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INLAND ACID SULFATE SOIL SYSTEMS ACROSS AUSTRALIA

THEMATIC VOLUME

Covering: distribution, properties, significance and biogeochemical processes of inland Acid Sulfate Soils (ASS) across Australia and overseas

Editors: Rob Fitzpatrick and Paul Shand

CRC LEME OPEN FILE REPORT 249

December 2008

CRC LEME is an unincorporated joint venture between CSIRO-Exploration & Mining, and Land & Water, The Australian National University, Curtin University of Technology, University of Adelaide, Geoscience Australia, Primary Industries and Resources SA, NSW Department of Primary Industries and Minerals Council of Australia, established and supported under the Australian Government's Cooperative Research Centres Program.

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Cover Photographs
Photograph of a typical inland Acid Sulfate Soil in the exposed creek-bed of Currency Creek, near north Goolwa, looking west towards the Adelaide Hills, South Australia showing:
(i) sulfuric material (pH < 4) with pale yellow mottles in a dark grey clay matrix between 10 cm to 30 cm (see close-up photo on right hand side with a pH indicator strip indicating a pH of 3.3),
(ii) black sulfidic material (iron sulfides) at depth (> 30 cm) and
(iii) trans-horizon polygonal cracks with very coarse columnar ped structures; the result of desiccation and dewatering of clayey subaqueous soils and sediments during wetting and drying cycles with a surface coating comprising mainly the reddish-orange mineral, schwertmannite, which has a pH ranging between 3 and 3.6.

Photographer: Rob Fitzpatrick©2008 CSIRO

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Headquarters: CRC LEME c/o CSIRO Exploration and Mining, PO Box 1130, Bentley WA 6102, Australia

Electronic copies of the publication in PDF format can be downloaded from the CRC LEME website: http://crcleme.org.au/Pubs/OFRSindex.html. Information on this or other LEME publications can be obtained from http://crcleme.org.au.
Hard copies will be retained in the Australian National Library, the J. S. Battye Library of West Australian History, and the CSIRO Library at the Australian Resources Research Centre, Kensington, Western Australia.

Reference:
Fitzpatrick, R. and Shand, P. 2008. Inland acid sulfate soil systems across Australia. CRC LEME Open File Report 249, CRC LEME, Perth, 303 pp.

Keywords: 1. Australia 2. Acid Sulfate Soils 3. Acid Sulphate Soils 4. Salinity 5. Environment 6. Exploration Geochemistry 7. Biogeochemistry 8. Hydrology

ISSN 1329-4768
ISBN 978 064 309625 7

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Published by: CRC LEME
c/o CSIRO Exploration and Mining
PO Box 1130, Bentley, Western Australia 6102.

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Lisa **Worrall**, Geoscience Australia/ CRC LEME (Foreword)

PREFACE

Inland Acid Sulfate Soils (ASS) form under a wide range of environmental conditions, from freshwater to saline environments in inland settings, through mechanisms involving an amazing diversity of soil and water conditions. The extent of their occurrence in Australia has only recently become apparent due to the drying of inland wetland and river systems in the current drought (2006 to 2008). In contrast, there is a much larger amount of published information for “coastal ASS” that have formed in modern-day coastal zones (i.e. those areas landwards of the coastal waters influenced by processes or activities that affect the coast and its values - as defined by NRMMC 2006). Hence, we define Inland ASS as those ASS, which occur inland of modern-day coastal zones. Inland ASS, provide an impressive array of management challenges and opportunities (e.g. mineral exploration). The publication of this monograph is contemporaneous with new occurrences and discoveries of inland ASS that have led to increasing interest in the soil-regolith zone as well as in wider environmental concerns. Investigations of inland ASS are greatly enhanced by prior knowledge of soils, regolith, wetland ecology, aquatic systems and detailed biogeochemistry. A plethora of recent studies of inland ASS across Australia and in some other parts of the world (e.g. Iraq and Brunei) have documented their distribution, properties, and significance. Some have resulted in general soil-landscape conceptual models that synthesise their biogeochemical and mineralogical characteristics and weathering histories. Unfortunately, much of this information is hidden in widely-scattered sources, both published and unpublished, that encompass a range of disciplines.

This CRC LEME (Cooperative Centre for Landscape Environments and Mineral Exploration) Thematic Volume or monograph (published here as a CRC LEME Open File Report) entitled: “Inland Acid Sulfate Soil Systems Across Australia” represents a first step in drawing together much of this scattered multi-disciplinary literature. The monograph aims to provide the framework for an up-to-date overview of fundamental principles, methods and importance of inland ASS to environmental, mineral exploration and policy issues across Australia.

This monograph presents the first compilation of ASS studies for inland environments in Australia showcasing a range of important investigations completed by CRC LEME, CSIRO Land and Water, Universities, State and Territory Departments, geological surveys and industry. The monograph effectively integrates and summarises research outcomes on inland ASS, covering soil and regolith science, geology, mineralogy, biogeochemistry, hydrology, policy and the assessment of potential natural hazards in the soil-regolith-water environment.

The introductory or overview chapters feature: (i) definitions of inland ASS types and ASS materials, (ii) general soil-landscape conceptual models emphasising their biogeochemical and mineralogical characteristics and weathering histories, (iii) risk assessment procedures and recommendations on field sampling and laboratory analytical methods, (iv) mapping procedures and distribution, (v) groundwater and surface water issues, (vi) processes and frameworks to control and manage environmental issues (soil degradation, water quality, toxic gasses, greenhouse gasses and climate change), (vii) implications for mineral exploration and forensic science, (viii) policy, strategic planning, communication and training issues. This is followed by a number of case studies mainly from across Australia, which highlight the variety of inland ASS and the environments in which they form.

The monograph will be a valuable resource for:
- soil, regolith and environmental scientists
- natural resource managers
- students
- anyone with an interest in Australia's unique environment
- mineral exploration
- farmers

The monograph fulfils the following key functions, each of which will be explained further:
- It is the first comprehensive reference on the distribution, properties and management of inland ASS.
- It is the first major compilation of case histories of inland ASS processes in different geochemical/geomorphic, mineralised and land use settings.
- It provides both public and government organisations with past and new information on the distribution, properties and significance of inland ASS in Australia, as a major environmental issue for land and water degradation.
- It makes recommendations on appropriate sampling, mapping and analytical procedures for inland ASS, including sampling and chemical analysis procedures (e.g. soil pH before and after hydrogen peroxide treatment, soil incubation, acid base accounting and X-ray diffraction) and data interpretation.
- It contributes to changes in government agency and industry practice to assess inland ASS (i.e. description, sampling, characterisation, analyses and mapping) for improved environmental risk assessment and management strategies.
- It develops national and some international understanding of the spatial distribution and biogeochemical processes leading to inland ASS formation.
- It provides recommendations on appropriate mineral exploration procedures embedded in the inland ASS conceptual process models.
- It contributes to State, national and international regulatory guidelines and frameworks to control and manage inland ASS in the environment.

To the knowledge of the editors there is currently no single work or book on the subject of inland ASS. Added to this, there recently has been a mini revolution in the way inland ASS are viewed. This work in progress will continue, especially taking into account the vast number of studies being undertaken across Australia in the current drought, with the aim of producing the definitive international book on inland Acid Sulfate Soils.

Hard Copies of this monograph are available from CRC LEME Head Office, and individual chapters and case studies are downloadable as PDF files from both the:
CRC LEME Web site (http://crcleme.org.au/Pubs/monographs.html) and
CSIRO Land and Water Acid Sulfate Soil Web site (http://www.clw.csiro.au/acidsulfatesoils/index.html)

REFERENCE

NRMMC 2006 Natural Resource Management Ministerial Council (2006) – Glossary of terms Page 50. Commonwealth of Australia Department of the Environment and Heritage, Canberra, ACT. National Cooperative Approach to Integrated Coastal Zone Management: Framework Implementation Plan. ISBN 0642550514.

Rob Fitzpatrick and Paul Shand
December 2008

ACKNOWLEDGEMENTS

The editors take this opportunity to express their appreciation to the authors for the spirit of cooperation and enthusiasm, which they have shown at all stages of our endeavours to produce the best possible regionally-orientated monograph on inland Acid Sulfate Soils. We look forward to continuing to work with current authors and new authors that have indicated their willingness to produce in the near future the defining international major reference book on inland Acid Sulfate Soils.

The editors express their deep appreciation to:

- Dr. Jock Churchman for the methodical, technical editing of most chapters,
- Mr Greg Rinder for the exacting drafting of many text figures over several years ,
- Ms Jan Mahoney for her great patience and skills in preparing the web-based delivery,
- Mrs Teleisia Tatafu for assisting in the final layout of the monograph,
- Drs Charles Butt and Graham Carr for their support and encouragement with mineral exploration applications,
- Drs Steve Rogers and Lisa Worrall for their encouragement and for supporing our work on Inland Acid Sulfate Soils during CRC LEME.

Finally we also wish to acknowledge the financial support, collaboration and encouragement from the management of CSIRO Land and Water and CRC LEME.

Rob Fitzpatrick and Paul Shand
December 2008

FOREWORDS

It is with pride and considerable pleasure that I write the foreword to this particular CRC LEME Open File Report. The Report is the first comprehensive summary of the research carried out on inland ASS systems under the umbrella of CRC LEME. It is also a testament to the vision, determination and courage of Rob Fitzpatrick and Paul Shand. Rob, Paul and their co-workers developed many of the protocols for assessing the extent and character of potential ASS in the Murray Basin before the risk of ASS conditions developing as the drought conditions intensified was recognised by the community and local, state and federal governments. This pre-emptive work meant that they could respond rapidly to urgent requests for advice on, and assistance with, devising appropriate environmental management strategies. The effectiveness of their response is one of CRC LEME's success stories and I congratulate everyone involved.

Dr Lisa Worrall
Chief Executive Officer
CRC LEME

The recent severe drought in Australia has elevated research into the occurrence and impacts of inland acid sulfate soils to a new level. Retreating water levels have exposed large areas of sulfidic subaqueous acid sulfate soils leading to the generation of acidity. These effects have been particularly severe in the Lower Murray and Lower Lakes region of South Australia where research has progressed beyond studying the occurrence of ASS to assessing the impacts on adjacent environments through the mobilisation and transport of acidity and solutes. Such questions involve harnessing skills in aqueous geochemistry, hydrodynamic modelling and ecological risk assessment. Perversely, never have things been 'so good' for ASS research in Australia.

A wide range of studies have documented the distribution, properties, significance and biogeochemical processes of inland ASS across Australia and in some other parts of the world e.g. Iraq, Brunei and the USA. Unfortunately much of this valuable information is dispersed across a wide range unpublished sources and is not easily accessible. This monograph provides an up-date overview of fundamental principles, methods and importance of inland ASS to environmental, mineral exploration and policy issues across Australia. An important aspect to note from the studies presented in this monograph is their collaborative nature, which spans not only a wide range of scientific disciplines, but covers a large number of scientific organisations (i.e. CSIRO, NatCASS, CRC LEME, various Universities and international institutions). Overall, this monograph is a timely and most welcome contribution to understanding inland ASS. I commend the efforts of CRC LEME, the editors and contributors for undertaking this exciting project.

Dr Simon Apte 7 December 2008
Theme Leader - Centre for Environmental Contaminants Research
Program Leader - Environmental Biogeochemistry
CSIRO Land and Water

Acid sulfate soils have existed and formed in coastal and inland environments over thousands of years, however, it is only in the last two decades that Australian communities have come to appreciate their significance and the consequences of poor management in particular.

Adverse impacts on aquatic ecosystems, water quality and infrastructure have been identified in coastal estuaries particularly in northern NSW and Queensland. While the severest impacts are on aquatic ecosystems, land management practices are the source of the problem and hold the key to addressing these impacts. Given the technical and bureaucratic complexity of managing problems at the land and water interface, a robust strategy is required if any real success is to be achieved.

A National Strategy for the Management of Coastal Acid Sulfate Soils was endorsed by three federal Ministerial Councils in 2000. Subsequently the National Committee for Acid Sulfate Soils (NatCASS) was established to facilitate implementation of the National Strategy across all States and Territories in Australia. This initiative joined technical experts and key coastal managers in a collaborative process to share existing knowledge and advance the identification of potential problems nationally. Policies and legislation have been developed to manage ASS under significant development pressure. Also, technologies and best management practices have been introduced to sensitive coastal areas already disturbed by drainage, excavation, and dredging or groundwater abstraction.

The nature, extent and significance of inland ASS are just starting to be understood. The Thematic Volume on inland ASS will prove an invaluable tool to those facing the difficult decisions on how to best manage the land and water practices which will avoid or mitigate ASS impacts. NatCASS commends the speed with which this technical reference has been compiled. It trusts that the experience and networks established to address coastal ASS problems will facilitate an effective response to the problems now facing inland ASS as a consequence of the unprecedented drought over southern Australia.

Dr John Williams
Chair
Australian National Committee of Acid Sulfate Soils (NatCASS)

Congratulations to CRC LEME and to the editors and authors for your vision in undertaking this ambitious publication project on inland Acid Sulfate Systems Across Australia, and to some extent, the world. It is my hope that this publication may stimulate other earth science organizations and agencies in other countries, such as the US Geological Survey and the Natural Resource Conservation Service of the US Department of Agriculture in the USA, to look again at the soils, regolith and underlying rocks of lands for which they are responsible for helping humankind to understand, to find and map those places, which are very extensive, that are underlain by and where soils have developed from sulfidic materials, which still lurk, waiting to rapidly oxidize upon human or natural exposure or dropping water tables, in the unoxidized zone of soil-geologic columns across broad swaths of landscapes - such as beneath the Cretaceous and Tertiary geologic sediments and sedimentary rocks along the East and Gulf Coasts of the eastern United States and probably on into Mexico to the south, commonly only a few meters beneath the modern soil/land surfaces. Humankind needs to know and understand these systems if they are to avoid catastrophes such as some of those that I am sure will be reported in your publication. Opportunities abound, but unfortunately lie underappreciated, for societies to be warned and taught about these systems that can be so dramatic in expressing their power upon the qualities of the waters that emanate from them as well as upon the properties of the soils that form upon them, and upon engineering structures put on and in them. Thank you for undertaking this tremendous project.

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Emeritus Professor of Soil Science
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Fitzpatrick Rob and Paul Shand 2008. Inland Acid Sulfate Soils: Overview and conceptual models. In *Inland Acid Sulfate Soil Systems Across Australia* (Eds. Rob Fitzpatrick and Paul Shand). pp 6-74. CRC LEME Open File Report No. 249 (Thematic Volume) CRC LEME, Perth, Australia.

