaminant flux.
Post reflooding recovery of sulfuric materials	Soil conditioning/water level manipulation	By reinstating natural wetting and drying cycles the acidification hazard of acid sulfate soil materials may be slowly reduced over decadal time periods. This management technique has been recently used with success in an inland freshwater wetland (i.e. Banrock Station). Whether this can be applied successfully to the much larger spatial scales, hydrological complexities and heterogeneous salinities of the CLLMM region requires further research.
	Rate of lake refilling	See key theme 'Contaminant mobilisation and transport'
	Monitoring	The Workshop identified that an early warning of acid sulfate soil antecedent conditions and knowing the state acid sulfate soils materials in the CLLMM region are critical to successfully responding to another drought. This information can be readily obtained through annual or bi-annual monitoring projects. The lack of pre-Millennium Drought baseline conditions resulted in difficulties in drawing conclusions (with high confidence) in a number of research projects. Workshop participants emphasised that that it is important this learning be communicated to managers. Monitoring efforts could be augmented using citizen science.

Key Theme	Discussion topic	Discussion outcomes
	Organic carbon	Soils that had oxidised during the Millennium Drought were found to be carbon limited. Therefore no or only low concentrations of carbon were available to promote alkalinity producing reduction reactions during the period immediately following reflooding. However, overall, the CLLMM system is carbon rich and over longer time periods the generation of pyrite is unlikely to be carbon limited. This distinction needs to be clarified in the summary report.
Benthic ecology and ecotoxicology impacts related to ASS	Aluminium	Aluminium frequently had hazard quotients that were considerably greater than other metals. Hence, further ecotoxicological research should prioritise this element. In particular, a revision of the ANZECC guideline value(s) for Al toxicity at lower pH values is needed. The speciation and in turn bioavailability of Al in the pH and redox dynamic acid sulfate soil systems is not yet fully understood.
	Mussel population recovery	Concerns were raised regarding the current status of recovery of mussels in the Lower Lakes. Due to the desiccation and acidification of marginal lake bed soils, dead mussels were ubiquitous during the Millennium Drought. Further research investigating the current population status and impacts the upwards flux of persisting sub-soil acidity has on the rate of recovery of the mussel population (and also other biota with carbonate exoskeletons) is required.
	Fish toxicology	Initial investigations showed that contaminants released from acid sulfate soils are bioavailable to benthic organisms. Further research is required to determine if acid sulfate soils are also impacting (or have the potential to impact) higher tropic level species such as fish.
	Was the structure/content of the ecotoxicological project appropriate?	The structure of the ecotoxicology project was appropriate for the small amount of information available when the program was initiated. In hindsight, workshop participants indicated it would have been structured in the same manner. The ecotoxicology project laid a good foundation and established in which directions further research should continue.

Key Theme	Discussion topic	Discussion outcomes
Development of an integrated CLLMM water quality response model	Acid sulfate soil terminology	The use of the correct acid sulfate soil terminology in the CLLMM region was established in 2007. It is suggested that the PASS and AASS terms used in the model are updated for both accuracy and consistency.
	Integrate findings from ecotoxicology project	There were a number of possible options discussed on how the findings of the ecotoxicology project could be effectively incorporated into the water quality response model. Possibilities included the use of Copper toxicity and identified synergistic metal mixtures to model an index value for potential ecotoxicological risk. Further research to investigate the possibility of linking geochemical module outputs with a toxicity 'score' would increase the scope and relevance of the model.
Conceptual models to aid the communication of complex ASS processes	Acid sulfate soil terminology	Soils or sub-aqueous soils should be used in place of sediments for accuracy.
	Models require updating	The conceptual models need to be brought up-to-date with recent findings, in particular the most recent findings from the ecotoxicological project. To increase the relevance of the conceptual models they also need to more clearly highlight the complex hydrology and heterogeneity of the CLLMM region (i.e. lakes, creeks, channels, wetlands, and easily disconnected areas etc.)