

Inland Acid Sulfate Soils in the Floodplain Wetlands of the Murray-
Darling Basin: Regional occurrence using rapid methods and the
impacts of reflooding on water quality

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I. DECLARATION

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II. ABSTRACT

A full appreciation of the extent and significance of acid sulfate soils (ASS) in Australia's inland environments has only recently been realised, in contrast to ASS in Australia's modern-day coastal zones, which have been well studied over the last four decades. Investigations into the inland ASS systems of the Murray-Darling Basin (MDB), Australia's largest river system, did not occur with any intensity prior to 2006. A number of key knowledge gaps exist concerning the occurrence, properties and behaviour of inland ASS systems in the MDB. These knowledge gaps, combined with the ecological and economic significance of the MDB, and the potential for environmental and infrastructure degradation through ASS acidification, provided the incentive for this research project.

The main objective was to advance the understanding of inland ASS in the MDB. This was achieved by answering two key research questions:

What is the prevalence and distribution of ASS with hypersulfidic and sulfuric materials in the floodplain wetlands of the MDB?

What are the dominant geochemical pathways taken following freshwater reflooding of inland ASS containing sulfuric materials and the timescales of impact?

The first research question was answered through a regional assessment of ASS in the MDB and represents the most extensive estimate of the basin-wide occurrence of inland ASS in the floodplain wetlands of the MDB thus far. As part of a government funded initiative, regional environmental officers collected approximately 7200 wetland soil samples, which were then submitted for soil incubation tests. The large number of samples requiring analysis, and the need for the rapid and robust classification of hypersulfidic materials led to the development of a simplified incubation method (see Chapter 2). This method was found to offer significant improvements over existing incubation methods. Firstly, the use of chip-trays as incubation vessels was found to offer many advantages in terms of transport, storage and analysis of soil samples compared with soil-slabs.

Secondly, the conditional extension of the incubation period resulted in the accurate classification of slowly acidifying hypersulfidic materials whilst maintaining a minimal test length.

Following its development, the simplified incubation method was used to assess the acidification potential of *ca.* 2500 profiles in over 1000 wetlands located throughout the MDB (see Chapter 3). The results of pH measurements made before and following soil incubation were used to estimate the prevalence and distribution of sulfuric and hypersulfidic ASS materials across the MDB. A total of 238 floodplain wetlands, representing 23% of the total wetlands assessed, were found to contain soils that severely acidified ($\text{pH} < 4$) when oxidised. The number of these soils, the majority of which are likely to be hypersulfidic ASS materials, indicates that inland ASS are prevalent in the floodplain wetlands of the MDB. As a result, the potential existence of inland ASS should be a key consideration for wetland management plans in any floodplain wetland located in the MDB.

The distribution of ASS materials in the MDB was investigated by dividing it into 13 geographical regions, whose boundaries roughly followed hydrological catchment boundaries. The distribution of acidification hazard was non-uniform throughout the MDB. The geographical regions with the greatest acidification hazard were in the southern MDB, downstream of the Murray-Darling confluence, and in catchments on the southern side of the Murray River channel in Victoria. The non-uniform distribution of ASS throughout the MDB has implications for the successful management of inland ASS in the MDB, whereby regions presenting the greatest acidification should receive much greater attention. Overall, the development of the simplified incubation method and the extensive broad-scale assessment of ASS in the MDB provided policy makers with a valuable screening tool, helping them to identify priority wetlands and regions that required more detailed IASS investigations.

The second research question was answered through two focused field studies, which applied in situ sampling and monitoring techniques to investigate the geochemical behaviour of severely acidified inland ASS materials following reflooding by freshwater. The reflooding of severely acidified inland ASS by freshwater has been suggested as a viable remediation method. However, this hypothesis is based on observations made in

coastal ASS systems following reflooding by sea water and had not yet been extensively documented in freshwater systems at the commencement of this research project.

In the first study, equilibrium dialysis membrane samplers were used to investigate in situ changes to soil acidity and abundance of metals and metalloids following the first 24 months of restored subaqueous conditions (see Chapter 4) In the second study, mesocosms were installed in situ to simulate reflooding and the key geochemical pathways were documented through continuous in situ redox monitoring and the use of in situ soil solution samplers (see Chapter 5).

In both studies, the strongly buffered low pH conditions of the oxidised sulfuric materials and the limited supply of external alkalinity in freshwater systems meant that soil acidity persisted for more than 24 months following reflooding. The persisting low pH conditions, along with insufficiently reducing redox conditions, and competitive exclusion by iron(III)-reducing bacteria were suspected to inhibit sulfate reduction. Following the eventual removal of the above limitations it is hypothesised that the lack of readily available soil organic carbon will further inhibit sulfate reduction. Under continued absence of net in situ alkalinity production, via the formation of reduced inorganic iron and sulfur species, observed trajectories indicate that neutralisation of soil acidity may take several years.

Small increases in soil pH confined to within 10 cm of the soil-water interface were observed after 24 months of subaqueous conditions. Substantial decreases in the concentrations of some metals and metalloids were observed to coincide with the small increases in soil pH, most likely owing to lower solubility and sorption as a consequence of the increase in pH. In the acidic porewaters, aluminium activity was consistent with a control by a solid phase aluminium species with stoichiometry Al:OH:SO_4 (e.g. jurbanite). In the same acidic porewaters, iron and sulfate activity were regulated by the dissolution of natrojarosite. Following the establishment of reducing conditions, the reductive dissolution of accumulated natrojarosite and schwertmannite phases was responsible for large increases in total dissolved iron. The differing physical properties and chemical characteristics, such as stored acidity and contaminant concentrations, of dominantly clayey soils and dominantly sandy soils, led to contrasting impacts on the transport of

solute following reflooding (diffusive versus advective flow, respectively) and timescales of recovery.

A number of key geochemical processes influencing the porewater concentrations of acidity, iron, aluminium, and metals and metalloids following reflooding by freshwater were observed in these severely acidified inland ASS systems. These physical and geochemical processes were summarised in two conceptual hydrogeochemical process models, which were used to distil complex information and convey it in a format readily understandable to a non-ASS specialist audience.

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I dedicate this thesis to my wife, Kimberley Creeper. Your endless encouragement, patience and love has meant everything. I couldn't have done this without your belief in me.

IV. PUBLICATIONS RELATED TO THIS THESIS

The University of Adelaide encourages the publication of papers during candidature and permits theses to be presented as either a collection of published papers or a combination of papers and conventional chapters. The main body of this thesis comprises four journal papers. Additionally, five peer reviewed conference papers and four scientific reports, which are related to this thesis, were published during candidature.

IV.1 Thesis research chapters (journal papers)

Creeper, N.L., R.W. Fitzpatrick and P. Shand. 2012. A simplified incubation method using chip-trays as incubation vessels to identify sulphidic materials in Acid Sulphate Soils. *Soil Use and Management*. **28**(3), 401-408. [doi: 10.1111/j.1475-2743.2012.00422.x](https://doi.org/10.1111/j.1475-2743.2012.00422.x).

Creeper, N.L., R.W. Fitzpatrick. and P. Shand. 2013. The occurrence of Inland Acid Sulphate Soils in the floodplain wetlands of the Murray–Darling Basin, Australia, identified using a simplified incubation method. *Soil Use and Management*. **29**(1), 130-139. [doi:10.1111/sum.12019](https://doi.org/10.1111/sum.12019).

Creeper, N.L., P. Shand, W.S. Hicks and R.W. Fitzpatrick. 2015. Porewater geochemistry of inland acid sulfate soils with sulfuric horizons following postdrought reflooding with freshwater. *Journal of Environmental Quality*. **44**(3), 989-1000. [doi:10.2134/jeq2014.09.0372](https://doi.org/10.2134/jeq2014.09.0372).

Creeper, N.L., W.S. Hicks, P. Shand, R.W. Fitzpatrick.. 2015. Geochemical processes following freshwater reflooding of acidified inland Acid Sulfate Soils: An in situ mesocosm experiment. *Chemical Geology*, **441**, 200-214. [doi:10.1016/j.chemgeo.2015.07.009](https://doi.org/10.1016/j.chemgeo.2015.07.009).

IV.2 Conference proceedings

Creeper, N.L., P. Shand, R.W. Fitzpatrick, J. Hutson. 2012. Behaviour of iron, aluminium and other selected metals following the rewetting of inland acid sulfate soils containing sulfuric material. 7th International Acid Sulfate Soil Conference: Towards Harmony between Land Use and the Environment. Vaasa, Finland. *Geological Survey of Finland Bulletin*. **56**: 26-28.

Creeper, N.L., R.W. Fitzpatrick and P. Shand. 2012. Rapid evaluation of acid sulfate soils in the floodplain wetlands of the Murray-Darling Basin using a simplified incubation method. In: Proceedings of the 5th Joint Australian and New Zealand Soil Science Conference: Soil solutions for diverse landscapes. L.L. Burkitt and L.A. Sparrow (eds.). Hobart, Australia. p. 735

Creeper, N.L., R.W. Fitzpatrick, P. Shand, P. Self and R. Kingham (2010). A systematic analysis procedure incorporating the chip-tray incubation method for the hazard assessment of Acid Sulfate Soils in the Murray Darling Basin. In: 19th World Congress of Soil Science, Soil solutions for a changing world, Symposium WG 3.1 Processes in acid sulfate soil materials. R. J. Gilkes and N. Prakongkep (eds.). Brisbane, Australia. p. 75-78

W.S. Hicks, N.L Creeper, J. Hutson, R.W. Fitzpatrick, S. Grocke and P. Shand. 2010. Acidity fluxes following rewetting of sulfuric material. In: Proceedings 19th World Congress of Soil Science, Soil solutions for a changing world, Division Symposium 2.1 Wetland soils and global change. R. J. Gilkes and N. Prakongkep (eds.). Brisbane, Australia. p. 9-12

Fitzpatrick, R. W., G. Grealish, P. Shand, R. H. Merry, N.L. Creeper, M. Thomas, A. Baker, B. Thomas, W. S. Hicks and N. Jayalath. 2010. Chip-tray incubation - A new field and laboratory method to support Acid Sulfate Soil Hazard Assessment, Classification and Communication. In: Proceedings 19th World Congress of Soil Science, Soil Solutions for a Changing World, Symposium WG 3.1 Processes in acid sulfate soil materials. R. J. Gilkes and N. Prakongkep (eds.). Brisbane, Australia. p. 28-31

IV.3 Scientific reports

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. p. 103. <http://www.clw.csiro.au/publications/science/2011/SAF-monitoring-ASS-Currency-Creek.pdf>

Fitzpatrick, R.W., G. Grealish, P. Shand, B.P. Thomas, R.H. Merry, N.L. Creeper, M.D. Raven and N. Jayalath. 2009. 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. CSIRO Science Report 01/09. p. 45. <http://www.clw.csiro.au/publications/science/2009/sr01-09.pdf>

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 CSIRO Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

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

V. LIST OF ABBREVIATIONS

Acid-Generating Potential (AGP)

Acid-Neutralising Capacity (ANC)

Australian and New Zealand Environment and Conservation Council (ANZECC)

Australian Height Datum (AHD)

Acid Sulfate Soils (ASS)

Acid Volatile Sulfur (AVS)

Acid Wetland (AW)

Below Ground Level (bgl)

Commonwealth Scientific and Industrial Research Organisation (CSIRO)

Coorong, Lower Lakes and Murray Mouth (CLLMM)

Guideline Trigger Value (GTV)

Inductively Coupled Plasma (ICP)

Inland Acid Sulfate Soils (IASS)

Mass Spectroscopy (MS)

Murray-Darling Basin (MDB)

Murray-Darling Basin Authority (MDBA)

Natural Resource Management (NRM)

Net Acid-Generating Potential (NAGP)

Optical Emission Spectroscopy (OES)

Reduced Inorganic Sulfides (RIS)

Saturation Index (SI)

Soil-Water Interface (SWI)

Visual basic for Applications (VBA)

World Reference Base (WRB)

X-ray diffraction (XRD).

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1.

Acid Sulfate Soils in the Environment

1.1 AN INTRODUCTION TO ACID SULFATE SOILS

Acid Sulfate Soils (ASS) are soils containing iron sulfide minerals (principally pyrite, FeS_2) or soils that are affected by the transformations of iron-sulfide minerals (see section 1.1.1). The iron sulfide minerals found in ASS accumulate naturally in anoxic environments through the reduction of iron and sulfate (see section 1.1.2). If left undisturbed, the accumulated iron sulfide minerals in ASS are often considered benign. However, if disturbed and exposed to oxidising conditions the accumulated iron sulfide minerals found in ASS will oxidise, and have the potential to generate sufficient sulfuric acid to severely acidify the soil ($\text{pH} < 4$) (see section 1.1.3). Because of this ASS pose a significant hazard to aquatic and terrestrial ecosystems and man-made infrastructure (see section 1.1.4) (Dent, 1986, Dent and Pons, 1995, Fanning and Fanning, 1989, Fitzpatrick and Shand, 2008a, Melville and White, 2013, Pons, 1973)

1.1.1 Description and classification

The distinguishing feature of ASS is either: severe acidification, with the oxidation of reduced inorganic sulfur (RIS) being a dominant source of that acidity, or the presence of RIS compounds in sufficient quantities to result in severe acidification upon oxidation. These are the main end-member materials recognised in ASS and have traditionally been termed sulfuric materials and sulfidic materials, respectively.

The term 'sulfidic', as used traditionally in soil classification systems (Isbell, 2002, Soil Survey Staff, 2014), differs from the general definition used by the broader scientific

community; who use the term to describe a material that contains sulfides. Additionally, the term 'sulfidic', as used traditionally in soil classification systems, does not accommodate sulfide containing soil materials that do not have the capacity to acidify, but do have the capacity to pose other sulfide related environmental hazards. To rectify these limitations, Sullivan, *et al.* (2009) proposed a number of conceptual changes, which were then later refined by Sullivan, *et al.* (2010). These changes included: altering the traditional definition of the term 'sulfidic' to bring it in line with the wider scientific community, replacing the term 'sulfidic' with a conceptually equivalent new term 'hypersulfidic', and introducing new terms 'hyposulfidic' and 'monosulfidic'. The existing terms 'sulfuric material' and 'sulfuric horizon' remained conceptually unchanged but definitions were updated to include recent improvements in the incubation method. The revised definitions of the above terms are as follows:

Sulfidic Material

A soil material containing detectable inorganic sulfides ($\geq 0.01\%$ sulfidic S)

Hypersulfidic material

Hypersulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by experiencing a substantial* drop in pH to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2 - 10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is either: a) until the soil pH changes by at least 0.5 pH unit to below 4, or b) until a stable** pH is reached after at least 8 weeks of incubation.

*A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.

**A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase.

In Soil Taxonomy, the term sulfidic material is used. Both classification systems aim to define the same ASS sub-type, but definitions differ slightly. For the complete definition of sulfidic material in Soil Taxonomy see Soil Survey Staff (2014).

Hyposulfidic material

Hyposulfidic material is a sulfidic material that (i) has a field pH of 4 or more and (ii) does not experience a substantial* drop in pH to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2 - 10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is until a stable** pH is reached after at least 8 weeks of incubation.

*A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.

**A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase.

Monosulfidic material

A soil material containing high concentrations of detectable monosulfides ($\geq 0.01\%$ acid volatile sulfide). Monosulfidic material is conceptually similar to Monosulfidic Black Ooze (MBO). However, it differs from MBO in that monosulfidic material encompasses a wider array of soil textures and consistencies. For example, monosulfidic material includes sands with $\geq 0.01\%$ acid volatile sulfide, which are excluded (on the basis of soil consistence) from being MBOs.

Sulfuric material

A soil material that has a pH less than 4 (1:1 by weight in water, or in a minimum of water to permit measurement) when measured in dry season conditions as a result of the oxidation of sulfidic materials (defined above). Evidence that low pH is caused by oxidation of sulfides is one of the following:

- Mottles and coatings with accumulations of jarosite or other iron and aluminium sulfate or hydroxysulfate minerals such as natrojarosite, schwertmannite, sideronatrite, tamarugite, etc.
- 0.05% or more by weight of water-soluble sulfate
- Underlying sulfidic material.

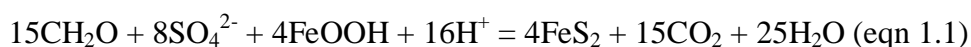
In Soil Taxonomy (Soil Survey Staff, 2014) the term sulfuric horizon is used, which for the most part, can be considered equivalent to the term sulfuric material in Australasian Soil

Classification (in soil taxonomy a sulfuric horizon must have a pH < 3.5). The complete definition of a sulfuric horizon can be found in Soil Survey Staff (2014).

The above definitions for the terms sulfidic, hypersulfidic, hyposulfidic, monosulfidic and sulfuric have since been adopted in the most recent versions of the Australian Soil Classification (Isbell and the National Committee for Soils and Terrain, In Press) and the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). These updated definitions have been used in Chapters 1 and 6. However, in the research chapters (Chapters 2 to 5) the latest revision of the soil classification system available at the time of publishing was used. This included previous revisions of The Australian Soil Classification (Isbell, 2002) and Soil Taxonomy (Soil Survey Staff, 2010). Throughout this thesis, the Australian Soil Classification is used in preference to Soil Taxonomy. However, in Chapters 4 and 5 Soil Taxonomy was most audience appropriate and was used as per the specific journal's requirements.

1.1.2 Formation of sulfides in hypersulfidic material (sulfidization)

The formation of sulfidies in hypersulfidic material principally involves the formation of acid generating Fe sulfide minerals. This process has been described as sulfidization by Fanning and Fanning (1989). Pyrite (FeS₂) is generally the most abundant, and thus the dominant acid generating mineral in ASS, as it is more stable than other Fe sulfide minerals such as monosulfides (e.g. FeS), although these minerals and elemental sulfur can also generate acidity. The formation of Fe sulfide minerals, in particular pyrite, occurs in waterlogged anoxic environments with a source of SO₄²⁻, Fe, and organic carbon. It involves a complex series of biogeochemical processes, however the overall reaction is summarised in equation 1.1 (Dent, 1986, Fanning and Fanning, 1989, Morse, *et al.*, 1987, Rabenhorst, *et al.*, 2006).



Fe reduction

The microbially mediated reduction of Iron(III) occurs under anoxic conditions, utilising organic matter as an electron donor, and producing Fe^{2+} (equation 1.2) (Anderson and Schiff, 1987).

*Sulfate reduction*

The conversion of oxidised forms of sulfur (e.g. SO_4^{2-}) to reduced forms (e.g. H_2S) is mediated by sulfate reducing bacteria under anoxic conditions. Sulfate functions as the terminal electron acceptor in the oxidation of organic matter, represented here in a simplified form CH_2O (equation 1.3) (Anderson and Schiff, 1987, Holmer and Storkholm, 2001).

*Formation of Fe sulfide minerals*

Following the consumption of oxygen and other electron acceptors such as nitrate and manganese, Fe(III) is first used as an electron acceptor in preference to SO_4^{2-} . So that Fe^{2+} is likely to be present when SO_4^{2-} is reduced to dissolved sulfides. The reduced products, Fe^{2+} and H_2S , can combine to form FeS (equation 1.4) (Anderson and Schiff, 1987).



Monosulfides are considered thermodynamically unstable and sulfide will generally be present as disulfides (FeS_2) through interaction of Fe^{2+} with H_2S (equation 1.5) or monosulfides will be converted to pyrite through reaction with elemental sulfur (equation 1.6) (Anderson and Schiff, 1987, Berner, 1984, Burton, *et al.*, 2006a, Postma and Jakobsen, 1996, Rickard and Luther, 2007, Schoonen and Barnes, 1991).

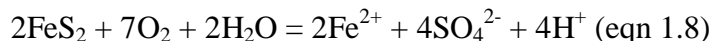


1.1.3 Oxidation of hypersulfidic material (sulfurization)

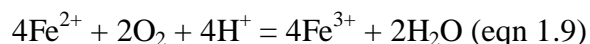
Iron sulfide minerals will continue to form under anoxic conditions as long as there is sufficient Fe, SO_4^{2-} , and labile organic matter available. Once formed FeS_2 is sparingly soluble and stable as long as anoxic conditions are maintained. However, if exposed to air, it will oxidise and release acidity. The process through which FeS_2 contained in hypersulfidic material is oxidised has been described as sulfurization by Fanning and Fanning (1989). The complete oxidation of pyrite and hydrolysis of Fe releases 4 moles of H^+ for each mole of FeS_2 oxidised (equation 1.7). However, this process involves a number of geochemical and biogeochemical reactions described by the following equations (Nordstrom, 1982, Singer and Stumm, 1970, van Breemen, 1973, Ward, *et al.*, 2004).



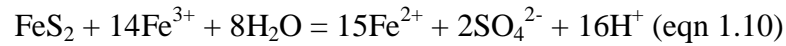
Oxygen acts as the initial oxidant, oxidising FeS_2 to Fe^{2+} . During this stage the chemical oxidation of pyrite at circum neutral pH proceeds relatively slowly (equation 1.8).



The aqueous Fe^{2+} product can then be further oxidised to ferric iron (equation 1.9).



As the initial acid producing reaction (equation 1.7) reduces the pH to ≤ 4.5 ferric iron becomes more stable in solution, however, at low pH, the rate of conversion of Fe^{2+} to Fe^{3+} slows considerably. The slow conversion of Fe^{2+} to Fe^{3+} at low pH is described as the rate limiting step in the rapid oxidation of pyrite by Fe^{3+} . As ferric iron concentrations increase under low pH conditions it becomes the primary oxidising agent of pyrite, oxidising pyrite while itself becoming reduced. The overall ferric driven oxidation of FeS_2 is rapid and is represented by equation 1.10. (equation 1.10). At low pH, iron oxidising bacteria also begin to catalyse the oxidation of Fe^{2+} , increasing the rate of reaction by a factor of 10^6 . If oxygen remains available, equations 1.9 and 1.10 form a self perpetuating loop increasing the rate of FeS_2 oxidation.



Ferric Fe can also be precipitated in a range of Fe(III) oxyhydroxide and hydroxy sulfate minerals (e.g. equation 1.11 and 1.12). Common Fe(III) phases found in oxidised ASS include jarosite, schwertmannite, ferric oxyhydroxides and goethite. The mineral formed depends largely on soil pH and redox conditions. Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) are only thermodynamically stable under low pH oxidising conditions, generally $< \text{pH } 2.8$ and $\text{pH } 2.8$ to 4.5 for jarosite and schwertmannite, respectively. These phases act as pH buffers and constitute a store of acidity (e.g. reverse of equation 1.12). At higher pH, more crystalline and thermodynamically stable minerals such as goethite (FeOOH) are formed (Bigham, *et al.*, 1996a, Bigham, *et al.*, 1996b, Burton, *et al.*, 2008b, Lawson, 1982).



Iron monosulfides existing in the sediments will also release acidity when oxidised (equation 1.13). However in comparison to pyrite, FeS only releases 2 moles of H^+ acidity for each mole oxidised. Additionally, FeS typically occurs in only small concentrations, progressively transforming to the more stable FeS_2 . However, elevated FeS concentration have been observed in some recently ($\sim \leq 20$ years) reduced soil materials, such as those in drainage channels (Sullivan, *et al.*, 2002). The oxidation and release of acidity from monosulfide phases will usually occur prior to FeS_2 oxidation as FeS phases have been shown to oxidise rapidly without microbial catalysis (Dent, 1986, Ward, *et al.*, 2004).



Sulfuric material

In a closed system, pyrite oxidation releases the equivalent H^+ acidity that is consumed during pyrite production (i.e. equation 1.1 and 1.7). The oxidation of accumulated FeS_2 in these closed systems will not theoretically result in the formation of sulfuric material upon oxidation. However, most natural systems are not closed. In ASS, acid neutralising capacity (ANC) is generally in the form of carbonates (CaCO_3) or dissolved alkalinity

(HCO_3^-). Carbonates are readily solubilised and can be transported away from the area of FeS_2 accumulation. Conversely, RIS are insoluble and remain within the soil. In natural ASS systems, soil acidification following the oxidation of hypersulfidic material is often the result of the removal of ANC from the soil. In coastal ASS systems ANC is removed from hypersulfidic material by tidal flushing. However, the processes involved in the separation of ANC from RIS in inland ASS systems is less well understood (Wallace, *et al.*, 2008). As pyrite accumulates, the soil develops an Acid Generation Potential (AGP). When the acid generation potential is greater than the available acid neutralising capacity ($\text{AGP} > \text{ANC}$) sulfuric material will form following the oxidation of hypersulfidic materials (Anderson and Schiff, 1987, Dent, 1986, Wallace, *et al.*, 2008)

The oxidation of hypersulfidic material is most often triggered by decreasing surface water levels or lowering of the water table. This can occur naturally as a result of seasonal rainfall variation, drought conditions, evapotranspiration, and tidal sea level fluctuations. It can also be a result of human activities such as dredging, excavation, and de-watering for the purpose of land reclamation for urban or agriculture development (Dent and Pons, 1995, Faltmarsch, *et al.*, 2008, Fitzpatrick, *et al.*, 2009, Thomas, 2010).

Environmental impacts associated with sulfuric material

The majority of environmental impacts posed by ASS are associated with sulfuric materials. The severely acidified porewaters of sulfuric material often contain high concentrations of mobile metals and metalloids (i.e. free aqueous ions or complexes). These acidic and metal rich porewaters can be transported from the ASS to surface waters, such as nearby streams, lakes or estuaries and cause significant ecological impacts (Astrom and Astrom, 1997, Astrom, 2001, Lawson, 1982, Rabenhorst and Fanning, 2006, Sammut, *et al.*, 1996, van Breemen, 1993, Wilson, *et al.*, 1999).

Sulfuric material can cause the severe stunting or death of acid or metal intolerant vegetation by exposing them to low pH, increased solute loads, Al toxicity and/or Fe stress (Ahern, *et al.*, 2004, Brinkman, *et al.*, 1993, Dent, 1986). The polluted waters leached from ASS can also have major detrimental effects on fish and other aquatic and benthic organisms. These effects are numerous and include habitat degradation, fish kills, infection and disease, community structures changes due to the removal or suppression of species, benthic smothering due to the formation of Fe flocs, and decline or failure of aquaculture

industries (Adams, *et al.*, 2013, Callinan, *et al.*, 1996, Cook, *et al.*, 2000, Hicks, *et al.*, 1999, Powell and Martens, 2005, Sammut, *et al.*, 1993, Sammut, *et al.*, 1995).

1.1.4 Distribution of acid sulfate soils

The global distribution of ASS is estimated at 50 million ha, covering parts of geographical regions including Australia, Africa, Central and South America, South and Southeast Asia, Scandinavia and Western Europe (Andriessse and van Mensvoort, 2006). In Australia ASS are most commonly associated with Holocene aged sediments deposited in low-lying coastal areas following the last post-glacial sea level rise. Australian ASS coverage is estimated at ~22 million ha, with ~6 million ha found along its modern-day coastal zones (<5 m Australian Height Datum (AHD)) in both sub-tropical and temperate environments such as mangroves, back swamps and estuarine systems (Fitzpatrick, *et al.*, 2008a). The remaining ~16 million ha of ASS in Australia is encountered in inland environments (those landward of modern-day coastal zones) such as river and stream channels, lakes, wetlands, drains, and floodplains. ASS in these environments are termed inland ASS (IASS).

ASS have historically been considered a coastal issue and consequently, this has been the focus for the majority of published research since the 1970s (Fitzpatrick, *et al.*, 2008a, Pons, 1973). In contrast, the extent of IASS was only beginning to be recognised in the late 1990s and 'the first compilation of ASS studies for inland environments in Australia' was published in 2008 (Fitzpatrick and Shand, 2008a). Hence, the reduced amount of published information available for IASS is principally due to the somewhat more recent discovery of the extent and existence of IASS systems in Australia.

1.2 INLAND ACID SULFATE SOILS IN THE MURRAY-DARLING BASIN

The IASS in the river and stream channels, lakes and wetlands of the lower Murray-Darling Basin (MDB) are the focus of this thesis. The formation of sulfidic materials in the MDB is attributed to two main anthropogenic disturbances: (a) the loss of climate driven wetting and drying cycles due to the construction of locks, weirs and barrages and (b)

salinisation of the MDB, in particular increased SO_4^{2-} inputs, due to primary industry development within the catchments.

Hydrological regime change

Due to Australia's climate the river systems in the MDB are subject to high variability in surface runoff and stream flow. Under natural conditions, this variability would produce regular periods of flooding, providing water to the floodplain wetlands, followed by periods of drying in years with low rainfall. The natural wetting and drying cycle of ephemeral wetlands in the MDB prevented the continuous accumulation of shallow acid generating RIS, whereby each dry period would remove pyrite accumulated during the previous wet period. The smaller amount of acidity released during the oxidation of the accumulated RIS could be more effectively dealt with in the freshwater systems (Fitzpatrick, *et al.*, 2009, Fitzpatrick, *et al.*, 2011).

Regulatory structures, such as dams, locks and weirs were installed throughout the MDB in the 1920s to 1940s to facilitate river navigation and agricultural development. As a consequence, these structures altered the natural pattern of flows of the MDB, buffering seasonal and yearly variations in surface runoff and steam flow, and leading to the loss of a natural drying cycle in many wetlands throughout the MDB. These new hydrological conditions in the regulated section of the MDB supported prolonged periods of inundation that favoured anoxic conditions and the on-going accumulation of acid generating RIS (Fitzpatrick, *et al.*, 2009, Fitzpatrick, *et al.*, 2011).

Increased SO_4^{2-} inputs

The formation of RIS is a naturally occurring process in freshwater inland systems. However, SO_4^{2-} concentration is an important factor controlling SO_4^{2-} reduction. Under low SO_4^{2-} concentrations typical of freshwater systems SO_4^{2-} reduction and in turn the production of acid generating RIS is restricted. However, under enhanced inputs of SO_4^{2-} the production of RIS is often stimulated resulting in greater accumulations of RIS in freshwater systems (Anderson and Schiff, 1987, Feng and Hsieh, 1998, Holmer and Storkholm, 2001, Kelly, *et al.*, 1995, Lamers, *et al.*, 2001).