CHAPTER 1

INLAND ACID SULFATE SOILS IN AUSTRALIA: OVERVIEW AND CONCEPTUAL MODELS

Rob Fitzpatrick[1] and Paul Shand[1]

[1]*CSIRO Land and Water/ CRC LEME, Adelaide, South Australia*

INTRODUCTION

Acid sulfate soils (ASS) is the common name given to all those soils with soil materials affected by iron sulfide minerals. These soils may either contain sulfuric acid or have the potential to form sulfuric acid in amounts that have a lasting effect on the main soil characteristics (Pons 1973; Dent 1986; Dent and Pons 1995), cause deoxygenation or release contaminants when the sulfide minerals are exposed to oxygen. In general, the following three broad genetic types of ASS materials are recognised (Fanning 2002):

- Potential or unripe ASS materials containing pyrite and/or monosulfides that are still waterlogged (i.e. contain sulfidic or monosulfidic materials – see definitions below).
- Actual, active or raw ASS material containing sulfuric acid and pyrite at shallow depths (sulfuric material – see definition below).
- Post-active or ripe ASS where after drainage there is an irreversible loss of water and soils becomes firm.

In general, ASS are associated with the following wide range of waterlogged/anaerobic and/or drained environments because these are ideal for the formation of sulfide minerals, predominantly pyrite (FeS_2):

- **Coastal environments** or modern-day coastal zones (i.e. those areas landwards of the coastal waters influenced by processes or activities that affect the coast and its values **-** as defined by NRMMC 2006) comprising "coastal ASS" in:
    - ***Estuarine systems***, ***mangrove swamps and backswamps***. (e.g. Box 2)
- **Inland environments** or those areas, which occur inland of modern-day coastal zones (as defined by NRMMC 2006**)**. Several case studies are summarised in this chapter which, together with the summary of historical observations (see Box 1) and case studies presented in this thematic volume (see Chapters 2 to 21, referenced below as: "Authors name 2008-Ch2 to Ch21"), provide a wide selection of examples dealing with "inland ASS" issues typical of inland environments encountered in:
    - ***River and stream channels*** (e.g. Fitzpatrick *et al*. 2008-Ch2,8; Simpson *et al*. 2008-Ch3),
    - ***Lakes*** (e.g. Degens *et al*. 2008-Ch11; Fitzpatrick *et al*. 2008-Ch2; Simpson *et al*. 2008-Ch3),
    - ***Wetlands*** (e.g. Fawcett *et al*. 2008-Ch18; Grealish *et al*. 2008-Ch21),
    - ***Seepages overlying mineralized zones*** (Skwarnecki and Fitzpatrick 2008-Ch4),
    - ***Disposal basins*** (***Evaporation)*** (e.g. Hicks and Fitzpatrick 2008-Ch6; Lamontagne *et al*. 2008-Ch14; Wallace *et al*. 2008-Ch15,16; Shand *et al*. 2008b),
    - ***Billabongs*** (e.g. Fitzpatrick *et al*. 2008-Ch19),
    - ***Drains*** (Degens *et al*. 2008-Ch10,11,13; Fitzpatrick *et al*. 2008-Ch12,17; Baker and Fitzpatrick 2008-Ch9),
    - ***Marshes*** (e.g. Fitzpatrick 2004),
    - ***Ground water systems*** (e.g. Shand *et al*. 2008-Ch5),
    - ***Sports fields*** (e.g. Hicks and Fitzpatrick 2008-Ch7) and
    - ***Floodplains*** (e.g. Willett 2008-Ch20).
- **Minespoil environments** comprising **"**minespoil ASS" and "acid–rock drainage'in:
    - ***Waste rock stockpiles and tailing impoundments*** (e.g. Milnes *et al*. 1992; Fitzpatrick *et al*. 1998).
    - ***Mine retention ponds*** (e.g. Fitzpatrick and Self 1997; Nordstrom and Alpers, 1999).

Iron sulfide minerals are one of the end products that form as part of the process of sulfate reduction (i.e., the use of SO_4^{2-} instead of O_2 during microbial respiration (Figure 1). Sulfate reduction is a natural process that occurs in virtually all lakes, rivers, wetlands and oceans. However, the quantities of sulfide minerals that will accumulate in a given environment are a function of many factors. The key general requirements for high rates of sulfate reduction and sulfide accumulation are:

- High concentrations of dissolved sulfate.
- Saturation of soils and sediments for periods long enough to favour moderately reducing conditions.
- Availability of labile carbon to fuel microbial activity.
- Availability of dissolved Fe or Fe containing minerals (e.g. Table 1).

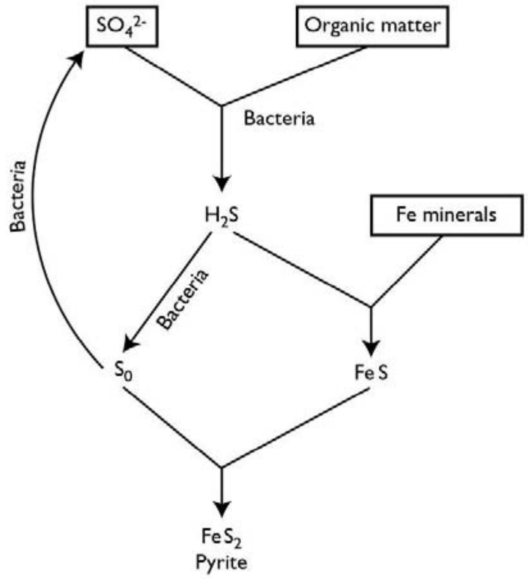


Figure 1. Schematic diagram for the formation of pyrite in anoxic environments (after Berner 1984).

Acidity derived from the oxidation of pyrite in ASS, together with associated toxic elements (*inter alia* heavy metals and other contaminants e.g. gases) contribute to environmental (soil, water, air), infrastructure (corrode concrete and steel), mineral exploration, and mining issues. In existing agencies in Australia (and overseas), these issues often fall between jurisdictions (e.g. agriculture, environment, fisheries/oceans, water, atmosphere, mineral exploration and mining) (see Fitzpatrick *et al*. 1998).

Although the consequences of the accumulation of iron sulfide minerals and/or sulfuric acid in inland soils have been known for more than a century (see Box 1 for historical summary), no single text has appeared, which has been entirely devoted to the topic of “inland Acid Sulfate Soils”. In the past, inland Acid Sulfate Soils have usually been dealt with as a subsection of major works dealing with salt-affected or saline soils (e.g. Box 1). In contrast, there is a much larger amount of published information, including several books on the topic of “coastal Acid Sulfate Soils” (e.g. Pons 1973; Dent 1986; Dent and Pons 1995; Lin et al. 2002) that have formed in modern-day coastal zones (i.e. those areas landwards of the coastal waters influenced by processes or activities that affect the coast and its values - as defined by NRMMC 2006). Coastal infrastructure development and primary industries around Australia are facing a $10 billion legacy of acid sulfate soils (e.g. National Working Party on Acid Sulfate Soil 2000). Public recognition of this serious problem has been reflected in government building legislation in several Australian states. In addition, there is gathering support from local government and industries to develop statutory requirements for rehabilitation.

Across much of inland Australia, there has been wide-ranging and fundamental shifts in the “environmental equilibrium” (Macumber 1991) brought about by the impact of European settlement (e.g. large scale clearing of trees and building of locks and barrages to contain water flow) and recent extreme drought conditions (i.e. lowering water levels in rivers, lakes and wetlands), which is providing a unique opportunity to study the various transformations of materials in inland ASS that is influencing this equilibrium. It is only over the past decade or so that the existence and extent of inland ASS has been realised (e.g. Box 1). Hence, the nature, type and distribution of inland ASS, the environments in which they occur (e.g. wetlands, river and

Table 1. Summary of the occurrence and distribution of secondary Fe oxides, sulfides, carbonates and salts in soil environments (modified from Bigham *et al.* 2002)

Mineral	**Dominant colour**	**Soil Environment**	**[†]Landscape position**
Hematite [α-Fe_2O_3]	Red (< 0.5mm) Reddish-purple (>0.5mm nodules, mottles, ferricretes)	Aerobic soils of the tropics, subtropics, arid/semiarid zones, and Mediterranean climates; greater amounts with warmer temperatures and lower organic matter contents.	Well drained upper parts.
Goethite [α-$FeO(OH)$]	Yellow (< 0.5 mm). Strong brown (>0.5mm nodules, ferricretes)	All weathering regimes; greater amounts with cool, wet climates (including higher altitudes and moist/cool aspects) and elevated organic matter.	Well drained upper parts and mottles in mid-slopes.[†]
Lepidocrocite [γ-$FeO(OH)$]	Orange (<0.5mm) Reddish-purple (>0.5mm)	Seasonally anaerobic, non-calcareous soils of cool-temperate climates (including higher altitudes and moist/cool aspects on mid to lower slopes).	Seasonally wet mid-slopes.
Ferrihydrite [$5Fe_2O_3.9H_2O$]	Reddish-brown	Soils subject to rapid oxidation of Fe in the presence of organic matter.	Seasonally wet foot-slopes and seeps.
Maghemite [γ-Fe_2O_3]	Brown.	Highly weathered soils of the tropics and subtropics derived from mafic rocks rich in precursor magnetite and/or soils subjected to burning in the presence of organic matter.	Well drained upper parts and foot-slopes after burning.
Schwertmannite [$Fe_8O_8(OH)_{4.6}(SO_4)_{1.7}$]	Reddish-orange	Sulfuric material in acid sulfate soils of both coastal and inland areas; anthropogenic sites including mines, spoils and tailings. pH between 3.5 and 4.5.	Poorly drained foot-slopes, seeps and bottom lands.
Jarosite [$KFe_3(SO_4)_2(OH)_6$] **Natrojarosite** [$NaFe_3(SO_4)_2(OH)_6$]	Pale yellow	Sulfuric material in acid sulfate soils of both coastal and inland areas; anthropogenic sites including mines, spoils and tailings. pH between 2.5 and 3.5.	Poorly drained foot-slopes, seeps and bottom lands.
[*]Sideronatrite [$Na_2Fe(SO_4)_2.OH.3H_2O$]	Pale yellowish green	Sulfuric material in acid sulfate soils in mostly inland or coastal back swamp areas; anthropogenic sites including mines, spoils and tailings. pH between 2.0 and 3.5.	Poorly drained foot-slopes, seeps and bottom lands.
Green Rust [$Fe(OH)_2$]	Greenish-blue	Strongly hydromorphic soils.	Poorly drained foot-slopes, seeps and bottom lands.
Akaganéite [β-$FeOOH$]	Bright Orange	Strongly hydromorphic and subaqueous soils.	As above and in saline rivers, lakes and ocean
Iron monosulfides [FeS]	Black	Strongly hydromorphic and subaqueous soils.	As above and in rivers and lakes.
Iron disulfides or pyrite [FeS_2]	Black	Strongly hydromorphic and subaqueous soils.	As above and in rivers and lakes.
Calcite and dolomite [$CaCO_3$] and [$CaMg(CO_3)_2$]	White	Calcareous soils.	Low rainfall regions.
Gypsum [$CaSO_{4X}\ 2H_2O$]	Very pale brown	Saline soils and saline acid sulfate soils.	Low rainfall regions.
Quartz [SiO_2]	Light grey	Sandy soils.	All landscape positions.

[†] Occurring only in specific soil horizons or sedimentary units.

[*] Widespread occurrences in sandy and peaty sulfuric materials in South Australia (Fitzpatrick *et al* 2000b; 2008c,d,e,f).

BOX 1 - HISTORICAL BACKGROUND OF INLAND ACID SULFATE SOILS

This brief, necessarily somewhat selective historical background provides a synopsis of inland ASS in Australia, but makes no claim to be comprehensive or to have recorded all useful individual contributions, but rather presents a broad overview.

Indigenous peoples of Australia

Indigenous peoples of Australia record creation stories about the remarkable changes that occurred both when the sea level began rising 18,000 years ago and when the current sea level stabilised about 5,000 years ago. The creation stories and oral traditions of indigenous people have been passed down from generation to generation, especially about the detailed knowledge of the nurseries (i.e. wetlands), which contain inland Acid Sulfate Soils. For example, the Ngarrindjeri people believe the land and water is a living body and that they are a part of its existence (Ngarrindjeri Tendi *et al*. 2007). In the Ngarrindjeri Nation *Yarluwar-Ruwe* plan (Ngarrindjeri Tendi *et al*. 2007) it is stated: “The land and waters must be healthy for the Ngarrindjeri people to be healthy. We say that if wetlands/nurseries die, our *Ngartji* (totem or special friend) die, then Ngarrindjeri will surely die.”

Early explorers in Australia

The first explorers to site and even settle in Australia possessed remarkable skills of observation. It is important to realise that the early explorers were not trained scientists and that their primary concerns were to delineate the major terrain features of the interior and to survive. Moreover, many of the early explorers originated or worked in environments quite different from Australia. In addition, at the time the Australian continent was being explored, the discipline of pedology (soil science) had not yet been established. Pedology is said to have had its origins as recently as 1882 in the work of its founder V. V. Dokuchaiev, a geologist employed by the Russian government.

Using horse drawn transport, early explorers' observations and reports on soils had mainly to do with pastoral or agricultural production more than with the natural history of wetlands or back swamps. Nevertheless, the following observations remain of interest with regard to past and current known occurrences of inland Acid Sulfate Soils:

Captain Charles Sturt was one of the earliest recorders of soil information. Following his previous experience along the Murrumbidgee, Murray and Darling rivers in 1828 to 1829, Sturt explored from Cawndilla near the Menindee Lakes westward into the north east deserts of South Australia in 1844-46. His journals (Sturt 1849) reveal him as an observant and inquisitive explorer. As he passed across the region of the South Australian border he records: "… we travelled over firm and open plains of clay and sand, similar to the soil of the plains of the Murray.” The following quotations from his published journal (Sturt 1849) reveal a few of his perceptions about the possible natural occurrences of inland Acid Sulfate Soils in wetlands: *Sunday, August 17th 1845 (Page 156):* “For the last six miles the country has fallen off greatly, the flats are broader and of a white clay with but little grass upon them. The sand hills are very high and the sand as red as brick, and from their summits the view to the NW is as dreary as can be imagined.... Surface water is becoming very scarce, and what we are obliged to use is ***as thick as a puddle and looks like a mixture of Magnesia and Rhubarb*** (Figure 2). ***The pools in truth are not more than two inches deep, and as it blows more or less violently every day the mud gets so mixed that it will not settle***. I may say that we have not had a drop of wholesome water since November......" (Figure 2). *Sunday September 7th 1845 (Page 180):* "Its channel was white as the driven snow and it was flanked by sand banks on which the marks of flood were 12 feet high. ***There was no water in the bed where we struck it, but the bed was too soft for us to cross with the horses*** so that we turned up it northerly, passing a long sheet of water on which the ***salt was coated like ice***. Tracing it upwards at a mile we crossed a high sand ridge, and beneath us saw the dry basin of this creek surrounded by samphire. Crossing it we took up our old course, and traversed flats of salt formation between sandy ridges dark with samphire bushes excepting where there were white patches thinly coated with salt, the shallow receptacles for water. ***The bottoms of these were spongy and soft “*** “The mineral salts in the waterholes such as this cause the clay sediments to settle, and also ***produce foul-smelling mud*** under the white crust” (Figure 2).

