

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

Nathan Leonard Creeper

Btech(Forensic and Analytical Chemistry), BSc(Hons)

2015

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

School of Biological Sciences
The University of Adelaide, Adelaide, Australia



THE UNIVERSITY
of ADELAIDE

I. DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Nathan Leonard Creeper

16 October 2015

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

solutes 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.

III. ACKNOWLEDGEMENTS

Thank you to my supervisor Rob Fitzpatrick (University of Adelaide and CSIRO) and my co-supervisors Paul Shand (CSIRO and Flinders University) and John Hutson (Flinders University). A PhD is a significant challenge for the student but it's by no means an easy task for the supervisors. They must provide guidance, encouragement, and enthusiasm in order to shepherd the student through the PhD maze. Congratulations, we made it.

I would also like to thank friends and colleagues at CSIRO and the University of Adelaide for their assistance with field and laboratory work and reviewing written work. To Andrew Baker, Gerard Grealish, Sonia Grocke, Warren Hicks, Peta Jacobsen, Nilmini Jayalath, Stuart McClure, Richard Merry, Luke Mosley, Robert Reid, Peter Self, Brett Thomas, Mark Thomas, and others, thank you your support has been paramount.

I acknowledge with gratitude the cooperation and financial support of the Australian Society of Soil Science, the Department of Environment, Water and Natural Resources, the Murray-Darling Basin Authority and the South Australian Environmental Protection Agency. I thank CSIRO Land and Water for providing me with equipment and logistic support that included office, library and laboratory facilities.

We thank Rob Kingham for his generous cooperation and allowing us to publish the incubation data used in Chapter 3.

To my parents Ron and Christine, my parents in-law John and Penny, my family and my friends. A special thank you for lending encouragement, perspective and providing an out whenever respite was sorely needed.

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).

VI.

Table of Contents

I	DECLARATION	i
II	ABSTRACT	iii
III	ACKNOWLEDGEMENTS	vii
IV	PUBLICATIONS RELATED TO THIS THESIS	ix
V	LIST OF ABBREVIATIONS	xiii
VI	TABLE OF CONTENTS	xv
VII	LIST OF FIGURES	xx
VIII	LIST OF TABLES	xxiv
1	ACID SULFATE SOILS IN THE ENVIRONMENT	1
1.1	An introduction to Acid Sulfate Soils	1
1.1.1	Description and classification	1
1.1.2	Formation of sulfides in hypersulfidic material (sulfidization)	4
1.1.3	Oxidation of hypersulfidic material (sulfurization)	6
1.1.4	Distribution of acid sulfate soils	9
1.2	Inland Acid Sulfate Soils in the Murray-Darling Basin	9
1.2.1	Post drought sulfuric material	11
1.2.2	Knowledge gaps addressed in this thesis	11
1.3	Rewetting of Inland Acid Sulfate Soils	15
1.3.1	Advantages over alternative remediation methods	15
1.3.2	Negative implications associated with the reflooding sulfuric materials	16
1.3.3	Knowledge gaps addressed in this thesis	17
1.4	Research Project	20
1.4.1	General significance of research project	21
1.4.2	Thesis structure	22
1.5	References	24

2	A SIMPLIFIED INCUBATION METHOD USING CHIP-TRAYS AS INCUBATION VESSELS TO IDENTIFY SULFIDIC MATERIALS IN ACID SULPHATE SOILS	35
2.1	Cover page	35
2.2	Author contributions	36
2.3	Abstract	37
2.4	Introduction	37
2.5	Materials and methods	39
	2.5.1 Sample collection and preparation for incubation	39
	2.5.2 Soil pH analysis	39
	2.5.3 Determining the precision of the chip-tray approach to the incubation method	39
	2.5.4 Simplified incubation method	39
2.6	Results and discussion	40
	2.6.1 The use of chip-trays in the simplified incubation method	40
	2.6.2 Determining the precision of the chip-tray approach to the incubation method	40
	2.6.3 Simplified incubation method	41
2.7	Conclusions	43
2.8	Acknowledgements	43
2.9	References	43
3	THE OCCURRENCE OF INLAND ACID SULPHATE SOILS IN THE FLOODPLAIN WETLANDS OF THE MURRAY–DARLING BASIN, AUSTRALIA, IDENTIFIED USING A SIMPLIFIED INCUBATION METHOD	45
3.1	Cover page	45
3.2	Author contributions	46
3.3	Abstract	47
3.4	Introduction	47
3.5	Methods	48
	3.5.1 Wetland selection	48
	3.5.2 Wetland rapid assessment	49
	3.5.3 Sample analysis	49
	3.5.4 Geographical regions	50