Over the past century, the MDB has undergone extensive changes in land use and water management which has led to widespread salinisation. There are a number of causes of

salinisation of the MDB floodplain, including land clearance, increased irrigation, agricultural leakage and over allocation of available water resources (Jolly, *et al.*, 2001). The high concentrations of SO_4^{2-} associated with salinisation induced greater rates of SO_4^{2-} reduction and aided the production of hypersulfidic material in the MDB (Baldwin, *et al.*, 2007, Rees, *et al.*, 2010).

1.2.1 Post drought sulfuric material

Extreme drought conditions in south-eastern Australia, from ~1997-2009, affected much of the MDB. Initially high water levels and connected water storages buffered low inflows as a result of reduced rainfall. However, as the drought conditions continued, becoming the worst drought in the MDB in recorded history, storages were exhausted and water levels dropped. During 2007-2009 the average river outflow was ~33% of the pre drought river outflow (Murray–Darling Basin Authority, 2010). Additionally, the allocation of water resources to agriculture during drought periods had not been adequately reduced, exacerbating the lowering of water levels. The lowering water levels resulted in the exposure and desiccation of hypersulfidic materials and the *en masse* oxidation of multi-decade (~80-100 years) pyrite accumulations, in turn forming sulfuric materials in wetlands, lakes and river channels particularly in the Lower MDB (Fitzpatrick, *et al.*, 2009, Mosley, *et al.*, 2014a, Murray-Darling Basin Authority, 2011).

1.2.2 Knowledge gaps addressed in this thesis

Distribution of IASS in the MDB

IASS systems in the MDB is an emerging field of research that commenced in earnest circa 2006 following the onset of severe drought conditions in the MDB. Despite decades of scientific investigation of the ecological, water quality, hydrological and geological features of wetlands in the MDB, the prevalence and significance of IASS in the MDB was only fully appreciated following their oxidation and acidification (Fitzpatrick and Shand, 2008b). In contrast, the distribution of coastal ASS in Australia is relatively well known.

There have been a small number of whole-basin investigations into the occurrence of IASS in the MDB. Hall, *et al.* (2006) sampled 81 wetlands to establish how common sulfidic sediments were in the MBD. It was concluded that 17 wetlands (21%) had levels of reduced sulfur that may be of concern. It was also stated that although the study did not have the statistical power to generalise its results over all wetlands in the MDB, the number of wetlands that contained reduced sulfidic sediments was high enough to suggest that the 'occurrence of IASS in the MDB is not uncommon'. In a similar study, Lamontagne, *et al.* (2006) also found that sediments containing sufficient reduced inorganic sulfur concentrations to be an environmental hazard were common in saline wetlands of the lower Murray River and their occurrence appeared to be a function of salinity and water regime, where sulfide concentrations were highest in saline perennial wetlands. Additionally, both Hall, *et al.* (2006) and Lamontagne, *et al.* (2006) did not provide adequate discussion on the distribution and hazards posed by hypersulfidic materials (i.e. soils that have the ability to acidify upon oxidation) in the MDB, instead focusing on the presence of reduced sulfides in wetlands soils. During the drought, a large number of detailed studies on individual wetlands or specific geographical regions were also conducted. For example, the occurrence of IASS with sulfuric and/or hypersulfidic materials in the lower lakes (Fitzpatrick, *et al.*, 2010a) and the middle-lower River Murray floodplain wetlands (Fitzpatrick, *et al.*, 2008b, Fitzpatrick, *et al.*, 2008c, Shand, *et al.*, 2008a, Shand, *et al.*, 2008b, Shand, *et al.*, 2009) had been covered in significant detail prior to the commencement of this study. The aforementioned studies highlighted that IASS may be ubiquitous in the floodplain wetlands of the MBD, however, if the prevalence of IASS in the MDB was to be properly assessed, the total number of wetlands investigated needed to be dramatically increased (see objective 2).

Previous studies into the basin-wide distribution of hypersulfidic materials which were conducted in the period 2003-2006, during the initial stages of the drought, occurred prior to the widespread oxidation and acidification of hypersulfidic materials throughout the MDB. As a result both Hall, *et al.* (2006) and Lamontagne, *et al.* (2006) used the distribution of sulfide containing soil materials to predict where acidification hazards relating to the formation of sulfuric materials will likely occur if drought conditions continued. The continuation of drought conditions following these studies allowed researchers to more accurately investigate the distribution of sulfuric materials under severe drought conditions. Assessment of the scale and hazards posed by sulfuric materials

in the MDB under severe drought conditions would provide valuable information to managers, allowing them to prioritise regional areas or individual wetlands that pose the greatest environmental hazard under continued low flow conditions, or if high flow conditions returned (see section 1.3.2). It would also assist in the allocation of water and monetary resources to minimise acidification if reduced flow conditions in the MDB are encountered in the future, as suggested by climate change models (see objective 2).

Accurate classification of hypersulfidic materials in the MDB

Laboratory tests are able to provide an indication of the probable acidification behaviour of hypersulfidic material, but cannot be expected to predict its exact in situ acidification behaviour. Hall, *et al.* (2006) and Lamontagne, *et al.* (2006) estimated the acidification potential of sulfide containing materials in the MDB by the calculating their net AGP (NAGP).

NAGP is defined as the difference between a soils potential to generate acidity (AGP) and its capacity to neutralise generated acidity (ANC) (i.e. $NAGP = AGP - ANC$) (Ahern, *et al.*, 2004). The bulk of the AGP of sulfidic materials can be estimated by determining its potential sulfidic acidity using the chromium-reducible Sulfur (S_{Cr}) method (Ahern, *et al.*, 2004, Sullivan, *et al.*, 2000). The S_{Cr} method directly measures RIS species (e.g. FeS_2 , FeS , and S^0) and avoids interferences from sulfur in sulfate, organic matter, or non acid generating sulfate minerals (e.g. gypsum). Thus, the S_{Cr} method is preferred over other non-direct methods and is generally considered to provide an accurate estimate of the in situ AGP of a sulfidic material.

To determine the effective ANC of soil materials the acid-reacted back-titration method (ANC_{BT}) is preferred but other methods are also commonly employed (Ahern, *et al.*, 2004). Estimating the effective in situ ANC of sulfidic material is difficult. Existing methods currently overestimate the effective ANC of a sulfidic material if it is not in a form that is readily available (e.g. ANC in the form of shells or other coarse carbonate fragments, or carbonates coated with sparingly soluble iron oxide coatings). Hence, the measurement of ANC in excess of AGP ($NAGP \leq 0$) is not a guarantee that soil acidification won't occur in situ. This is because ANC_{BT} and other methods used to estimate effective ANC do not account for kinetic factors, such as the rate of acid

production compared to the rates at which the neutralising materials become available for buffering.

The use of temporal testing methods, such as the incubation method, take these kinetic effects into account. The incubation method attempts to simulate the natural oxidation behaviour of a sulfidic material by exposing the soil to the atmosphere whilst maintaining it in a moist state over a period of time. By letting the soil ‘speak for itself’ (Dent, 1986), the incubation method often provides a better indication of a soil materials potential acidification behaviour than calculation of its NAGP. For this reason, the incubation method underpins the identification and classification of ASS in Soil Taxonomy (Soil Survey Staff, 2014), the World Reference base (IUSS Working Group WRB, 2014), the Australian Soil Classification (Isbell, 1996), and the Acid Sulfate Soil Working Group, International Union of Soil Sciences (Sullivan, *et al.*, 2010). By using incubation methods in addition to the series of analytical methods to calculate NAGP (Shand, *et al.*, 2008a), the distribution and hazards posed by hypersulfidic materials in the MDB can be more effectively mapped (see objective 2).

Various forms of the incubation method have been used in the study of ASS for some time (Andriessse, 1993, Dent, 1986). Currently, both Soil Taxonomy (Soil Survey Staff, 2014) and the Australian Soil Classification (Isbell, 1996) specify the use of 10mm thick slabs of soil material and an incubation period of 8 weeks (or until the soil pH changes by at least 0.5 pH units to below 4). Recently, the incubation method has undergone improvements. Sullivan, *et al.* (2010) noted that the currently recommended 8 week incubation period can result in false-negative determination in slowly acidifying hypersulfidic materials. To combat this it was suggested that the maximum duration of the incubation period is changed from 8 weeks to ‘until a stable pH is reach after at least 8 weeks of incubation’. A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase (Sullivan, *et al.*, 2010).

Although incubation to a stable pH should be considered best practice, this approach has considerable implications in terms of time, practicality and cost. In many instances, the scope of a study does not permit incubation until a stable pH is achieved, whether it be due to logistical or time constraints. In these instances a simplified incubation method that

results in significant time and labour savings, whilst still accurately classifying ASS materials, and function as a suitable 'next best alternative' is required (see objective 1).

The use of chip-trays as incubation vessels in the incubation method has seen continuous development and use in ASS investigations since 2007 (Fitzpatrick, *et al.*, 2010b). Chip-trays offer a number of advantages over traditional soil-slabs methods, particularly during field sampling, transport, storage during incubation and analysis, and archival storage. The incubation of soil samples in chip-trays, and in soils slabs, produce similar incubation conditions (Sullivan, *et al.*, 2010). However, the precision of the chip-tray approach to the incubation method has not been determined. Due to their advantages, it is expected the use of chip-trays in incubation experiments will become increasingly common. If this is to be the case, it must be demonstrated that the chip-tray approach can provide an acceptable level of precision for testing a soil material acidification potential in the incubation method (see objective 1). Further comprehensive testing, which provides evidence of the advantages offered by chip-trays, will also help to establish the practicality and suitability of chip-trays in ASS investigations (see objective 1).

1.3 REWETTING OF INLAND ACID SULFATE SOILS

The oxidation and acidification of ASS should not be considered an irreversible process. Each of the oxidation reactions outlined in section 1.1.3 are reversible in principle by those outlined in section 1.1.2. This is the basis for suggesting the inundation of severely acidified ASS by a water body as an appropriate method to remediate ASS with sulfuric materials.

1.3.1. Advantages over alternative remediation methods

Traditional methods for the management of sulfuric materials have usually involved the addition of ANC (e.g. agricultural lime (mainly CaCO_3) or slaked lime (Ca(OH)_2)) to neutralise soils acidity. The addition of neutralising agents to ASS has a number of practical drawbacks. To be effective they must be physically thoroughly mixed through the acidified soil, and as the acidification of ASS commonly occurs at large scales, large

volumes of neutralising agent are often required. This makes the addition of neutralising agents to remediate ASS with sulfuric materials difficult, excessively laborious, and expensive. In addition, physical disturbance and the addition of chemical ameliorants is not appropriate in ecologically significant environments.

The reflooding of ASS with sulfuric materials is considered to be an effective means of remediation as it has the potential to: (a) minimise further generation of acidity from pyrite oxidation by excluding atmospheric oxygen (b) consume acidity by introducing an external source of alkalinity (i.e. surface water alkalinity), (c) immobilise pH sensitive elements (e.g. Al, Co, Cu, Ni, Pb, Zn) by increasing pH and (d) establish reducing conditions necessary to promote alkalinity generating geochemical reactions. Hence, the reflooding of ASS with sulfuric materials has the potential to be an effective, low-cost and passive remediation technique suitable for large scales. It is also the most suitable remediation technique for use in ecological significant environments.

1.3.2 Negative implications associated with the reflooding sulfuric materials

The reflooding of severely acidified ASS has a number of potential negative implications that require careful management. The negative implications almost always occur during the period following reflooding, up until the formation of FeS₂. These include:

Mobilisation and transport of elements upon reflooding

Under low pH high Eh conditions, such as those found in sulfuric materials, the mobility of many elements is enhanced (e.g. Al, Cd, Cu, Fe, Mn, Ni, Pb, Zn). Upon reflooding, these materials can be readily transported to surface waters either directly or via sub-surface flow, often in concentrations which may be toxic to local ecosystems (Astrom, 1998, Simpson, *et al.*, 2010). However, increases in pH to circum-neutral conditions driven by reflooding will result in the pH-dependent immobilisation of many of these species. Hence, reflooding has the potential to minimise the release of many elements if circum-neutral pH conditions can be established quickly following reflooding.

Continued pyrite oxidation

Pyrite oxidation can continue following reflooding. In the absence of oxygen, exhausted by aerobic microorganisms, pyrite can be oxidised by aqueous Fe^{3+} species (eqn 1.10) or dissolution of neighbouring Fe(III) solid phases releasing further acidity if pH is sufficiently low or other oxidising agents are present.

Second event element mobilisation

During reductive processes the mobilisation of some elements is enhanced (e.g. As, Cr, Fe), this can result in a secondary event of element mobilisation upon the establishment of reducing conditions following reflooding (Burton, *et al.*, 2008a, Warren and Haack, 2001). The reductive dissolution of Fe and Al acid oxidation products releases Fe^{2+} and Al^{3+} and other adsorbed and co-precipitated metals and can liberate further acidity (Collins, *et al.*, 2010, Jones, *et al.*, 2011, Totsche, *et al.*, 2003). The reduction of SO_4^{2-} to S(-II) species, can lead to toxic concentrations of HS^- and H_2S (Dent, 1986).

Formation of iron monosulfides

The formation of highly reactive iron monosulfides, often considered as a precursor to pyrite (eqn 1.6), following reflooding, means that water levels need to be maintained following inundation. Periods of oxidation that would result in their rapid oxidation and release of stored acidity and co-precipitated elements needs to be avoided (Burton, *et al.*, 2006b, Bush, *et al.*, 2004, White, *et al.*, 1997)

1.3.3 Knowledge gaps addressed in this thesis

Much of the current knowledge on the behaviour of severely acidified ASS following reflooding has been established in coastal environments with land elevations within the tidal range (Johnston, *et al.*, 2009, Johnston, *et al.*, 2010, Portnoy and Giblin, 1997). The majority of these studied environments are also located in tropical climates. Following the realisation of the extent of IASS in the MDB (see section 1.2), it became important to investigate the behaviour of severely acidified ASS following reflooding in these inland freshwater environments (see objective 3).

The impacts following the reflooding of severely acidified IASS with freshwater can be severe in terms of acidification and contaminant mobilisation (Hicks, *et al.*, 2003, McCarthy, *et al.*, 2006, Mosley, *et al.*, 2014b, Shand, *et al.*, 2010). Additionally, the commonly held view that reflooding of severely acidified IASS as an effective means of remediation is currently unproven. The direct application of knowledge gained in coastal ASS environments to IASS environments, without caveats, would be inappropriate. This is due to a number of expected differences in geochemical pathways and hydrological scenarios of the contrasting systems. These differences include:

Alkalinity concentration, supply and delivery

The concentration of alkalinity in sea water systems is relatively constant at ~ 2.5 mmol/L HCO_3^- . Conversely, alkalinity concentrations in freshwater systems of the MDB are highly variable, and are often lower than sea water concentration at $\sim \leq 1$ mmol/L HCO_3^- . Hence, for the same volume of reflooding water the neutralising capacity of freshwater can be less than that of sea water, making freshwater a much less effective neutralising agent. Tidal sea water systems have a continuous supply of external alkalinity that is regenerated diurnally with each tidal cycle. In IASS systems alkalinity present in the reflooding water can function as a once off initial 'charge'. This is particularly the case for wetlands and other small disconnected water bodies. In larger lake systems or riparian wetlands where exchange with the river channel is possible additional alkalinity may be available, however, exchange is likely to be diffusion limited. A possible exception to this is wind driven seiche-events in large water bodies with sufficient fetch, such as Lake Alexandrina in the lower MDB. In sea water systems, the tidal cycle provides an effective means to rapidly distribute renewed alkalinity from the incoming tide.

Lower initial concentrations, limited resupply, and the less effective distribution of alkalinity in highly acidified freshwater IASS systems has the potential to impact the effectiveness of reflooding as a remediation technique. A number of reports (e.g. Shand, *et al.*, 2010) have demonstrated some impacts of limited external alkalinity supply, such as, prolonged periods of metal mobilisation, surface water acidification, and projected several-year recovery timescales. However, these impacts vary with differing soil physical and chemical properties and under differing rewetting scenarios in IASS systems. Further research is required to constrain the range of impacts of lower external alkalinity supply

and to provide scientific evidence that can assist in management decisions and risk assessments for IASS expected to undergo reflooding.

Water level security

In sea water ASS systems, water height fluctuates between a known and predictable tidal range and is unaffected by short-term climate variations. In Australian freshwater IASS systems, water heights can change greatly with climate variation. Australia's climate is highly variable and characterised by cyclic periods of drought, which are predicted to worsen with climate change. The limited security of water levels in inland systems, such as the MDB, when compared to sea levels, means that surface water levels sufficient to prevent the exposure of wetland soils containing IASS materials may not be able to maintained at all times. This places IASS systems that undergo rehabilitation by reflooding at greater risk of unwanted future oxidation events. This is particularly hazardous if the oxidation event occurs during a period where the formation of FeS_2 is not favoured and reactive monosulfide species are abundant. During this period, the highly reactive nature of FeS increases the propensity for the soil to undergo rapid acidification and release their store of co-precipitated elements (see section 1.1.3). There remains considerable uncertainty in the approximate timescales for recovery of severely acidified IASS, however, it is recognised that they present at least short-term acidification hazards and are likely to present ongoing and long-term management challenges. The timescales of recovery, with reference to the commitment of water resources, is therefore a subject worthy of investigation.

Soil differences

There is a large diversity in ASS types in inland systems owing to a wide variety of soil forming factors and landscape types. The environments in which they occur and the types of hazards they pose to surrounding ecosystems and infrastructure can also differ greatly. Fitzpatrick, *et al.* (2009) suggest that this makes IASS more complex than their coastal equivalents. Knowledge of the geochemical processes of reflooded sulfuric ASS in inland freshwater systems needs to be improved in order to minimise damage to the surrounding ecosystem when they are reflooded. The complexity and variety of IASS types makes the construction of predictive models difficult. This thesis intends to add valuable knowledge to the still growing understanding of reflooded IASS systems in the MDB by investigating a number of these processes in the highly acidified IASS in the Lower Lakes region.

Trace element behaviour following reflooding

In theory, freshwater reflooding of severely acidified IASS has the potential to immobilise and prevent the off-site transport of many pH and redox sensitive trace elements by increasing pH and decreasing Eh. The incorporation of trace elements into solid phase FeS₂ is a means of long term trace element sequestration and a key outcome of remediation of sulfuric materials by reflooding (Burton, *et al.*, 2006c). However, there is limited research on the release and transport of trace metals and acidity following reflooding in the complex and often extremely acidified IASS environments (see objective 3). This has hampered the construction of predictive models aimed at assessing the hazards of inland sulfuric materials that under go reflooding and prevented their effective management.

Iron, Aluminium and Sulfur geochemistry

There remains considerable uncertainty in the rates of recovery and geochemical pathways taken following the reflooding of severely acidified IASS. The success of remediation by freshwater reflooding relies on the timely suppression of a number of environmental hazards (see section 1.3.2) by the establishment of circum-neutral pH conditions, establishment of a reducing environment and ultimately the re-formation of FeS₂. It is relatively unknown how the complex geochemical processes involving Fe, Al and S in dynamic Eh-pH systems may delay the pedogenesis of sulfuric material to hypersulfidic or hyposulfidic material. How these delays might impact surface water and ground water quality in severely acidified freshwater IASS systems is also not well known (see objective 3). Without this knowledge, it is impossible to properly manage the impacts of reflooding severely acidified IASS and assess its effectiveness as a potential method of remediation.

1.4 RESEARCH PROJECT

This thesis comprises combined field and laboratory studies of IASS in the MDB. Its general aim is to advance the understanding of ASS in the inland freshwater systems of the MDB. The previous discussions presented in sections 1.2 and 1.3 were used to highlight a number of knowledge gaps relating to IASS in the MDB. The knowledge gaps chosen to be addressed in this thesis are encompassed in the following two sub theme research questions (both with a number of specific objectives).

What is the prevalence and distribution of IASS with hypersulfidic and sulfuric materials in the floodplain wetlands of the MDB?

Objective 1. *Develop a simplified incubation method that: (a) takes advantage of the benefits provided by chip-trays, (b) further demonstrates the suitability of chip-trays as incubation vessels, (c) manages large numbers of samples efficiently and in a timely manner; and (d) more accurately identifies slowly acidifying hypersulfidic materials (see section 1.2.4)*

Objective 2. *More accurately determine the distribution of ASS materials in the MDB by: (a) dramatically increasing the number of assessed wetlands in the MDB, (b) using the incubation method to more accurately determine the acidification potential of hypersulfidic materials, and (c) establish the distribution of sulfuric materials in the MDB under severe drought conditions at the height of the recent millennium drought (see section 1.2.4)*

What are the dominant geochemical pathways taken following freshwater reflooding of inland ASS containing sulfuric materials and the timescales of impact?

Objective 3. *Use in situ sampling techniques to: (a) investigate the behaviour and fate of trace elements and acidity following the freshwater reflooding of severely acidified IASS, (b) identify the physio-chemical processes that control Fe, Al, and SO_4^{2-} solubility following freshwater reflooding of severely acidified IASS, (c) highlight issues that may compromise the effectiveness of freshwater remediation of IASS compared to the tidal sea water remediation of coastal ASS, and (d) construct conceptual models that describe the evolution of a severely acidified IASS system in the lower MDB that undergoes freshwater reflooding (see section 1.3.3)*

1.4.1 General significance of research project

The MDB is Australia's largest and most iconic river system. It is located in the south east of Australia and covers ~1 million km², representing 14% of the Australian continent. The

MDB contains ~30 000 wetlands that support a variety of natural ecosystems and thousands of species of native flora and fauna, some of which are threatened species. Sixteen wetland complexes within the MDB are recognised for their international importance and listed under the Ramsar convention and many others are important to Australians' on a national, state, or regional level. The MDB is prominent in the history and folk lore of Australia and has been the traditional lands of aboriginals for more than 50 000 years. Currently, over 2.1 million people live within the MDB and a further 1.3 million people outside the MDB are dependent on its water resources. The MDB generates ~40% of Australia's gross income derived from irrigated agriculture production, including cotton, cereals, rice, horticulture, and livestock. Mining, manufacturing, and tourism in the MDB also contribute to Australia's economy

Much of the MDB is in poor health as a result of various anthropogenic factors. ASS have been recognised as one of these factors and pose a major threat to the ecology, amenity and economy of the MDB. Due to their recent recognition, research into IASS in the MDB is playing 'catch-up' with the evolving climate conditions. It is of the utmost importance that research into all aspects of IASS in the MDB firstly occurs. It is then important that it continues with intensity and looks to the future. At the next significant climate shift that drives a further evolution of IASS in the MDB the required research should be well developed and available to assist the relevant management authorities in protecting the significant resource that is the MDB.

1.4.2 Thesis Structure

This thesis is composed of four published research chapters and unpublished introductory and concluding chapters. The published research chapters make up the contents of Chapters 2 to 5 and are equivalent to the results chapters in a traditional thesis format. Each published results chapter is self contained and includes independent introduction, methods, results, discussion, and conclusion sections. However, a cover page precedes each published chapter to provide a brief background information and outline of the context of the chapter within the thesis as a whole. Overall introductory and concluding remarks are made in Chapters 1 and 6, respectively.

Chapters 2 to 5 are multi authored. The contributions of each author are ascribed in a standard form provided by the University of Adelaide at the beginning of each research chapter. To conform to the relevant journal's 'requirements for authors' the classification system (e.g. Australian Soil Classification or Soil Taxonomy) and spelling used (e.g. sulfidic or sulphidic) are not consistent throughout this thesis. When referring to these chapters, such as in the table of contents, consistency with the published manuscript takes precedence over, and at the expense of, whole-thesis consistency

Chapter 1. Provides a small introductory background overview to ASS. It reviews literature most relevant to the research objectives, identifying knowledge gaps, and defines the research objectives of the thesis.

Chapter 2. Comprises a manuscript published in Soil Use and Management. It details the development of a simplified incubation method that offers improvements over existing methods. The development of the simplified incubation method addresses research objective 1 and was required in order to properly address research objective 2 .

Chapter 3. Comprises a manuscript published in Soil Use and Management. It aims to addresses research objective 2 by determining the basin-wide distribution of hypersulfidic and sulfuric materials in the MDB .

Chapter 4. Comprises a manuscript published in Journal of Environmental Quality. It uses in situ sampling techniques to focus on the initial period of remediation of sulfuric material following reflooding by a freshwater body. The results are used to addresses research objective 3.

Chapter 5. Comprises a manuscript published in Chemical Geology. It uses a novel experimental design to conduct ponded water experiments that simulate the post-drought reflooding of sulfuric materials. The results focus on the initial period following the freshwater inundation of sulfuric material addresses research objective 3.

Chapter 6. Provides an overall synthesis of the findings contained in Chapters 2 to 5 and their significance, and includes recommendations for future work.

Chapter 7. Appendices A to C. (A) *Contains the supplementary information published alongside the manuscripts in Chapters 4 and 5. (B) Contains a selection of conference abstracts and media associated with the work of this thesis. (C) A digital appendix containing the raw data relating to Chapters 2 to 5, not published within the manuscripts or in its supplementary material.*

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2.

A Simplified Incubation Method Using Chip-trays as Incubation Vessels to Identify Sulphidic Materials in Acid Sulphate Soils

Soil Use and Management, 2012, **28**(3), 401-408.

DOI: [10.1111/j.1475-2743.2012.00422.x](https://doi.org/10.1111/j.1475-2743.2012.00422.x)

This chapter examines the development of a simplified incubation method to determine the acidification potential of ASS in an efficient and timely manner. When this paper was published the incubation method had existing definitions in both the Australian Soil Classification (Isbell, 2002) and Soil Taxonomy (Soil Survey Staff, 2014). However, a number of limitations with these definitions had been identified. I elected to develop the simplified incubation method and use it in place of the existing methods as it offered a number of improvements over the fixed 8 week incubation period defined in Australian Soil Classification and Soil taxonomy. A catalyst for this work was provided by a Murray-Darling Basin Authority commissioned project (Murray-Darling Basin Authority, 2011), which required assessment of the acidification potential of over 7000 soil samples. This method, once developed, was used to determine the acidification potential of those samples, and investigate the occurrence of ASS in the MDB in the following chapter (Chapter 3).

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Name of Co-Author	Rob W. Fitzpatrick		
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Creeper, N.L., Fitzpatrick, R.W. & Shand, P. (2012). A simplified incubation method using chip-trays as incubation vessels to identify sulphidic materials in Acid Sulphate Soils.
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3.

The Occurrence of Inland Acid Sulphate Soils in the Floodplain Wetlands of the Murray–Darling Basin, Australia, Identified Using a Simplified Incubation Method

Soil Use and Management, 2013, **29**(1), 130-139.

DOI: [10.1111/sum.12019](https://doi.org/10.1111/sum.12019)

This chapter applies the incubation method developed in the previous chapter (Chapter 2) to assess the occurrence of IASS in the floodplain wetlands across the MDB. It aims to address the first of two key research questions "What is the prevalence and distribution of ASS with hypersulfidic and sulfuric materials in the floodplain wetlands of the MDB?". Data reported in this chapter originated from an earlier project carried out for the Murray-Darling Basin Authority (Murray-Darling Basin Authority, 2011). Regional environmental officers collected approximately 7200 wetland soil samples from over 1000 floodplain wetlands throughout the MDB. These samples were submitted to me for cataloguing and soil incubation analyses. This chapter represents an original interpretation and reporting of data collected from those samples.

Statement of Authorship

Title of Paper	The occurrence of Inland Acid Sulphate Soils in the floodplain wetlands of the Murray–Darling Basin, Australia, identified using a simplified incubation method
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Contribution to the Paper	Supervised original development of work. Assisted with data interpretation and manuscript revisions following review.		
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4.

Porewater Geochemistry of Inland Acid Sulfate Soils with Sulfuric Horizons Following Postdrought Reflooding with Freshwater

Journal of Environmental Quality, 2015, **44**(3).

DOI: [10.2134/jeq2014.09.0372](https://doi.org/10.2134/jeq2014.09.0372)

This chapter deals with porewater geochemical processes following the rewetting of severely acidified IASS. An unprecedented drought in the MDB led to the exposure and oxidation of hypersulfidic IASS in the Finniss River and Currency Creek. Two major studies (Fitzpatrick et al., 2009; Fitzpatrick et al., 2011), which investigated the properties and extent of ASS in the Finniss River and Currency Creek wetland systems, provided substantial background to this chapter, in particular the representative selection of study sites. The break of the drought flooded the Finniss River and Currency Creek and provided a unique opportunity to study the in situ changes that occur when these soils are rewet. The results of the study contributes original research towards understanding of the geochemical changes to sulfuric IASS following freshwater reflooding and helps support the effective management of these hazardous soils, which in Chapter 3 were found to be common in floodplain wetlands of the MDB.

This manuscript was the feature article and appeared on the front cover of the May 2015 JEQ issue. A synopsis of this chapter was also featured in the Crops, Soils and Agronomy news magazine: the official monthly magazine of the American Society of Agronomy, Crop Science Society of America and Soil Science Society of America (SSSA). It was also featured on the SSSA news webpage and social media. The published popular magazine, webpage articles and social media posts are provided in Appendix B.

Statement of Authorship

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Contribution to the Paper	Supervised original development of work. Assisted with site selection, sampling and preparation of manuscript.		
Signature		Date	11/04/2015

Creeper, N.L., Shand, P., Hicks, W.S. & Fitzpatrick, R.W. (2015). Porewater geochemistry of inland acid sulfate soils with sulfuric horizons following postdrought reflooding with freshwater.
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5.

Geochemical processes following freshwater reflooding of acidified inland Acid Sulfate Soils: An in situ mesocosm experiment

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The extent and threat posed by IASS in the Lower Lakes region has only been fully recognised in recent years. In 2008, a series of CSIRO technical reports investigating the properties and distribution of IASS in the Lower Lakes Region established that these soils were widespread in the region (Fitzpatrick et al., 2010; Fitzpatrick et al., 2008a; Fitzpatrick et al., 2008b). The reports also highlighted that the remediation of the lower lakes area will most likely involve rewetting following the return to higher environmental flows. A subsequent report, which this chapter builds upon, used small scale water containment structures to model the response of sulfuric IASS to post-drought reflooding and quantify the potential for contaminant mobilisation in the Lower Lakes region (Hicks et al., 2009). In the original report, I assisted with experimental design and installation, was responsible for ongoing field and laboratory work, and assisted with data interpretation and the preparation of the client report. This paper expands from the original client report by extending the period of observation by ≥ 100 days, to a total of 200 days, assessing solute transport in greater detail, and investigating complex geochemical transformations of Al, Fe, and their associated products and reactants following freshwater reflooding. This further investigation of geochemical changes following the freshwater reflooding of IASS supports the conclusions of Chapter 4 and will assist with the management of these soils that in Chapter 3 were found to be common in the MDB.