Hill (1969; first published 1937) from “*Water Into Gold*” noted on page 12: “In the late 1830’s Lake Bonney was described as a fine lake of fresh water about 30 miles in diameter. Thousands of ducks were on the water” and page 15: “In marked contrast, in 1841 ***a sulphurous silence lay over Lake Bonney. The bed of the lake was as dry as a bone***”.

Figure 2. Typical waterhole between sandy ridges in the Strzelecki Creek showing white salts (left photo) and subaqueous black monosulfidic ooze (right photo) exposed by breaking the pinkish-white salt crust in the water using a geological hammer; site probably bypassed by Sturt on 18th August 1845 when full of water but proved to be dry on his return in October 1845.

BOX 1 – *continued: HISTORICAL BACKGROUND-*

The early scientists in Australia

The early reports on soils (1898 to 1922) in NSW were mostly concerned with their qualities for crop production, which also culminated in the publication by H I Jenson (1914) entitled: "Soils of New South Wales" – with no mention of the occurrences of inland ASS. However, Jenson (1914) identified blue coloured coastal soils in swamps that contained iron sulfide, which formed by reduction of sulfate and iron, and became acidic after being drained.

An occurrence of inland Acid Sulfate Soil was recognised as a potential problem as early as 1914 following drainage of the "Seven Mile Swamps and land below it in Western Australia (Woodward 1914): - "- during the early years this swamp land was very productive; now, however, the lower lying portions have become so highly saturated with mineral solutions as to tender it perfectly infertile" - - leaving a red-brown encrustation after the subsidence, and thus it is claimed was the primary cause of the damage." - - the whole trouble can be directly attributed to the decomposition of pyrite which is present in soil and subsoil of the swamp itself in considerable quantity……the decomposition of the pyrites is, however brought about by either, or rapidly by both, of the following conditions: firstly, by the drainage of the land which permits the access of the air into the soil, and secondly, by cultivation, which opens up the soil, thus exposing pyrites to the atmosphere. Teakle and Southern (1937) also recognised sulfide bearing soils in the Herdsman Lake in Western Australia.

Detailed field survey investigations of Australian soils commenced by Taylor and England (1929) in the Renmark Irrigation District on the River Murray in South Australia (Wells and Prescott 1983). By 1940, all then existing irrigation in SA had been investigated/mapped, including the irrigated drained Phragmites swamps on the lower Murray River (Taylor and Poole 1931a) between Murray Bridge and Wellington. Significantly, these soil survey investigations also included the lake bed of Lake Albert, which was being considered for drainage and development as an irrigated pasture/cropping area similar to the swamps (Taylor and Poole 1931b). This soil survey required unique subaqueous soil inspections and sampling techniques. At that time, they noted the presence of what we now call inland Acid Sulfate Soils, one soil having a pH of 3.9, and they successfully argued that the lake should not be drained for agriculture. Some of their original soil samples were retrieved from the CSIRO Land and Water soil archive in Canberra, and analysed for pH and pH after peroxide treatment for comparison with the original measurements made 78 years previously (Fitzpatrick *et al*. 2008c). In this case, the original, 1930s results can be taken as the original pH values and the 2007 pH values used as a long-term incubation experiment as they show the effects of exposure of the soils to the atmosphere.

The early soil scientists and pedologists who produced soil maps of Australia were often unaware of, and thus did not consider, acid sulfate soils (e.g. Prescott, 1931; Stephens, 1952, 1956, 1962; Northcote *et al*. 1960-68). A plausible explanation for this may be found in the following statement by Fanning and Fanning (1989): "- - perhaps this was because most Russian and American soil scientists lived and worked primarily in the centres of large continents, upon the extensive soils used for agriculture and forestry in those areas, rather than near seacoasts where ASS are more common, extensive and important". In general, soil scientists have only become more aware of ASS processes since 1973 when the first international symposium on ASS was held (Pons 1973; Dost 1973) and in Australian coastal floodplains following the comprehensive study by Walker (1972) – who specifically warned of the dangers of continuing the draining of sulfidic materials. In fact, according to Pons (1973), acid sulfate soils were recognised in Europe over 250 years ago.

Recent scientific investigations in Australia- post 1990

Various stages can be discerned in the development of our current understanding of inland ASS in Australia. They overlap and are not clearly separated in chronological order, but a sequential development can nevertheless be detected in the efforts made to provide an explanatory account of occurrences and processes of inland ASS in Australia. Our examination of the following various disciplines points to their initiation by key workers in Australia who largely succeeded in blending fundamental soil science, geology, hydrology and vegetation with innovative observations or research on inland ASS to produce results of either indirect or direct practical application:

Pedology, classification, biogeochemistry, mineralogy, dryland salinity, first use of term "Inland Acid Sulfate Soils": Fitzpatrick (1991), Fitzpatrick *et al*. (1992, 1993, 1996, 1998; 2008a,b,c,d), Fitzpatrick and Self (1997), Isbell (1996)

Saline and acid groundwater systems, geology and dryland salinity: Macumber (1991), Corom *et al*. (2001), Salama *et al*. (1999), Shand *et al*. (2008-Ch5), Degens *et al*. (2008-Ch10); Appleyard and Cook (2008).

Geology, regolith, geochemical mineralisation and mineral exploration: Skwarnecki *et al*. (2002); Skwarnecki and Fitzpatrick (2003).

Water quality, vegetation, freshwater wetlands in Murray Darling Basin: Hall *et al*. (2006) and Baldwin (2007).

Soil chemistry, monosulfides and dryland salinity: Sullivan *et al*. (2000, 2002a, 2004)

Atlas of Australian Acid Sulfate Soils: regional mapping of inland ASS: Fitzpatrick *et al*. (2006, 2008,a,c,d, 2009; 2008-Ch2).

stream channels), and the potential impacts on surrounding ecosystems make them more complex than their coastal equivalents, and a detailed and robust national strategy has yet to be developed. A clear understanding of the basic processes involved in inland ASS is essential for an overall view of what is happening in these complex systems and why. Hence, with a view to gaining a fuller understanding of the pedological, hydrological, biogeochemical and mineralogical processes, conceptual soil-regolith-landscape process models have been constructed to display mechanisms that occur in toposequences (e.g. Figure 3) to explain causes of land/water degradation and to aid with mineral exploration (e.g. Fitzpatrick *et al* 1996; Fitzpatrick *et al*. 2000a; Fritsch and Fitzpatrick 1994; Skwarnecki and Fitzpatrick 2003a.b; Fitzpatrick *et al*. 2008a,b,c,d) and are summarised in this chapter and in several other chapters in this monograph (e.g. Fitzpatrick *et al*. 2008-Ch2,8,12,17; Fawcett *et al*. 2008-Ch18; Skwarnecki and Fitzpatrick 2008-Ch4; Hicks and Fitzpatrick 2008-Ch6; Shand *et al*. 2008-Ch5 and Willett 2008-Ch20).

The purpose of this introductory chapter is to briefly review available information on these fascinating and critically important inland Acid Sulfate Soils across Australia, by summarising:

- Historical observations (Box 1), current established concepts, standard terminologies and definitions.
- Sampling and laboratory analytical methods and risk assessment procedures.
- Soil classifications, mapping procedures and distribution.
- Conceptual models to illustrate the range of pedological, regolith, groundwater, surface-water, biogeochemical, mineralogical and weathering processes involved.
- Implications for soil/water degradation and mineral exploration.
- Frameworks to underpin best management practices by highlighting how coloured cross-sectional diagrams or toposequences and photographs of soil-regolith help local community groups to understand complicated scientific processes and terminology.

SOIL-LANDSCAPE PROPERTIES AND PATTERNS: TOPOSEQUENCES

Soils mean different things to different people. Soil scientists (pedologists) view soils as being made up of different size mineral particles (sand, silt, and clay) and organic matter. They have complex biological, chemical, physical, mineralogical and hydrological properties that are always changing with time. Acid sulfate soils are particularly prone to change, especially when sulfidic materials are exposed to air (see processes below). Agronomists, farmers and gardeners on the other hand see soil as a medium for growing crops, pastures and plants primarily in the top 50 cm of the Earth's surface. Engineers regard soil as material to build on and excavate, and are usually concerned primarily with moisture conditions and the capacity for soil to become compacted and support structures. All agree, however, that soils are strongly affected during land degradation and furthermore, that pedological approaches are crucial to understanding land degradation processes, and how knowledge of these processes contribute to effective Natural Resources Management (e.g., McKenzie *et al*. 2004; Fitzpatrick 2008).

The following checklist of six key soil morphological descriptors has been compiled from standard techniques used in soil science (McDonald *et al*. 1990; Schoeneberger *et al*. 2002) for assessing soil properties for Natural Resources Management. These include observations of depth changes in colour, consistence, texture, structure, segregations/coarse fragments (carbonates and ironstone) and abundance of roots in the different layers or horizons (e.g. Fitzpatrick *et al*. 1999). Morphological descriptors are useful in assessing soil conditions because:

- They are rapid field and laboratory assessments, and may serve as proxies for other methods, such as for mineralogy and geochemistry, which are generally complex and more costly to carry out; and
- They can be used in research to evaluate causes for variation in soil conditions induced by anthropogenic activities, land management, hydrology and weather conditions.

Soil Colour and toposequences patterns

Soil colour is usually the first property recorded in a morphological description of soils (and may be the only feature of significance to a layperson). Colour provides an indicator of redox status because soil colour depends upon the type of Fe oxides and other minerals present, and the soil’s position in the landscape relates to soil aeration and organic matter content (Bigham and Ciolkosz 1993; Fitzpatrick *et al*. 1999; Bigham *et al*. 2002).

Upslopes - freely drained soils

Uniform high chroma red and yellow colours (hues) indicate oxidising conditions, and are usually present in the upper parts of landscapes (Figure 3, Table 1). The Fe oxides dominating such aerobic soils are mainly hematite and goethite. Red soils are nearly always better drained than yellow soils.

Downslopes – periodically saturated soils

Under wet and anaerobic conditions, hematite and goethite can become soluble through the action of anaerobic bacteria. Soluble Fe^{2+} may move to aerobic zones either lower in the profile, or down slope to re-oxidize and form a new Fe oxide (Figure 3). Consequently, distinctive colour patterns are formed. In some cases, the re-oxidized Fe may form various types of ferricretes as indicated in Figure 2. When the Fe oxides have been fully depleted from soils, and organic matter levels are low, then the soil colours will have low chroma colours, grey and blue tints (or even, white) in an A2 (or E) horizon (Figure 3), indicating reducing, waterlogged, hydric or aquic conditions. In the same soil layer, mixtures of bright red or yellow soil matrices containing dark grey or bluish blotches (mottles) indicate periodic conditions of water saturation (e.g. Vepraskas 1992; Schoeneberger *et al*. 2002).

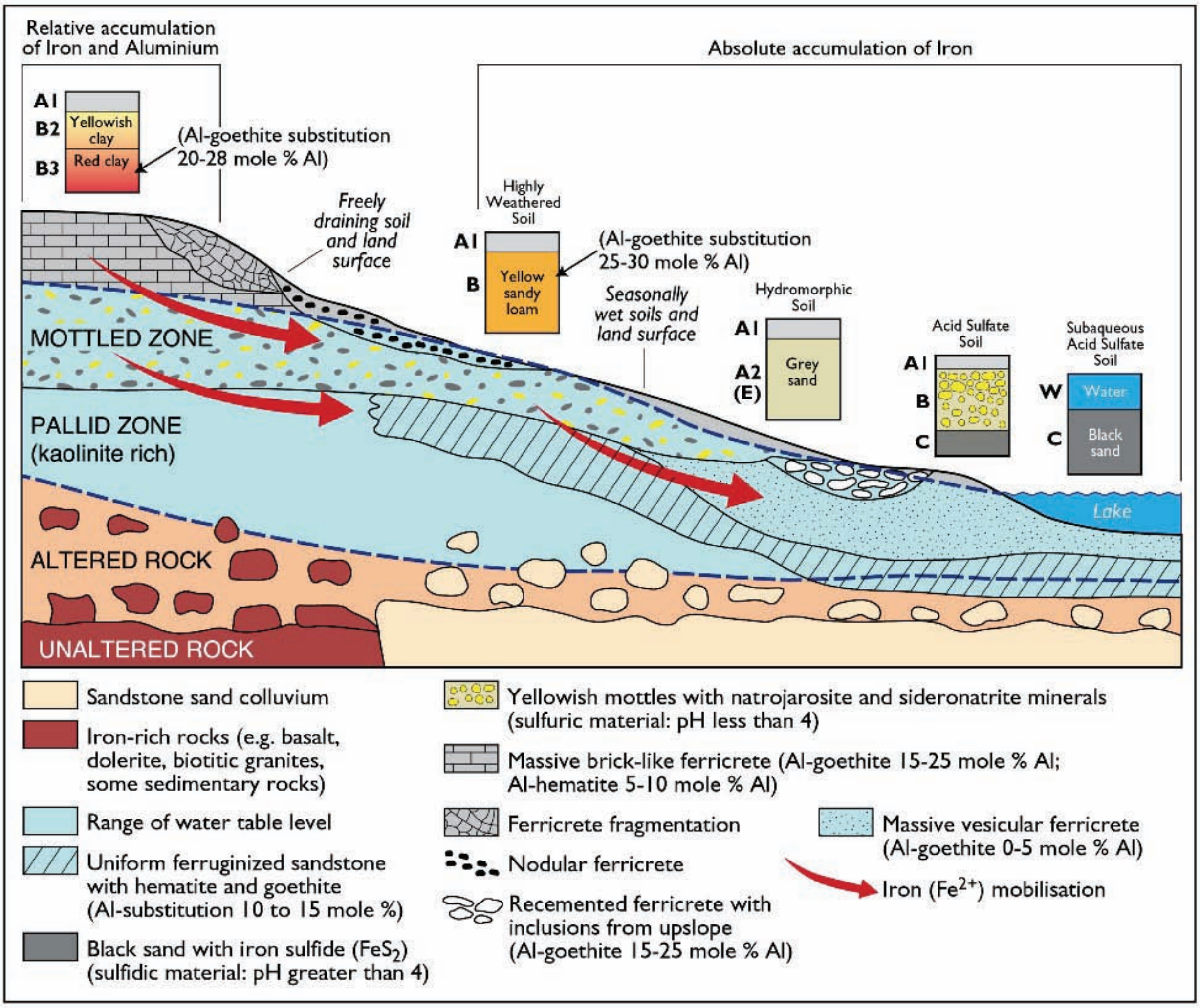


Figure 3. Generalised cross section or toposequence illustrating the multi-process formation of red-yellow-grey-black soils and ferricretes down a hillslope. The schematic representation demonstrates the relationship between hydrology, topography, geology, soil mineralogy and dominant soil profile horizons. It also demonstrates the changes in soil patterns down slope from freely drained soils (red-yellow) to hydromorphic soils (grey waterlogged or hydric soils with mottles) to subaqueous soils (permanently submerged under at least 2.5 m water). The toposequence also indicates some of the different modes and forms of Fe oxide accumulation and/or transformation in relation to landscape features indicated in Table 1 (modified after Fitzpatrick 1988, 2008; McKenzie *et al*. 2004).