3.6	Results	50
3.6.1	Acidification of soils in the floodplain wetlands in the MDB	50
3.6.2	Proportion of soil samples within an AW that were ultra-acidic or became ultra-acidic following incubation	51
3.6.3	Location of ultra-acidic soils or soils that became ultra-acidic following incubation within an AW	52
3.7	Discussion	52
3.7.1	General discussion	52
3.7.2	Sources of ultra-acidic soils in the floodplain wetlands of the MDB	53
3.8	Conclusions	54
3.9	Acknowledgements	55
3.10	References	55
4	POREWATER GEOCHEMISTRY OF INLAND ACID SULFATE SOILS WITH SULFURIC HORIZONS FOLLOWING POST-DROUGHT REFLOODING WITH FRESHWATER	57
4.1	Cover page	57
4.2	Author contributions	58
4.3	Abstract	59
4.4	Introduction	59
4.5	Materials and Methods	60
4.5.1	Selection of sampling locations	60
4.5.2	Porewater sampling and characterization	61
4.6	Results	61
4.6.1	General properties	61
4.6.2	Iron and Sulfate	63
4.6.3	Trace element behavior	64
4.7	Discussion	65
4.7.1	Soil structure impacts on infiltration and rate of recovery	65
4.7.2	Changes in Iron and Sulfate concentrations	65
4.7.3	Changes in contaminant concentrations	67
4.8	Conclusions	68
4.9	Supplementary material	69
4.10	Acknowledgements	69

4.11	References	69
5	GEOCHEMICAL PROCESSES FOLLOWING FRESHWATER REFLOODING OF ACIDIFIED INLAND ACID SULFATE SOILS: AN IN SITU MESOCOSM EXPERIMENT	71
5.1	Cover page	71
5.2	Author contributions	72
5.3	Abstract	73
5.4	Introduction	73
5.5	Materials and Methods	74
	5.5.1 Study site location, climate and hydrological history	74
	5.5.2 Construction of field installation	75
5.6	Results	77
	5.6.1 Solid phase characterization	77
	5.6.2 Porewater properties	77
	5.6.3 Iron and aluminium solid-phase equilibria	79
5.7	Discussion	81
	5.7.1 Solute transport following reflooding	82
	5.7.2 Solid phase Fe speciation and control on Fe solubility	83
	5.7.3 Solid phase Al speciation and control on Al solubility	84
5.8	Conclusion	86
5.9	Acknowledgements	86
5.10	Supplementary material	86
5.11	References	86
6	CONCLUSIONS AND FUTURE RESEARCH PRIORITIES	89
6.1	Introduction	89
6.2	Inland Acid Sulfate Soils in the Murray-Darling Basin	90
	6.2.1 Identification of sulfidic materials by the simplified incubation method	91
	6.2.2 The prevalence and distribution of IASS in the MDB	92
	6.2.3 Limitations of conclusions and suggested future research	93
6.3	Freshwater Reflooding of Inland Acid Sulfate Soils with Sulfuric Materials	94
	6.3.1 Neutralisation of soil acidity following reflooding by freshwater	95
	6.3.2 Metal(loid) behaviour following reflooding	96

6.3.3	Iron and sulfur reduction	97
6.3.4	Limitations of conclusions and suggested future research	98
6.4	References	100
7	APPENDIX A. SUPPLEMENTARY MATERIAL	103
7.1	Chapter 4	103
7.2	Chapter 5	110
8	APPENDIX B. CONFERENCE ABSTRACTS AND MEDIA	123
8.1	Chapters 2 and 3	123
8.1.1	Conference abstract	124
8.2	Chapter 4	128
8.2.1	Conference abstract	128
8.2.2	CSA News magazine article	131
8.2.3	Soil Science Society Digital Library News website article	132
8.2.4	Journal issue front cover image	133
8.2.5	Social media	133
9	APPENDIX C. DIGITAL DATA FOR CHAPTERS 2 TO 5	135
9.1	Chapter 2	CD
9.2	Chapter 3	CD
9.3	Chapter 4	CD
9.4	Chapter 5	CD