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Author Contributions

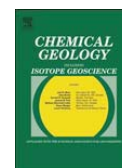
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Name of Co-Author	Rob W. Fitzpatrick		
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Signature		Date	11/04/2015



Geochemical processes following freshwater reflooding of acidified inland acid sulfate soils: An in situ mesocosm experiment



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ABSTRACT

In their oxidised form, inland acid sulfate soils (IASS) with sulfuric horizons ($\text{pH} \leq 3.5$) contain substantial acidity and pose a number of threats to surrounding ecosystems. In their reduced form, IASS with sulfidic material are relatively benign. Freshwater reflooding has the potential to return oxidised IASS with sulfuric horizons to a reduced and benign state. This study uses mesocosms installed in situ to simulate reflooding in two sulfuric IASS profiles, one sandy textured and the other a cracking clay, and to document key geochemical consequences resulting from their reflooding. During the assessed period of 200 days of subaqueous conditions, reducing conditions were established in parts of the former sulfuric horizons in both the sandy textured and clayey textured IASS. In the permeable sandy IASS, acidity was removed from the sulfuric horizon and displaced downward in the profile by advective piston flow, and thus not completely neutralised. The removal of acidity away from the soil surface was critical in preventing surface water acidification. In contrast, solute transport in the less permeable clayey IASS was diffusion dominated and acidity was not removed from the sulfuric horizon following reflooding and no increase in pH was observed. In the absence of piston flow, a diffusive flux of acidity, from the soil to surface water, resulted in surface water acidification. In the acidic porewaters of the reflooded sulfuric horizons, results indicated dissolved aluminium was controlled by an aluminium species with stoichiometry $\text{Al}:\text{OH}:\text{SO}_4$ (e.g. jurbanite). In the same acidic porewaters, iron and sulfate activity appeared to be regulated by the dissolution of natrojarosite. Following the establishment of reducing conditions, the reductive dissolution of natrojarosite and schwertmannite was responsible for large increases in total dissolved iron. We did not observe any indirect evidence indicating the existence of sulfate reduction during the assessed period. It is likely that insufficiently reducing conditions, competitive exclusion by iron-reducing bacteria, and persisting low pH inhibited sulfate reduction during the assessed period. With insufficient in situ alkalinity generation, IASS are likely to continue to pose an environmental hazard following reflooding and remediation is likely to be slow. A number of geochemical processes involved in the remediation of sulfuric horizons were observed in this study. The key geochemical and physical processes affecting porewater chemistry, in particular Fe and Al, are summarised in a conceptual hydrogeochemical model, so that observations made in this study may be applied to other regions containing IASS with sulfuric horizons that are expected to be reflooded with freshwater.

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1. Introduction

In Australia, inland acid sulfate soil (IASS) coverage is estimated at 157,000 km², which is substantially greater than the estimated 58,000 km² of acid sulfate soils located in Australia's coastal environments (Fitzpatrick et al., 2008a). Many of the IASS found in Australia

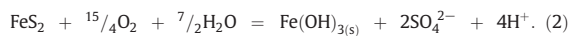
Abbreviations: AHD, Australian height datum; bgl, below ground level; CLLMM, Coorong, Lower Lakes and Murray Mouth; IASS, inland acid sulfate soils; MDB, Murray–Darling Basin; RIS, reduced inorganic sulfur; SI, saturation index; SWI, sediment–water interface; XRD, X-ray diffraction.

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are in the lakes, wetlands and river banks of the Murray–Darling Basin (MDB) (Creeper et al., 2013; Fitzpatrick et al., 2009). Inland acid sulfate soils are soils that contain, or are affected by transformations of sulfide minerals (e.g. pyrite, FeS_2) (Dent and Pons, 1995; Soil Survey Staff, 2014). In their reduced state, IASS consist of sulfidic materials ($\text{pH} > 3.5$) which contain iron sulfide minerals (e.g. pyrite, FeS_2), formed by the microbially catalysed reduction of Fe(III) and SO_4^{2-} (Eq. (1), overall reduction reaction). On exposure to air, the pyrite contained in sulfidic materials oxidizes, resulting in severe soil acidification and the formation of sulfuric horizons ($\text{pH} \leq 3.5$), especially where the soils have limited acid neutralising capacity (Eq. (2), overall oxidation reaction). A sulfuric horizon comprises a soil material ≥ 15 cm thick, with a $\text{pH} \leq 3.5$ and evidence that the low pH value is caused by sulfuric acid

from pyrite oxidation (Soil Survey Staff, 2014). A further consequence of severe soil acidification is the mobilisation of Fe, Al and other contaminants into porewaters, and often into nearby surface waters (Astrom, 2001). At the time of this study, drought conditions in the MDB of Australia had led to the decline of water levels in the Lower Lakes region, and the exposure of IASS that had previously been submerged for a continuous period of time, ~100 years. Once exposed, ca. 200 km² of IASS in the Lower Lakes severely acidified due to the oxidation of pyrite accumulated during this period and formed sulfuric horizons (Fitzpatrick et al., 2010).



The freshwater reflooding of IASS with sulfuric horizons ($\text{pH} \leq 3.5$) can be natural (e.g. climate driven, such as the break of a drought) or management driven (e.g. for the purpose of remediation). The freshwater reflooding of severely acidified IASS has the potential to provide an effective means of remediation through (a) preventing further pyrite oxidation by minimising the ingress of oxygen into the soils via inundation (b) neutralising acidity by introducing an external source of alkalinity (i.e. surface water alkalinity), and (c) establishing the reducing conditions necessary to promote alkalinity generating geochemical reactions and the reformation of pyrite (Anderson and Schiff, 1987). However, many of these hypotheses originate from studies of coastal acid sulfate soils following marine tidal reflooding, which have demonstrated its success as a remediation method (Johnston et al., 2009a, 2009b; Portnoy and Giblin, 1997). Directly applying the conclusions of marine tidal reflooding, without caveats, to freshwater reflooding of IASS would be inappropriate due to differences in geochemical pathways and hydrological scenarios. For example, in the absence of a diurnal tidal cycle, freshwater systems do not have the same continuously regenerative external supply of anions such as HCO_3^- and SO_4^{2-} . A smaller number of studies have shown that freshwater reflooding shows promise as a viable remediation technique (Johnston et al., 2014; Virtanen et al., 2014). However, in the highly acidified IASS systems of the MDB, freshwater reflooding has led to surface water acidification and a heightened risk of ecological damage through persisting periods of low pH, increased metal mobilisation and off-site transportation of acidity and metal(oids) (Baker and Shand, 2014; Creeper et al., 2015; Hicks et al., 2009b; Mosley et al., 2014b; Shand et al., 2010). There remains considerable uncertainty in the rates of recovery and geochemical pathways taken following freshwater reflooding of IASS. The freshwater reflooding of severely acidified IASS has the potential to be a suitable remediation technique for use in ecologically significant wetlands and lakes, such as the Ramsar listed Lower Lakes region (Ramsar Convention, 1998). Many other existing techniques, such as the mechanical application of a neutralising agent, are either not practical or may cause environmental damage. Hence, the continued research of freshwater reflooded IASS is of high importance.

In this study, we used mesocosms installed in situ to monitor the response of IASS with sulfuric horizons, one sandy textured and the other a cracking clay, to freshwater reflooding. The main objectives were to: (i) examine the transport of existing acidity and identify key geochemical transformations of Fe and Al during the initial phase of reflooding, and (b) identify the key physical and geochemical processes that appear to be influencing the likely trajectory towards remediation under continued reflooded conditions. We aim to summarise the identified physical and geochemical processes in a conceptual hydrogeochemical model to explain changes in porewater chemistry, in particular Fe and Al, following freshwater reflooding, so that it can be applied to other

regions containing IASS with sulfuric horizons that are expected to be reflooded with freshwater.

2. Materials and methods

2.1. Study site location, climate and hydrological history

Point Sturt and Boggy Creek study sites are located in Lake Alexandrina, a part of the Coorong, Lower Lakes and Murray Mouth (CLLMM) region of the MDB, South Australia (Fig. 1). The CLLMM region is a Ramsar listed wetland of international importance that provides habitat for internationally significant flora and fauna species, including migratory waterbirds and nationally threatened species of native fish (Ramsar Convention, 1998). Lake Alexandrina is a large (ca. 650 km²), shallow freshwater lake that forms at the terminus of the River Murray. The Point Sturt study site was located on the then dry shoreline of Lake Alexandrina (lat. 35.499° S, long. 138.958° E), at an elevation ranging from −0.3 to −0.4 m Australian height datum ((AHD); 0 m AHD = mean sea level) (Fig. 1). The Boggy Creek study site was located in the dry bed of the Boggy Creek watercourse fringing Hindmarsh island (lat. 35.533° S, long. 138.917° E), at an elevation ranging from −0.05 to −0.4 m AHD (Fig. 1). Boggy Creek is connected at both ends to the Mundoo channel, which is connected to Lake Alexandrina.

The CLLMM region has a mediterranean climate, characterised by cool to mild wet winters and extended hot and dry summers. Median maximum and minimum air temperatures for days 0–100 (July–November) of the study period were 17 °C and 9 °C, respectively (Fig. S1a). Median, maximum and minimum air temperatures for days 100–200 (November–March) were 25 °C and 15 °C, respectively. At both study sites, median soil temperature 20 cm below ground level (bgl) was 13 °C for days 0–100 and 18 °C for days 100–200. Over the assessed period, total rainfall was 243 mm and total class A pan

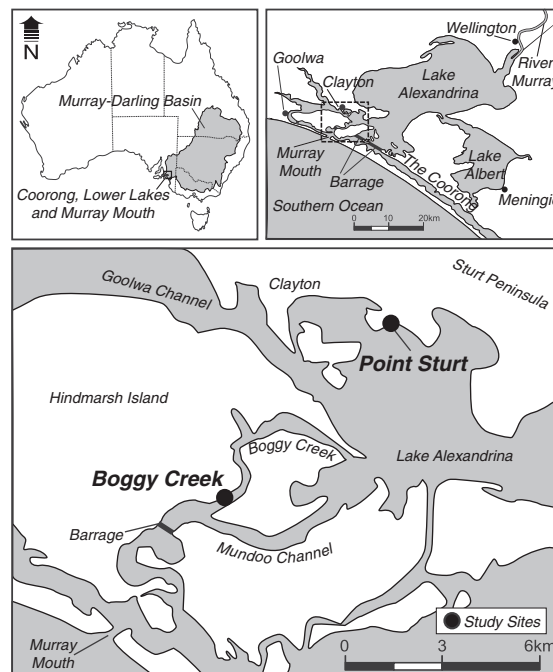


Fig. 1. Locality of Point Sturt and Boggy Creek study sites in Lake Alexandrina and in the CLLMM region and the locality of the CLLMM region within the MDB and Australia.

evaporation was 996 mm, with evaporation rates ranging from 0.8 mm/d to 13.2 mm/d (Fig. S1b). For the majority of the assessed period, daily evaporation exceeded daily rainfall. Local measurement of pan evaporation ceased in 2003, consequently, interpolated daily observations from Silo Data Drill (Jeffrey et al., 2001) have been used. A previous comparison indicated a difference of ± 0.2 mm/d between measured and interpolated evaporation data (Hicks et al., 2010).

The hydrological regime of both study sites is controlled by the water height of Lake Alexandrina. During sufficient freshwater flows from the River Murray, Lake Alexandrina was historically maintained at a full supply level of approximately +0.75 m AHD by the use of upstream river locks and downstream barrages that disconnect Lake Alexandrina from a coastal lagoon (the Coorong) and the Southern Ocean (Fig. 1). The water height of Lake Alexandrina remained at a level higher than the elevation of both Boggy Creek and Point Sturt study sites from the 1920s until 2007. During this period, Boggy Creek and Point Sturt were under continuous subaqueous conditions. The loss of climate driven wetting and drying cycles due to the construction of locks and barrages, combined with increased SO_4^{2-} inputs due to primary industry development within the catchment resulted in the accumulation of reduced iron sulfides (e.g. pyrite) (Fitzpatrick et al., 2009).

Low inflows, caused by the severe Millennium Drought in south-eastern Australia (ca. 1997–2010), and high evaporation rates resulted in the lowering of the water height in Lake Alexandrina in 2007. The water level of Lake Alexandrina dropped below the elevation of the Boggy Creek and Point Sturt study sites in summer 2007/2008, reaching its lowest level of -0.93 m AHD in late 2009. When the soils at Point Sturt and Boggy Creek drained, sulfidic material that had accumulated during the long subaqueous period oxidised and formed sulfuric horizons. When the experiment commenced in July 2009, soils at both study sites had remained severely acidified since their initial desiccation in late 2007. The reflooding experiment occurred under drought conditions with only the soils inside the ponded mesocosms experiencing subaqueous conditions.

2.2. Construction of field installation

2.2.1. Mesocosms/containment structures

Water tanks (ca. 2 m tall with a diameter of 2 m) constructed from polyvinyl chloride (PVC) were used as containment structures for the in situ reflooding mesocosm experiment (Fig. 2a) (Hicks et al., 2009b). A photograph of the in situ mesocosm installations is provided in Fig. 3. The bottom and tops of the water tanks were removed and then pushed into the soils to a depth of 1 m with an excavator. The diameter of the water tanks was sufficient to adequately simulate one dimensional vertical transport that would occur during a whole-of-lake water level rise. Freshwater used to reflood the mesocosms was collected from the River Murray as it flows into Lake Alexandrina. The supply water used to reflood the mesocosms was typical of the freshwater that would reflood the study sites under natural conditions and its general chemistry remained consistent throughout the assessed period.

2.2.2. Solid phase sampling and analysis

Prior to this study (July 2009), representative soil profiles from both study sites were sampled and characterised by Fitzpatrick et al. (2010). Here, we describe and classify these soils according to Keys of Soil Taxonomy (Soil Survey Staff, 2014) and the Australian acid sulfate soil identification key (Fitzpatrick, 2013). Soil mineralogy in the sulfuric horizons was identified by X-ray diffraction (XRD) or supported qualitatively through visual observation and retained acidity measurement (Fitzpatrick et al., 2010). Retained acidity is commonly used in ASS studies to indicate the presence of Fe or Al hydroxy sulfate minerals, such as natrojarosite (Ahern et al., 2004). Chromium reducible sulfur (Ahern et al., 2004; Sullivan et al., 2000), another commonly used method in

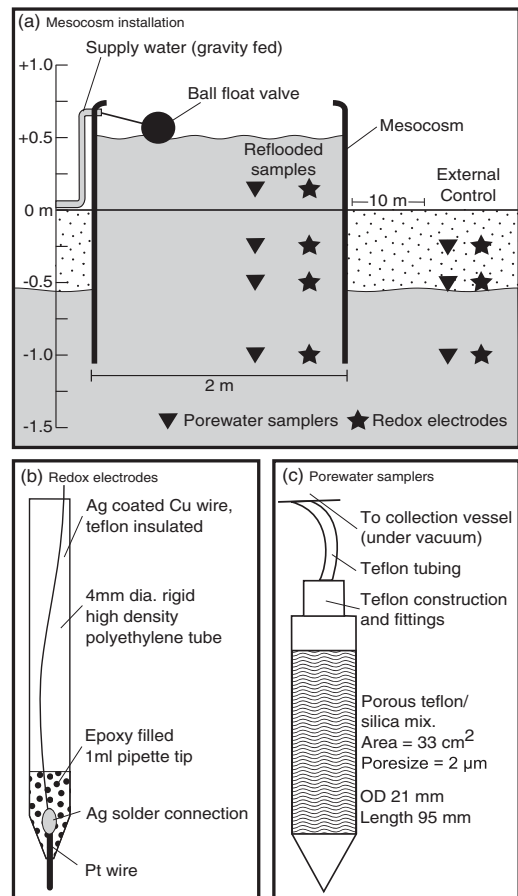


Fig. 2. Illustration of (a) mesocosm installation (not to scale), (b) Pt tipped redox electrode construction, and (c) porewater solution samplers.

ASS studies, was used to quantify reduced inorganic sulfide phases, principally pyrite, in the sulfidic material at both study sites.

2.2.3. Surface water and porewater sampling and analysis

At both study sites, soil solution samplers (Prenart Super Quartz soil water sampler, Prenart Equipment Aps) were installed inside and external to the mesocosm at 0.2 m, 0.5 m, and 1.0 m bgl (Fig. 2a,c). Soil solution samples were obtained by applying a vacuum (initial pressure ca. -80 kPa) to the solution samplers over a period of 24 h. Bottles constructed of high density polyethylene (HDPE) with PTFE fittings and tubing, doubled as both vacuum and sample collection vessels. A sealed system between soil solution sampler and sample collection vessel minimised the exposure of reduced waters to atmospheric oxygen. Porewater was then transferred to new acid washed and rinsed 125 mL polyethylene bottles. Surface water samples were collected by submerging new acid washed and rinsed 125 mL polyethylene bottles ca. 25 cm under the water surface (mid water column). Surface water and porewater samples were stored overnight at 4 °C before being filtered through 0.22 µm membrane filters. Samples were acidified for the determination of Al, Ca, Fe, K, Mg, Na, and S concentrations by ICP-OES and un-acidified sample was used to determine Cl^- (Ion Chromatography), pH and alkalinity or acidity (auto-titrator) (APHA, 2012; Cook et al., 2000; Kirby and Cravotta, 2005).

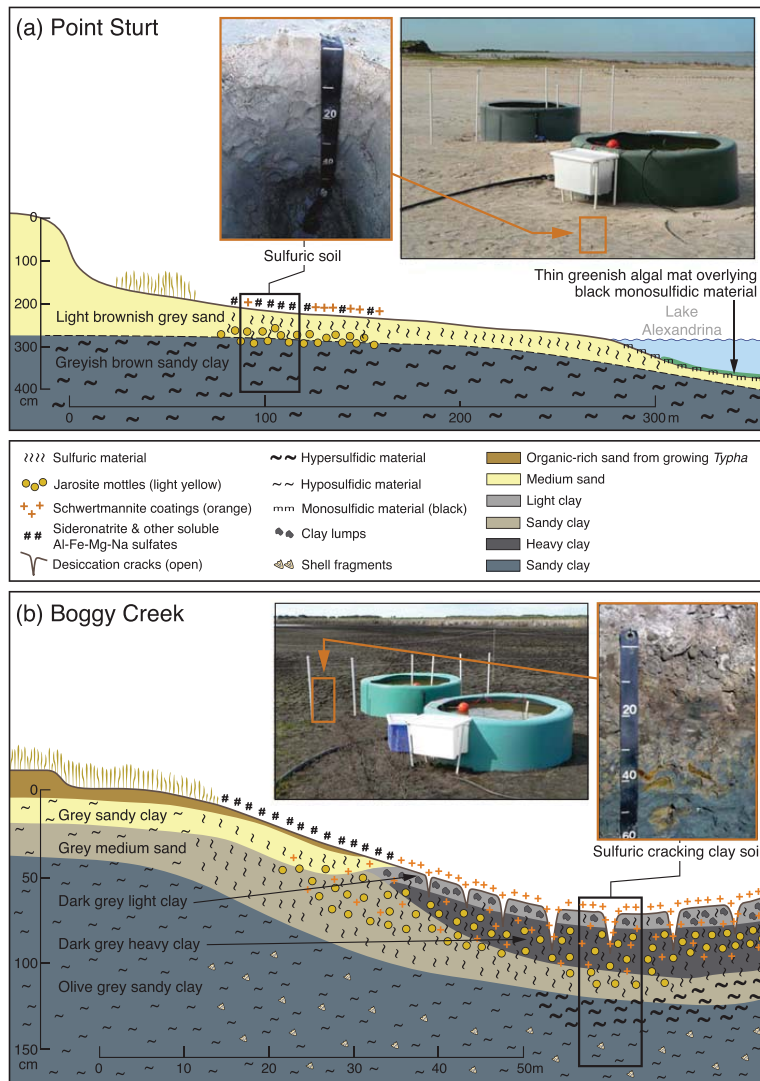


Fig. 3. Cross-section soil-regolith diagrams of Point Sturt and Boggy Creek study sites showing spatial and down profile heterogeneity with inset colour photographs of soil profiles prior to reflooding and study site's landscape. Adapted from Baker et al. (2011).

2.2.4. Soil Eh and temperature monitoring

New platinum redox electrodes were fabricated (Dowley et al., 1998; Thomas, 2010) (Fig. 2b), and installed in duplicate inside the mesocosms 10 cm above the sediment–water interface, 0.2 m bgl, 0.5 m bgl and 1.0 m bgl; and external to the mesocosm at depths of 0.2 m, 0.5 m, and 1.0 m bgl (Fig. 2a). Duplicate redox electrodes were installed at the same depth to assess the heterogeneity of the soil and its response to water regime change. An Ionode™ intermediate junction Ag/AgCl/KCl gel electrode (IJ14) was used as the reference electrode and redox measurements were recorded on a data logger once per hour (Dowley et al., 1998). Additionally, a thermocouple installed 20 cm bgl, was used to record soil temperature at hourly intervals. Measured field redox potentials observed in natural systems usually represent mixed potentials and do not relate directly to a single dominant redox couple (Lindberg and Runnells, 1984), making accurate thermodynamic

calculations difficult. However, in systems where the redox potential is primarily controlled by a single redox couple, interpretations assuming thermodynamic redox equilibrium become more meaningful. For example, Eh measurements have been found useful in strongly poised acid sulfate soil systems dominated by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple (Bartlett, 1986; Fiedler et al., 2007; Langmuir and Whitmore, 1971; van Breemen, 1973a).

2.2.5. Thermodynamic calculations

In this study, in situ measurements of temperature, pH, Eh and total solute concentrations were used to examine the temporal trends in soil redox status and for thermodynamic calculations. Thermodynamic calculations to determine the saturation index (SI) for selected Fe and Al minerals are provided in the supplementary material (see section S2.1). Construction of the Fe–S–Na–H₂O and Al–S–K–H₂O predominance

diagrams and activities used is also detailed in the supplementary material (see section S2.2).

3. Results

3.1. Solid phase characterization

The spatial heterogeneity and soil morphology at the Point Sturt and Boggy Creek study sites are summarised in cross-section soil-regolith diagrams (Fig. 3). Colour soil profile pictures of both study sites are also provided in Fig. 3, and show soil matrix colour, texture changes and mottling. Site photos in Fig. 3 show the experimental installations at both study sites and provide information about the surrounding landscape, and surface features such as the desiccation cracking at Boggy Creek.

Prior to reflooding, the soil profile at the Point Sturt study site comprised a sulfuric horizon ($\text{pH} \leq 3.5$) above the water table (ca. 50 cm bgl), overlying sulfidic material below the water table. Soil texture at this site was dominantly a medium sand (ca. $\geq 95\%$ sand and $\leq 5\%$ clay), changing to a sandy clay texture (ca. 45–55% clay) 70 cm bgl (Fig. 3a). Soil Fe–S mineralogy was dominated by jarosite and schwertmannite in the sulfuric horizon above the water table and pyrite in the sulfidic material below the water table (Fitzpatrick et al., 2008b, 2008c). This profile classified as a Typic Sulfaquept in Soil Taxonomy (Soil Survey Staff, 2014) but is referred to here as a sulfuric sandy soil for simplicity and in accordance with the Australian acid sulfate soil identification key (Fitzpatrick, 2013). The Australian acid sulfate soil identification key is used in preference, as it was designed for audiences who may not be experts in soil classification systems.

Prior to reflooding, the soil profile at the Boggy Creek study site comprised a sulfuric horizon ($\text{pH} \leq 3.5$) above the water table (ca. 40 cm bgl), overlying sulfidic material below the water table (Fig. 3b). Soil texture at this site was a sandy clay (ca. 45–55% clay) to 38 cm bgl with a small sandy (ca. $\geq 95\%$ sand and $\leq 5\%$ clay) 10 cm thick band 12 cm bgl. Deep hexagonal desiccation cracking of at least 30 cm deep was observed in the sulfuric horizon. Ped diameters ranged from 20 to 30 cm and were partially infilled by the outwash of sandy material from the creek banks. Soil Fe-mineralogy was dominated by jarosite and schwertmannite in the sulfuric horizon above the water table (Fitzpatrick et al., 2008b, 2008c). Common pale yellow diffuse mottles of natrojarosite and minor orange–yellow mottles of schwertmannite were visually observed on crack faces in the sulfuric horizon. In the sulfidic material below the water table, Fe-mineralogy was dominated by pyrite. This profile classified as a Hydraquentic Sulfaquept in Soil Taxonomy (Soil Survey Staff, 2014) but is referred to here as a sulfuric cracking clay soil for simplicity and in accordance with the Australian acid sulfate soil identification key (Fitzpatrick, 2013).

At both study sites, severely acidic ($\text{pH} < 2.5$) salt efflorescences had accumulated on the soil surface by evapoconcentration during the preceding dry period. These surface efflorescences comprised schwertmannite, sideronatriite, and other Al–Fe–Mg–Na sulfate minerals (Fitzpatrick et al., 2008b, 2008c). The selected Boggy Creek and Point Sturt study sites provide a contrast in soil physical and chemical properties and represented the two dominant IASS subtypes in Lake Alexandrina under drought conditions, namely sulfuric sandy soils (Point Sturt) and sulfuric cracking clay soils (Boggy Creek).

3.2. Porewater properties

3.2.1. External control samples

The results for analysed parameters in the external control samples are provided in Fig. S2 (pH, acidity or alkalinity, Cl^- , and SO_4^{2-}), Fig. 4 (Eh) and Fig. S3 (Fe and Al). Immediately prior to reflooding, there was general agreement between external control results and internal mesocosm samples for equivalent parameters. Following reflooding,

external control results demonstrated sensor stability and general stability for analysed parameters throughout the assessed period. Changes to equivalent parameters in the internal reflooded samples not observed in the external control samples are considered a result of reflooding.

3.2.2. Sulfuric sandy soil (Point Sturt)

3.2.2.1. Surface water. The chemistry of the overlying surface water initially approximated the chemistry of the supply water apart from a temporary decrease in pH of 1 unit within 1 day of reflooding. After ca. 50 days of subaqueous conditions the chemistry of the surface water began to differ from the supply water, which was likely due to rainfall inputs and evapoconcentration. The Eh of the overlying water remained oxidising throughout the assessed period (Fig. 4a). Over the assessed period, the pH of the surface water increased from 7.9 to a maximum of 9.9 (Fig. 5a). Alkalinity increased along with the pH, increasing from 1.5 mmol/L HCO_3^- to a maximum of 2.6 mmol/L HCO_3^- . Total dissolved Fe and Al concentrations in the surface water remained below detection limit throughout the assessed period.

3.2.2.2. Shallow porewater (20 cm bgl). Prior to reflooding, porewaters 20 cm bgl were oxidising and unsaturated (>700 mV) (Fig. 4b), severely acidic ($\text{pH} < 3$) and highly buffered (>15 mmol/L H^+) (Fig. 5a,b, respectively). Following reflooding the oxic and acidic layer 20 cm bgl became reducing with circum-neutral pH over the assessed period (Fig. 4b). A redox response to reflooding was observed 40 days after reflooding, with Eh decreasing sharply from >700 mV to values as low as -200 mV (Fig. 4b). pH values increased, from a minimum of pH 2.6 to values ≥ 7 after ca. 175 days of subaqueous conditions (Fig. 5a). Initially, high acidity buffered pH increases but after ca. 50 days of subaqueous conditions, close to the time of the decrease in Eh, the majority of dissolved acidity had been removed allowing pH to increase (Fig. 5a). Chloride and SO_4^{2-} concentrations 20 cm bgl decreased by an order of magnitude or more, to concentrations approaching those of the surface water 10 days after reflooding (Fig. 5c,d, respectively). Total dissolved Fe and Al concentrations 20 cm bgl were highest immediately following reflooding, decreasing by ca. 3 orders of magnitude after ca. 10–50 days of subaqueous conditions (Fig. 6a and b, respectively).