Valley bottom - subaqueous soils permanently submerged under water

In the last decade, the US Department of Agriculture's (USDA) definition of soils has changed to include environments that are permanently submerged under water (Soil Survey Staff 1999). Subaqueous soils form in sediments found in shallow permanently flooded environments (Figure 3; Table 3). Excluded from the definition of subaqueous soils are any areas "permanently covered by water too deep (typically greater than 2.5 m) for the growth of rooted plants" (Stolt 2006).

Pedologists have been studying these subaqueous soils in shallow subtidal lagoons or lakes (e.g. Taylor and Poole 1931b; Box 1) and so have described their benthic substrates from a pedological perspective i.e. characterising the morphological (colour, structure), physical (texture, compressibility), chemical (pH, salinity), mineralogical (layer silicates, Fe oxides) and biological (roots, plants) properties. Once the benthic materials and underlying sediments are described as soils, investigators can easily identify the relationship between the soils and their position on the landscape (e.g. Bradley and Stolt 2003; Demas and Rabenhorst 1999). An understanding of these relationships enables land managers to identify the best location for specific land uses and to better predict the potential impact of proposed changes (like dredging or drainage) on subaqueous soils, especially if they contain sulfidic materials (see definitions below) and the ecosystems they support.

INLAND SALT-AFFECTED AND ACID SULFATE SOILS

Saline (or salt-affected) soils are those with relatively large amounts of soluble salts such as chloride or sulfate containing salts. The soluble salts found in saline soils are generally of three types: chlorides, **sulfates** and carbonates. Most saline soils in Australia have high amounts of chloride salts (e.g. Gunn and Richardson 1979, Isbell *et al*. 1983). However, in many parts of the Australia (e.g., Mount Lofty Ranges, South Australia; Fitzpatrick *et al*. 1996; Dundas Tablelands, Victoria and Murray Darling Basin) and overseas (e.g. Iraq: Fitzpatrick 2004b) extensive areas of saline soils also contain surface accumulations of sulfate-rich salts, and sulfide minerals at depth (acid sulfate soils). Saline soils with high amounts of Na_2CO_3 may also occur and are usually associated with coarse-textured soils.

Hence, it is important to briefly review the nature and properties of salt-affected soils because many agriculturists, hydrologists, agronomists, and even some soil scientists have experienced much confusion in differentiating between saline soils on the one hand and acid sulfate soils on the other (e.g. see Box 1). Part of the problem stems from the fact that, in many cases, certain soils are simultaneously acid sulfate soils and saline soils, with the latter sometimes evolving from the former as a result of the formation of sulfate-containing salts from the oxidation of sulfides. Therefore it is first necessary to draw a clear distinction between these two groups of soils, which, fortunately, is relatively easy, before attempting to clarify the definitions of the various materials in ASS. However, it is impossible to separate the effects of salinity totally from those of ASS (especially those with sulfuric materials) as they go hand in hand, while the level of salt that might be present in an ASS is of utmost importance in determining how certain subtypes of ASS will behave from a physical and chemical point of view.

Types of saline landscapes and soils

Soils with high salt concentrations (as defined by high EC) dehydrate plant cells because the dissolved salts decrease the osmotic potential of soil water. Water flows from the high osmotic potential (low salt concentration in the plant cell) to low osmotic potential (high salt concentration in soil). Thus, plants cannot extract water from soil when the soil solution has a lower osmotic potential than the plant cells. The effect on plants is similar to drought stress, with impaired plant growth and productivity, and may cause death if excessive. For many crops, yields are reduced when the soil extract EC (EC_{se} where SE = Saturation Extract) reaches 4 dS/m (US Salinity Laboratory Staff 1954) and decline proportionately as EC levels increase above that concentration. Some crops, such as sugar beet, are tolerant to EC levels between 4 and 8 dS/m. At an EC of 16 dS/m the growth and yields of most crops are affected.

When saline soils occur naturally, this is referred to as primary salinity (i.e., primary groundwater associated salinity (GAS) [Figure 4; Fitzpatrick 2008]). Secondary salinity results from human activities such as irrigation or land clearing in areas that are not irrigated (also referred to as “dryland salinity”) (Wood 1924; National Land and Water Resources Audit, 2001b, Ghassemi et al 1995; Keren 2000; Tanji 2002). Both primary and secondary salinity affect plant growth by causing dehydration and toxic conditions.

Before salt-affected landscapes can be managed, the type of saline land must be determined using the hydrological characteristics, and the category of salt-affected soil from the dominant geochemical properties (Figure 4). Salt-affected soils form under vastly different environmental conditions under the influence of diverse hydrological, morphological, geochemical, mineralogical and physical processes.

Types of saline soils include:

- Groundwater associated salinity (GAS) comprises salt-affected soils in rain fed areas that have direct or capillary contact with saline groundwater tables, and categories defined by the following hydrological and geochemical environments: (i) primary (natural) or secondary (anthropogenic) , (ii) alkaline (Na_2CO_3-dominant, pH >9), (iii) halitic (NaCl-dominant), (iv) gypsic ($CaSO_4$-dominant), (v) sulfidic (pyrite-dominant, pH >4.0), (vi) sulfuric (sulfuric acid dominant, pH <4.0), and (vi) sodic, that possess elevated exchangeable sodium percent (ESP) on clay surfaces
- Non-groundwater associated salinity (NAS) comprises salt-affected soils in rain fed areas that have no direct contact with saline groundwater tables, and with categories defined by the following soil chemical environments: (i) sodic ($ESP \geq 5$), and (ii) saline (electrical conductivity, $EC_{se} \geq 2$ dS/m; where SE = Saturation Extract) conditions in the solum (A- and B-horizons, typically <1.2 m deep)
- Irrigation associated salinity (IAS) comprises salt-affected soils in irrigated areas with shallow (surface IAS) or deep (subsoil IAS) saline water tables.

Various terms are in use to describe saline land in Australia. The classification scheme presented in Figure 4 features a unified, process-based scheme to promote clear communication and management of types of saline land, including those with sulfidic and sulfuric materials.

Saline soils and saline ASS form under different environmental conditions and thus have diverse hydrological, morphological, chemical, physical and biological properties (Figures 2 and 4). There is no universally accepted definition for saline soils and ASS. The definition used depends on the discipline and the type of measurements taken. For example:

- Hydrogeologists distinguish primary and secondary saline soils (e.g., Coram *et al.* 2001; George *et al.* 1997).
- Plant and soil scientists use the distribution of salt-tolerant plant species and/or the approximate range of soil electrical conductivity (EC) to distinguish slightly, moderately or severely affected saline soils (e.g. Allan 1994); and
- Scientists in other disciplines may use:
  - measurements of pH (3.5–8.5), exchangeable Na percentage, the Na adsorption ratio and EC to identify sodic–saline soils (e.g. Soil Survey Staff 1987; Naidu *et al.* 1995, Northcote and Skene 1972);
  - measurements of pH (> 9), presence of Na_2CO_3 and high EC to distinguish alkaline saline soils
  - pH (< 3.5 or 4), presence of sulfur and high EC to distinguish acid sulfate saline soils (Fitzpatrick *et al.* 1996; Fanning 2002); and
  - apparent electrical conductivity (EC_a) intensities and patterns using geophysics (Rhoades *et al* 1999).

The definition is further complicated by the fact that soil salinity may also not be associated with a permanent saline groundwater table. In Australia, most studies of salinisation processes focus on primary and secondary salinity (e.g., George *et al.* 1997; Coram *et al.* 2001; Salama *et al.* 1999, Clarke *et al.* 2002) or the processes occurring in sodic soils (e.g., Isbell *et al.* 1983; Rengasamy and Sumner 1998; Shaw *et al.* 1998; Fitzpatrick *et al.* 1994). Non-groundwater associated salinity (NAS) comprises several categories of salt-affected soils (Figure 4) in rain fed areas that have no direct contact with saline groundwater water tables (e.g. Fitzpatrick et al. 2003d; Herriot 1942 and Kennewell 1999, Maschmedt 2000; Rengasamy 2002).

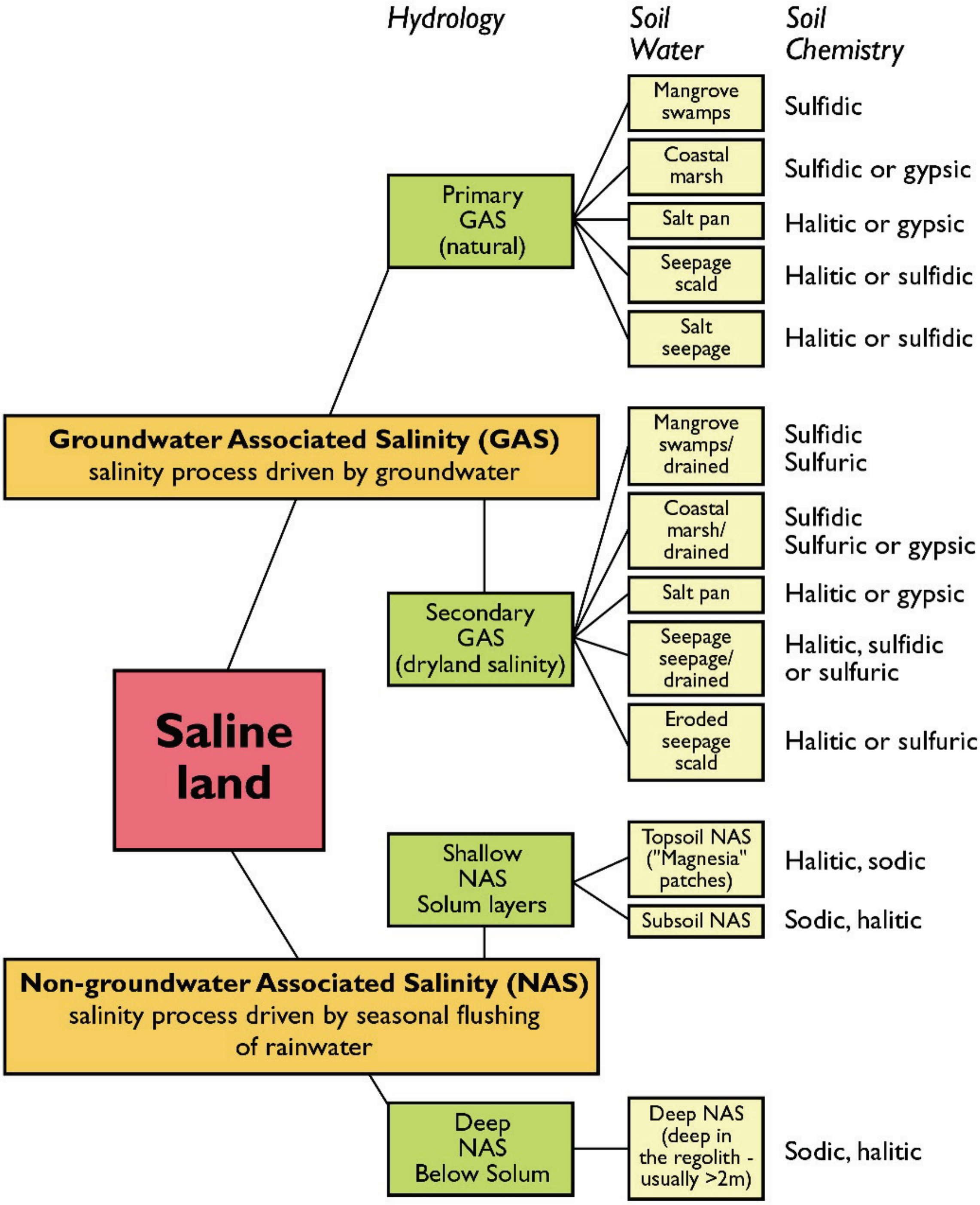


Figure 4. Categories of saline land as defined by hydrology, soil water status and soil chemistry (from Fitzpatrick 2008; after SCAV 1982; Williams and Bullock 1989; Fitzpatrick *et al*. 2003c). Where GAS = Groundwater Associated Salinity and NAS = Non-groundwater Associated Salinity.

DEFINITIONS OF MATERIALS IN ACID SULFATE SOILS

Sulfidic Material

Soil horizons that contain sulfide minerals are called sulfidic materials (Isbell 1996; Soil Survey Staff 2003) and can be environmentally damaging if exposed to air (reaction with oxygen) by disturbance.
Saturated, organic-rich soil conditions promote reducing conditions and the activation of the SO_4^{2-}/S^{2-} redox couple. This process produces pyrite (FeS_2) i.e. sulfidic material (Soil Survey Staff 2003, Isbell 1996), in reactions (Equations 1 to 4) as follows:

- Sulfate reduction: $2H^+ + SO_4^{2-} + 2(CH_2O) = 2CO_2 + H_2S + 2H_2O$ Eqn 1
- H_2S reacts with Fe^{2+} to precipitate FeS, which can be converted to pyrite:
  - $H_2S + Fe^{2+} = FeS + 2H^+$ Eqn 2
  - $H_2S + FeS = FeS_2 + H_2$ Eqn 3
- H_2S also reduces Fe^{3+} minerals to form pyrite:
  - $4H_2S + 2Fe(OH)_3 = 2FeS_2 + 6H_2O + H_2$ Eqn 4

Pyrite-rich soil materials are termed sulfidic material, because they have the ingredients necessary to produce sulfuric materials (e.g. Pons 1973; Fanning 2002; Fitzpatrick *et al*. 1996). They are waterlogged, mineral or organic subsoil materials that contain oxidisable sulfur compounds, usually pyrite, that have a field pH of 4 or more but which will become acidic (pH < 4) when drained (Isbell 1996). Sulfidic material is identified by a drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 10 mm thick layer is incubated wet (i.e. at field capacity) for 8 weeks.