VII. LIST OF FIGURES

VII.1 Chapter 2

- Figure 1.* (a) Illustration of an empty chip-tray. (b) Photograph of labelled chip-trays filled with soil samples. Chip-trays are commonly used in the mining and other industries for the storage of soil, sediment and rock chip core samples. Chip-trays are of polypropylene construction with overall dimensions of 51 cm x 3.5 cm x 5 cm (L x H x W) and are divided into 20 individual compartments with internal dimensions of ca. 2.5 cm x 3 cm x 5 cm. 38
- Figure 2.* Flow chart of the simplified pH incubation method.*(Isbell, 1996). 39
- Figure 3.* Box plots and the 95% confidence intervals of pH incubation results over 15 weeks of incubation for two samples (X and Y, 20 replicates each). 41
- Figure 4.* Acidification behaviour of nine soil samples over an incubation period of 36 weeks. Symbols represent mean values and error bars represent the minimum and maximum values recorded. 42

VII.2 Chapter 3

- Figure 1.* Flow chart of the multi-tiered wetland selection process. 49
- Figure 2.* Geographical regions used to investigate the occurrence of inland acid sulphate soils in the Murray–Darling Basin and locality of the wetlands assessed. 50
- Figure 3.* Cumulative frequency plots of the minimum pH in a wetland following incubation. 52
- Figure 4.* Percent of samples within a wetland that contained soils that were ultra-acidic or became ultra-acidic following incubation for all geographic regions. 53
- Figure 5.* Percent of soils that were ultra-acidic or became ultra-acidic following incubation at each site and sampling depth for all geographical regions. 54
- Figure 6.* The proportion of Acid Wetlands (AW) in a geographical region represented on a map of the Murray–Darling Basin and in bar charts. Cross-hatching in the bar chart represents the proportion of AW that contained sulphuric material at the time of assessment. 55

VII.3 Chapter 4

- Figure 1.* Top left: the study area within the Murray Darling-Basin. Top right: the location of the study area in relation to the mouth of the Murray River. Bottom: Lake Alexandrina, and positions of the 4 sampling locations in the Finnis River and Currency Creek catchments. 60
- Figure 2.* Down profile morphological characteristics and trends in soil pore-water pH, chloride, and alkalinity/acidity of each sampling location. SWI is at 0 cm depth. Post-rewet/+5 (○). Post-rewet/+24 (▼). Morphological characteristics prior to rewetting from left to right; texture, redoximorphic features (Jar. = Jarosite, Sch. = Schwertmannite), soil cracking, and, matrix color (moist Munsell color). 62
- Figure 3.* Down profile soil porewater trends of total dissolved Fe and SO_4^{2-} concentrations and their chloride ratios. Note differing x-axis scales for some plots. Post-rewet/+5 (○). Post-rewet/+24 (▼) 64
- Figure 4.* Down profile soil porewater trends of Al, Cr, Mn, Ni and Zn. Dashed line represents GTV. Post-rewet/+5 (○). Post-rewet/+24 (▼) 66
- Figure 5.* Conceptual process model illustrating initial recovery in the first 24 months after rewetting for dominantly clay textured and dominantly sand textured profiles 67
- Figure 6.* Plots demonstrating non-conservative behavior (relative to Cl) of Fe, Al, Cr, and Ni. Dashed line represents conservative behavior (i.e. Na). Left of dashed line represents a % loss beyond what would be expected conservatively. Right of line represents a % gain beyond what would be expected conservatively. 67
- Figure 7* Relationship between trace metal concentration and porewater pH for 5 months after rewetting and 24 months after rewetting. 68

VII.4 Chapter 5

- Figure 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. 74

- Figure 2.* Illustration of (a) mesocosm installation (not to scale), (b) Pt tipped redox electrode construction, and (c) porewater solution samplers. 75
- Figure 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). 76
- Figure 4.* Temporal redox changes following reflooding. Sulfuric sandy soil (Point Sturt): (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. 78
- Figure 5.* Temporal changes for pH, acidity or alkalinity, Cl^- , and SO_4^{2-} in the reflooded 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). 79
- Figure 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). 80
- Figure 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), $\text{Fe}(\text{OH})_3$ -amorph (grey circle), goethite (white triangle), pyrite (cross). 80
- Figure 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), $\text{Al}(\text{OH})_3$ -amorph (black triangle), jurbanite (grey circle), alunite (white triangle), basaluminite (cross). 81

Figure 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. 83

Figure 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 acidic 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) Ground water 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. 85

VIII. LIST OF TABLES

VII.1 Chapter 3

<i>Table 1</i>	Sampling locations for the rapid assessment of a 'wet' and 'dry' wetland	50
<i>Table 2.</i>	Upstream and downstream boundaries for geographical regions	51