3.2.2.3. Deep porewater (50 cm and 100 cm bgl). The 50 cm bgl sampling depth was below the groundwater level and had not oxidised or acidified during the drought. Hence, porewaters 50 cm bgl were reducing (ca. -134 mV) with circum-neutral pH values prior to reflooding (Figs. 4c and 5a, respectively). The redox environment 50 cm bgl remained strongly reducing (ca. -150 mV) for the first 125 days of subaqueous conditions, but Eh increased over time to become weakly reducing (0–150 mV) after 200 days of subaqueous conditions (Fig. 4c). Acidity initially showed an increasing trend, and pH 50 cm bgl decreased to values of ≤ 4 within 50 days of subaqueous conditions (Fig. 5a) and remained ≤ 4 for the remainder of the assessed period. Existing alkalinity 50 cm bgl was consumed 3 days after reflooding (Fig. 5b). Increasing acidity levels continued for a further 13 days after reflooding, reaching a maximum of 8.3 mmol/L H^+ , but returned to concentrations ≤ 1.2 mmol/L H^+ after ca. 50 days of subaqueous conditions. Porewater SO_4^{2-} concentrations increased with increasing acidity. After ca. 50 days of subaqueous conditions, Cl^- and SO_4^{2-} concentrations decreased with decreasing acidity (Fig. 5c, d, respectively). Initial total dissolved Fe concentrations were 2 orders of magnitude higher (3.62×10^{-4} mol/L) than Al concentrations (3.71×10^{-6} mol/L) (Fig. 6a and b, respectively). This differed from observations 20 cm bgl where initial Fe and Al concentrations were both $>1 \times 10^{-3}$ mol/L. Dissolved Al concentrations 50 cm bgl increased by ca. 2.5 orders of magnitude during the first 10 days of subaqueous conditions (Fig. 6b). Total dissolved Fe concentrations also increased during the first 10 days of subaqueous conditions, but increases were <1 order of

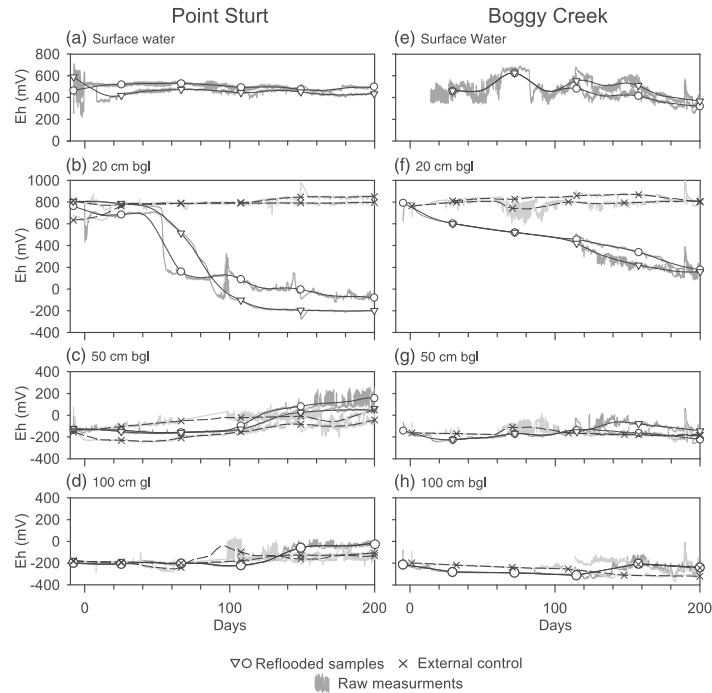


Fig. 4. Temporal redox changes following reflooding. Sulfuric sandy soil (Point Start): (a) Surface water, (b) 20 cm bgl, (c) 50 cm bgl, and (d) 100 cm bgl. Sulfuric cracking clay (Boggy Creek): (e) Surface water, (f) 20 cm bgl, (g) 50 cm bgl, and (h) 100 cm bgl. Shown along with redox changes for external control samples for comparison.

magnitude (Fig. 6a). Iron and Al concentrations decreased after 10 days of subaqueous conditions. At the end of the assessed period, total dissolved Fe and Al concentrations 50 cm bgl were greater than Fe and Al concentrations 20 cm bgl, where prior to reflooding Fe and Al concentrations had been greater.

Porewater 100 cm bgl was circum-neutral (Fig. 5a) and well buffered (Fig. 5b) prior to reflooding. Redox conditions 100 cm bgl were initially strongly reducing (≤ -200 mV) following reflooding but became weakly reducing when Eh increased from ≤ -200 mV to ca. -30 mV after 125 days of subaqueous conditions (Fig. 4d). Eh increased immediately following a decrease in pH from 7.4 to 6.5 during days 100–140 after reflooding (Fig. 5a). The majority of dissolved alkalinity 100 cm bgl was removed approximately 15 days after reflooding (Fig. 5b). The weakly reducing (ca. -30 mV) and slightly more acidic (pH 6.5) conditions after 140 days of subaqueous conditions persisted to the end of the assessed period. Total dissolved Fe and Al concentrations 100 cm bgl remained below detection limits during the assessed period.

3.2.3. Sulfuric cracking clay soil (Boggy Creek)

3.2.3.1. Surface water. Following reflooding, surface water alkalinity decreased, from a starting value of 1.4 mmol/L HCO_3^- to a minimum of 0.1 mmol/L HCO_3^- 102 days after reflooding (Fig. 5f). After 102 days of subaqueous conditions alkalinity increased due to evapoconcentration, returning to ca. 1 mmol/L HCO_3^- by the end of the assessed period. During the same period surface water pH decreased from an initial value of 8.2 to a minimum of 5.6 (Fig. 5e). After 102 days of subaqueous conditions, pH then increased with increasing alkalinity, reaching a maximum of 9.2 units 143 days after reflooding. During the period from 143 days after reflooding to the end of the assessed period, large fluctuations in surface water pH, between ca. pH 6.0 and ca. 9.2 were

observed. Throughout the assessed period, the surface water remained oxidising (Fig. 4e). Dissolved Al and total dissolved Fe concentrations were below detection limits in the surface water throughout the assessed period.

3.2.3.2. Shallow porewater (20 cm bgl). Porewater 20 cm bgl was strongly acidic (pH < 3) and well buffered in terms of pH (> 11 mmol/L H^+) prior to the reflooding (Fig. 5e,f, respectively). A large temporary spike in pH was observed 20 cm bgl 1 day after reflooding, increasing from an initial value of 3.0 to 7.9 (i.e. pH of the supply water) (Fig. 5e). At the same time, large temporary decreases in acidity (Fig. 5f), Cl^- (Fig. 5g) and SO_4^{2-} (Fig. 5h) concentrations were also observed. In all instances, the new concentrations approximated those of the supply water. Within ≤ 1 day (total of 3 days of subaqueous conditions) pH and acidity values and Cl^- and SO_4^{2-} concentrations had returned to initial values. Otherwise, pH and Cl^- and SO_4^{2-} concentrations 20 cm bgl changed little during the assessed period. However, changes in Eh and acidity were observed. Prior to reflooding the porewater 20 cm bgl was strongly oxidising (ca. 740 mV), but following reflooding became weakly oxidising, reaching a minimum of 178 mV (Fig. 4f). Following a decrease in Eh 50 days after reflooding, acidity increased, reaching a maximum of 22 mmol/L H^+ 116 days after reflooding (Fig. 5f). Total dissolved Fe concentrations 20 cm bgl increased by ca. 1 order of magnitude during the assessed period, from a minimum of 2.0×10^{-4} mol/L to a maximum of 6.6×10^{-3} mol/L (Fig. 6c). Dissolved Al concentrations 20 cm bgl were highest prior to reflooding (2.56×10^{-3} mol/L) and changed little for ca. 50 days of subaqueous conditions before decreasing by ca. 1.5 orders of magnitude, to 1.13×10^{-4} mol/L (Fig. 6d).

3.2.3.3. Deep porewater (50 cm and 100 cm bgl). Initial pH values 50 cm bgl and 100 cm bgl were 7.8 and 8.1 respectively, and both were well

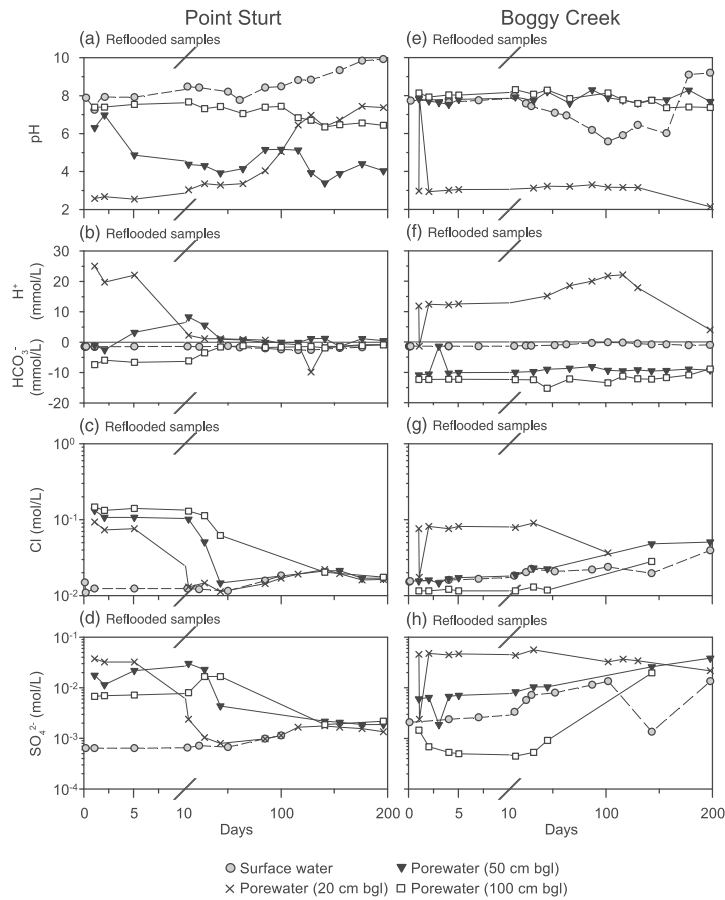


Fig. 5. Temporal changes for pH, acidity or alkalinity, Cl^- , and SO_4^{2-} in the reflowed samples during the assessed period. Sulfuric sandy soil (Point Sturt): (a) pH, (b) acidity or alkalinity, (c) Cl^- , and (d) SO_4^{2-} . Sulfuric cracking clay (Boggy Creek): (e) pH, (f) acidity or alkalinity, (g) Cl^- , and (h) SO_4^{2-} . Sampling depths: surface water (grey circle), 20 cm bgl (cross), 50 cm bgl (black triangle), 100 cm bgl (white square).

buffered with respect to pH with ≥ 10.8 mmol/L HCO_3^- (Fig. 5e,f, respectively). Redox conditions 50 cm bgl and 100 cm bgl remained reducing (ca. -200 mV) during the assessed period and were in general agreement with the external control. Three days after reflooding, a rapid temporary loss of alkalinity was observed 50 cm bgl (Fig. 5f). Alkalinity was not consumed completely, hence pH 50 cm bgl decreased by only 0.3 units (Fig. 5e). Sulfate concentrations 50 cm bgl also showed a rapid temporary decrease 3 days after reflooding (Fig. 5h). By the next sampling period, 4 days after reflooding, pH, alkalinity, and SO_4^{2-} values 50 cm bgl had returned to their initial values and showed little change during the remainder of the assessed period. Immediately prior to reflooding, external control Cl^- concentrations 50 cm bgl and 100 cm bgl were approximately half an order of magnitude lower than those inside the mesocosms (Fig. 5g). After reflooding, external control Cl^- concentrations remained stable during the assessed period but inside the mesocosms, Cl^- concentrations increased, approaching concentrations similar to the external controls. Total dissolved Fe concentrations 50 cm bgl were lower than detection limit during the majority of the assessed period, apart from a period between 10 and 50 days of sub-aqueous conditions where total dissolved Fe concentrations were ca. 1×10^{-5} mol/L (Fig. 6c). Dissolved Al concentrations were also $\leq 1 \times 10^{-5}$ mol/L during the assessed period (Fig. 6d).

3.3. Iron and aluminium solid-phase equilibria

Saturation indices were calculated to qualitatively assess temporal changes in solid phase speciation following reflooding for the selected Fe minerals: goethite, $\text{Fe}(\text{OH})_3$ -amorph, natrojarosite, schwertmannite, and pyrite and Al minerals: gibbsite, $\text{Al}(\text{OH})_3$ -amorph, basaluminite, jurbanite and alunite. Saturation indices for the selected Fe and Al minerals are plotted for porewaters 20 cm and 50 cm bgl (Figs. 7 and 8, respectively). Saturation indices for selected Fe and Al minerals were not determined in the surface waters and 100 cm bgl, as total dissolved Fe and Al concentrations were below detection limit and/or Eh and pH showed little to no response following reflooding.

3.3.1. Iron solid-phase equilibria

3.3.1.1. External control samples. In the external control samples 20 cm bgl and 50 cm bgl, saturation indices varied between a narrow range in both sulfuric soil subtypes during the assessed period (Fig. S4). This was due to relatively stable Eh, pH and dissolved Fe concentrations (Fig. S3). In both sulfuric soil subtypes, natrojarosite and schwertmannite were indicated to be saturated to supersaturated in the external acidic porewaters 20 cm bgl at the beginning of the

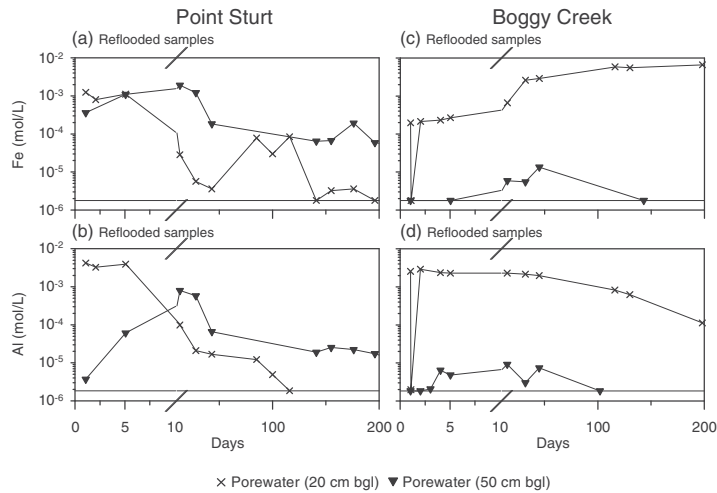


Fig. 6. Temporal changes for total dissolved Fe and Al in the reflooded samples during the assessed period. Sulfuric sandy soil (Point Sturt): (a) Fe and (b) Al. Sulfuric cracking clay (Boggy Creek): (c) Fe and (d) Al. Sampling depths: 20 cm bgl (cross) and 50 cm bgl (black triangle).

assessed period (Fig. S4a,c). Goethite remained moderately supersaturated 20 cm bgl throughout the assessed period. $\text{Fe}(\text{OH})_3\text{-amorph}$ was weakly subsaturated and pyrite was very strongly subsaturated in the oxidised external porewaters 20 cm bgl in both sulfuric soil subtypes (Fig. S4a,c).

Pyrite was weakly subsaturated in the external circum-neutral pH and reduced porewaters 50 cm bgl in both sulfuric soil subtypes, becoming moderately subsaturated later in the assessed period in the sulfuric sandy soil due to a small increase in redox potential (Fig. S4b,d). Goethite (weakly supersaturated) and $\text{Fe}(\text{OH})_3\text{-amorph}$ (weakly subsaturated) were indicated to be close to equilibrium (notional) 50 cm

bgl. Schwertmannite and natrojarosite were moderately to strongly subsaturated 50 cm bgl in both sulfidic soil subtypes during the assessed period (Fig. S4b,d).

3.3.1.2. Internal reflooded samples. Saturation indices for the reflooded soils inside the mesocosms were more variable than the external control values, highlighting a response to reflooding. Goethite was generally indicated to be weakly supersaturated in the porewaters 20 cm bgl in both sulfuric soil subtypes (Fig. 7). In the sulfuric sandy soils at Point Sturt natrojarosite was in notional equilibrium 20 cm bgl for the first 5 days following reflooding. Schwertmannite and natrojarosite became

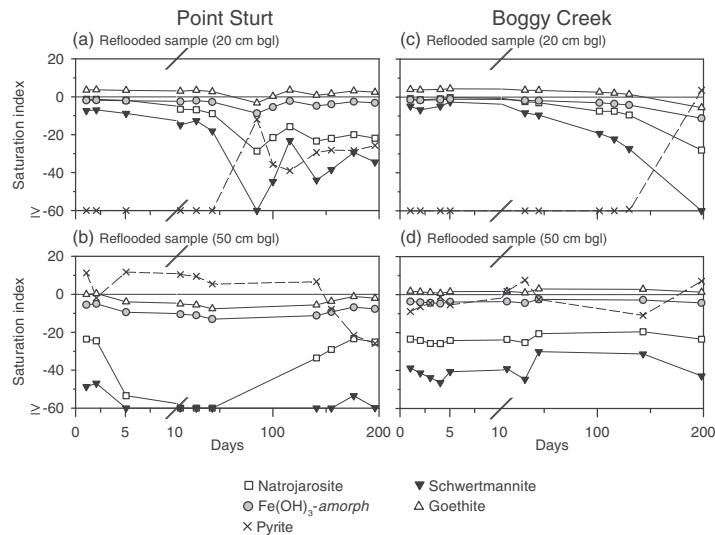


Fig. 7. Temporal changes in the saturation index for selected Fe minerals during the assessed period. Sulfuric sandy soil (Point Sturt): (a) reflooded sample (20 cm bgl), (b) reflooded sample (50 cm bgl). Sulfuric cracking clay (Boggy Creek): (c) reflooded sample (20 cm bgl), (d) reflooded sample (50 cm bgl). Fe minerals: natrojarosite (white square), schwertmannite (black triangle), $\text{Fe}(\text{OH})_3\text{-amorph}$ (grey circle), goethite (white triangle), and pyrite (cross).

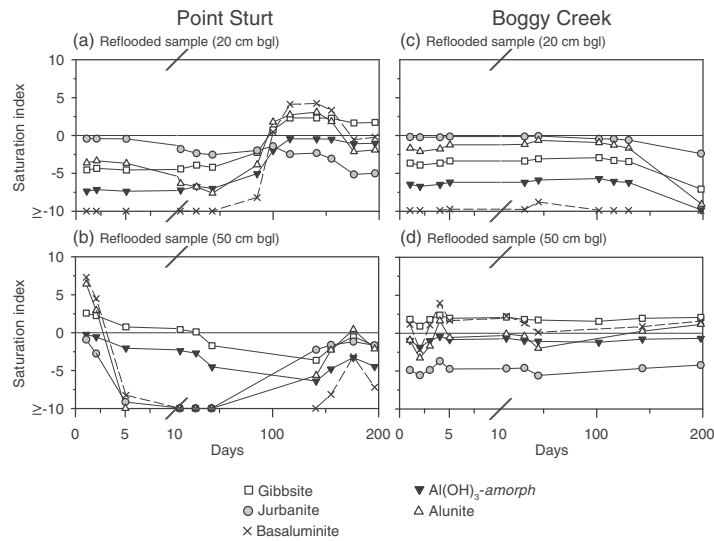


Fig. 8. Temporal changes in the saturation index for selected Al minerals during the assessed period. Sulfuric sandy soil (Point Sturt): (a) reflooded sample (20 cm bgl), (b) reflooded sample (50 cm bgl). Sulfuric cracking clay (Boggy Creek): (c) reflooded sample (20 cm bgl), (d) reflooded sample (50 cm bgl). Al minerals: gibbsite (white square), $\text{Al}(\text{OH})_3\text{-amorph}$ (black inverted triangle), jurbanite (grey circle), alunite (white triangle), and basaluminite (cross).

increasingly subsaturated following reflooding, trending from weakly subsaturated to moderately subsaturated over the assessed period. $\text{Fe}(\text{OH})_3\text{-amorph}$ was weakly subsaturated over the assessed period. In the sulfuric cracking clay soil at Boggy Creek, natrojarosite was in notional equilibrium for ca. 100 days following reflooding. During the same period schwertmannite was weakly subsaturated.

Immediately following reflooding, pyrite was very strongly subsaturated 20 cm bgl in both soil subtypes (Fig. 7a,c). After ca. 50 days after reflooding $\text{SI}_{\text{pyrite}}$ increased rapidly, from -139 to -17 , in the sulfuric sandy soil at Point Sturt. This was a result of a rapid decrease in Eh between ca. 50 and 100 days after reflooding (Fig. 4b) and increase in Fe^{2+} activity (Fig. 6a) (i.e. greater IAP). In the sulfuric cracking clay at Boggy Creek soil $\text{SI}_{\text{pyrite}}$ 20 cm bgl also increased during the assessed period, from -152 immediately following reflooding, to 0.64 and in notional equilibrium at the end of the assessed period, 200 days after reflooding (Fig. 7c). In both soil subtypes, pyrite saturation indices were less variable 50 cm bgl than they were at 20 cm bgl. In the sulfuric sandy soil, $\text{SI}_{\text{pyrite}}$ indicated that pyrite was most often supersaturated throughout the assessed period (Fig. 7b). However, between ca. 150 days after reflooding and the end of the assessed period pyrite became subsaturated. In the sulfuric cracking clay soil 50 cm bgl, pyrite SI values were most often <0 , indicating pyrite remained weakly subsaturated following reflooding.

3.3.2. Aluminium solid-phase equilibria

3.3.2.1. External control samples. In both sulfuric soil subtypes, jurbanite generally remained saturated to weakly subsaturated throughout the assessed period and closest to equilibrium in the external porewaters 20 cm bgl (Fig. S5). In the sulfuric sandy soils at Point Sturt, all other minerals were subsaturated 20 cm bgl; in order from weak to strong subsaturation alunite $>$ gibbsite $>$ $\text{Al}(\text{OH})_3\text{-amorph}$ $>$ basaluminite. In the sulfuric cracking clay soil at Boggy Creek, alunite was supersaturated for 100 days following reflooding, and gibbsite, $\text{Al}(\text{OH})_3\text{-amorph}$, and basaluminite remained subsaturated throughout the assessed period. In the higher pH external porewaters 50 cm bgl of the sandy soil,

$\text{Al}(\text{OH})_3\text{-amorph}$ was closest to equilibrium during the assessed period. In the cracking clay soil 50 cm bgl, gibbsite remained weakly supersaturated and $\text{Al}(\text{OH})_3\text{-amorph}$ weakly subsaturated throughout the assessed period (Fig. S5).

3.3.2.2. Internal reflooded samples. Immediately following reflooding, jurbanite was in notional equilibrium with the reflooded samples 20 cm bgl in the sulfuric sandy soil at Point Sturt, however, jurbanite became increasingly subsaturated as pH increased and SO_4^{2-} activity decreased (Fig. 8a). In the sulfuric cracking clay soils at Boggy Creek jurbanite appeared to be in equilibrium with the reflooded samples 20 cm bgl for ca. 125 days of subaqueous conditions (Fig. 8c). After 125 days of subaqueous conditions, saturation indices of all selected minerals decreased as Al^{3+} activity decreased. In the sulfuric sandy soil, SO_4^{2-} was the dominant controlling species on alunite and jurbanite saturation in the reflooded porewaters 50 cm bgl. Following increases in SO_4^{2-} activity, $\text{SI}_{\text{alunite}}$, $\text{SI}_{\text{basaluminite}}$ and $\text{SI}_{\text{jurbanite}}$ rapidly decreased to minima ≥ -10 , respectively (Fig. 7b). $\text{SI}_{\text{gibbsite}}$ and $\text{SI}_{\text{Al}(\text{OH})_3\text{-amorph}}$, whose IAP are not affected by SO_4^{2-} activity, did not vary as greatly but generally decreased, trending towards weak subsaturation by the end of the assessed period. In the cracking clay soil 50 cm bgl, gibbsite and $\text{Al}(\text{OH})_3\text{-amorph}$ behaved similarly to the external porewaters, owing to only small changes in pH and Al activity following reflooding (Fig. 8d).

4. Discussion

The biogeochemical cycling of elements such as Fe and S are closely linked in acid sulfate soil environments, and dominated by the master variables pH and Eh. In contrast, pH is the dominant control on Al, although Al geochemistry can also be linked to redox processes through incorporation in Fe minerals such as goethite and to complexation processes through its association with dissolved organic matter (Astrom and Corin, 2000; Yvanes-Giuliani et al., 2014). In natural environments, particularly those involving wetting–drying cycles, transport has a major influence on how soils respond to acidification and recovery.

The data from this mesocosm study is used to develop a conceptual model of the geochemical functioning and recovery of contrasting textural soils in a freshwater lake impacted by severe drought.

4.1. Solute transport following reflooding

4.1.1. Sulfuric sandy soil (Point Sturt)

After 5 days of subaqueous conditions, acidity 20 cm bgl began to decrease, losing the majority of existing acidity between 5 and 10 days of subaqueous conditions (Fig. 5b). The acidity at this depth was ≥ 10 times the equivalent alkalinity present in the surface water, hence, insufficient alkalinity was present in the 0.5 m depth of surface water to neutralise the acidity in the sulfuric horizon. Additionally, no decrease in surface water alkalinity was observed, hence, the removal of acidity from the sulfuric horizon was unlikely to be a result of mixing and neutralisation by alkalinity in the surface water. Following the decrease in shallow acidity 20 cm bgl, a concurrent loss of alkalinity and subsequent increase in acidity deeper in the profile at 50 cm bgl was observed. Previously alkaline waters, such as those 50 cm bgl, would not become acidic if mixing and neutralisation dominated. These results indicate that existing acidity 20 cm bgl was displaced downwards. Upon reflooding, the surface water infiltrated the unsaturated soil acting as a displacing fluid piston, and displacing acidity originally at shallower depth (20 cm bgl) downward ahead of a piston front. Examination of Cl^- (a conservative parameter) and SO_4^{2-} porewater concentrations supports the hypotheses that solute transport in the sandy soil at Point Sturt was dominated by downwards advective piston flow (Fig. 5c,d, respectively), to concentrations approaching those of the surface water 10 after reflooding.

Any existing acidity 20 cm bgl not neutralised by the alkalinity in the infiltrating surface water was displaced downward. The downward advective piston flow resulted in a decrease of alkalinity and increasing acidity 50 cm bgl between ca. 5 and 13 days after reflooding (Fig. 5b). Between ca. 15 and 50 days after reflooding acidity 50 cm bgl decreased. Again, the loss of acidity in the overlying layer 50 cm bgl coincided with a decrease in alkalinity in the deeper layer 100 cm bgl. Acidity is associated with elevated SO_4^{2-} concentrations (Eq. (2)), which, along with Cl, shows the progression of the displaced acidic porewater to greater depths over time. The arrival of displaced acidity from above is signalled by elevated SO_4^{2-} concentrations, and its replacement by infiltrating surface water from above is signalled with decreasing SO_4^{2-} concentrations, as it is displaced further downwards.

In summary, during the assessed period, solute transport in the sulfuric sandy soil at Point Sturt was controlled by downward advective piston flow. The mesocosm design, reflooding an initially desiccated profile, provided a good one dimensional representation of lake reflooding, whereby vertical flow was dominant in the unsaturated zone. Studies conducted after this experiment also allowed us to confirm the realistic simulation of post-drought reflooding by the *in situ* mesocosm design. In July 2010 large unseasonal rainfall events at the break of drought resulted in the uncontrolled reflooding of the external control solution samplers at both study sites. Data collection at the external control samplers continued for a short time under re-flooded conditions, with results showing the same downwards displacement of shallow acidity observed in the mesocosm (unpublished data). Soil monitoring around Lake Alexandrina following reflooding, also showed that in permeable sandy profiles around Lake Alexandrina, acidity was transported deeper into the profile following reflooding (Baker and Shand, 2014).

The observation of downwards advective piston flow in the sandy soil at Point Sturt has potentially positive management outcomes for the recovery of severely acidified IASS following reflooding that have high permeability, such as the sandy textured profiles along the shore lines of Lake Alexandrina. Upon reflooding, there are a number of different sources of acidity that could contribute to surface water acidification, including H^+ acidity, dissolved acidic cations, acidic cations

adsorbed to oxides and on cation exchange sites and solid phase acidity, such as sparingly soluble 'acidic' oxyhydroxide and oxyhydroxy sulfate minerals. By displacing shallow acidity and acidic cations away from the sediment–water interface (SWI), piston flow can limit the sources of near SWI acidity to solid phase acidity, reducing the risk of surface water acidification (Hicks et al., 2010). Removing acidity from shallow soil layers also has the potential to limit interaction between sensitive benthic organisms and the higher concentrations of metal(loid)s often associated with acidic porewaters (Corbin et al., 2012; Simpson et al., 2010; Stauber et al., 2008). In the absence of downward advective flow the potential for surface water acidification in freshwater systems is considerable (Mosley et al., 2014c; Shand et al., 2010). In freshwater systems, surface water alkalinity is not recharged diurnally by tidal cycles as in coastal systems. Hence, the capacity for a freshwater system to prevent surface water acidification can rely heavily on the initial concentration of alkalinity in the surface water. Surface water alkalinity can also be lower in freshwater systems than in coastal marine systems.

Upscaling the mesocosm results to that of the lake will depend on a number of factors, and will be scenario dependent, for example the rate of reflooding, and the amount and quality of water introduced. In a lake system, surface water mixing exchange and dilution may be greater than observed in the constrained tank system. Therefore, observations made in the mesocosms will most accurately simulate constrained or closed systems such as hydraulically disconnected small water bodies (i.e. wetlands and small lakes). Larger water bodies where large dilution factors and alkalinity exchange is possible will generally reduce the potential for surface water acidification when compared to observations made in the mesocosms. However, we have demonstrated that the alkalinity present in 0.5 m depth of freshwater can be insufficient to neutralise subsurface acidity (Hicks et al., 2009b). In larger water bodies with restricted dilution and alkalinity exchange the amount of acidity in the soil profile compared with the water column may still be an issue.

4.1.2. Sulfuric cracking clay soil (Boggy Creek)

Large temporary changes in the concentrations of a number of analytes were observed 1 day after reflooding 20 cm bgl and 3 days after reflooding 50 cm bgl. The rate of change was too high for low permeability clayey soils such as those at the Boggy Creek study site. Preferential flow via macropores and cracks greatly enhances advective solute transport in soils. The large temporary changes to analyte concentrations were a result of rapid infiltration of the surface water via extensive desiccation cracking of the clayey soil and other macropores into the unsaturated soils layers ca. 0–50 cm bgl following reflooding. Analogous to the observations in the sandy soil at the Point Sturt, this initial period of advective flow in the cracking clay soil at Boggy Creek resulted in shallow porewater acidity being displaced downwards. However, unlike the downward advective flow observed in the sulfuric sandy soil, advective solute transport in the cracking clay soil ceased once the air-filled pore spaces became waterlogged soon after reflooding. This is consistent with much smaller seepage rates in the cracking clay at Boggy Creek compared to the sandy soil at Point Sturt.

After the temporary period of advective flow, solute transport in the sulfuric cracking clay became diffusion dominated, consistent with the lower hydraulic conductivity expected for the clayey soil. In the absence of continued piston flow, we observed a net upwards flux of acidity from soil to the overlying water column, ultimately resulting in surface water acidification (see Section 4.2.1) (Fig. 5e). A series of recent studies have highlighted the potential of surface water acidification following freshwater reflooding of IASS with shallow sulfuric horizons (Mosley et al., 2014a, 2014b, 2014c). During the oxidation of IASS, sandy textured soils are normally considered to be at higher risk of acidification due to limited buffering capacity compared to clays. Because of this, they often attract a management priority. However, during reflooding, clay textured soils may pose a greater risk of surface water acidification due to the limited downward flux. This represents a reversal of

management priority between sands and clays during the rehabilitation of IASS by reflooding.