Sulfuric material

Sulfuric materials have a pH less than 4 (1:1 by weight in water, or in a minimum of water to permit measurement). Exposure of pyrite to the air results in the oxidation of pyrite, with each mole of pyrite yielding 4 moles of acidity (Eqn 1.5).

$$FeS_2 + 15/4O_2 + 7/2H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \qquad \text{Eqn 5}$$

This process may transform sulfidic material to sulfuric material (Isbell 1996) i.e. the material has a pH < 4 (a sulfuric horizon is one with pH < 3.5 according to Soil Survey Staff 2003: USDA Taxonomy). Acidification occurs if the amount of acidity produced exceeds the buffering capacity of soil. Evidence that low pH is caused by oxidation of sulfides within a soil profile is provided by one of the following:

- Bright yellowish mottles and coatings of e.g. jarosite or natrojarosite; schwertmannite (orange), sideronatrite (bright yellowish-green), metavoltine (golden) (Table 1, Figures 5, 31)
- Underlying sulfidic material (Figures 5, 28 and 29).

Figure 5. Acid Sulfate Soil with sulfuric material in drained wetlands adjacent to the Murray River (left), which shows extensive cracking and accumulation of natrojarosite (Table 1) scale-like, bright golden yellow crystals of metavoltine [$K_2Na_6Fe^{2+}Fe^{3+}_6(SO_4)_{12}O_2\ 18H_2O$] (right) and white crystals of alunogen [$Al_2(SO_4)_3\ 17H_2O$] formed under acidic conditions (pH < 2.5) due to sulfide oxidation and silicate dissolution during drying and evaporation of soil porewater. These localised solutions were rich in ferrous and ferric iron and also contained leached potassium and sodium. The sulfuric material, which also contains hexahydrite and gypsum developed after drainage; watertable levels dropped from 40 cm in June 2007 to below 90 cm in November 2007. Due to severe drought conditions, large sections of riverbank and wetlands that once contained high levels of un-oxidized iron sulfide (pyrite) became exposed. Sulfidic material (pH>4), which contain un-oxidized pyrite, occurs below the water table shown (middle) (Modified from Fitzpatrick *et al* 2008a).

If the amount of acidity produced exceeds the buffering capacity of soil, then acidification occurs. Once sulfidic materials are drained they may transform to sulfuric materials.

Sulfuric materials form in the hydromorphic zone following dewatering or drainage as water levels drop (e.g. by either drought conditions, cattle pugging or dredging operations), which exposes pyrite in the upper layers of the soil profile to oxygen. When this happens, pyrite is oxidised to sulfuric acid (Eqn 5) causing the soil pH to drop typically from around neutral (pH 7) to below 4, which causes dissolution of layer aluminosilicates (clay) in the soil. The oxidation of the pyrite and associated rise in acidity also causes major cations and associated anions (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, SiO_4^{4-}), trace elements, and metal ions (such as Fe^{3+} and Al^{3+}) to be released. This acid, together with toxic elements that are leached from ASS, can kill fish and oysters, contaminate groundwater, and may corrode concrete and steel. These impacts can be measured in terms of:

- poor water quality with loss of amenity, damage to estuarine environments and reduction of wetland biodiversity
- the need for rehabilitation of disturbed areas to improve water quality and minimize impacts
- loss of fisheries and agricultural production, and
- additional maintenance of community infrastructure affected by acid corrosion.

Monosulfidic black ooze material

Monosulfidic black ooze (MBO) is a subaqueous or waterlogged organic-rich material that contains appreciable concentrations of monosulfides (Sullivan *et al.* 2002; Bush *et al*. 2004; Burton *et al*. 2006a, 2006b, 2008). MBO's are specific materials characterised by their gel-like consistence (Figure 6). This material has a field pH of 4 or more, commonly > pH 7-8, but may not become extremely acidic (pH <4) when drained. The recognition of the occurrence and importance of monosulfides in soil materials led in 2005 to the inclusion of monosulfidic materials as a distinguishing property within mapping units of the Australian Atlas of Acid Sulfate Soils (Fitzpatrick *et al*. 2008a; 2008-Ch2). High nutrient environments together with the activity of algae and micro-organisms generate redoximorphic conditions, which result in the formation of black, smelly soils containing Fe monosulfides. When subaqueous materials rich in monosulfides are resuspended, for example during the flushing of drains by high runoff events, they rapidly oxidise to potentially remove most of the oxygen from the water column (Sullivan *et al*. 2002a). This can lead to fish kills, especially in enclosed areas such as aquaculture ponds or in estuaries. Hence, MBO is reactive if exposed to oxygen, but is harmless if left undisturbed.

Monosulfidic soil materials have the ability to favourably affect surrounding environments by immobilizing potential metal pollutants (Simpson *et al*. 1998). However, when a drain is cleaned, alunite supergroup minerals (especially alunite and jarosite) and Fe oxyhydroxy-sulfate salts (e.g., schwertmannite) may precipitate on the soil surface along the drain edges. These soluble salts dissolve during rain events and contribute to MBO formation, acidity and metal content in drainage waters.

ACIDITY IN FARMING SYSTEMS

Soil acidity is a severe soil degradation problem in Australia that can greatly reduce the production potential of farming systems (e.g. Helyar and Porter 1989, White *et al.* 2000). The National Land and Water Resources Audit (NLWRA 2001a) estimated that 50 million hectares of the agricultural zone are already suffering from acidification of soil surface layers and 20 million ha from subsoil acidification, and that these are 'probably markedly affecting yields'. Much of this problem occurs in productive agricultural zones. It causes production losses within paddocks, and also longterm and off-site effects. Soil acidification can be determined by assessing the pH of a soil. Soil pH can be measured in water (pHw) or calcium chloride (pH_{Ca}). A 1:5 mix of soil:CaC_{l2} solution (0.01M strength calcium chloride) strength is used to estimate the concentration of hydrogen ions in the soil solution. Development of acidity in soils is a natural process, especially in the high rainfall regions of southern Australia. Some soils are inherently acidic because of the high rates of leaching in these regions.

Figure 6. Monosulfidic black ooze (MBO) material in Acid Sulfate Soil exposed in a shallow backswamp/wetland (Paiwalla wetland adjacent to the River Murray; see Fitzpatrick *et al*. 2008d). MBO, if mobilised into water, is able to remove dissolved oxygen from that water.

DRAINAGE AND DISTURBANCE OF SALT-AFFECTED AND ACID SULFATE SOILS

Generally speaking, most drainage and disturbance of saline ASS soils is caused by human action, though some erosion and vegetation changes can result from natural processes, and periods of low recharge (drought). Processes resulting in changed soil and groundwater levels can be summarised as follows:

- *Engineering* - groundwater pumping, construction of drains (Sinclair Knight Merz 2001)
- *Improved farming systems using vegetation* - reducing recharge, lowering of water tables by using deep-rooted plants (e.g. Barrett-Lennard *et al* 2003)
- *Erosion* - e.g. local lowering of the water table by gully formation and deepening; removal of surface soil layers by wind or sheet erosion to produce scalds and expose hardpans
- *Agriculture* - e.g. tillage, pugging by cattle creating densipans or introducing oxygen to sulfidic discharge areas.
- *Drought conditions* - causing the lowering of water levels in rivers and water tables (ground and surface waters).

Understanding water table hydrology, soil properties and processes is fundamental to selecting the best options for drainage and the most appropriate management of the soils when they are drained.

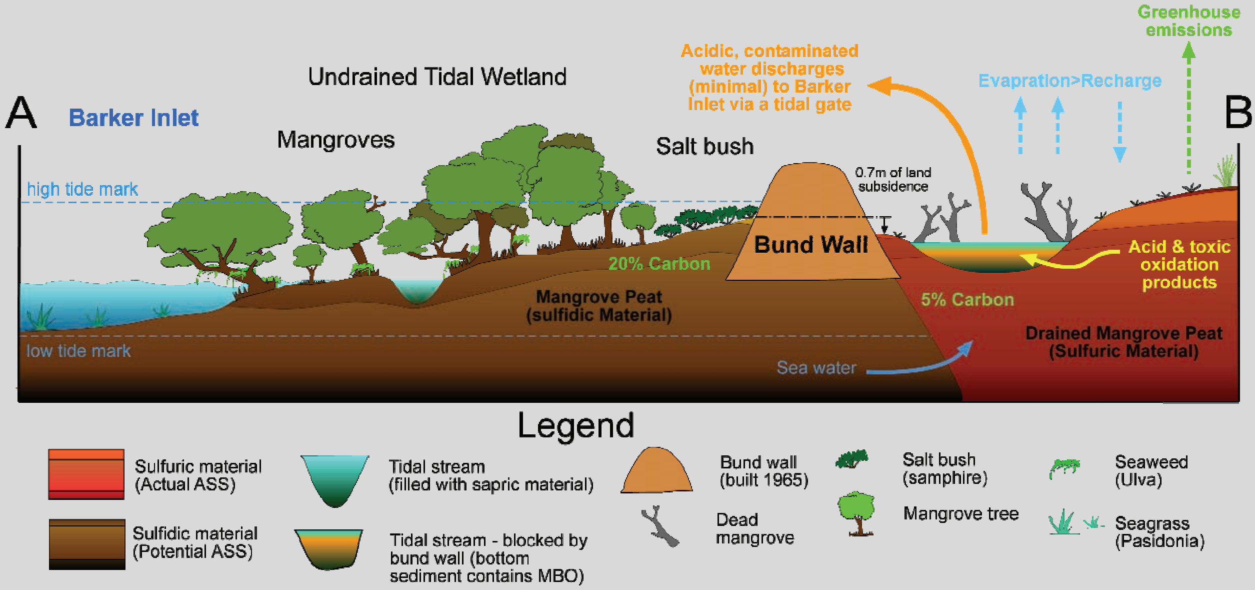
ATLAS OF AUSTRALIAN ACID SULFATE SOILS

Australia contains a wide range of ASS types in different physical settings such as in inland wetlands (e.g. Figures 5 and 6) and coastal environments (e.g. see BOX 2 showing an undrained and drained estuarine, mangrove swamp and back swamp). Various sources of organic matter fractions (i.e., sapric and hemic materials), minerals (e.g., pyrite, jarosite and gypsum), and micro-scale weathering pathways and mechanisms occur under drained (e.g. through levee bank construction) and undrained (ranging from natural tidal to intertidal, to supratidal zones) conditions. Ultimately, they pose different environmental hazards requiring tailored and site-specific management options.

The Atlas of Australian Acid Sulfate Soils (ASS) is a new web-based hazard assessment tool with a nationally consistent legend, which provides information about the distribution and properties of both coastal and inland ASS across Australia (Fitzpatrick *et al*. 2008-Ch2). This tool is available on ASRIS (Australian Soil Resource Information System: www.asris.gov.au) and every polygon or mapping unit is attributed with information pertaining to: (i) classes of "probability of occurrence", (ii) levels of confidence relating to the quality of data source, and (iii) additional descriptors such as desiccation cracks. The Atlas is a constantly evolving national map of available ASS information, which also includes priority case studies at a range of localities across Australia. (e.g. http://www.clw.csiro.au/acidsulfatesoils/index.html).

BOX 2
EXAMPLES OF COASTAL ACID SULFATE SOILS IN THE BARKER INLET ESTUARY

In several parts of the Barker Inlet estuary in the Gulf St Vincent near Port Adelaide in South Australia, bund walls were constructed across tidal zones comprising mangrove and samphire swamps nearly 50 years ago to cut off tidal flushing. The following schematic cross-section illustrates how the former back barrier sand ridge at Gillman has effectively been drained/disturbed causing: (i) mangrove trees and samphire vegetation to die and (ii) development of a 2 m thick soil profile with sulfuric material because pyrite framboids in and surrounding decomposed mangrove pneumatophores have oxidised to form jarosite mottles and acidity where neutralising by alkaline materials is limited:



Schematic soil-landscape cross section at Gillman in Barker Inlet showing how normal tidal dynamics were interrupted by a bund wall (levee banks constructed since 1935) causing oxidation of sulfidic materials and monosulfidic black ooze (MBO) to occur, which contributes to degraded "saline" acidic land with sulfuric materials, denuded vegetation, reduction of wetland biodiversity, poor estuarine and stream water quality, ground subsidence, increase in greenhouse gas emissions and loss of amenity (after Fitzpatrick et al. 2008f).

Excluding seawater from the original sulfidic material underlying this area has caused the surface to dry and oxidise the sulfide minerals to produce sulfuric acid (pH commonly between 2.5 and 3.5) and bright yellow mottles of jarosite were identified by Fitzpatrick *et al.* (2008f). Coatings of jarosite and Fe oxides form rapidly along large root channels during various periods of drying. Some small, unoxidized pyrite framboids still occur in the underlying sandy, sulfuric horizons. In the upper horizons (0-58 cm), the oxidation of pyrite in organic residues caused precipitation of Fe oxides and lenticular gypsum crystals, which are now being leached out of the profile (Fitzpatrick *et al*. 2008f).

In Australia, ASS occupy an estimated 215,000 km^2 of which 58,000 km^2 is coastal ASS and 157,000 km^2 is inland ASS (Fitzpatrick *et al*. 2008-Ch2). In the coastal zone, 41,000 km^2 are exposed at some point during the tidal cycle with the remaining 17,000 km^2 being permanently subaqueous. Finally, 126 km^2 of ASS with sulfuric material have been mapped.

Coastal ASS occur in coastal estuaries and tidal flats, much of which are close to major population centres in Australia such as in the Barker Inlet estuary near Port Adelaide (BOX 2; Fitzpatrick *et al.* 2008f). At the time of writing, considerable effort is being expended in Australia to document and map the occurrence of inland ASS across Australia. For example, major new occurrences have been documented in freshwater river and wetland systems (e.g. Murray River, Lower Lakes and Coorong in South Australia, Fitzpatrick *et al.* 2008a,b,c,d,e, 2009; Shand *et al.* 2008a,b), artificially drained landscapes (e.g., WA wheatbelt cropping region, Fitzpatrick *et al.* 2005; Degens *et al.* 2008-Ch10,11 13; Fitzpatrick *et al.* 2008-Ch12,17) and upland landscapes experiencing altered groundwater drainage where mineralisation occurs (e.g., Mount Lofty Ranges, SA: Fitzpatrick *et al.* 1996; and Dundas Tablelands, Victoria: Fawcett *et al.* 2008-Ch18, Gardner *et al.* 2004a,b) (e.g. see examples listed in Table 4).

