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

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 whist 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 (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.

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.

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.

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.

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

VII. LIST OF FIGURES

VII.1 Chapter 2

VII.2 Chapter 3

VII.3 Chapter 4

VII.4 Chapter 5

VIII. LIST OF TABLES

VII.1 Chapter 3