4.2. Solid phase Fe speciation and control on Fe solubility

4.2.1. Dissolution of acid oxidation products following reflooding

Inland acid sulfate soils with sulfuric horizons often contain a range of acidic oxidation products in the form of sparingly soluble oxyhydroxide and oxyhydroxy Fe-SO_4^{2-} precipitates (e.g. schwertmannite and natrojarosite). These precipitates can accumulate on the soil surface, and also exist more diffusely in the soil matrix (Fig. 3). Prior to reflooding, natrojarosite was predicted to control Fe solubility in the acidic porewaters 20 cm bgl in both sulfuric soil subtypes (Fig. 8). This observation agrees with a number of other studies that have shown natrojarosite to be common at low pH ($\text{pH} < 3$), and as a companion phase to schwertmannite at low to moderate pH (i.e. pH ca. 3–5) (Acero et al., 2006; Bigham et al., 1996; Collins et al., 2010). Examination of the $\text{Fe-S-Na-H}_2\text{O}$ predominance diagrams show porewater Eh-pH conditions occupying a small area within the stability field of natrojarosite, supporting natrojarosite as the most stable phase (Fig. 9).

Following reflooding, natrojarosite and schwertmannite became increasingly subsaturated 20 cm bgl in the sulfuric sandy soil at Point Sturt over the assessed period (Fig. 7a). During the first 10 days of reflooding, Fe behaved conservatively with respect to Cl^- , with decreases a result of dilution, not solubility or reaction. However, between 10 and ca. 60 days after reflooding, Fe concentrations were not depleted in accordance

with what would be expected for conservative behaviour under decreasing Cl^- concentrations (Fig. 5c). It is probable that natrojarosite and/or schwertmannite was dissolving to maintain the pre-reflooded equilibrium when Fe and other soluble reaction products were removed from the soil layer by piston flow. The release of Fe adsorbed on mineral surfaces and exchange sites may also have supplied Fe to the porewaters. Both natrojarosite and schwertmannite were present prior to reflooding and undergo dissolution following reflooding as pH increases (Burton et al., 2006; Dent, 1986; van Breemen, 1975). The dissolution of Fe(III) oxyhydroxy sulfate minerals and supply of Fe into the aqueous solution during this period acted to buffer the porewater to low pH (Fig. 5a). This resulted in a different trend in the coupling of Eh and pH from that commonly observed, whereby Eh-pH conditions travel along the upper boundary line of the Fe^{2+} stability field, maintaining coupling between Fe(III) minerals and Fe^{2+} solubility, ultimately controlling maximum Fe concentrations (Glover et al., 2011; Johnston et al., 2009b). This coupling has not always been observed (i.e. observation of a near vertical line in a predominance diagram) in highly acidic IASS, such as documented in this study, and in other highly acidic IASS wetland soils in the lower River Murray region (Mosley et al., 2014a; Shand et al., 2011).

After 50 days of subaqueous conditions, Eh 20 cm bgl dropped rapidly in the sulfuric sandy soil (Fig. 4b). With the rapid drop in Eh, redox conditions crossed from the natrojarosite stability field into the stability field for aqueous Fe^{2+} species (Fig. 9a). Under the new Eh-pH conditions Fe(III) solid phases, such as schwertmannite and natrojarosite

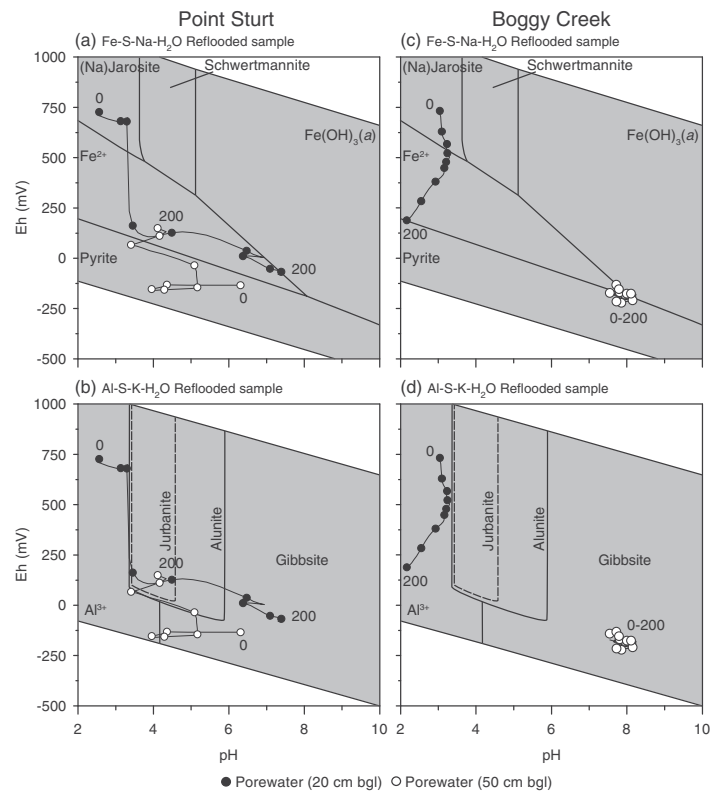


Fig. 9. Eh-pH predominance diagram for Fe-S-Na-H₂O and Al-S-K-H₂O systems. Start (0 days) and end (200 days) points are labelled, each data point between represents a time period of 25 days. Sulfuric sandy soil (Point Sturt): (a) Fe-S-Na-H₂O reflooded samples, (b) Al-S-K-H₂O reflooded samples. Sulfuric cracking clay (Boggy Creek): (c) Fe-S-Na-H₂O reflooded samples, (d) Al-S-K-H₂O reflooded samples. Sampling depths: 20 cm bgl (black circle), 50 cm bgl (white circle). Equilibrium values for solid phases and element concentrations are given in supplementary material.

would no longer stable and could be expected to undergo reductive dissolution. This observation is consistent with total dissolved Fe increasing by an order of magnitude sometime between ca. 40 and 85 days after reflooding (Fig. 6a). The saturation indices for natrojarosite and schwertmannite became more strongly subsaturated during this period, also supporting a conclusion that the reductive dissolution of Fe(III) minerals is exerting a controlling influence on Fe following reflooding. After ca. 125 of subaqueous conditions, total dissolved Fe 20 cm bgl decreased (Fig. 6a) along with an associated increase in pH (Fig. 4c). Examination of the Fe–S–Na–H₂O predominance diagram showed close proximity to the Fe(OH)₃-*amorph* stability field boundary, where a new equilibrium was established, whereby porewater Fe solubility was regulated by the dissolution and reformation of Fe(OH)₃-*amorph* (Fig. 9a).

A similar observation of Fe solubility control by Fe(III) minerals following reflooding was made in the sulfuric cracking clay at Boggy Creek. An increase in total dissolved Fe 20 cm bgl (Fig. 6c), along with a concurrent increase in acidity (Fig. 5f) and decreasing pH (Fig. 5e), was observed between 45 and 116 days after reflooding. The release of Fe into solution also coincided well with transition from natrojarosite to Fe²⁺ stability field (Fig. 9c), and a decrease in saturation indices for natrojarosite and schwertmannite (Fig. 7c). Again, we conclude that the increase in dissolved Fe 20 cm bgl represented the reductive dissolution of natrojarosite or schwertmannite solid phases.

The reductive dissolution of schwertmannite and/or natrojarosite in the sulfuric cracking clay, and the resulting upwards flux of acid and acidic cations, resulted in the consumption of surface water alkalinity and its acidification. We do not consider that cation exchange reactions played a dominant role in the consumption of surface water alkalinity in the sulfuric cracking clay. Cation exchange reactions are rapid, and any impacts resulting from displacement of acidic cations should be observed almost immediately following reflooding, and not delayed like observed here. This differs from what is expected and documented in coastal environments. When acid sulfate soils with sulfuric horizons are reflooded by sea water its high ionic strength commonly leads to cation exchange reactions following reflooding, whereby Na⁺ displaces acid and acidic cations.

4.2.2. Reformation of pyrite following reflooding

4.2.2.1. Shallow porewater (20 cm bgl). Saturation indices, in both sulfuric soil subtypes, indicated that pyrite became less strongly subsaturated, but not supersaturated, in the sulfuric horizon following reflooding. Increases in SI_{pyrite} were driven by substantial decreases in Eh, and in the case of the sandy soil at Point Sturt also an increase in pH. In the sulfuric sandy soil, the Fe–S–Na–H₂O predominance diagram shows Eh–pH conditions closely approached the indicated stability field for pyrite following the Eh drop, and subsequent pH increase (Fig. 9a). In the sulfuric cracking clay soil at Boggy Creek, the Fe–S–Na–H₂O predominance diagram shows that at the end of the assessed period, 200 days after reflooding, Eh–pH conditions 20 cm bgl plotted along the pyrite/Fe²⁺ stability field boundary (Fig. 9c). SI_{pyrite} also indicated pyrite to be in notional equilibrium with the porewater 200 days after reflooding (Fig. 7c).

The reflooding of IASS with sulfuric horizons is expected to encourage natural anoxic microbial processes that ultimately result in the reformation of reduced inorganic sulfur (RIS) species, such as pyrite. However, the formation of pyrite involves a complex series of biogeochemical processes, all of which require a number of conditions to be met. This includes the need for sufficient concentrations of SO₄²⁻, Fe²⁺, and labile organic carbon, acceptable Eh and pH conditions, and the elimination of more favourable electron acceptors (e.g. O₂, NO₃⁻, Mn⁴⁺ and Fe³⁺). During the assessed period, covering the first 200 days of subaqueous conditions following reflooding, we observed the consumption and exclusion of O₂, and the reduction of Fe(III) (see Section 4.2.1), and by inference NO₃⁻ and Mn⁴⁺ reduction. However, despite drops in Eh, we did not observe any indirect

evidence demonstrating the existence of SO₄²⁻ reduction in the shallow porewaters 20 cm bgl, such as decreases in SO₄²⁻ and Fe²⁺ and increases in HCO₃⁻, following reflooding. However, we did not attempt to measure reduced sulfide species (S²⁻, HS⁻, H₂S) directly, and it was not possible to analyse for FeS or FeS₂ without irreversible site disturbance. We suspect that SO₄²⁻ reduction 20 cm bgl remained inhibited during the assessed period by insufficiently reducing conditions, competitive exclusion by iron-reducing bacteria, and in the case for sulfuric cracking clay persisting low pH (Koschorreck, 2008; Postma and Jakobsen, 1996).

We did not measure organic carbon, which may also inhibit RIS production, if its supply is limited, once pH and Eh conditions become suitable. However, there was an abundance of algae observed in the surface waters and on the sediment surface at both study sites, which suggests that carbon may not be limiting. Their respiration is reflected in the diurnal variation of redox potential in the surface waters (Fig. 4a, e). Other reflooding studies have consistently indicated that prolonged periods (≥5–10 years) are required for the full remediation of highly acidified acid sulfate soil systems (Creeper et al., 2015; Johnston et al., 2014; Shand et al., 2010).

4.2.2.2. Deep porewater (50 cm bgl). In both soil subtypes, porewaters 50 cm bgl were reducing with circum-neutral pH prior to reflooding. It was also known that pyrite was present in the reduced soil layers 50 cm bgl in both soil subtypes prior to reflooding (Hicks et al., 2009b). Following reflooding, pyrite was in notional equilibrium or supersaturated for the majority of the assessed period in the sulfuric sandy soil at Point Sturt. Following the arrival of acidic porewater displaced from 20 cm bgl, Fe–S–Na–H₂O predominance diagram shows Eh–pH conditions continued to remain within the stability field of pyrite. However, a small increase in Eh, between 100 days and the end of the assessed period, caused Eh–pH conditions to move within close proximity, and parallel to, the FeS₂/Fe²⁺ stability field boundary, before then moving across it (Fig. 9a). A small increase in acidity and a temporary increase in Fe was observed as Eh–pH conditions moved from the pyrite to Fe²⁺ stability field. A relatively rapid drop in pH, from 5.2 to 3.4, was also observed following the increase in redox values. During this period, porewater 50 cm bgl appeared to be poorly buffered, with fluctuations in pH occurring readily. The source of the released dissolved Fe following the less reducing redox conditions, and increased Fe²⁺ solubility, is unknown. However, possibilities include the release of adsorbed Fe²⁺ or the oxidation of the now instable pyrite by an oxidising agent (e.g. O₂, Fe³⁺, Mn⁴⁺) following the infiltration of slightly more oxalic water.

In the sulfuric cracking clay soil at Boggy Creek, porewater Eh–pH values 50 cm bgl occupied a small area at the junction of Fe²⁺, pyrite and Fe(OH)₃-*amorph* stability fields following reflooding (Fig. 9c). Saturation indices indicated pyrite was weakly subsaturated throughout the assessed period, and hence expected to undergo dissolution. Although SI_{pyrite} indicates the dissolution of pyrite 50 cm bgl was thermodynamically favourable following reflooding, we did not observe an increase in reaction product activities (i.e. Fig. 7d).

4.3. Solid phase Al speciation and control on Al solubility

4.3.1. Jurbanite in acidic porewaters (20 cm bgl)

In both sulfuric soil subtypes, jurbanite appeared to exert a controlling influence on aluminium concentration in the acidic porewaters 20 cm bgl prior to reflooding (Fig. 8). However, Eh–pH conditions indicate aqueous Al³⁺ as the most stable phase prior to reflooding (Fig. 9b,d). Following reflooding, increasing pH 20 cm bgl in the sandy soil at Point Sturt resulted in jurbanite and alunite becoming more strongly subsaturated. Conversely, in the sulfuric cracking clay soil at Boggy Creek, low pH persisted and jurbanite remained in notional equilibrium throughout the assessed period. The apparent control of Al activity in low pH (pH < 4.5) acid sulfate soil porewaters by a species

with the stoichiometry Al:OH:SO₄, presented here as jurbanite (Al(OH)SO₄·5H₂O), has received attention in a number of studies (Jones et al., 2010; Karathanasis et al., 1988; Totsche et al., 2003; van Breemen, 1973b, 1994; Vuai et al., 2003). Currently, the constancy of the IAP for a mineral with assemblage Al:OH:SO₄, is considered fortuitous and simply an artefact of the conservative behaviour of Al and SO₄²⁻ in porewaters with pH < 4.5 (Bigam and Nordstrom, 2000). In a later study by Hicks et al. (2009a), a number of observations contrary to the above were made, and the existence of a mineral with stoichiometry Al:OH:SO₄ was re-questioned. In a recent study, conducted in close proximity to Point Sturt and Boggy Creek study sites, thermodynamic calculations also showed Al in apparent equilibrium with jurbanite (Mosley et al., 2014a). X-ray diffraction did not identify jurbanite in the suspended material of surface waters, however, its identification by XRD can be difficult if poorly crystalline. We did not attempt to isolate jurbanite or another mineral with similar stoichiometry, however, the observations of this study add to a number of

existing studies showing Al activity regulated by a constant IAP_{Al(OH)SO₄}. Furthermore, a number of the contradictory observations made by Hicks et al. (2009a), were also observed in this study. Correlation between SO₄²⁻ activity and pH and SO₄²⁻ and Al³⁺ activity was very poor in the porewaters of both sulfuric soil subtypes. We believe that a completely satisfactory explanation for the apparent control of Al³⁺ activity by a notional Al(OH)SO₄ mineral species in acidic pH < 4.5 acid-sulfate waters is not available. Further research is still required before regarding the potential existence of a notional Al(OH)SO₄ mineral species in acid-sulfate waters as implausible.

4.3.2. Control of Al solubility in circum-neutral pH porewaters (50 cm bgl)

Aluminium activity in natural waters with circum-neutral pH and lower SO₄²⁻ activities is usually controlled by pH and gibbsite or Al(OH)₃-amorph solubility (Bache, 1974; Nordstrom, 1982). This is consistent with our observations, where gibbsite and Al(OH)₃-amorph were closest to equilibrium with the circum-neutral pH porewaters 50 cm bgl

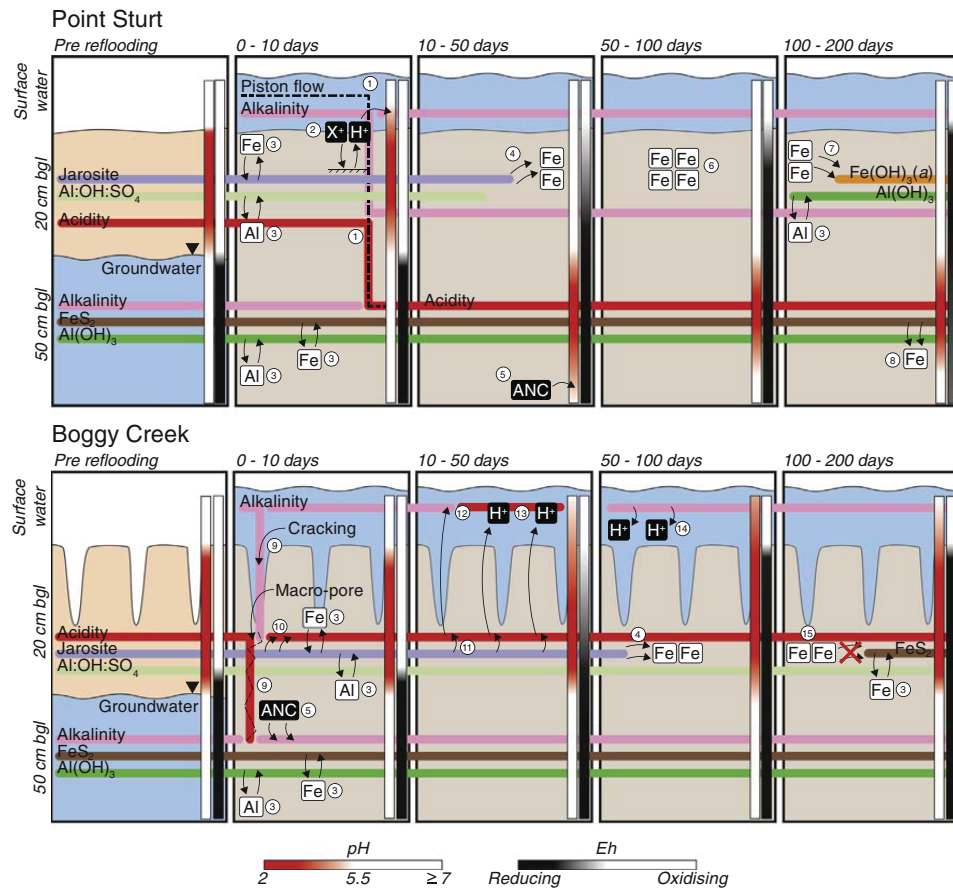


Fig. 10. Conceptual process diagram summarising key geochemical changes following freshwater reflooding of a sulfuric sandy soil (Point Sturt) and sulfuric cracking clay soil (Boggy Creek). (1) Advective piston flow displaces shallow acidity downwards in permeable soils. (2) Displacement of acidity cations (effect weakened by low ionic strength of freshwater vs. tidal marine reflooding). (3) Fe/Al solubility controlled by indicated mineral species. (4) Reductive dissolution of retained acidity phases (i.e. jarosite and schwertmannite). (5) Groundwater acid neutralising capacity consumes displaced acidity. (6) Aqueous Fe most stable species (as a result of Fe(III)(s)-Fe²⁺(aq) decoupling). (7) Aqueous Fe species precipitate out of solution as Fe(OH)₃-amorph. (8) Release of Fe into solution by FeS₂ dissolution. (9) Advective flow along air-filled macropores in cracked clay soils immediately following reflooding (mixing with infiltrating surface water displaces acidity downwards). (10) Dissolution of retained acidity phases release acidity; neutralising surface water alkalinity inputs following reflooding and re-establishing equilibrium. (11) Continued dissolution of retained acidity phases to maintain equilibrium releases further acidity. (12) Upwards diffusion of acidity consumes surface water alkalinity. (13) Surface water acidifies as a result of continued upwards diffusion of acidity (14) Replenishment of surface water lost through evaporation results in evapoconcentration of alkalinity and neutralisation of surface water acidity. (15) Sulfate reduction in the presence of ferrous iron inhibited by persisting low pH.

prior to reflooding (Fig. 8). Following reflooding, saturation indices for gibbsite and $\text{Al}(\text{OH})_3\text{-amorph}$ remained relatively consistent in the cracking clay soil at Boggy Creek, owing to only small changes in pH and Al activity following reflooding. The constructed Al–S–K–H₂O predominance diagram also shows Eh–pH conditions 50 cm bgl within the stability field for gibbsite during the assessed period (Fig. 9). In the sulfuric sandy soils at Point Sturt, SO_4^{2-} was a controlling ionic species on alunite and jurbanite saturation in the reflooded porewaters 50 cm bgl. Increases in SO_4^{2-} , following the displacement of acidic porewater with elevated SO_4^{2-} from 20 cm bgl to 50 cm bgl (Fig. 5d), resulted in large rapid decreases in S_{alunite} , $S_{\text{basaluminite}}$ and $S_{\text{jurbanite}}$. Gibbsite and $\text{Al}(\text{OH})_3\text{-amorph}$, whose IAPs are not affected by SO_4^{2-} activity remained stable during this period. After ca. 80 days of subaqueous conditions S_{alunite} and $S_{\text{jurbanite}}$ increased, approaching weak subsaturation ca. 125 days after reflooding. This is consistent with the Al–S–K–H₂O predominance diagram, which shows Eh–pH conditions moving along and into the stability fields of alunite and jurbanite (see Section 4.2.1) (Fig. 9).

5. Conclusions

The assessed period covered the first 200 days of subaqueous conditions following the reflooding of IASS with sulfuric horizons. Starting conditions, prior to reflooding, of the sulfuric sandy soil (Point Sturt) and cracking clay sulfuric soil (Boggy Creek) were similar. However, following reflooding, these two profiles with contrasting textures behaved differently. In the dominantly sandy soil, solute transport following reflooding was controlled by downward advective piston flow. The displacement of shallow acidic porewater deeper into the profile prevented the upward flux of acidity and acid oxidation products into surface water, and allowed surface water quality to be maintained. In the much less permeable cracking clay soil solute transport was diffusion limited. Here, acidic porewaters remained close to the SWI and the upward flux of acidity and acid oxidation products resulted in surface water acidification.

During the assessed period, a sharp drop in redox potential in the previously oxic sulfuric horizons was observed following reflooding in both sulfuric soil subtypes. We also observed the apparent dissolution of schwertmannite and natrojarosite that had formed during the formation of the sulfuric horizons, their control of Fe solubility following reflooding, and the release of Fe into solution following their reductive dissolution. Al solubility appeared to be controlled by jurbanite or alunite in the acidic porewaters and by gibbsite or $\text{Al}(\text{OH})_3\text{-amorph}$ in circum-neutral pH porewaters. Additional future work, to identify precipitating Al–S solid phases in these severely acidic reflooded IASS systems is required to confirm the existence of the predicted equilibria controls on Al solubility observed in this paper. A number of challenges, including low concentrations and the poorly crystalline nature of many of these Al solid phases (e.g. jurbanite and tamarugite), means that their identification will likely require synchrotron techniques, such as Al and S K-edge XANES and micro-XRD analyses.

The freshwater reflooding of the IASS with sulfuric horizons resulted in major changes to the geochemistry of both systems. A conceptual hydrogeochemical model was developed to explain and summarise key geochemical and physical processes affecting porewater chemistry, in particular Fe and Al, following reflooding (Fig. 10). The observation of these transformations, their locality in the profile and the timescales involved provides important information for modelling reflooding events of severely acidified IASS. The results of this study are also of wider relevance to other locations where drained and severely acidified IASS might be expected to undergo reflooding by freshwater and it is important that such observations are incorporated into their management.

This and other studies (Creeper et al., 2015; Mosley et al., 2014b; Shand et al., 2010) have highlighted a number of problems associated with freshwater reflooding of severely acidified IASS. The reflooding of severely acidified IASS in the MDB following the break of the drought

was largely uncontrolled and the continued monitoring of these systems is recommended. For example, some significant geochemical transformations, namely the production of RIS species, fell outside the period assessed in this study. These transformations can result in further physio-chemical changes to the system and it is important they are documented in future research. At this stage, further research is required before freshwater reflooding can be recommended as a viable technique to remediate severely acidified IASS. Hence, in instances where the opportunity for controlled reflooding exists, delaying reflooding until further research can provide a more complete picture should be considered.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2015.07.009>.

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6.

Conclusions and future research priorities

6.1 INTRODUCTION

At the commencement of this research project, the MDB was experiencing the worst drought conditions in recorded history. Water levels were at their lowest levels in over 80 years and thousands of wetlands, lake margins and the banks of river and stream channels had dried out. Prior to widespread exposure and drying of soils, the full extent of IASS in the MDB was not well known, and was considered by many to be of minor importance and confined to a small number of isolated locations. The knowledge deficit of IASS systems, combined with the ecological and economic significance of the MDB, and the potential for environmental and infrastructure degradation through ASS acidification, provided the incentive for this research project.

Throughout this research project, under continued drought conditions, large numbers of reports, papers, and conference presentations were published, rapidly growing the body of knowledge on IASS in the MDB. The itinerary of this research project adds to this body of knowledge, further advancing our understanding of IASS systems in the MDB.

The aims of this research project were initially focused on providing an overview and context followed by more focused site studies. This was achieved by answering the first of two key research questions set out in section 1.4.

What is the prevalence and distribution of ASS with hypersulfidic and sulfuric materials in the floodplain wetlands of the MDB?

Upon establishing the prevalence of IASS in the MDB two detailed geochemical focused studies were designed to answer the second of two key research questions set out in section 1.4.

What are the dominant geochemical pathways taken following freshwater reflooding of inland ASS containing sulfuric materials and the timescales of impact?

Conclusions are made at the end of each stand alone research chapter. The sections below are used to provide a dot point review of these conclusions and demonstrates how answering the key research questions has added to the understanding of IASS systems in the MDB. Conclusions that address the specific objectives of the first and second key research questions are presented in sections 6.2 and 6.3, respectively. Limitations of the work and recommendations for future research projects are presented at the end of each sub section.

6.2 INLAND ACID SULFATE SOILS IN THE MURRAY-DARLING BASIN

A number of limitations of existing incubation methods were identified in section 1.2.4. These limitations were addressed by the development of a simplified incubation method using chip-trays in Chapter 2, thus accomplishing objective 1 (see section 6.2.1).

Objective 1. Develop a simplified incubation method that can: (a) manage large numbers of samples efficiently and in a timely manner; and (b) more accurately identify slowly acidifying hypersulfidic materials.

At the commencement of this research project the prevalence of IASS in the MDB had only been estimated. These estimations indicated that reduced sulfides were likely to be common in the MDB, however, a number of shortcomings were recognised and described in section 1.2.2. These shortcomings were addressed through an extensive basin-wide study in Chapter 3 that used the simplified incubation method developed in Chapter 2 to determine the acidification hazard of over 1000 wetlands in the MDB, thus accomplishing objective 2 (see section 6.2.2).

Objective 2. *More accurately determine the distribution of ASS materials in the MDB by: (a) dramatically increasing the number of assessed wetlands in the MDB, (b) using the incubation method to more accurately determine the acidification potential of sulfide containing materials, and (c) establish the actual distribution of sulfuric materials in the MDB under severe drought conditions.*

The conclusions arising from the development of a new rapid approach, which incorporates a simplified incubation method and the basin-wide study into prevalence of IASS in the MDB are:

6.2.1 Identification of hypersulfidic materials by a simplified incubation method

Conclusion 1. *The simplified incubation method classifies slowly acidifying hypersulfidic materials more reliably than incubation methods that use a fixed incubation period of 8 weeks (e.g. Isbell, 2002). Sullivan, et al. (2010) proposed that the incubation period should extend beyond 8 weeks, until a stable pH is achieved. This protocol was adopted by the MDBA for the detailed assessment of Ramsar wetlands in the MDB (Murray-Darling Basin Authority, 2010). Since these works were published, the Australian Soil Classification (Isbell and the National Committee for Soils and Terrain, In Press) no longer uses a fixed 8 week incubation period, instead adopting incubation until a stable pH is achieved.*

Conclusion 2. *The simplified incubation method offers an optimal compromise between efficiency and accuracy when incubation to a stable pH is not practical.*

Conclusion 3. *The use of chip-trays as incubation vessels provides an acceptable level of precision (0.1 pH units with 95% confidence) for pH incubation measurements.*

Conclusion 4. *The use of the existing chip-tray approach to the incubation method (Fitzpatrick, et al., 2010) provided a number of advantages over soil-slabs (Isbell, 2002), such as time savings and increased convenience in the field sampling, transport, analysis, and archival storage of samples. Chip-trays were successfully*

used by non-soil specialist regional wetland officers to rapidly sample ASS soil samples from over 1000 floodplain wetlands throughout the MDB. These samples were subsequently used for testing acidification potential using the simplified incubation method (see conclusion 5 below).

Conclusion 5. The simplified incubation method and the use of chip-trays to incubate soil samples was tested and proved to function successfully in Chapter 3, when they were used to determine the acidification potential of ca. 7200 soil samples.

6.2.2 The prevalence and distribution of IASS in the MDB

Conclusion 1. This extensive basin-wide screening study provided a robust method to estimate the prevalence of IASS in the MDB. The results of this study, together with the detailed investigations of selected wetlands contracted by the MDBA (Murray-Darling Basin Authority, 2011), provides an accurate regional assessment of the prevalence and distribution of IASS in the floodplain wetlands of the MDB.

Conclusion 2. The simplified incubation method developed in this thesis and the rapid desktop and wetland assessment protocols developed by the MDBA (Murray-Darling Basin Authority, 2009), functioned as a reliable screening method to detect IASS in the floodplain wetlands of the MDB and rank the acidification hazard of MDB regions. The valuable information provided by this extensive basin-wide screening study facilitated the allocation of limited funds to target regions and individual wetlands with severe acidification hazards. These funds were used for detailed field and laboratory investigations.

Conclusion 3. This extensive basin-wide screening study found that IASS are both prevalent and widespread throughout the MDB with hypersulfidic or sulfuric materials present in 238 of the 1055 wetlands assessed and observed in 11 out of 13 regions.