METHODOLOGY FOR SAMPLING AND LABORATORY SOIL ANALYSIS

Field observations and sampling

A generalised protocol has been developed by CSIRO Land and Water to describe and collect inland ASS samples for soil and water analyses (e.g. Figure 7; Fitzpatrick et al. 2008b,c,d). At each site, the geomorphological characteristics are identified and sampling sites are topographically related in short transects or hydro-toposequences (e.g. Figure 3) that extend from the shore/banks (lakes, billabongs and river channel) to lowest points (i.e. dry wetlands) or to the deepest depth at which it is practical to sample using waders (i.e. wet wetlands). This typically includes sub-aerial soils (freely drained), hydrosols (periodically saturated waterlogged soils) and subaqueous soils as shown in the soil toposequence displayed in Figure 3. The general flowchart for soil sample collection and analysis is shown on Figure 7. Samples are collected in chip trays (e.g. see Figures 9 and 10): one for visualisation (detailed soil morphology descriptions) where compartments are filled to ¾ full with preferably undisturbed clods/samples and used for long-term storage (soil archival system), and a second for ageing or incubation (see below); in addition to samples collected in sealed plastic bags and bottles. Water samples are also collected in wetlands, river channels, lakes and soil pits for the analysis of a wide range of solute concentrations. The parameters pH, Eh (redox), DO (dissolved oxygen), Temperature (^{o}C), EC (electrical conductivity or more correctly SEC: specific electrical conductance) and turbidity are measured on-site. Subaqueous soil samples are usually obtained by wading and using a range of implements: spades, D-auger and gouge auger to a maximum of about 90 cm depth.

Air is excluded as far as possible from the samples in sealed plastic bags and bottles. On return to the laboratory, the soils are kept cool at 4°C until analysed. Samples (soils and salt efflorescences) for XRF and detailed sulfide analysis (S_{CR}) for acid-base accounting are air dried at 80°C (e.g. Ahern *et al.* 1998; 2004). Moisture contents are recorded and bulk densities estimated. Recorded locations and long-term storage of the oven dried samples and air dried/moist samples kept in chip trays allow for future re-sampling and analysis, if required, and are used for incubation (ageing) experiments to follow the course of potential acidification and confirm ASS status.

Laboratory methods to assess acid generation potential

In order to assess the acid generation potential (AGP) of acid sulfate soils, a range of methodologies is used. This requires several parameters to be measured, as highlighted on Figure 7. An important consideration is also the mineralogical composition of the soils, which may either enhance or neutralise acid generating potential. These analyses also need to be combined with field observations and placed into the geological and hydrogeological setting, so that laboratory data can be extrapolated and interpreted at the larger landscape scale (e.g. Fitzpatrick *et al*. 2008b,c,d,e; Shand *et al*. 2008a,b).

In nature, a number of oxidation reactions of sulfide minerals (principally pyrite: FeS_2) may occur which produce acidity, including:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

$$4FeS_2 + 15O_2 + 10H_2O \rightarrow 4FeOOH + 8H_2SO_4$$

A range of secondary minerals, such as jarosite, sideronatrite and schwertmannite (Table 1) may also form, which act as stores of acidity i.e. they may produce acidity upon dissolution. Therefore, any assessment needs to include the presence of such minerals in the soil.

There is some debate as to the most realistic methodology to estimate if a soil will acidify. The most effective methodology may vary according to the local environment and associated mineralogy. In most studies of inland ASS conducted by CSIRO Land and Water (e.g. Fitzpatrick *et al*. 2008c), a combination of the following three most generally accepted methodologies for ASS testing has been used: pH testing in water (pH_W) and after treatment with hydrogen peroxide (pH_{FOX}) (approximately 1:1 soil solution slurry; hydrogen peroxide pH adjusted to 5), acid-base accounting (e.g. Ahern *et al*. 2004, Sullivan *et al*. 2002b), and incubation experiments (Figure 7). These have different strengths and weaknesses. The current practice in CSIRO Land and Water is to use all of the above techniques (i.e. pH_{FOX}, acid-base accounting, and ageing/incubation) and, where possible, to monitor changes in the field during periods of drying to assess the most likely scenarios of acid generation and neutralisation (e.g. Fitzpatrick *et al*. 2008 c, d; Shand *et al*. 2008a).

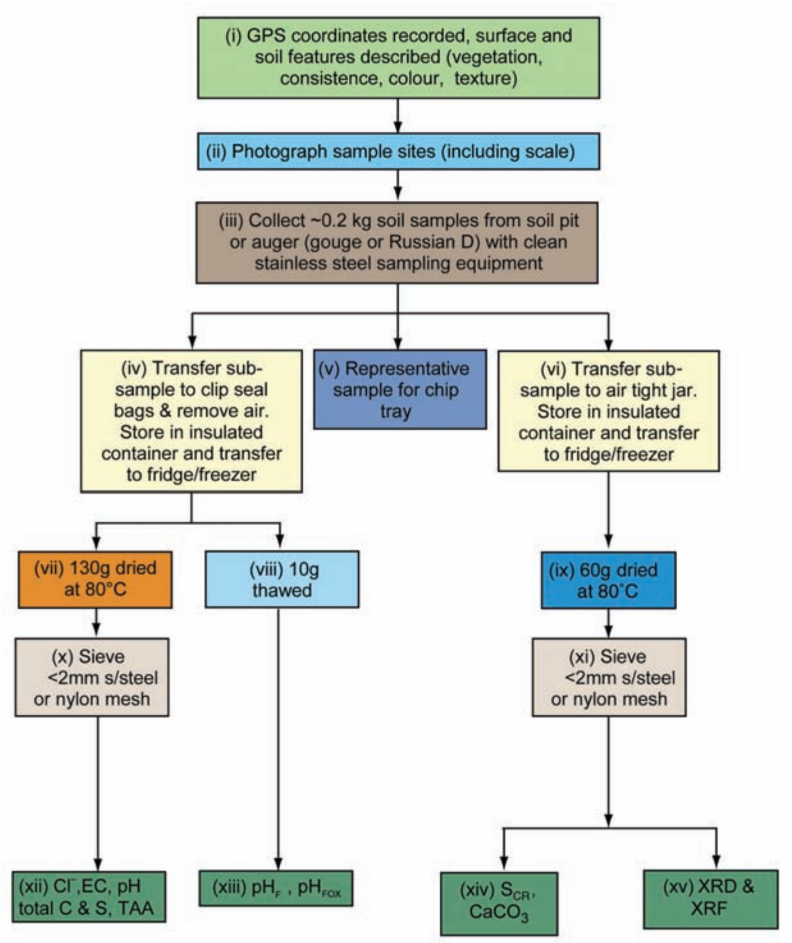


Figure 7. General flow chart for soil sampling and analysis (from Fitzpatrick et al. 2008d)

Soil pH after treatment with hydrogen peroxide (pH_{FOX})

Hydrogen peroxide (H_2O_2) is a strong oxidising agent and is used to encourage the oxidation of sulfide minerals (principally pyrite: FeS_2), hence the production of acidity.

Peroxide addition oxidises sulfide minerals and organic matter, the former oxidising to sulfuric acid:

- Sulfidic material + hydrogen peroxide ---> sulfuric acid + iron sulfate minerals + heat

Since peroxide is a very strong oxidising agent, it can be argued that the resultant pH measured is a worst-case scenario as in nature oxidation is rarely complete. In nature, the presence of carbonate minerals such as calcite ($CaCO_3$) may neutralise acid produced. However, in some cases the carbonate may not fully dissolve due to slow dissolution rates (reaction kinetics) and the peroxide pH measurement may reflect this. The dissolution rates of individual minerals may be largely controlled by a number of factors, hence additional tests based on measuring the carbonate content are recommended.

All inland ASS soil samples should be subjected to the following laboratory analyses: soil pH in: (i) water and (ii) 30% hydrogen peroxide with pH adjusted to ca. pH 5 (Ahern *et al*. 2004). Since ASS soil samples are mostly wet or moist, soil to solution ratios will vary, but should approximate a soil:water ratio of 1:1 and with H_2O_2 (pH_{FOX}) up to 1:5 as the amount required to complete the reaction may vary, usually 5 to 10 ml. In the case of pH_{FOX}, pH measurement should be made after frothing and fuming subsides (see Figure 7; example of effect) and the mixture cools to room temperature. The reaction can be very violent and produce a great amount of heat, so hydrogen peroxide addition should be completed with caution. The variations in soil:solution ratios (and therefore ionic strength of the suspensions) introduces errors compared to usual laboratory pH measurements (see Rayment and Higginson 1992) with controlled soil-to-solution ratios, but these are not thought to be significant in the context of inland ASS investigations. All pH measurements should be made at 20°C or 25°C (record the temperature) using a calibrated laboratory pH meter.

Figure 8: Photographs of the peroxide test in the field used to assess the presence of ASS (sulfidic material). Note the change in colour of the pH test strips indicating the drop in pH. Frothing and fuming are caused by the reaction of peroxide with organic matter and peroxide decomposition catalysed by metal ions. Colour changes to orange and yellow are more indicative of acid formation (from Fitzpatrick *et al.* 2008c).

Colour changes to orange-brown may indicate change in iron oxidation state and removal of colour-masking organic matter. It is most noticeable when MBO is present.

Comparing the water pH to the peroxide pH indicates, where the peroxide pH drops to below about 4, that the materials present may have the potential to acidify significantly and produce sulfuric materials due to the presence of sufficient sulfidic material that converts to sulfuric material. If the peroxide pH does not acidify significantly, the material is likely to contain sufficient acid neutralising capacity to avoid sulfuric conditions. Samples containing MBO may not necessarily achieve a final pH less than 4. The laboratory reactions are relatively quick and may not attain a true equilibrium, thereby indicating less acidic conditions than may actually be reached by natural, prolonged oxidation. However, poorly buffered sands are likely to reach the indicated pH, although Fitzpatrick *et al.* (2008c) have observed field pH values as low as 2.5 in clayey soils of the River Murray and the Lower Lakes.

The final pH and reaction vigour can then be interpreted to qualitatively assess soil or sediment materials (Figure 8, Table 2). pH_{FOX} is a useful screening technique especially for rapid assessment of ASS. However, pH_{FOX} is not a definitive method and should not be used independently of the definitive methods for recommendations of the soil materials to be assessed for ASS risk.

Table 2. Soil rating scale for the pH_{FOX} test. If the field pH in hydrogen peroxide (pH_{FOX}) is at least one unit below field pH, it may indicate potential ASS. The greater the difference between the two measurements, the more indicative the value is of sulfidic material. The lower the final pH_{FOX} value is, the better the indication of a positive result (modified from Ahern *et al.* 2004).

pH_{FOX}	**Indication of ASS**
<3	High probability; but requires appropriate additional laboratory tests for conclusive determination.
3–4	Probable; but requires appropriate additional laboratory tests for conclusive determination.
4–5	Sulfides may be present in small quantities or may be unreactive, or neutralising material is present. Requires appropriate additional laboratory tests for conclusive determination.
>5	Combined with little drop from field pH, little net acid generation potential is indicated. Requires appropriate additional laboratory tests for conclusive determination.

Incubation of Soil Material

The following concept underlying the formal Australian Soil Classification (Isbell 1996) definition for identification of sulfidic material (as described below) is used to identify inland ASS with subsoil, waterlogged, mineral or organic materials that contain oxidisable sulfur compounds, usually iron disulfide (e.g. pyrite, FeS_2), with field pH of 4 or more but which will become extremely acid when drained. Sulfidic material is identified by a drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 10 mm thick layer is incubated at field capacity for 8 weeks.

This test currently being used by Fitzpatrick *et al.* (2008c,d) to determine sulfidic material in inland ASS is a slight modification of this incubation procedure, which involves the following steps:

- Incubate mineral or organic soil materials, which have a natural pH (1:1 soil:water) value > 4, for a minimum of 8 weeks as a layer 1 cm thick under moist conditions, while maintaining contact with the air at room temperature.
- Measure the pH and observe whether there is a drop in pH of 0.5 units or more to a value of 4.0 or less within a minimum of 8 weeks, including wetting and drying cycles.

Collection and storage of moist samples in chip trays (Figures 9 and 10) produces similar conditions, and thus chip trays are suitable for incubation testing (Fitzpatrick *et al.* 2008 c,d,e). Incubation tests have the advantage of not requiring 30% hydrogen peroxide, which should only be handled by a trained operator. The recommended procedure is a modification of the duration of incubation from the fixed 8 weeks in the formal Australian Soil Classification definition, to that proposed by Sullivan *et al.* (2009) where a stable pH is reached after at least 8 weeks of incubation.

In the laboratory, the 1 cm thick layer of soil in each chip tray compartment will be either: (i) covered by a 1 mm thick piece of sponge (Figures 9 and 10) or (ii) kept moist (Figure 10), which allows slow oxygen diffusion into the moist soil sample and potential formation of sulfuric acid from sulfidic materials, with the aim to mimic field conditions of drying soils. The sponge materials used should be pre-leached with distilled water and the pH of the sponge checked to confirm that the material is inert. The sponges used were found not to alter the pH (Fitzpatrick *et al.* 2008c). In the chip tray, the sponge covering the soil sample is moistened and allowed to stand at room temperature (20 to 25 °C) for a minimum of 8 weeks with occasional checking and re-moistening of the sponge with distilled water. Dampening is best achieved using a mist sprayer.

After at least 8 weeks ageing (see Figure 10), the soils were visually checked for the formation of those secondary minerals which indicate significant acidification, e.g. jarosite, sideronatrite. Since the solution in contact with the soil in the chip tray compartments is in equilibrium with the exterior soil material, a pH indicator strip (Merck item numbers: pH 2.5-4.5: 1.09541.0001; pH 4.0-7.0: 1.09541.0002; pH 6.5-10.0: 1.09543.0001) is used to indicate the pH of the exterior soil material of the sample. A pH value of 4 or less confirms that a sulfidic soil material in the field soil is likely to develop into sulfuric material on drying. pH values much greater than this indicate that the soil materials are unlikely to acidify significantly.