Conclusion 4. *The distribution of ASS materials in the floodplain wetlands of the MDB is non-uniform. Regions downstream of the Murray–Darling confluence, and in catchments on the southern side of the Murray River channel in Victoria present the greatest acidification hazard.*

Conclusion 5. *Severely acidified ($\text{pH} < 4$) soils, many likely to be ASS with sulfuric material, were common in the floodplain wetlands of the MDB during severe drought conditions. This highlighted the vulnerability of hypersulfidic ASS materials to undergo oxidation and acidification in arid and semi-arid inland environments where water levels are affected by climatic variability and change or water management decisions, such as those in the MDB.*

Conclusion 6. *This study added value by repurposing and reinterpreting legacy data provided by the MDBA. The legacy data was used to its full potential to produce a peer reviewed paper in an international journal and its repurposing represented an efficient use of limited research funding.*

Conclusion 7. *Samples and associated data produced in this study have been catalogued for easy retrieval in the CSIRO National Soil Archive and the National Soil Database (NatSoil). Archiving this extensive database of MDB wetland soils will allow it to be used in future work in the decades to come.*

6.2.3 Limitations of conclusions and suggested future research

Archived database of 7200 MDB wetland soil samples

Soil samples analysed in Chapter 3 have been placed in archival storage along with accompanying analytical data. The large number of geo-referenced soil samples collected from 1055 wetlands distributed throughout the MDB basin represents a considerably valuable resource. This resource is available, via NatSoil, to anyone wishing to conduct further investigations on the archived soil samples and accompanying database. For example, due to the small sample volume available (*ca.* 20 to 30g) Fourier Transform Infrared Spectroscopy and magnetic susceptibility investigations would be ideally suited. Further suggestions include: (a) ascertaining the existence of a relationship between

acidification potential and multiple element concentrations (e.g. Fe and SO_4^{2-}), (b) investigation of wetland soil organic matter concentrations in MDB wetland soils, and (c) sulfide reformation rates following rewetting of chip tray soil samples.

Prevalence of monosulfidic materials in the MDB

The prevalence and distribution of sulfidic and sulfuric materials in the MDB were investigated in Chapter 3. However, it did not provide an indication of the prevalence and distribution of sulfide containing soils that do not acidify upon oxidation (e.g. hyposulfidic and monosulfidic materials). Soils that contain high concentrations of reduced sulfides, but also have high acid neutralising capacity, may present a number of hazards not related to acidification. Monosulfides are often the dominant form of reduced sulfide in these soils. Soils with enhanced monosulfide concentrations can deoxygenate surface waters if resuspended and due to their high reactivity can rapidly release co-precipitated metals when oxidised. Visual observation of monosulfidic soil materials were documented during the sampling or incubation analysis of soil samples in Chapter 3, but results were not published due to lack of analytical data (e.g. Acid Volatile Sulfur (AVS) measurements) (Ahern, *et al.*, 2004). Monosulfidic materials were visually observed in most of the regions and appeared to occur more commonly in regions along the Darling anabranch (unpublished data). The widespread visual observation of monosulfidic soil materials demonstrated a need for a future investigation into the prevalence and distribution of these ASS materials in the MDB. Since the completion of this study, the prevalence of monosulfidic materials has been highlighted in several detailed surveys throughout the MDB that included AVS measurements (Murray-Darling Basin Authority, 2011). The information gained from these detailed studies needs to be combined with the qualitative information of this study so that future research into monosulfidic materials in the MDB can better target the most hazardous regions.

6.3 FRESHWATER REFLOODING OF INLAND ACID SULFATE SOILS WITH SULFURIC MATERIALS

The pedological and mineralogical behaviour of sulfuric material following reflooding by freshwater has been illustrated in detailed cross-sectional conceptual models (Fitzpatrick, *et al.*, 2009, Fitzpatrick, *et al.*, 2012). However, a lack of detailed field monitoring and

laboratory investigations has meant the behaviour and fate of metals and acidity following the freshwater reflooding of sulfuric materials is less well known (Hicks, *et al.*, 2009, Johnston, *et al.*, 2014, Shand, *et al.*, 2010). The reflooding of sulfuric materials in tidal marine system has received greater attention. In these systems the behaviour and fate of metals and acidity in sulfuric material following reflooding by seawater is well established (e.g. Johnston, *et al.*, 2009, Johnston, *et al.*, 2012). However, a number of key differences between sea water and freshwater reflooding and between coastal and inland ASS environments were identified in section 1.3.3. The implications of these key differences on the geochemical pathways taken during remediation were investigated in Chapters 4 and 5. The implementation of two in-situ experiments allowed for the collection of detailed geochemical data. The results of both studies contribute original research towards understanding the key (bio)geochemical transformations following freshwater reflooding of severely acidified IASS, thus accomplishing objective 3.

Objective 3. Use in situ sampling techniques to: (a) investigate the behaviour and fate of trace elements and acidity following the freshwater reflooding of severely acidified IASS, (b) identify the physio-chemical processes that control Fe, Al, and SO₄ solubility following the freshwater reflooding of severely acidified IASS, (c) highlight issues that may compromise the effectiveness of the freshwater remediation of IASS with reference to the tidal sea water remediation of coastal ASS, and (d) construct detailed conceptual models that describe the evolution of severely acidified IASS system of the lower Murray floodplains that undergo freshwater reflooding.

The conclusions arising from these studies are:

6.3.1 Neutralisation of soil acidity following reflooding by freshwater

An important first step in the remediation of severely acidified sulfuric material is the neutralisation of soil acidity. Reflooding with freshwater provides external sources of alkalinity that has the potential to neutralise soil acidity. However, there are a number of concerns that the low alkalinities typical of surface waters in the MDB (when compared to sea water) would be insufficient to neutralise soil acidity in a timely manner.

Conclusion 1. *The complete neutralisation of soil acidity for a strongly acidified IASS reflooded by freshwater is expected to take more than 2 and likely several years.*

Conclusion 2. *Desiccation cracking in clay textured soils provides a mechanism for surface water alkalinity to access deep soil acidity, increasing the rate of neutralisation when compared to diffusion through the SWI.*

Conclusion 3. *Soil acidity is removed more quickly from permeable sandy soils. In the case of deep sandy profiles acidity may be displaced downwards by piston flow. Piston flow reduces the chance of surface water acidification..*

Conclusion 4. *A single charge of alkalinity contained in a freshwater column < 2 m deep is likely to be insufficient to neutralise existing soil acidity. The potential for alkalinity exchange or renewal is diminished in freshwater systems (i.e. no tidal cycle), and alkalinity will often function as a single dose. In the absence of alkalinity renewal, the potential for surface water acidification in freshwater systems is high.*

6.3.2 Metal(loid) behaviour following reflooding

The mobility of trace metals and metalloids following reflooding is of major concern. If their mobility is not suppressed, the potential for off-site transport presents an ongoing risk to the surrounding ecosystem. The mobility of trace metal(loid)s following reflooding of sulfuric materials in inland freshwater environments is largely unknown and until now had not been investigated in such detail.

Conclusion 1. *Trace metal(loid)s remained mobile following reflooding where low pH conditions persisted. Small pH increases near the SWI after 2 years of subaqueous conditions resulted in substantial decreases in concentrations of pH sensitive trace metal(loid)s.*

Conclusion 2. *Metal(loid) contamination (e.g. Al, As(V), B, Cr(VI), Mn, Ni and Zn) exceeded ANZECC water quality guidelines for ≥ 2 years of subaqueous conditions (ANZECC & ARMCANZ, 2000). Exceedances occurred in an environmentally significant Ramsar listed site.*

Conclusion 3. *Immediately following reflooding, exchange reactions resulted in the release of metals into solution, however the effect was observed to be diminished when compared to tidal marine reflooding, likely due to lower ionic strength of freshwaters.*

Conclusion 4. *In acidic porewaters, Al activity was consistent with control by a notional solid phase Al species with stoichiometry Al:OH:SO₄ and equilibrium constant of jurbanite.*

Conclusion 5. *In acidic porewaters, total dissolved Fe concentrations were buffered by the dissolution of acid oxidation products (e.g. natrojarosite and schwertmannite)*

6.3.3 Iron and sulfur reduction

The ultimate objective of remediation by reflooding is the removal or burial of Fe(III) and SO₄²⁻ to reform pyrite. Before the latter occurs, Fe(III) and SO₄²⁻ must proceed through a number of microbially mediated pH and redox sensitive reduction reactions (see section 1.1.2). The timescales involved for these complex geochemical transformations in inland freshwater systems had not been investigated in detail before these studies.

Conclusion 1. *A drop in redox potential, from strongly oxidising to moderately reducing, was observed in the dried and oxidised soil layer above the water table within ca. 50 days of subaqueous conditions.*

Conclusion 2. *A drop in redox potential separate from a delayed increase in pH resulted in a decoupling between $Fe(III)_{(s)}$ and $Fe^{2+}_{(aq)}$. The reductive dissolution of existing $Fe(III)$ phases and the lack of a mineralogical equilibrium control on Fe^{2+} solubility resulted in high Fe^{2+} porewater concentrations.*

Conclusion 3. *Indirect evidence indicating the production of reduced iron sulfide species such as, reduction in SO_4^{2-} and Fe^{2+} , increases in HCO_3^- , black colouration and H_2S odours were not readily apparent within 2 years of subaqueous conditions. However, I did not attempt to measure reduced sulfide species directly. Low organic matter concentrations are known to limit sulfate reduction and may become a factor slowing remediation in the future. However, at the current stage of recovery (i.e. ≤ 2 years of subaqueous conditions) I believe prevailing low pH and competitive exclusion by $Fe(III)$ reducing bacteria or insufficiently reducing redox conditions are more likely to be limiting SO_4^{2-} reduction.*

Conclusion 4. *In the absence of dissolved sulfide, produced via SO_4^{2-} reduction, Fe^{2+} is expected to continue to exist in solution. In an insufficiently reducing environment that does not favour SO_4^{2-} reduction, an increase in pH may result in the oxidation and incorporation of Fe^{2+} into a ferrihydrite phase and not a reduced Fe-S solid phase. The resulting decrease in Fe^{2+} is likely to be only temporary, and Fe^{2+} will be re-released following the eventual reductive dissolution of ferrihydrite.*

6.3.4 Limitations of conclusions and suggested future research

A number of key geochemical transformations fell outside of the assessed periods of both studies. Namely the reduction of sulfate to S(-II) species and the formation and burial of FeS_2 , or the less crystalline FeS . At this stage, further research is required to determine in detail how freshwater reflooding should be used as a technique to remediate severely acidified IASS in freshwater systems. The reflooding of sulfuric IASS in the MDB following the break of the drought was largely uncontrolled due to the very large flows at the break of the drought. However, in instances where the opportunity for human controlled reflooding exists (i.e. water control structures), the possibility of delaying reflooding until further research can provide a more complete picture should be

considered. Controlling the rate of reflooding may also allow the study of the recovery process, whilst minimising risks to surrounding ecosystems. The chief research priority remains the continued observation of reflooded IASS as they undergo remediation. The slow indicated remediation timescales means monitoring may be required for several years. Once SO_4^{2-} reduction becomes thermodynamically favoured investigations should focus on reductive iron, sulfate and organic carbon cycling. Additionally, due to the expectation of more frequent drought periods of greater severity in the future due to climate change, investigations should also be mindful of the impacts of future oxidation events in the remediated or partially remediated reflooded IASS.

The following are suggestions for future research priorities:

What is the distribution and morphology of contemporary RIS species?

The form of RIS species accumulated (e.g. FeS_2 or FeS) will determine the reactivity of the soils during future oxidation events. The distribution of RIS in the soil profile will also determine the reactivity of the soils during future oxidation events. If the distribution of RIS is skewed towards the soil surface, the potential of an acidification event during a shallow draw down episode is increased. Acidification may also occur more rapidly as oxygen can more readily access shallower soil layers. The size and morphology of FeS_2 crystals will may also have implications of the rate of acidification in a future oxidation event. Rates of pyrite oxidation are strongly influenced by surface area, therefore the formation of smaller crystal size or pyrite framboids may increase the susceptibility of an ASS to rapid oxidation and acidification.

What is the impact of in situ alkalinity generation on remediation rates?

Geochemical reactions involved in the reformation of pyrite and iron monosulfide species generate alkalinity. Do the timescale required for remediation decrease substantially where external alkalinity and alkalinity derived from Fe-S reductive processes are jointly responsible for the consumption of acidity?

What is the distribution and morphology of generated alkalinity?

Alkalinity generated during the production of pyrite is stoichiometrically equivalent to the acidity released when oxidised. Divergence from this equivalency by the off-site removal of alkalinity will directly impact the severity of acidification during a subsequent oxidation

event. In sea water coastal ASS environments carbonates are removed by tidal flushing. In IASS environments this is not possible, however, the widespread acidification of IASS in the MDB indicate that a mechanism for removal must exist. Investigation into the spatial distribution of RIS relative to carbonates and the controlling processes involved could help with predictions of acidification severity in future oxidation events.

What are the factors limiting the production of pyrite during remediation?

The factors limiting SO_4^{2-} reduction are likely to change as the soil undergoes remediation. The relative abundance of different electron acceptors, the abundance of electron donors compared to electron acceptors, the molecular complexity of available organic matter, prevailing Eh-pH conditions and the microbial community structure are some of the variables that can all alter the rates of S(-II) production. Can recovery timescales be enhanced by management interventions that remove these limitations, for example the addition of different forms of organic carbon?

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7.

Appendix A. Supplementary Material

7.1 CHAPTER 4

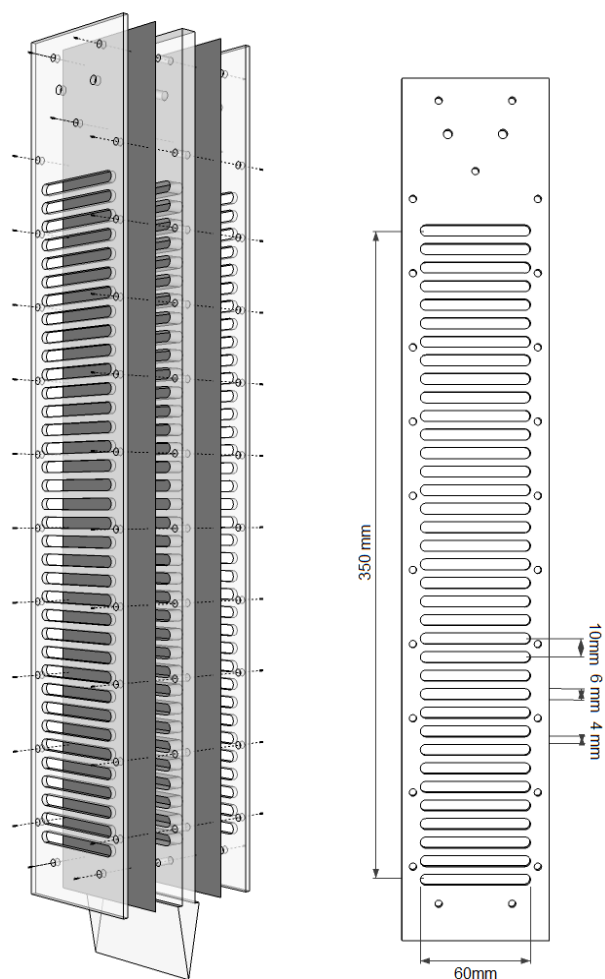


Fig. S1. Diagram of peeper used in study. Polysulfone membrane illustrated in dark grey

7.1.1 Soil Classification

Currently no subgroup exists in Soil Taxonomy (Soil Survey Staff, 2014) that adequately describes a subaqueous soil with a *sulfuric horizon*, as observed at the Finnis River and Currency Creek sampling locations in the study. This presents little issue if these soils exist in this transient state for a short period of time (e.g. during transformation from Hydraquentic Sulfaquept to Sulfic Hydraquent). However, in some instances it is expected that these soils will persist for a number of years. In these cases, it would be appropriate to have the ability to classify these soils accurately within Soil Taxonomy. Fitzpatrick and Grealish (personal communication) have proposed the subgroups Hydraquentic Sulfowassepts and Typic Sulfowassepts to describe the active subaqueous ASS in Finnis River and Currency Creek, respectively (Table S1). This also involves the creation of the Inceptisol sub order, Wassepts, and the great group Sulfowassepts. These proposals are currently being drafted by Fitzpatrick and Grealish (personal communication) for USDA-NRCS for consideration to be included in revised versions of the US Keys to Soil Taxonomy.

Table S1. Cross-reference between sampling location labels used in this study and previous studies and classification of soil profiles by Soil Taxonomy⁷ and the easy to understand Australian ASS identification key⁹.

Sampling locations ¹	Previous sampling location reference	Depth (cm bgl)	Prior to rewetting (pre-rewet/-5)		Post rewetting (post-rewet/+24)			
			Sulfuric horizon⁵/Sulfidic material⁶	Soil Class ⁷	Sulfuric horizon⁵/Sulfidic material⁶	Soil Class ⁷	Australian ASS identification key ⁹	
Fin_N	FIN26M3-4 ²	0 - 5	Sulfuric		Sulfuric			
	FC10740 ³	5 - 17	Sulfuric		Sulfidic			
	LF01-B ⁴	17 - 40	Sulfuric	Hydraquentic Sulfaquept	Sulfuric	Hydraquentic Sulfowassept		Sulfuric subaqueous clayey soil
		40 - 60	Sulfuric		Sulfuric			
		60 - 80	<i>Sulfidic</i>		<i>Sulfidic</i>			
Fin_S	FIN28 ²	0 - 10	Sulfuric		Sulfidic			
	FC1001 ³	10 - 35	Sulfuric	Hydraquentic Sulfaquept	Sulfuric	Hydraquentic Sulfowassept		Sulfuric subaqueous clayey soil
		35 - 75	<i>Sulfidic</i>		<i>Sulfidic</i>			
Cur_N	CUR 25 ²	0 - 5	Sulfuric		Sulfidic			
	FC1062 ³	5 - 15	Sulfuric	Typic Sulfaquept	Sulfidic	Typic Sulfowassept		Sulfuric subaqueous soil
		15 - 35	Sulfuric		Sulfuric			
Cur_S	CUR 18 ²	0 - 5	Sulfuric		Sulfidic			
	FC1029 ³	5 - 20	Sulfuric	Typic Sulfaquept	Sulfuric	Typic Sulfowassept		Sulfuric subaqueous soil
		20 - 50	Sulfuric		Sulfuric			
		50 - 75	<i>Sulfidic</i>		<i>Sulfidic</i>			
		75 - 90	<i>Sulfidic</i>		<i>Sulfidic</i>			

1. Sampling location label used in this document

2. Sampling location label used in (Fitzpatrick, *et al.*, 2009a, Fitzpatrick, *et al.*, 2009b)

3. Sampling location label used in (Fitzpatrick, *et al.*, 2011)

4. Sampling location label used in (Baker, *et al.*, 2010, Baker, *et al.*, 2011)

5. Acid sulfate soil horizon (Soil Survey Staff, 2014)

6. Acid sulfate soil material (Soil Survey Staff, 2014)

7. Soil Taxonomy subgroup (Soil Survey Staff, 2014)

8. Hydraquentic Sulfowassept and Typic Sulfowassept are new subgroup proposals to Soil Taxonomy.

9. Australian acid sulfate soil identification key (Fitzpatrick, 2013, Fitzpatrick, *et al.*, 2008)

7.1.2 Surface water and porewater quality

The concentrations of trace elements at all sampling locations were assessed for exceedances of guideline trigger values (GTV) for metals and metalloids in south central Australian freshwater lakes (ANZECC & ARMCANZ, 2000). The GTV for protection of 95% of species were used and GTV were adjusted for elements known to change toxicity with water hardness, and where hardness algorithms were available (i.e. Cd, Cu, Ni, Pb, and Zn). For porewaters, the more widely used water quality GTV that offer protection to 95% of species (of varying sensitivities) were used in place of the proposed interim sediment quality guidelines for metals and metalloids (ANZECC & ARMCANZ, 2000). A summary of exceedances of GTV can be found in Table S2. A selection of detailed down profile distributions of trace metals (Al, Cr, Mn, Ni, Zn) is presented in Figure 4.

The concentrations of many metals at the Finnis River and Currency Creek sampling locations exceeded GTV (Table S2) on the 1st sampling occasion (Post-rewet/+5). There was a large decrease in the number of GTV exceedances in the surface waters and porewaters of the 4 sampling locations on the 2nd sampling occasion (Post-rewet/+24). The reduction in the number of GTV exceedances indicates there has been an important reduction in the eco-toxicological risk between the 1st and 2nd sampling occasions. However, although the concentrations of a number of trace metals had in some instances reduced significantly (Fig. 4) there were still GTV exceedances in some of the porewaters at some of the sampling locations 24 months after inundation for Al, As(V), B, Cr(VI), Mn, Ni and Zn (Table S2).

Post rewet/+5 (Post rewet /+24)						
	Al (mg L ⁻¹)	As (V) (µg L ⁻¹)	B (mg L ⁻¹)	Cd (µg L ⁻¹)	Cr (VI) (µg L ⁻¹)	
GTV (mg L ⁻¹) Extreme hardness (400mg L ⁻¹ CaCO ₃)	0.055	13	0.370	2.0	1.0	
Surface water	<0.1	<0.004	0.54	<0.01	<0.01	2.00
0-15 cm bgl	1.89	<0.004	1.24	<0.01	<0.01	8.40
15-30 cm bgl	34.3	0.04	<1	2.65	0.400	17.2
Surface water	<0.1	0.068	<1	<0.05	0.200	<0.1
0-15 cm bgl	38.1	3.59	1.69	1.82	3.00	21.6
15-30 cm bgl	135	26.2	2.42	3.43	5.00	54.4
Surface water	<0.1	0.064	1.27	<0.05	<0.1	2.00
0-15 cm bgl	74.8	1.757	3.27	2.66	3.60	26.0
15-30 cm bgl	85.7	2.384	3.19	2.89	3.20	24.6
Surface water	<0.1	0.005	<1	<0.05	0.300	<0.1
0-15 cm bgl	388	120	1.36	1.48	4.20	182.4
15-30 cm bgl	401	188	2.14	1.88	4.10	207.6

		Post rewet/+5 (Post rewet /+24)						
		Cu ($\mu\text{g L}^{-1}$)	Mn (mg L^{-1})	Ni ($\mu\text{g L}^{-1}$)	Pb ($\mu\text{g L}^{-1}$)	Zn ($\mu\text{g L}^{-1}$)		
GTV (mg L^{-1}) Extreme hardness ($400\text{mg L}^{-1} \text{CaCO}_3$)		12.7	1.9	99.4	91.2	72.3		
	Surface water	3.0	2.38	10.0	21.0	10.0	0.400	
Fin_N	0-15 cm bgl	3.0	22.7	518	19.8	236	1.60	
	15-30 cm bgl	6.0	49.0	718	40.2	1750	16.4	
	Surface water	6.0	0.665	16.8	2.6	18.0	2.80	
Fin_S	0-15 cm bgl	38	8.21	381	28.2	732	160	
	15-30 cm bgl	28	18.6	735	29.6	1070	530	
	Surface water	6.0	0.345	11.2	1.00	20.0	<0.4	
Cur_N	0-15 cm bgl	7.0	24.7	674	22.6	1180	115	
	15-30 cm bgl	7.0	23.7	623	19.6	1080	159	
	Surface water	10	0.1236	5.00	6.00	56.0	2.00	
Cur_S	0-15 cm bgl	40	25.3	1870	51.8	894	252	
	15-30 cm bgl	40	26.7	1960	20.8	846	270	

Table S2. Summary of exceedances of guideline trigger values for 95% level of species protection (ANZECC/ARMCANZ 2000). 0-15 cm and 15-30 cm are below ground level (bgl). Reported values represent maximum concentrations within depth range. Exceedances are marked in *italics*. GTV for Al assumes pH > 6.5 no GTV exists for waters with pH < 6.5. GTV for arsenic assumes all arsenic is As (V). The GTV for Chromium assumes all Chromium is Cr (VI). Hardness dependant algorithms have been used to modify GTV for Cd, Cu, Ni, Pb, and Zn (400 mg L⁻¹ CaCO₃).

7.2 CHAPTER 5

7.2.1 Saturation indices

Saturation indices were calculated for goethite, $\text{Fe}(\text{OH})_3\text{-}amorph$, (natro)jarosite, schwertmannite, pyrite, gibbsite, $\text{Al}(\text{OH})_3\text{-}amorph$, jurbanite, alunite, and basaluminite by the following procedure:

Molar concentrations for Al^{3+} , Fe^{2+} , Fe^{3+} , HS^- , and SO_4^{2-} , were determined via PHREEQC (WATEQ4F database) (Ball and Nordstrom, 1991; Parkhurst and Appelo, 2013) using total solute concentrations for Al, Fe and S, respectively, as well as in situ temperature, pH and Eh.

Activities (a_i) for Al^{3+} , Fe^{2+} , Fe^{3+} , H^+ , HS^- , K^+ , Na^+ , OH^- , and SO_4^{2-} were then calculated from the product of the solute concentration (c_i in mol/L) and activity coefficient (γ_i), via the extended Debye-Huckel equation.

$$a_i = c_i \gamma_i$$

where

$$\log \gamma_i = -AZ_i^2 \frac{\mu^{1/2}}{1 + Bd_i \mu^{1/2}}$$

and

$$\mu = \frac{1}{2} \sum c_i Z_i^2$$

A and B are temperature dependant constants ($A = 0.5085$, $B = 0.3285 \times 10^{10}$ at 25 °C), Z_i is the integer ionic charge, d_i is the effective distance of closest approach (effective diameter), and μ is the ionic strength of the aqueous solution (Langmuir, 1997; Lindsay, 1979).

Solute activities were then used to calculate ion activity products (IAP). The IAP for the dissolution reaction of a solid, $A_{(s)} + B = 2C + D$, is defined as

$$IAP = \frac{C^2D}{B}$$

and

$$pIAP = 2pC + pD - pB$$

The activity of a pure solid (i.e. $A_{(s)}$) is 1 by convention and is thus excluded from the IAP. The equilibrium constant (pK) for the same dissolution reaction is defined as.

$$pK = 2pC_e + pD_e - pB_e$$

Where the subscript e denotes the solute activity at equilibrium. When the measured solute activities are in equilibrium with the solid $pK = pIAP$. If $pIAP > pK$ then the soil solution is supersaturated with respect to the products and solid is expected to precipitate. If $pIAP < K$ then the soil solution is undersaturated with respect to the products and the solid is expected to dissolve. By subtracting $pIAP$ from the equilibrium constant, a measure of disequilibrium between the measured activities of solutes in solution and their activities at equilibrium is obtained. Thus the saturation index (SI) is defined as

$$SI = pK - pIAP$$

Where if $SI > 0$, the solution is supersaturated with respect to the expected equilibrium activities, and if $SI < 0$, the solution is undersaturated. The equilibrium constant and its source, the $pIAP$, and the SI for assessed minerals is provided in Table S1.

Table S1. Chemical equations for the dissolution of selected Fe and Al minerals and their corresponding IAP and equilibrium constant, with source of values referenced.

Mineral	Equation	Ion activity product	Equilibrium constant	Reference
Gibbsite	$\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	$\text{pIAP}_{\text{gibbsite}} = \text{pAl}^{3+} - 3\text{pH}$	$\text{pK} = -8.11$	Nordstrom et al. (1990)
Jurbanite	$\text{AlOHSO}_4 + = \text{Al}^{3+} + \text{SO}_4^{2-} + \text{OH}^-$	$\text{pIAP}_{\text{jurbanite}} = \text{pAl}^{3+} + \text{pSO}_4^{2-} + \text{pOH}$	$\text{pK} = 17.23$	Nordstrom (1982)
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ = \text{K}^+ + 3\text{Al}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O}$	$\text{pIAP}_{\text{alunite}} = \text{pK}^+ + 3\text{pAl}^{3+} + 2\text{pSO}_4^{2-} - 6\text{pH}$	$\text{pK} = 1.4$	Adams and Rawajfih (1977)
Basaluminitite	$\text{Al}_4(\text{OH})_{10}\text{SO}_4 + 10\text{H}^+ = 4\text{Al}^{3+} + \text{SO}_4^{2-} + 10\text{H}_2\text{O}$	$\text{pIAP}_{\text{basaluminitite}} = 4\text{pAl}^{3+} + \text{pSO}_4^{2-} - 10\text{pH}$	$\text{pK} = -22.7$	Adams and Rawajfih (1977)
$\text{Al}(\text{OH})_3\text{-}amorph$	$\text{Al}(\text{OH})_3\text{-}amorph + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	$\text{pIAP}_{\text{Al}(\text{OH})_3\text{-}amorph} = \text{pAl}^{3+} - 3\text{pH}$	$\text{pK} = -10.8$	Nordstrom et al. (1990)
$\text{Fe}(\text{OH})_3\text{-}amorph$	$\text{Fe}(\text{OH})_3\text{-}amorph + 3\text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O}$	$\text{pIAP}_{\text{Fe}(\text{OH})_3\text{-}amorph} = \text{pFe}^{3+} - 3\text{pH}$	$\text{pK} = -4$	Ball and Nordstrom (1991)
Jarosite-Na	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ = \text{Na}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O}$	$\text{pIAP}_{\text{jarosite-Na}} = \text{pNa}^+ + 3\text{pFe}^{3+} + 2\text{pSO}_4^{2-} - 6\text{pH}$	$\text{pK} = 5.28$	Ball and Nordstrom (1991)
Schwertmannite	$\text{Fe}_8\text{O}_8(\text{OH})_{4.8}(\text{SO}_4)_{1.6} + 20.8\text{H}^+ = 8\text{Fe}^{3+} + 1.6\text{SO}_4^{2-} + 12.8\text{H}_2\text{O}$	$\text{pIAP}_{\text{schwertmannite}} = 8\text{pFe}^{3+} + 1.6\text{pSO}_4^{2-} - 20.8\text{pH}$	$\text{pK} = -18$	Bigham et al. (1996)
Goethite	$\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$	$\text{pIAP}_{\text{goethite}} = \text{pFe}^{3+} - 3\text{pH}$	$\text{pK} = 1$	Ball and Nordstrom (1991)
Pyrite	$\text{FeS}_2 + 2\text{H}^+ + 2\text{e}^- = \text{Fe}^{2+} + 2\text{HS}^-$	$\text{pIAP}_{\text{pyrite}} = \text{pFe}^{2+} + 2\text{pHS}^- - 2\text{pH} - 2\text{pe}$	$\text{pK} = 18.5$	Ball and Nordstrom (1991)

7.2.2 Eh-pH predominance diagrams

The phreeplot program was used to construct the Fe-S-Na-H₂O and Al-S-K-H₂O predominance diagrams (Kinniburgh and Cooper, 2004). Phreeplot uses an embedded version of PHREEQC for calculations (Parkhurst and Appelo, 2013). The provided WATEQ4F database was used with the addition of schwertmannite (Table S1). The following element concentration were used: Fe (1g/L); Al (0.1g/L); S (2.5 g/L); Na (2 g/L); Cl (2.5g/L); Ca (0.5 g/L); Mg (0.8 g/L); K (0.2 g/L).

7.2.3 Supplementary figures

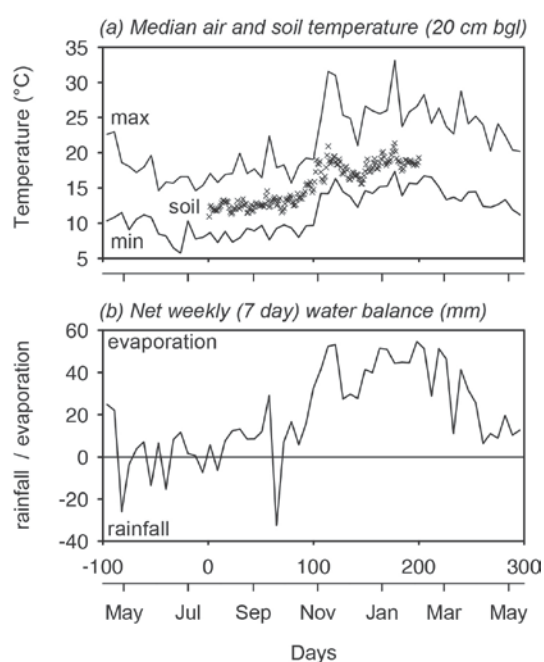


Fig. S1. Climate data for assessed period. (a) Median maximum and minimum air temperature (solid lines) and median soil temperature 20cm bgl (crosses). (b) Net weekly (7 day) water budget; positive number represents net evaporation and negative number represents net rainfall.

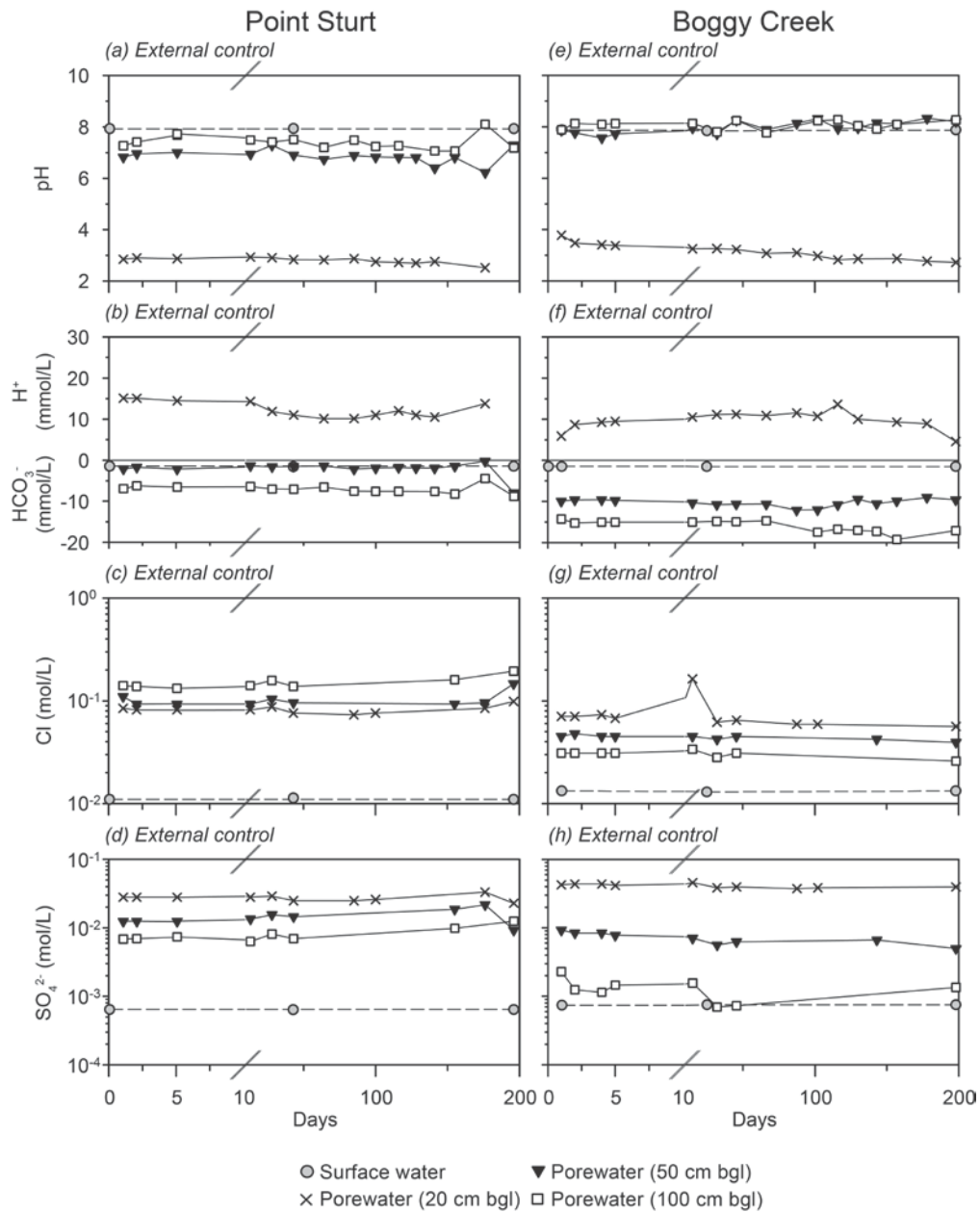


Fig. S2. Temporal changes for pH, acidity or alkalinity, Cl⁻, and SO₄²⁻ in the external control samples during the assessed period. Sulfuric sandy soil (Point Sturt): (a) pH, (b) acidity or alkalinity, (c) Cl⁻, and (d) SO₄²⁻. Sulfuric cracking clay (Boggy Creek): (e) pH, (f) acidity or alkalinity, (g) Cl⁻, and (h) SO₄²⁻. Sampling depths: surface water (grey circle), 20 cm bgl (cross), 50 cm bgl (black triangle), 100 cm bgl (white square).

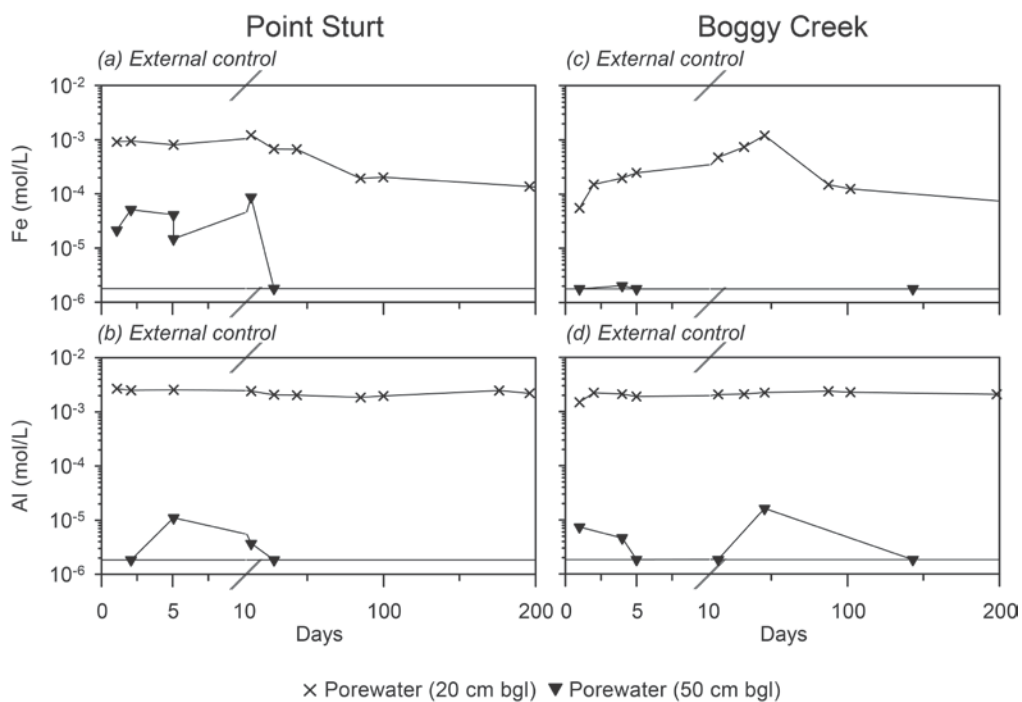


Fig. S3. Temporal changes for total dissolved Fe and Al in the external control samples during the assessed period. Sulfuric sandy soil (Point Sturt): (a) Fe and (b) Al. Sulfuric cracking clay (Boggy Creek): (c) Fe and (d) Al. Sampling depths: 20 cm bgl (cross) and 50 cm bgl (black triangle).

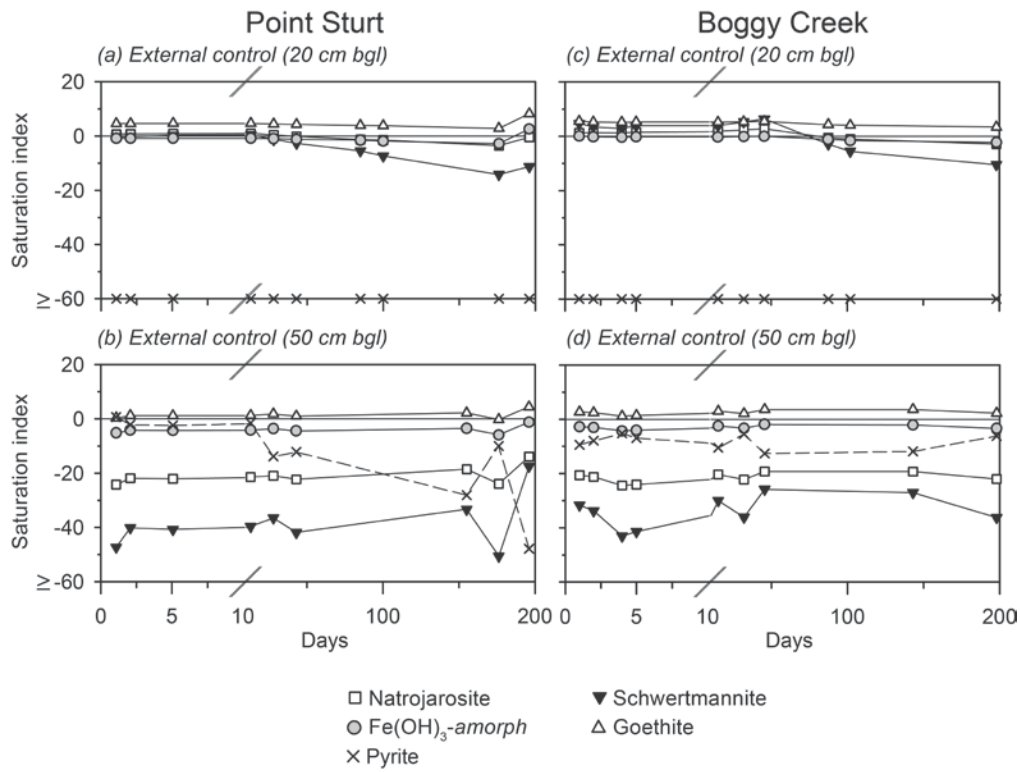


Fig. S4. Temporal changes in the saturation index for selected Fe minerals during the assessed period. Sulfuric sandy soil (Point Sturt): (a) external control (20 cm bgl), (b) external control (50 cm bgl). Sulfuric cracking clay (Boggy Creek): (c) external control (20 cm bgl), (d) external control (50 cm bgl). Fe minerals: natrojarosite (white square), schwertmannite (black triangle), Fe(OH)₃-amorph (grey circle), goethite (white triangle), pyrite (cross).

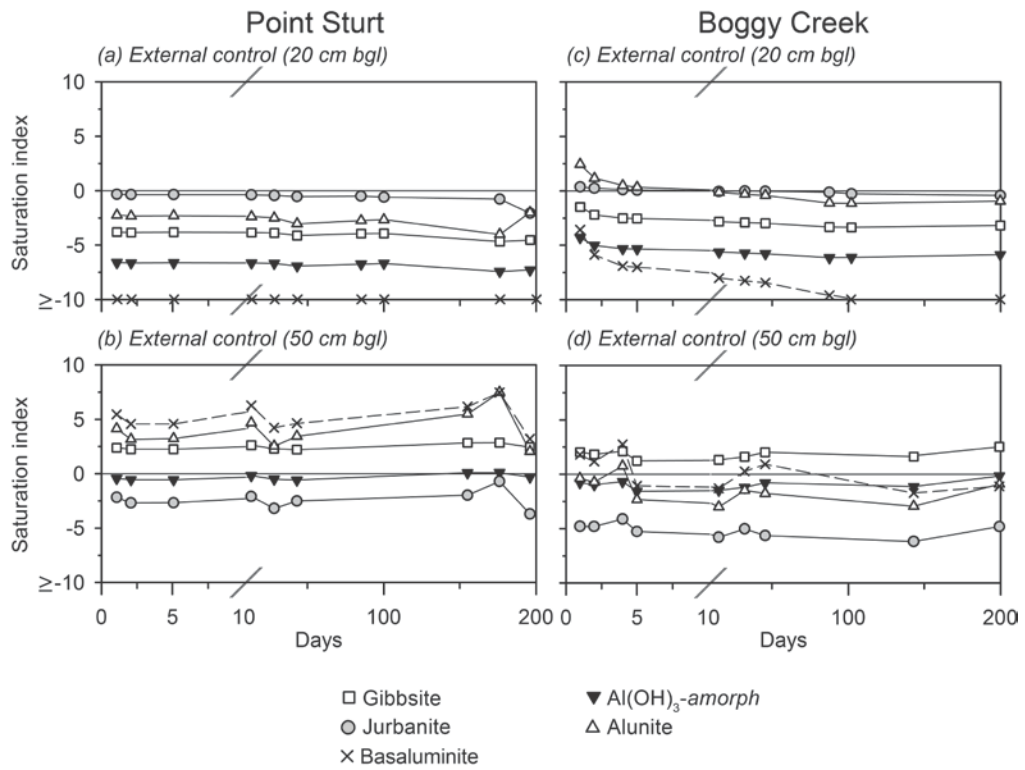


Fig. S5. Temporal changes in the saturation indices for selected Al minerals during the assessed period. Sulfuric sandy soil (Point Sturt): (a) external control (20 cm bgl), (b) external control (50 cm bgl). Sulfuric cracking clay (Boggy Creek): (a) external control (20 cm bgl), (b) external control (50 cm bgl). Al minerals: gibbsite (white square), Al(OH)₃-amorph (black triangle), jurbanite (grey circle), alunite (white triangle), basaluminite (cross).

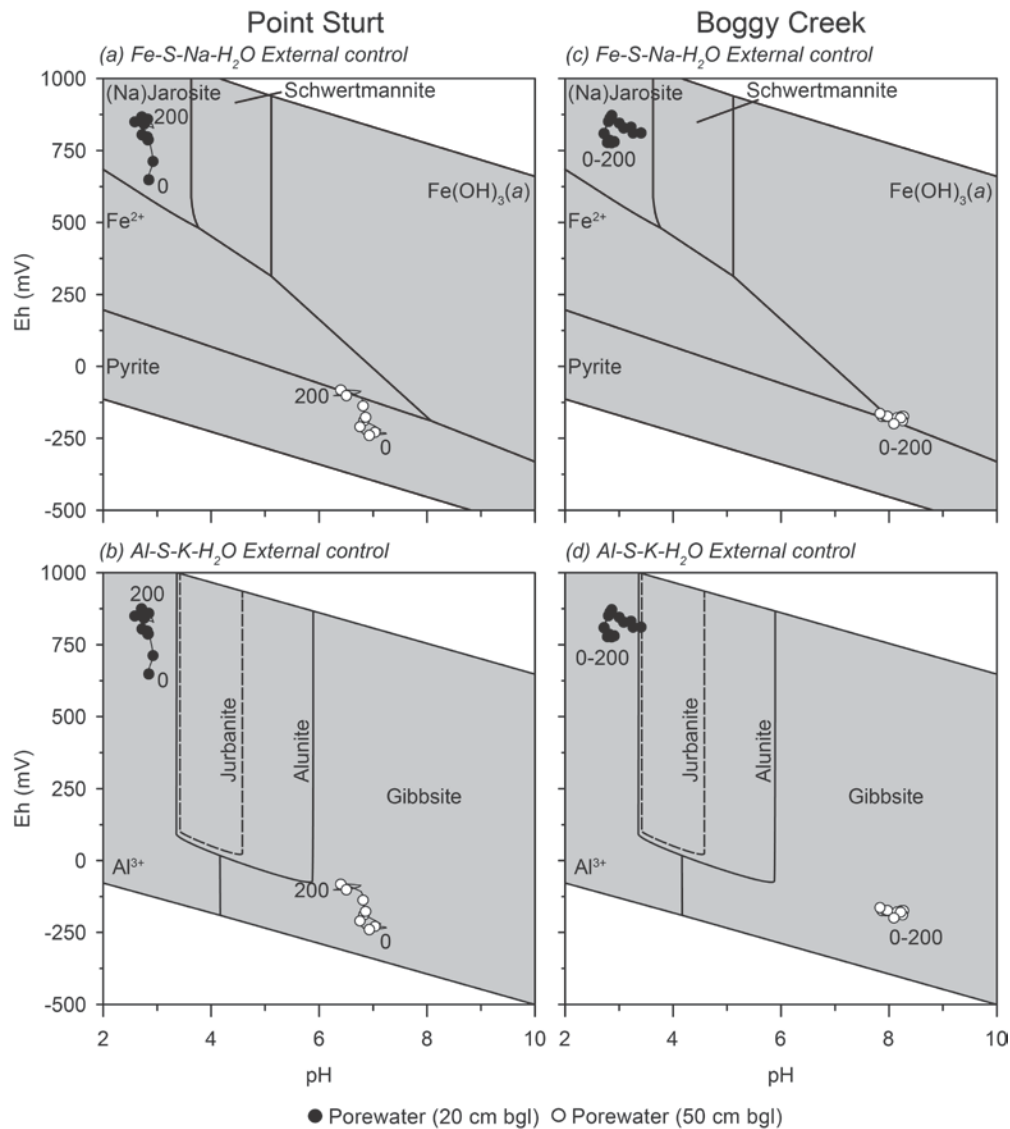


Fig. S6. Eh-pH predominance diagram for Fe-S-Na-H₂O and Al-S-K-H₂O systems. Start (0 days) and end (200 days) points are labelled, each data point between represents a time period of 25 days. Sulfuric sandy soil (Point Sturt): (a) Fe-S-Na-H₂O external control, (b) Al-S-K-H₂O external control. Sulfuric cracking clay (Boggy Creek): (c) Fe-S-Na-H₂O external control, (d) Al-S-K-H₂O external control. Sampling depths: 20 cm bgl (black circle), 50 cm bgl (white circle). Equilibrium values for solid phases and element concentrations are given in supplementary material.

7.2.4 Supplementary data tables

Table S2. Summary of minimum, median, and maximum results for selected parameters at the Point Sturt study site for the periods 0-10, 11-100, and 101-200 days after reflooding.

	Eh (mV)	pH	Alkalinity (mEq/L HCO ₃ ⁻)	Acidity (mEq/L H ⁺)	Cl ⁻ (mmol/L)	SO ₄ ²⁻ (mmol/L)	Fe (mmol/L x10 ³)	Al
<i>Point Sturt: Surface water 0 to 10 days after reflooding</i>								
min.	483	7.25	1.39	-	11	0.645	-	0.482
median	483	7.83	1.43	-	12.4	0.645	-	0.482
max.	494	7.93	1.58	-	621	31.2	-	0.482
<i>Point Sturt: Surface water 11 to 100 days after reflooding</i>								
min.	502	7.77	1.28	-	11.6	0.656	-	1.48
median	518	8.43	1.58	-	12.4	0.718	-	1.48
max.	531	8.49	2.35	-	18.3	1.15	-	1.48
<i>Point Sturt: Surface water 101 to 200 days after reflooding</i>								
min.	355	8.03	1.14	-	-	-	-	-
median	481	9.55	1.56	-	-	-	-	-
max.	504	10	2.6	-	-	-	-	-
<i>Point Sturt: Porewater 20 cm bgl 0 to 10 days after reflooding</i>								
min.	708	2.55	-	19.8	73.3	32.3	802	3260
median	721	2.58	-	22.1	76.2	32.3	1110	3930
max.	725	2.68	-	25	93.1	37.5	1250	4230
<i>Point Sturt: Porewater 20 cm bgl 11 to 100 days after reflooding</i>								
min.	110	3.04	0.402	0.71	11.3	0.802	3.58	4.93
median	440	3.36	0.402	1.17	14.4	1.04	28.5	16.9
max.	688	5.05	0.402	2.3	16.9	2.39	78.2	99
<i>Point Sturt: Porewater 20 cm bgl 101 to 200 days after reflooding</i>								
min.	-73.7	6.37	0.8	-	16.1	1.35	3.24	-
median	-6.88	6.84	1.08	-	19.2	1.67	3.58	-
max.	52.1	7.44	9.82	-	22	1.77	84.5	-
<i>Point Sturt: Porewater 50 cm bgl 0 to 10 days after reflooding</i>								
min.	-134	4.87	1.03	3.24	107	11.5	362	3.71
median	-134	6.31	1.77	3.24	107	17.7	731	32.4
max.	-134	6.98	2.51	3.24	133	21.9	1100	61.2
<i>Point Sturt: Porewater 50 cm bgl 11 to 100 days after reflooding</i>								
min.	-158	3.93	0.048	0.75	14.7	4.37	184	66
median	-145	4.35	0.0575	3.3	50.8	22.9	1220	578
max.	-132	5.17	0.067	8.31	102	30.2	1920	797
<i>Point Sturt: Porewater 50 cm bgl 101 to 200 days after reflooding</i>								
min.	-54.3	3.4	0.073	0.497	16.9	1.87	59.1	17.4
median	79.7	3.99	0.725	1.19	19	1.98	66	20.7
max.	159	5.13	1.38	1.23	21.4	2.19	193	25.4

	Eh (mV)	pH	Alkalinity (mEq/L HCO ₃ ⁻)	Acidity (mEq/L H ⁺)	Cl ⁻ (mmol/L)	SO ₄ ²⁻ (mmol/L)	Fe (mmol/L x10 ³)	Al
<i>Point Sturt: Porewater 100 cm bgl 0 to 10 days after reflooding</i>								
min.	-206	7.39	5.94	-	133	6.77	-	5.56
median	-204	7.4	6.61	-	141	6.98	-	5.56
max.	-204	7.54	7.36	-	147	7.18	-	5.56
<i>Point Sturt: Porewater 100 cm bgl 11 to 100 days after reflooding</i>								
min.	-225	7.06	1.15	-	62.1	8.02	-	3.71
median	-208	7.41	1.69	-	113	16.7	-	3.71
max.	-193	7.67	6.15	-	130	16.7	-	3.71
<i>Point Sturt: Porewater 100 cm bgl 101 to 200 days after reflooding</i>								
min.	-211	6.35	0.868	-	17.5	1.87	-	-
median	-70.9	6.52	1.43	-	18.9	2.03	-	-
max.	-24	6.84	1.84	-	20.3	2.19	-	-

Table S3. Summary of minimum, median, and maximum results for selected parameters at the Boggy Creek study site for the periods 0-10, 11-100, and 101-200 days after reflooding.

	Eh (mV)	pH	Alkalinity (mEq/L HCO ₃ ⁻)	Acidity (mEq/L H ⁺)	Cl ⁻ (mmol/L)	SO ₄ ²⁻ (mmol/L)	Fe (mmol/L x10 ³)	Al
<i>Boggy Creek: Surface water 0 to 10 days after reflooding</i>								
min.	460	7.65	1.39	-	11.3	0.593	-	3.15
median	460	7.81	1.41	-	15.5	2.08	-	3.28
max.	460	7.95	1.42	-	16.6	2.6	-	3.45
<i>Boggy Creek: Surface water 11 to 100 days after reflooding</i>								
min.	460	6.19	0.316	-	18.3	3.33	4.67	3.04
median	469	7.27	1.13	-	20.9	7.18	4.67	3.87
max.	581	7.98	1.35	-	22.6	11.5	4.67	4.71
<i>Boggy Creek: Surface water 101 to 200 days after reflooding</i>								
min.	366	5.58	0.123	-	19.7	1.35	-	-
median	422	6.27	0.772	-	24	13.5	-	-
max.	508	9.2	2.35	-	39.5	13.5	-	-
<i>Boggy Creek: Porewater 20 cm bgl 0 to 10 days after reflooding</i>								
min.	726	2.94	1.4	11.9	17.5	2.39	197	1.98
median	740	3.01	1.4	12.3	76.2	45.8	223	2370
max.	754	7.92	1.4	12.6	81.8	47.9	269	2930
<i>Boggy Creek: Porewater 20 cm bgl 11 to 100 days after reflooding</i>								
min.	498	3.12	-	15.2	79	43.7	661	1980
median	570	3.22	-	18.5	84.6	50	2600	2170
max.	659	3.3	-	20	90.3	56.2	2900	2310

	Eh (mV)	pH	Alkalinity (mEq/L HCO ₃ ⁻)	Acidity (mEq/L H ⁺)	Cl ⁻ (mmol/L)	SO ₄ ²⁻ (mmol/L)	Fe (mmol/L x10 ³)	Al
<i>Boggy Creek: Porewater 20 cm bgl 101 to 200 days after reflooding</i>								
min.	178	2.14	-	4	36.7	16.7	36.9	4.89
median	437	3.16	-	19.8	36.7	27.9	5680	370
max.	472	3.17	-	22.1	36.7	36.8	6610	830
<i>Boggy Creek: Porewater 50 cm bgl 0 to 10 days after reflooding</i>								
min.	-176	7.53	1.4	-	14.7	1.87	-	2.06
median	-169	7.71	10.3	-	16.1	6.45	-	4.82
max.	-162	7.83	10.8	-	17.2	7.08	-	6.45
<i>Boggy Creek: Porewater 50 cm bgl 11 to 100 days after reflooding</i>								
min.	-223	7.59	8.13	-	18.9	8.33	5.53	3.02
median	-210	7.92	8.98	-	22.6	10.4	5.91	7.41
max.	-179	8.3	9.96	-	23.1	10.4	13.5	9.19
<i>Boggy Creek: Porewater 50 cm bgl 101 to 200 days after reflooding</i>								
min.	-222	7.6	8.91	-	48	26	-	-
median	-164	7.77	9.34	-	49.4	32.3	-	-
max.	-137	8.28	9.56	-	50.8	38.5	-	-
<i>Boggy Creek: Porewater 100 cm bgl 0 to 10 days after reflooding</i>								
min.	-234	7.92	12.3	-	11.6	0.5	-	-
median	-230	8.03	12.3	-	11.6	0.609	-	-
max.	-225	8.13	12.3	-	12.1	1.46	-	-
<i>Boggy Creek: Porewater 100 cm bgl 11 to 100 days after reflooding</i>								
min.	-289	7.84	12.2	-	11.6	0.448	-	-
median	-285	8.18	12.4	-	11.8	0.531	-	-
max.	-257	8.31	15.3	-	13	0.916	-	-
<i>Boggy Creek: Porewater 100 cm bgl 101 to 200 days after reflooding</i>								
min.	-312	7.36	8.89	-	28.2	19.8	-	-
median	-254	7.58	11.8	-	28.2	19.8	-	-
max.	-206	8.13	13.4	-	28.2	19.8	-	-

7.2.5 References

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8.

Appendix B. Conference Abstracts and Media

8.1 CHAPTERS 2 AND 3

8.1.1 Conference abstract presented at the 19th World congress of soil science conference abstract. Brisbane, Australia

8.2 CHAPTER 4

8.2.1 Conference abstract presented at the 7th International acid sulfate soil conference abstract. Vassa, Finland

8.2.2 Crop Soil Agronomy News magazine article

8.2.3 Soil Science Society Digital Library News website article

8.2.4 Journal issue front cover image

8.2.5 Social media

8.1.1 19th World congress of soil science conference abstract. Brisbane, Australia

A systematic analysis procedure incorporating the chip-tray incubation method for the hazard assessment of Acid Sulfate Soils in the Murray-Darling BasinNathan Creeper^{A,B}, Rob Fitzpatrick^{A,B}, Paul Shand^A and Peter Self^A and Rob Kingham^C^ACSIRO Land and Water, Urrbrae, SA, Australia, Email nathan.creeper@csiro.au^BEarth and Environmental Sciences, The University of Adelaide, South Australia, Australia^CWetlands Unit, Murray-Darling Basin Authority, Canberra, ACT, Australia**Abstract**

During a Murray-Darling Basin wide assessment of Acid Sulfate Soils (ASS), soil samples from over 3500 soil profiles were collected by staff from state and regional Natural Resource Management (NRM) agencies and submitted for pH incubation analysis. The large number of soil samples triggered the requirement for a new systematic analysis procedure to be developed.

A reliable and systematic analysis procedure using chip trays was successfully developed and tested, which allowed: (i) a rapid and convenient means to incubate the soils in order to assess the hazards of soil acidification on all samples based mainly on pH incubation measurements and (ii) streamlined data acquisition for a wide range of ASS subtypes covering over 8,000 soil samples.