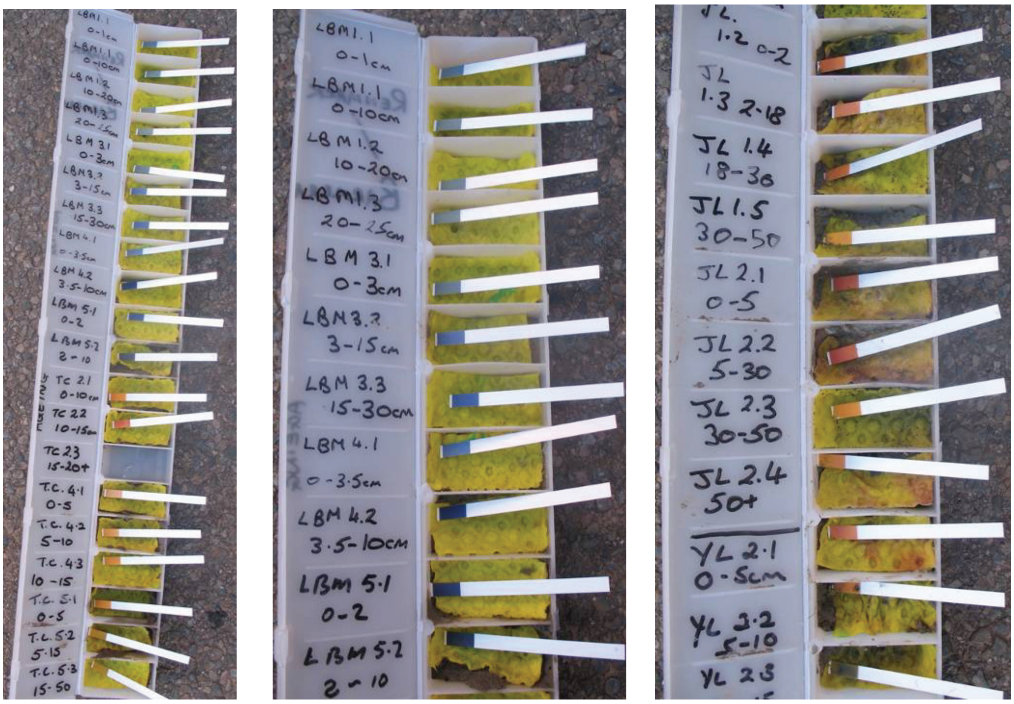


Figure 9. Examples of aged samples from a range of localities across Australia. Left hand side: view of chip tray showing samples from Lake Bonney (top half: LBM 1.1. to LBM 5.2; Fitzpatrick *et al*. 2008e) and lower half samples from Tanyaca Creek near Renmark (lower half TC 2.1 to TC 5.3) aged for 8 weeks. Middle: close-up view of Lake Bonney samples with pH indicator strips clearly indicating they are all neutral to alkaline (blue colour - pH 6 to 7). Right hand side: view of samples from Jaeschke and Yatco Lagoons indicating aged samples are all acid (red colour - pH 3.9 to 4.8).

Sulfur and acid-base accounting

Sulfur chemistry

In soils, total sulfur is an inexpensive, convenient measure to screen samples for acid sulfate soil potential. However, this analysis also measures non-acid generating sulfur; therefore, the total sulfur determination may greatly overestimate the maximum potential environmental risk from sulfide oxidation, so that when a trigger value is exceeded, more detailed analysis is usually required. Interpretation is complicated by the presence of sulfate salts (containing oxidised S) such as gypsum, which do not produce acidity. Directly measuring the amount of reduced inorganic sulfur in a sample using the chromium reduction method has become the accepted standard for further investigation (Ahern *et al*. 2004; Sullivan *et al*. 2002b). Chromium reducible sulfur (commonly written as either S_{CR} or CRS) can be directly equated with the acid generating potential (AGP) of a soil or sediment, and is one component of the net acidity, the others being the existing or actual acidity and the acid neutralising capacity. The difference between reduced inorganic sulfur and total sulfur is generally the quantity of sulfate plus organic sulfur in the sample. Further analysis is required to separate the individual contributions of these components.

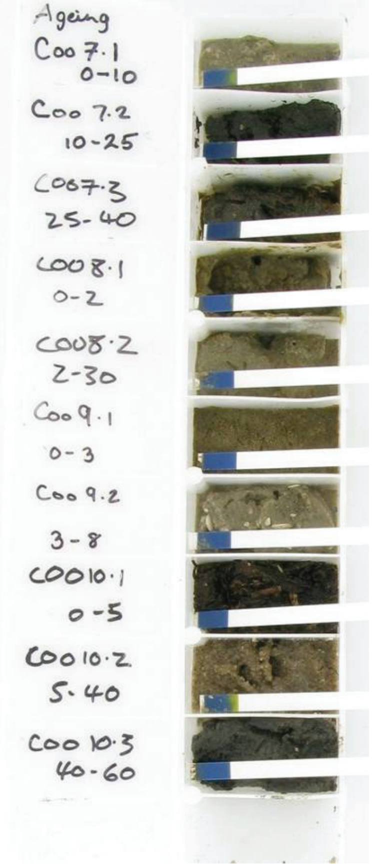
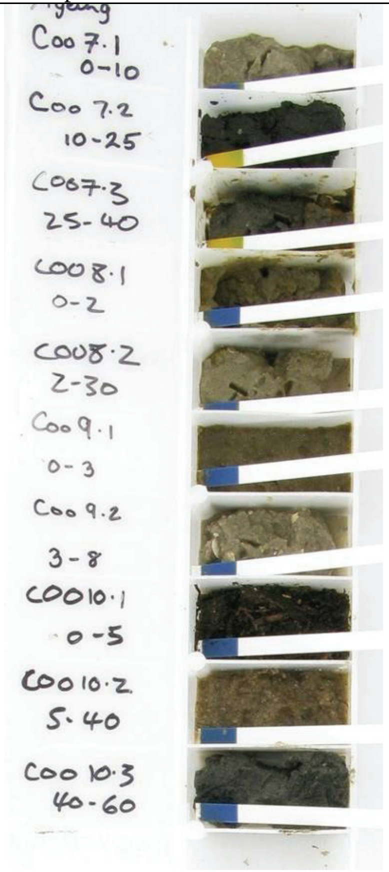
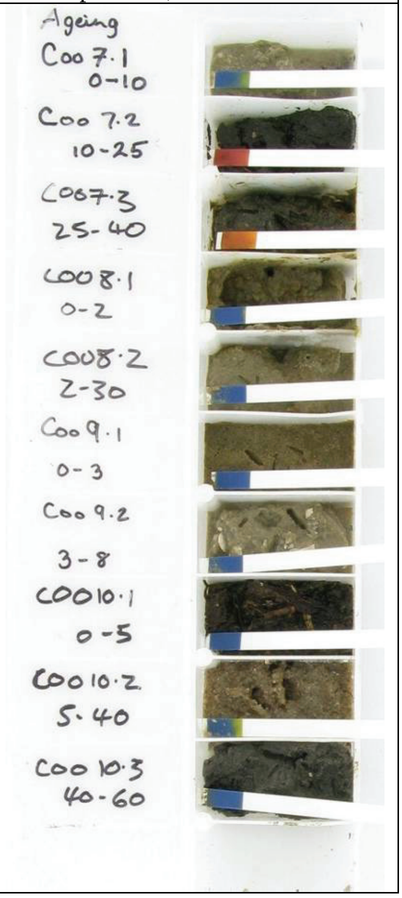
Field testing 15th July 2008	**8 weeks** 4th September 2008	**10 weeks** 18th September, 2008
		

Figure 10. Chip trays showing incubation of soil samples from the Coorong (Coo 7.1 to Coo 10.3) that have been tested for pH using pH indicator strips: (i) sampled in the field, (ii) after ageing for 8 weeks and (iii) 10 weeks. Here pH indicator strips indicate that most samples remain alkaline or neutral (blue colour >pH 7) with only two becoming acidic after ageing for 10 weeks (red or pink colour - pH 3.9 to 4).(From Fitzpatrick *et al.* 2008f)

Acid-Base Accounting

Acid-base accounting (ABA) is used to assess both the potential of a soil material to produce acidity from sulfide oxidation and also its ability to neutralise any acid formed (e.g. Sullivan *et al*. 2002b). The standard ABA applicable to ASS is as described in Ahern *et al*. (2004) as shown below:

Net Acidity = Potential Sulfidic Acidity + Existing Acidity – measured ANC/FF

The components in this ABA are further discussed below and by Ahern *et al*. (2004).

Potential Sulfidic Acidity

The Potential Sulfidic Acidity is most easily and accurately determined by assessing the chromium reducible sulfur. This method was developed specifically for analysing acid sulfate soil materials (Sullivan *et al*. 2000) to, *inter alia*, assess their Potential Sulfidic Acidity (PSA) also known as the ‘acid generation potential’ (AGP). The method is also described in Ahern *et al*. (2004), which includes the chromium reducible sulfur (S_{CR} or CRS: Method Code 22B) and its conversion to PSA and AGP.

Existing Acidity

This is the sum of the Actual Acidity and the Retained Acidity (Ahern *et al*. 2004).

Titratable Actual Acidity (TAA) is a measure of the actual acidity in acid sulfate soil materials that have already oxidised or partially oxidised. TAA measures the sum of both soluble and exchangeable acidity.

The Retained Acidity is the acidity 'stored' in minerals such as jarosite, schwertmannite and other hydroxy sulfate minerals (Table 1). Although these minerals may be stable under acidic conditions, they can release acidity to the environment when these conditions change. Hence, pH can be highly misleading in ASS systems – given that pH is commonly used as an indicator of acidity in acid sulfate soil waters. For example, data from acid sulfate soil-affected acidic waters at East Trinity (Hicks *et al.* 1999) demonstrated that pH is a poor indicator of acidity in this ASS system because the pH correlated poorly with acidity, because hydrolysing salts such as iron or aluminium sulfates may contribute to the measured acidity. The methods for determining both TAA and Retained or Stored Acidity are given by Ahern *et al.* (2004).

Acid Neutralising Capacity (ANC)

Soils with pH > 6.5 may potentially have ANC in the form of (usually) carbonate minerals, principally of calcium, magnesium and sodium. The carbonate minerals present are estimated by titration, and alkalinity present expressed in $CaCO_3$ equivalents. By accepted definition (Ahern *et al*. 2004), any acid sulfate soil material with a pH < 6.5 has a zero ANC. The methods for determining ANC are given by Ahern *et al.* (2004).

Fineness Factor (FF)

This is defined by Ahern *et al*. (2004) as "A factor applied to the acid neutralising capacity result in the acid base account to allow for the poor reactivity of coarser carbonate or other acid neutralising material. The minimum factor is 1.5 for finely divided pure agricultural lime, but may be as high as 3.0 for coarser shell material". Fine grinding of soil materials may lead to an over-estimate of ANC when carbonates are present in the form of hard nodules or shells. In the soil environment, they may provide little effective ANC when exposure to acid may result in the formation of surface crusts (iron oxides or gypsum), preventing or slowing further neutralisation reactions. For reasons including those above, the use of the "Fineness Factor" also applies to those naturally occurring alkalinity sources in soil materials as measured by the ANC methods.

Mineralogy

The following method is an example of an appropriate method used by Fitzpatrick *et al*. (2008c). The soil samples or salt efflorescences are ground in an agate mortar and pestle and either back pressed into steel holders or deposited onto Si low background holders (depending on how much sample is available). XRD patterns are recorded with a PANalytical X'Pert Pro Multi-purpose Diffractometer using Co K-alpha radiation, variable divergence slit, post diffraction graphite monochromator and fast X'Cellerator Si strip detector. The diffraction patterns are recorded in steps of 0.05° 2 theta, with a total counting time of 30 minutes, and logged to data files for analysis using HighScore Plus.

SOIL CLASSIFICATION SYSTEMS

Classifying soils (for a particular purpose) involves the ordering of soils into groups with similar properties and for potential end uses. According to Fitzpatrick (2004a) the historical evolution of soil-classification systems currently used in Australia have national (e.g. Prescott 1931; Isbell 1996), regional (e.g. Schoknecht 2001), and special-purpose (e.g. Fitzpatrick *et al*. 2003a) applications, which can be traced as follows:

- General-purpose soil classifications that have been used in Australia since 1931 to communicate soil information and soil distributions at national scales (e.g. Prescott 1931; Isbell 1996).
- State and regional ''user-friendly'' soil classifications designed both to assist with communication of soil information and to account for the occurrence of soils that impact on existing and future industry development and prosperity (e.g. Schoknecht 2001; Fitzpatrick *et al.* 2008-Ch2).
- Special-purpose and more-technical classification systems for single-purpose application that involve using detailed soil-assessment criteria with recommendations for soil-management practices have been developed for a range of specific Australian industries (e.g. Fitzpatrick *et al*. 2003a,b; Table 3).

Australia's current national soil classification system is the Australian Soil Classification (ASC; Isbell 1996). This is based on several internationally recognized systems and allows international technology transfer, because similar soils anywhere in the world can be identified and successful management practices can be copied or correlated without need for extensive local trials. However, the Australian Soil Classification and other internationally recognised classification systems such as Soil Taxonomy (Soil Survey Staff 1999;

2003) require considerable expertise and experience. Therefore, a simplified Soil Identification Key (See Table 3) specific for inland ASS was developed, initially for ASS in the River Murray and Lower Lakes systems to identify and classify the various subtypes of ASS and non-ASS (Fitzpatrick *et al*. 2008b,c,d,e). The key is to assist users who are not experts in soil classification systems to easily identify types and subtypes of ASS. The key uses a collection of plain language names for ASS types and subtypes in accordance with the legend for the Atlas of Australian ASS (Fitzpatrick *et al*. 2008c) and separates out the same soil classes as would occur if the ASC or Soil Taxonomy was to be used. It recognises 5 Soil Types (Table 3) and 16 Soil Subtypes (Fitzpatrick *et al*. 2008c).

This key is based on easily observable soil features and simple tests (e.g. pH). Attributes include water inundation (subaqueous soils), soil cracks, structure, texture, colour, features indicating waterlogging and ‘acid’ status: already acidified, i.e. sulfuric material, or with the potential to acidify, i.e. sulfidic material, and the depths at which they occur or change in the soil profile. Hence, it has the potential to deliver soil-specific land development and soil management packages to advisors, planners and engineers.

The key consists of a systematic arrangement of soils into 5 Soil Types, each of which can be further divided into up to 16 Soil Subtypes. The key layout is bifurcating, being based on the presence or absence of particular soil profile features (i.e. using a series of questions set out in a key). A soil is allocated to the first type whose diagnostic features it matches, even though it may also match diagnostic features further down the key. The soil types and subtypes in the Soil Identification Key are largely in the same order as occurs in the Australian Soil Classification (Isbell 1996) and Keys to Soil Taxonomy (Soil Survey Staff 2003). A collection of plain language soil type and subtype names was developed. The 5 ASS types in the Key (Table 3) are: (i) Subaqueous Soils, (ii) Organic Soils, (iii) Cracking Clay Soils, (iv) Sulfuric Soils and (v) Sulfidic Soils. These are further sub-divided into 16 subtypes based on occurrence of monosulfidic black ooze material (MBO), sulfidic material, sulfuric material and clayey or sandy layers. The key permits easy identification of ASS types and subtypes, which describe practical, surrogate methods to assist users to estimate treatment categories and risk classes (High, medium, low and very low).