Key Words

pH, incubation, Acid Sulfate Soils, wetland, Murray-Darling Basin, chip-tray.

Introduction

Acid Sulfate Soils (ASS) is the name given to those soils containing soil materials affected by iron sulfide minerals. These soils either contain sulfuric materials or have the potential to generate sulfuric materials in amounts that have an effect on soil pH. The Murray-Darling Basin (MDB) is currently experiencing the worst drought conditions in recent history. Declining water levels have caused non-acidic soils with previously accumulated sulfide minerals in wetlands, creeks, and lakes to be exposed to the atmosphere and undergo oxidation reactions, which generates sulfuric material and can turn these soil material acidic (pH < 4). Following their oxidation, ASS can cause detrimental impacts on the surrounding ecosystem in a variety of ways. The release of sulfuric acid and toxic elements can lead to the acidification of water bodies and toxic impacts of wetland ecosystems, aquatic biota and human health. Additionally, the disturbance of monosulfidic material can cause the surface waters to become rapidly deoxygenated.

The MDB ASS Risk Assessment Project, initiated by the Murray-Darling Basin Authority (MDBA), aims to assess the spatial extent of, and risks posed by these hazards in wetlands of environmental significance, as well as those that could pose a risk to surrounding waters. These wetlands were subjected to a tiered assessment process, whereby wetlands were screened through a desktop assessment stage, followed by a rapid on-ground appraisal (RAP), and then detailed on-ground assessment if results of previous stages indicate an increased likelihood of occurrence of ASS. More than 19,000 wetlands underwent desktop assessment, and this identified approximately 1,450 wetlands considered to have a higher likelihood of ASS occurrence which required further assessment. The RAPs were performed by state and regional NRM agency staff that had completed one of the six ASS rapid assessment training courses.

During the RAP, wetland soil samples were collected from up to 3 different soil profiles within a wetland representing a toposequence. As part of the RAP these soil samples were then submitted for incubation analysis. pH incubation is a method whereby ASS are kept in a moist state and exposed to the atmosphere allowing them to undergo oxidation reactions in an attempt to simulate the natural acidification behaviour of the soil. If the soil in question is hypersulfidic the pH will reduce substantially during incubation to a pH < 4, as a result of sulphide oxidation and hence pose an acidity hazard (Sullivan *et al.* 2009a,b). The use of pH incubation for classification is often considered preferable to other methods, such as peroxide addition, because the result of the experiment is arguably more representative of what would be expected to occur in the field (Dent 1986).

A total of 1,329 wetlands from South Australia (SA), New South Wales (NSW), Victoria and Queensland (QLD) were assessed resulting in over 8,000 soil samples being submitted for pH incubation analysis. The

large number of samples triggered the requirement for, and allowed the testing of, a new systematic analysis procedure.

Methods

The analysis procedure and associated pH incubation method using plastic chip-trays (Fitzpatrick *et al.* 2010) for the analyses of MDB soil samples is illustrated in the flow chart outlined in Figure 1. It illustrates the systematic order in which observations and analyses were conducted. Sections of the flow chart are examined further under subheadings below.

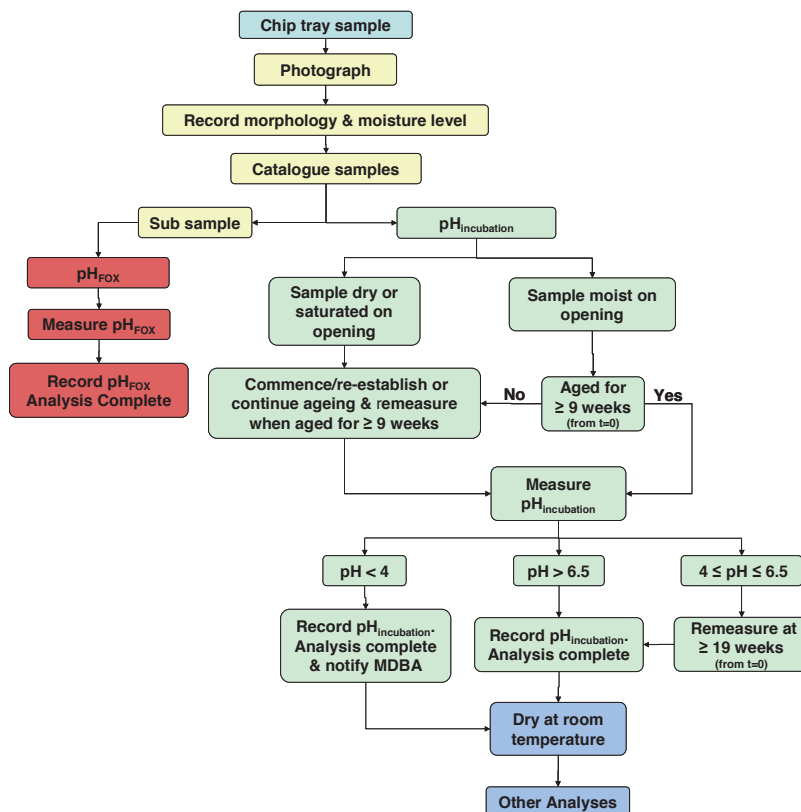


Figure 1. Flow chart of the analysis procedure and pH incubation method of chip-tray samples

Sample collection and preparation

Approximately 50g of soil was collected at up to 3 depths (0-5cm, 5-30cm, and >30cm), designated as top, middle and bottom and placed into chip-trays (Figure 2). This was repeated for up to three different profiles selected along a toposquence. The samples were then moistened if dry to initiate incubation before wrapping the chip-tray tightly in Gladwrap® to prevent desiccation and spillage during transport and posting to the laboratory. Thus, the incubation period start date is the date of collection in the field. The practical consequence of this is that all samples for a wetland can be analysed simultaneously without the need to consider, for example, which samples were moist in the field and which were dry and not moistened until a later stage.

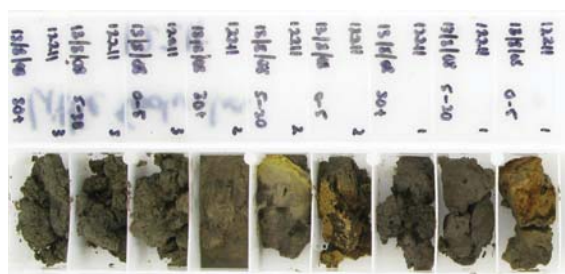


Figure 2. Photograph of plastic chip-tray filled with soil from a wetland in South Australia.

In previous studies, small squares of non-antibacterial sponge were placed in chip-trays over the soil samples to help reduce desiccation. This was later revised when many sponges were found to be decomposed upon opening in the laboratory. The addition of organic matter from the decomposition of the sponge had the potential to adversely affect results. The sponges were also found to remove the permanent marker labelling. Due to this the use of sponges was discontinued. Also in support of this move, it was later realised that the chip-tray construction was ideally suited to prevent excessive desiccation, whereby a slightly moistened sample has been found to remain at or slightly below field capacity for periods up to 9 weeks without attention.

Photography

Photographs of chip-tray samples from each wetland were obtained for reference purposes. Each photograph was acquired using an Ortary Photosmile™ light box, which provided consistent lighting for natural white-balanced and shadow-free photographs.

Basic morphology and moisture level

A simplified soil morphology description was collected for each sample. Descriptors were chosen on the added usefulness of the information they provide in relation to ASS hazard. Chosen descriptors include moisture status, colour, consistence, texture, and any other comments. Because a high sample throughput was essential for this project each morphology descriptor was refined to a limited number of choices. These are shown in Figure 3. To further assist with sample throughput, a virtual tick sheet was created in Visual Basic for Applications (VBA), which allowed the user to rapidly input morphology data by simply clicking on the appropriate buttons. When completed the virtual tick sheet would then insert the recorded information into an Excel® spreadsheet in the required format. Albeit limited, the simplified soil morphology description allowed the capture of key morphology information that otherwise would not have been collected.

The screenshot shows a software interface for data entry. At the top, there's a 'Wetland ID' field with '80002' and a 'Sample Collected' section with three rows (S1, S2, S3) and three columns (Top, Mid, Bot). Each cell contains a 'Y' or 'N'. Below this is a 'Moisture Status' section with four columns: Dry, Slightly Moist, Moist, Saturated. A 'Comments' section has three columns: Top, Mid, Bot. The 'Top' column contains 'White salts' and 'Possibly monosulfides'. Below these are three rows of color selection grids for 'Matrix Colour', 'Mottle Colour', and 'Consistency'. The 'Consistency' section has columns for 'Gel', 'Very Weak', 'Weak', 'Strong', 'Loose', 'Sand', 'Loam', 'Clay', and 'Organic'. A pop-up dialog box is open over the 'Consistency' section, titled 'Select categories that must be entered', with checkboxes for 'Moisture', 'Matrix Colour', 'Mottle Colour', 'Consistency', and 'Texture'. The 'Moisture', 'Matrix Colour', and 'Texture' checkboxes are checked.

Figure 3. Screen capture of virtual tick sheet with details filled out for wetland ID 80002.

The moisture status of each sample was recorded on a scale of 1 to 4. This was done each time the chip-tray was opened. During the incubation period moisture is required for the oxidation reactions to occur. Hence, this observation was used to determine whether or not a sample had been aging between the time of collection in the field and first opening in the laboratory or any subsequent openings.

pH peroxide (pH_{FOX})

As part of the analysis procedure soils were subjected to the peroxide field oxidation method (pH_{FOX}). The method involves measuring the soil pH after the rapid oxygenation of reduced inorganic sulfur materials caused by the addition of hydrogen peroxide. pH_{FOX} provides another means of assessing the acidity hazard.

pH incubation

All soil samples, except for soil surface efflorescences, were submitted for pH incubation analysis. The soil

sample was homogenised by mixing with a glass rod while deionised water was added until an approximate soil-to-solution ratio of 1:1 was achieved. These steps and the pH measurement take place in the chip-tray. All pH measurements were obtained using an Ionode™ intermediate junction electrode that was calibrated at pH 4 and 7 at the beginning and end of each sample batch. The electrode was connected to a WP-81 TPS™ pH meter and referenced against temperature with a Pt sensor.

If a sample was found to have a moisture status of 2 or 3 (slightly moist or moist) on receipt it was stored and allowed to undergo incubation for ≥ 9 weeks starting from the date of collection. If a sample was found to be dry or saturated (moisture status 1 or 4) the appropriate amount of water was added or subtracted before incubating the sample for ≥ 9 weeks starting from that date.

If a soil sample was found to acidify to a pH < 4 after an incubation period of 9 weeks or more, that sample was classified as hypersulfidic material and analysis for that sample was considered complete. Additionally, if a soil sample did not acidify over the same period to a pH below 6.5 analysis was also considered complete. In the case that the pH of a sample lies between a pH of 4 and 6.5 ($4 \leq \text{pH} \leq 6.5$) incubation is continued for a further ≥ 10 week period (i.e. total incubation period ≥ 19 weeks) before pH re-measurement. For these samples, analysis was considered complete after this second incubation period.

Samples were discriminated this way because it was reasoned that if after ≥ 9 weeks of incubation the pH of a sample did not drop below a pH of 6.5 the sample will not age to a pH < 4 given more time. This assumption was based on the fact that if a sample has a pH of > 6.5 it still contains an amount of acid neutralising capacity (ANC) and, hence, has ability to buffer acidity and resist changes in pH.

Ideally sample analysis would continue until a stable pH was obtained as suggested in recent literature (Sullivan *et al.* 2009b). However, when the scope of the project does not allow for this it is suggested that this method of sample discrimination is adopted as a suitable alternative.

Results and Discussion

The systematic analysis procedure has functioned successfully throughout the project allowing the large number of samples to be managed and analysed efficiently and accurately. The analysis procedure has so far been used in the identification of over 400 wetlands containing hypersulfidic soils. Conversely, the analysis procedure has identified approximately 930 wetlands that are unlikely to contain ASS with hypersulfidic materials, a potentially greater achievement when considering the necessity for economical assignment of finite funds and time.

Conclusion

The use of the chip-tray pH incubation method like other incubation methods is considered favourable over other methods for classification of hypersulfidic materials because it is a direct measurement and produces a more realistic result for testing of hypersulfidic soil materials in ASS by allowing the soil to “speak for itself” (Dent 1986). However, incubation methods are also very time exhaustive in that in some instances it can require > 19 weeks to give a conclusive determination and that soil samples must be periodically monitored for moisture status during the incubation. The systematic analysis procedure presented here provides a tested means that streamlines data acquisition, assures correct hazard identification, and is able to handle these and other problems even with very large sample numbers.

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8.2.1 7th International acid sulfate soil conference abstract. Vassa, Finland

Geologian tutkimuskeskus, Opas 56 – *Geological Survey of Finland, Guide 56, 2012*
 Peter Österholm, Markku Yli-Halla and Peter Edén (eds.)

BEHAVIOUR OF IRON, ALUMINIUM AND OTHER SELECTED METALS FOLLOWING THE REWETTING OF INLAND ACID SULFATE SOILS CONTAINING SULFURIC MATERIAL

by

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In this study, *in situ* equilibrium dialysis samplers, commonly known as peepers (Fig. 1a), were used to determine high resolution depth profiles of pore water chemistry and to assess the mobilisation and transport of dissolved constituents in previously dried Inland Acid Sulfate Soils (IASS) containing sulfuric material.

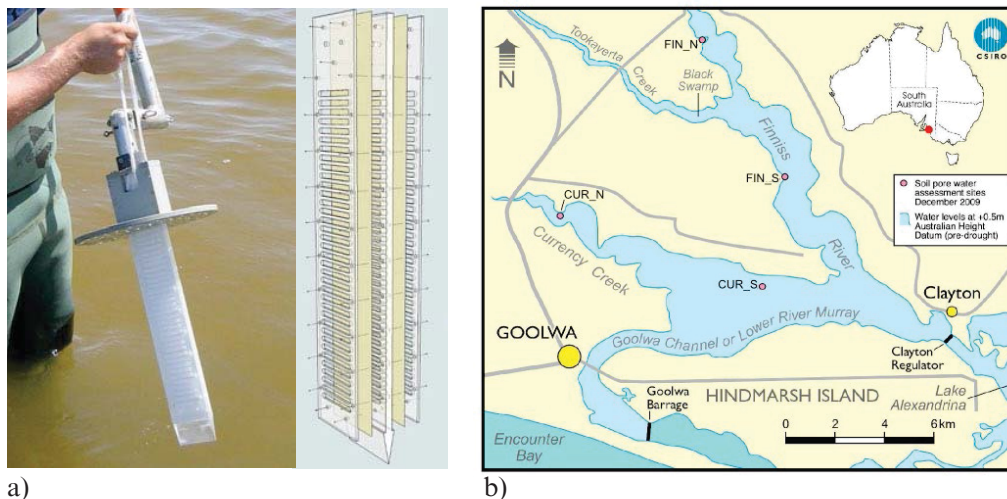


Fig. 1. (a) Photo showing specialised peeper installation apparatus with peeper ready to be deployed and diagram of peepers used in this study. The polysulfone membrane is coloured yellow in diagram for clarity (usual colour is white). (b) Locality map showing the 4 sites where peepers were installed.

Peepers are multi-chambered samplers typically constructed of a plastic such as Perspex, in which each chamber is filled with deoxygenated and deionised water. Each chamber is then sealed with a permeable inert polysulfone membrane (pore size ca. 0.45 mm). Once installed, dissolved pore water constituents diffuse across the membrane until equilibrium is reached. Typically, equilibrium is reached in around 2 weeks for Hesslein-style peepers, similar to those used in this study (Hesslein 1976, Teasdale et al. 1995), after which the peepers can be removed and the chamber contents analysed for the required parameters.

The Finnis River and Currency Creek tributaries, located to the west of Lake Alexandrina in the lower reaches of the River Murray in South Australia, experienced low water levels due to severe drought conditions. Water levels in the Finnis River and Currency Creek tributaries were at their lowest in 2007 and 2008, and during this period contained approximately 2000 ha of sulfuric soils (Fitzpatrick et al., 2011). Due to large areas of acidified IASS and the continued lowering of water levels, a water regulator was installed to raise the water levels in the Finnis River and Currency Creek and prevent further areas of IASS being exposed. Subsequent rainfall and the pumping of water from Lake Alexandrina into the tributaries led to the rewetting of the Finnis River and Currency Creek in September 2009. The rewetting of the tributaries provided a unique opportunity to study the changing properties and recovery of IASS containing sulfuric material following a rewetting event.

Peepers were installed at 4 rewetted sites in the Finnis River and Currency Creek tributaries (2 in each tributary) that were known to contain sulfuric material (Fig. 1b). Peepers were first installed at all 4 sites in January 2010, 5 months after the initial rewetting. They were then re-installed in August 2011, 24 months after the initial rewetting. Soil pore waters were analysed for pH, EC, acidity or alkalinity, and major and trace elements. Soil pore water analyses were also supported by measurements of soil pH, pH following incubation, soil Eh, and acid base accounting (Fitzpatrick et al. 2011).

At all sites, much of the profile remained acidic after 24 months of subaqueous conditions. Following 5 months of inundation, ≤ 5 cm of the uppermost sediment was partially neutralised to $\text{pH} > 4$. Below this, soil classified as sulfuric material prior to the rewetting event remained sulfuric and unaffected by rewetting. After 24 months of subaqueous conditions, an improvement of an additional 1–3 pH units in the uppermost 5 to 10 cm of the soil profile occurred at some sites. Below 10cm, an increase of <1 pH unit was typically observed.

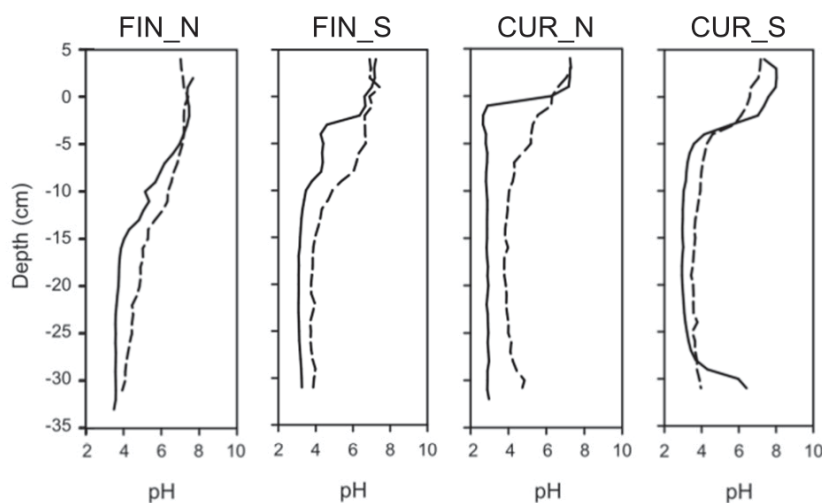


Fig. 2. Soil pore water pH profiles. Solid line = first sampling (5 months after rewetting). Dashed line = second sampling (24 months after rewetting).

Over time there has been an improvement in soil pore water quality, although many solutes still exceeded ANZECC guideline values (ANZECC/ARMCANZ 2000) after 24 months of subaqueous conditions. After 5 months of subaqueous conditions, ANZECC guideline trigger values were exceeded for Al, As, B, Cd, Cr, Cu, Mg, Ni, Pb, and Zn, with most being exceeded at all sites and over the majority of the depth-profile, including the top 5 cm. Twenty-four months after the initial rewetting event, a reduction in concentration to below ANZECC guideline trigger values has been observed at some sites for Al, As, Cd, Cr, Cu, Ni Pb, and Zn.

The detailed *in situ* sampling has demonstrated that the timescales involved for the recovery (i.e. neutralisation or removal of acidity and the re-establishment of reducing conditions) of rewetted IASS containing sulfuric material can exceed 24 months. Currently, geochemical modelling tools are being used to develop conceptual models of soil behaviour following the rewetting of an IASS containing sulfuric material.

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8.2.2 Crop Soils Agonomy News magazine

Published May 1, 2015

Porewater Geochemistry of Inland Acid Sulfate Soils with Sulfuric Horizons after Postdrought Freshwater Reflooding



Around 2007–2010, at the end of Australia's Millennium Drought, previously submerged lake beds in the large Ramsar-listed wetlands of Lake Alexandrina and Lake Albert in the lower Murray–Darling Basin in South Australia became exposed. More than 20,000 ha of fertile, irrigated farmland and ecologically diverse wetlands quickly turned into dried-out wastelands of cracked soil and mud. Much of the subaqueous soil in this area contained iron sulfide minerals. When submerged, this "sulfidic mud" is harmless, but the drought exposed the area to the air for the first time in more than 100 years. This allowed the sulfide in the soil to react with oxygen in the air to produce sulfuric acid resulting in the formation of acid sulfate soils with sulfuric horizons (pH < 3.5) and extremely acidic (pH < 2) sulfate-rich salt efflorescences.

Following the break of the drought in 2010, floodwaters inundated the oxidized and severely acidified acid sulfate soils to return subaqueous soil conditions to the whole area. However, the apparent pristine water surface hides a problem that hasn't gone away. In several areas, beneath the surface at the soil–water interface lie acid sulfate soils with sulfuric horizons. But now, these soils have no or little buffering capacity—in other words, little ability to keep the pH level stable. Before the Millennium Drought, these subaqueous soils had some buffering capacity to acidification because they contained calcium carbonate minerals. Now, these minerals have been destroyed by the acidity and cannot reform quickly.

In a new study published in the May–June 2015 issue of the *Journal of Environmental Quality*, a group of Australian researchers at the Acid Sulfate Soils Centre (ASSC) and CSIRO used equilibrium dialysis membrane samplers (peepers) to investigate in situ changes to soil acidity and abundance of metals and metalloids following the first 24 months of restored subaqueous conditions.

The rewetted sulfuric horizons remained severely acidified (pH ~4) or had retained acidity with jarosite visibly present after five months of continuous subaqueous conditions. A further 19 months of subaqueous conditions resulted in only small additional increases in pH (~0.5–1 pH units), with the largest increases occurring within the uppermost 10 cm of the soil profile.

The authors found that substantial decreases in the concentrations of some metals and metalloids occurred with time, due largely to lower solubility and sorption as a consequence of the increase in pH over 24 months of

subaqueous conditions. In deeper parts of the profiles, porewater remained strongly buffered at low-pH values (pH < 4.5) and experienced little progression toward anoxic circumneutral pH conditions over the 24 months of subaqueous conditions. The authors have proposed that low-pH conditions inhibited the activity of sulfate-reducing bacteria and, in turn, the in situ production of alkalinity critical for remediation.

They also believe the low concentration of alkalinity in the freshwater system and the initial highly buffered low pH conditions is slowing recovery. With little or no net alkalinity production, alkalinity in the surface water is likely the only method of neutralization readily available. With its supply limited by diffusion from the surface water to the soil, recovery is likely to continue at a slow rate until pH levels are raised sufficiently to where the microbial formation of pyrite begins to actively produce alkalinity in situ. The authors recognize that the timescales involved for a sulfuric horizon rewetted by a freshwater body to recover from acidic conditions could therefore take decades or longer.

Adapted from Creeper, N.L., P. Shand, W.S. Hicks, and R.W. Fitzpatrick. 2015. Porewater geochemistry of inland acid sulfate soils with sulfuric horizons following post-drought reflooding with freshwater. *J. Environ. Qual.* 44(3). View the full article online at <http://dx.doi.org/doi:10.2134/jeq2014.09.0372>



Photo taken during Australia's Millennium Drought of extremely acidic (pH < 2.5) sulfate-rich salt efflorescences (e.g., sideronatriite) that have accumulated on the surface of an acid sulfate soil with sulfuric horizons.

doi:10.2134/csa2015-60-5-5

May 2015

CSA News 13

8.2.3 Soil Science Society Digital Library News website article

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Soils acidified during Australia's historic drought will be slow to recover

May 11, 2015

By R. Fitzpatrick, et al.

In the years 2007 to 2010, at the end of Australia's Millennium drought, previously submerged lake beds in the large, Ramsar-listed wetlands of Lake Alexandrina and Lake Albert in South Australia became exposed. Overall, more than 20,000 ha of fertile, irrigated farmland and ecologically diverse wetlands in the lower Murray-Darling Basin quickly turned into dried-out wastelands of cracked soil and mud.

Much of the subaqueous (submerged) soil in this area contained iron sulfide minerals. When submerged, this "sulfidic mud" is harmless, but the drought exposed the area to the air for the first time in more than 100 years. This allowed the sulfide in the soil to react with oxygen in the air, producing sulfuric acid and forming acid sulfate soils with sulfuric horizons (pH < 3.5) and extremely acidic (pH < 2) sulfate-rich salt efflorescences.

Following the drought's break in 2010, floodwaters inundated the oxidized and severely acidified acid sulfate soils, returning subaqueous soil conditions to the whole area. However, the apparent pristine water surface hides a problem that hasn't gone away.

In a new study in the May-June issue of the *Journal of Environmental Quality*, a group of Australian researchers at the Acid Sulfate Soils Centre (ASSC) and CSIRO used equilibrium dialysis membrane samplers (peepers) to investigate *in situ* changes to soil acidity and the abundance of metals and metalloids following the first 24 months of restored subaqueous conditions.

The authors explain that in several areas, acid sulfate soils with sulfuric horizons lie beneath the surface at the soil-water interface. But now, these soils have no or little buffering capacity—in other words, little ability to keep the pH level stable. Before the Millennium drought, these subaqueous soils had some buffering capacity to acidification because they contained calcium carbonate minerals. Now, these minerals have been destroyed by the acidity and cannot reform quickly.

When the researchers investigated these soils, they found that the rewetted sulfuric horizons indeed remained severely acidified (pH ~4) or had retained acidity, with jarosite visibly present after five months of continuous subaqueous conditions. A further 19 months of subaqueous conditions resulted in only small additional increases in pH (~0.5-1 pH units), with the largest increases occurring within the uppermost 10 cm of the soil profile.

In deeper parts of the profiles, porewater remained strongly buffered at low pH values (pH <4.5) and experienced little progression toward neutral pH conditions over the 24 months of subaqueous conditions. The authors have proposed that low pH conditions inhibit the activity of sulfate-reducing bacteria and, in turn, the *in situ* production of alkalinity critical for remediation.

They also believe the low concentration of alkalinity in the freshwater system and the initial highly buffered low pH conditions is slowing recovery. With little or no net alkalinity production, alkalinity in the surface water is likely the only method of neutralization available. With its supply limited by diffusion from the surface water to the soil, recovery is likely to continue at a slow rate until pH levels are raised to the point where microbial formation of pyrite begins to actively produce alkalinity *in situ*. The authors conclude that the timescales involved for a sulfuric horizon rewetted by a freshwater body to recover from acidic conditions could be decades or longer.

Adapted from Creeper, N.L., P. Shand, W.S. Hicks, and R.W. Fitzpatrick. 2015. Porewater geochemistry of inland acid sulfate soils with sulfuric horizons following post-drought reflooding with freshwater. *J. Environ. Qual.* 44(3). View the full article online at <http://dx.doi.org/doi:10.2134/jeq2014.09.0372>

This story originally appeared in the May 2015 issue of *CSA News* magazine.

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Acid sulfate soils in the lower Murray-Darling Basin of South Australia. These soils were acidified after being exposed to the air during Australia's Millennium drought. Although they're now submerged once more, a new study suggests they will be slow to recover from acidification.

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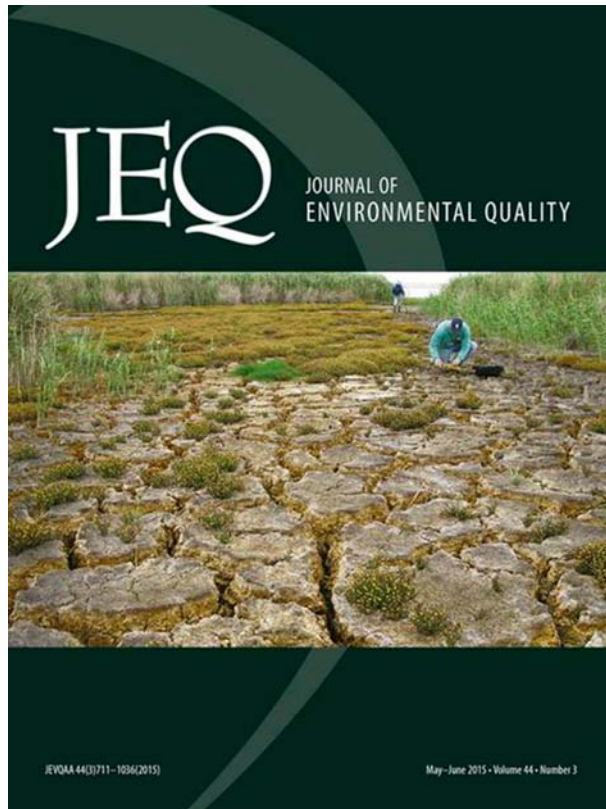
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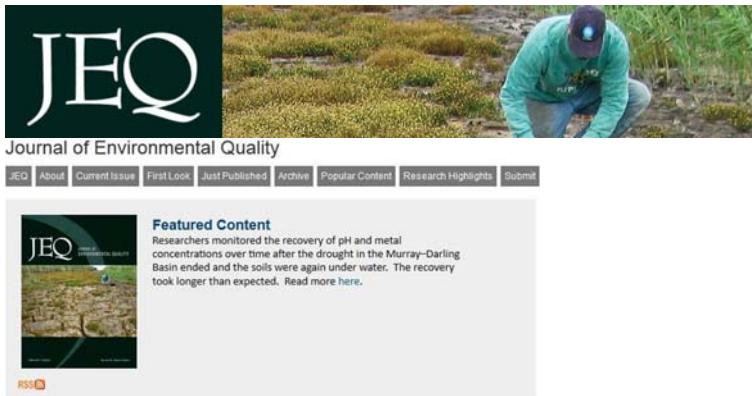
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8.2.4 Journal issue front cover image



8.2.5 Social media



9.

Appendix C. Digital Data Appendix for Chapters 2 to 5

NOTE:

Data for research chapters 2 to 5 are held on a CD in the print copy of the thesis kept in the University of Adelaide Library.