SOIL AND LANDSCAPE FIELD INDICATORS AND CONCEPUAL MODELS

This section summarises approaches and procedures developed at CSIRO Land and Water and CRC LEME over two decades to:

- Identify the best set of soil and landscape field indicators of soil-landscape condition for a region.
- Construct appropriate 3D and 4D mechanistic models of soil-regolith and water processes that explain and predict the processes giving rise to geochemically variable salt-affected and acid sulfate soils using a toposequence approach (soil landscape cross-sections), which integrates pedological, hydrological, geological, biogeochemical and mineralogical information.
- Publish easy-to-use pictorial manuals that incorporate field indicators and mechanistic models to be used by land managers and which provide land-use options that help prevent the spread of “saline” inland ASS.

Field indicators linked to landform elements are useful for identifying inland ASS and salt-affected soils and increasing awareness of the extent of salinity and ASS among landholders and regional advisers. Standard descriptive soil indicators such as visual indicators (e.g. colour) and consistency are often used by farmers, regional advisers and scientists in the field to identify and report attributes of soil quality (Fitzpatrick *et al*. 1999). For example, as discussed above, soil colour can provide a simple means to recognise or predict salt-affected and ASS-affected wetlands caused by poor drainage (Figure 2), which provide a low-cost alternative to difficult and costly methods to document saline water table depths and to estimate water duration in soils. Visual indicators of salinity and ASS may be obvious (e.g., white or yellow salt accumulations on soil surfaces) or subtle (e.g., subsoil mottling patterns, strong pedality). Analytical indicators include pH (acidity/alkalinity), electrical conductivity (as a measure of salinity) and clay dispersion (sodicity).

Table 3. Summary soil identification key for inland ASS types in the lower Murray Darling Basin/Lower Lakes. After finding the Soil Type use to find the soil subtype (from Fitzpatrick et al 2008b,c,d,e,f).

Diagnostic features for Soil Type	Soil Type	
Does the soil occur in shallow permanent flooded environments (typically not greater then 2.5 m)? No ↓ Yes →	Subaqueous soil 	1
Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	Organic soil 	2
Does the soil develop cracks at the surface OR in a clay layer within 100 cm of the soil surface OR have slickensides (polished and grooved surfaces between soil aggregates), AND is the subsoil uniformly grey coloured (poorly drained or very poorly drained)? No ↓ Yes →	Cracking clay soil 	3
Does a sulfuric layer (pH<4) occur within 150 cm of the soil surface, AND is the subsoil uniformly grey coloured (poorly drained)? No ↓ Yes →	Sulfuric soil 	4
Does sulfidic material (pH>4 which changes on ageing to pH<4) occur within 100 cm of the soil surface, AND is the subsoil uniformly grey coloured (poorly drained)? No ↓ Yes →	Sulfidic soil 	5
Other soils	Other soils	6

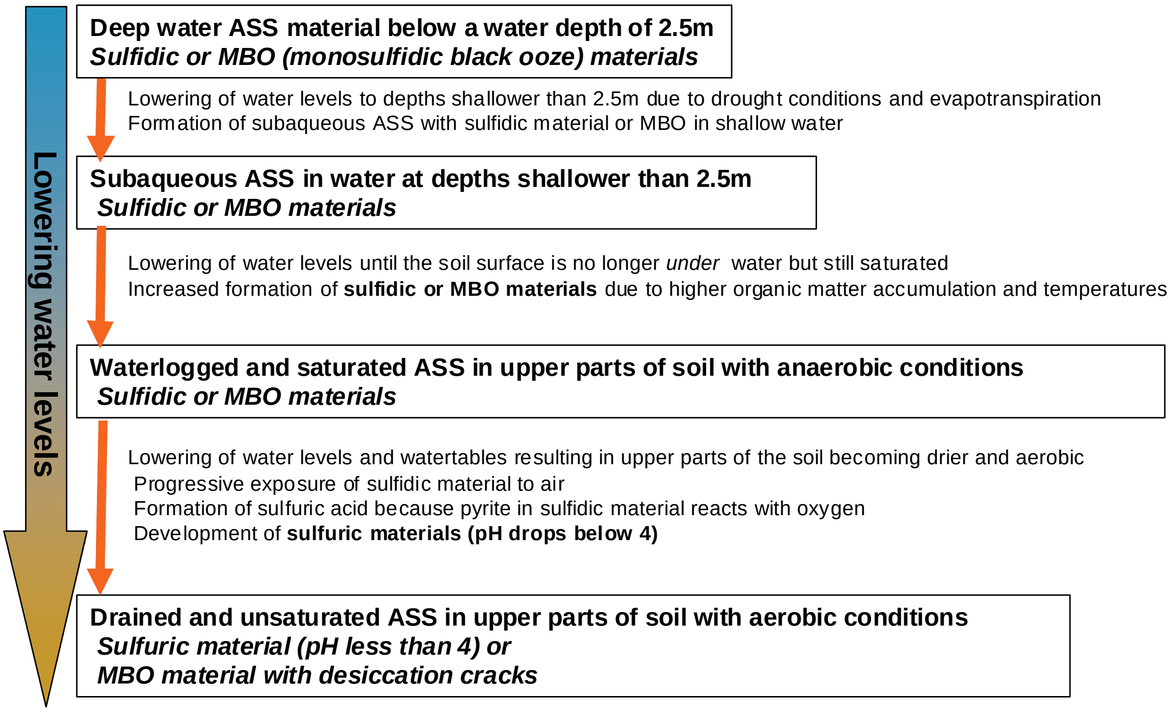
Where: Subaqueous soil is defined as above. Cracking clay is confirmed by field observation, cracks and texture. Organic material is confirmed by field observation and laboratory data (organic carbon, clay); Sulfuric material is confirmed by field observation (pH measurement using pH strips or pH meter). Sulfidic material is initially inferred from field observations (e.g. peroxide pH) and confirmed by sampling, CRS measurement and/or incubation for 8 weeks (Isbell 1996).

Combining descriptive and analytical indicators has provided vital information about soil-water processes leading to improved management and remediation of saline land, as demonstrated in several case studies from Australia, China and Iraq listed in Table 4 and in this monograph covering the following wide range of environmental systems: **in river channels** (Fitzpatrick *et al*. 2008-Ch2,8), **lakes** (e.g. Degens *et al*. 2008-Ch11; Fitzpatrick *et al*. 2008-Ch2), **wetlands** (e.g. Fawcett *et al*. 2008-Ch18; Grealish *et al*. 2008-Ch21), **evaporation basins** (e.g. Lamontagne *et al*. 2008-Ch14; Wallace *et al*. 2008-Ch15,16), **billabongs** (e.g. Fitzpatrick *et al*. 2008-Ch19), **drains** (Degens *et al*. 2008-Ch10,11 13; Fitzpatrick *et al*. 2008-Ch12,17), **marshes in Iraq** (Fitzpatrick 2004b), **seepages overlying mineralized zones** (Skwarnecki and Fitzpatrick 2008-Ch4), **ground water systems** (Shand *et al*. 2008-Ch5) and **floodplains** (Willett 2008-Ch20).

GENERALISED CONCEPTUAL SOIL-REGOLITH MODELS

Prolonged extreme drought conditions are continuing to cause water levels to recede in the freshwater Lakes Alexandrina and Albert. Following declining water levels, sulfidic material in the anaerobic soils become oxidised and transformed to sulfuric material (pH <4), with consequent potential water quality, ecological and public health issues.

Studies by CSIRO Land and Water developed a conceptual model (Figure 11) to explain four sequential drying phases and the development of different ASS Subtypes that occur: deep water sulfidic ASS → subaqueous ASS → waterlogged and saturated ASS → drained and unsaturated ASS (Fitzpatrick *et al*. 2008a,c,d). By applying this model, Fitzpatrick *et al*. (2008c) integrated locally detailed field survey and laboratory data and used the Australian Soil Classification (Isbell 1996) to derive fourteen subtypes of ASS conforming to the map legend of the Atlas of Australian ASS.



Deep water ASS material below a water depth of 2.5m
Sulfidic or MBO (monosulfidic black ooze) materials

Lowering of water levels to depths shallower than 2.5m due to drought conditions and evapotranspiration
Formation of subaqueous ASS with sulfidic material or MBO in shallow water

Subaqueous ASS in water at depths shallower than 2.5m
Sulfidic or MBO materials

Lowering of water levels until the soil surface is no longer *under* water but still saturated
Increased formation of **sulfidic or MBO materials** due to higher organic matter accumulation and temperatures

Waterlogged and saturated ASS in upper parts of soil with anaerobic conditions
Sulfidic or MBO materials

Lowering of water levels and watertables resulting in upper parts of the soil becoming drier and aerobic
Progressive exposure of sulfidic material to air
Formation of sulfuric acid because pyrite in sulfidic material reacts with oxygen
Development of **sulfuric materials (pH drops below 4)**

Drained and unsaturated ASS in upper parts of soil with aerobic conditions
Sulfuric material (pH less than 4) or
MBO material with desiccation cracks

Figure 11. Generalised conceptual model showing the sequential transformation of four Classes of ASS due to lowering of water levels from "Deep-water ASS" → "Subaqueous ASS" → "Waterlogged and saturated ASS" (all containing sulfidic material with high sulfide concentrations and pH>4) to → "Drained and unsaturated ASS" containing sulfuric material (pH<4) in the upper soil layers (from Fitzpatrick *et al*. 2008a,c,d).

Table 4. Case studies from geochemically variable inland saline and/or acid sulfate environments where soil indicators and hydro-pedologically based toposequence models have been incorporated in land management manuals, reports and other publications (modified from Fitzpatrick 2008)**

Locality of case study	**Hydrological Type**			**Geochemical Category of salt-affected soil**					
Key references	GAS	NAS	IAS	Alk	Hal	Gyp	Sulfidic	Sufuric	Sodic
Herrmanns and Keynes, Mt. Lofty Ranges, SA. (Fitzpatrick *et al*. 1996, 1997, 2003b, 2008-Ch1; Skwarnecki *et al*. 2002; Cox *et al*. 1996)	D (s)	M			M	S	D	M	S
Dairy Creek, Mt. Lofty Ranges., SA. (Fitzpatrick *et al*. 1996,1997, 2003b; Skwarnecki *et al*. 2002)	D (s)				M	S	S	D	S
Mt. Lofty Ranges., SA. (Skwarnecki and Fitzpatrick 2003; 2008-Ch4)	D (s)	M			M	S	D		S
Loveday disposable basin, Murray R, SA: (Lamontagne *et al*. 2004; 2008-Ch14; Wallace *et al*. 2008-Ch15,16; Hicks & Fitzpatrick 2008 Ch6).	D (s) (p)	M		S	M	S	D	M	M
Lakes Albert and Alexandrina, River Murray below Lock 1, SA (Fitzpatrick *et al*. 2008a,c,d)	M		M		M	M	D	D	M
Tilley Swamp, SA (Fitzpatrick *et al*. 2008-Ch17)	D (s) (p)	M	M	S	S	S	S		M
Lake Bonney, SA (Fitzpatrick *et al*. 2008e)	D (s) (p)		M	S	S	S	D	M	
Noora Basin (Shand *et al*. 2008b)	D					D			M
Telford Basin, South Australia (Bourman *et al*. 1995)	D (s) (p)					D		M	M
Jamestown, SA. (Fitzpatrick *et al* 2003d; Thomas *et al*. 2008a, b)	M (s) (p)	D		D	M	M	M		D
MDB Salt Interception Scheme. (Shand *et al*. 2008-Ch5)	D (s)	M				S	M	M	M
Cook plains (Hollingsworth *et al*. 1996)	D(s/p)	M		M	M	M	M		M
Victorian wetlands above Lock 8-9 (Shand *et al*. 2008a)									
Woorndoo, Victoria (Cox *et al*. 1999; Fitzpatrick *et al*. 2003b)	D (s) (p)	M		M	S	S	S		S
Gatum, Dundas Tablelands, Victoria (e.g. Brouwer and Fitzpatrick 2002; Fitzpatrick and Brouwer 2003)	D (s)	M			M	M	S		S
Merriefields, Dundas Tablelands, Vic. (Gardner *et al*. 2004a, b; Fawcett *et al*. 2008-Ch18).	D (s)	M			M	S	D	M	S
Rouse Hill, NSW. (Cox *et al*. 2002)	D (s)	M		M	S	M	M		S
Tareena Billabong & Salt Creek, NSW (Fitzpatrick et al. 2008-Ch19)	GAS (s)		M				M		M
Wheat belt, WA: (Fitzpatrick *et al*. 2003c; 2005; 2008-Ch12,17; Degens *et al*. 2008-Ch10,11 13; Lee, 2002)	D (s) (p)	M			M	D	M	D	M
Magela Creek Plain, East Alligator River, N.T. (Willett 2008-Ch20)	D (s)	M					D	M	
Brunei (Grealish *et al*. 2008-Ch21)	D (s)						D	S	
North China Plain, China. (Fitzpatrick *et al*. 2002; Fitzpatrick & Merry 2002)	D (s)		M	S	S	M	M		S
Mesopotamian marshlands, Iraq (Fitzpatrick 2004b).	D (s)		S	S	S	D	S		D
East Texas, USA (Fanning and Fanning 1989 p 313)	D (s) (p)					M	D	D	

GAS = Groundwater Associated Salinity, (p) = Primary (naturally saline); (s) = Secondary (anthropogenic salinity). NAS = Non-groundwater Associated Salinity. IAS = Irrigation Associated Salinity. D = Dominant; S=Sub-dominant; M=Minor. Alk = Alkaline (sodium carbonate dominant, pH >9); Hal = Halitic (sodium chloride dominant); Gyp = Gypsic (gypsum dominant) or Mg-sulfate salts; Sulfidic = pyrite rich and pH >4.0; Sulfuric = sulfuric acid dominant, pH <4.0); Sod = Sodic (high ESP), SA = South Australia; Vic = Victoria; NSW = New South Wales, WA = Western Australia.

DESCRIPTIVE, EXPLANATORY AND PREDICTIVE TOPOSEQUENCE MODELS

Conceptual process models enable researchers to develop, refine and present mechanistic understanding of complex soil-regolith environments (Fritsch and Fitzpatrick 1994). These models are graphic, cross-sectional representations of soil-regolith-bedrock profiles that illustrate vertical and lateral changes that occur along toposequences. They are used to explain the complex pedological, hydrological and biogeochemical interactions that occur in the regolith environment (e.g. Fitzpatrick and Merry 2002).

Three categories of conceptual toposequence models have been described, which are:
- Descriptive soil-regolith models.
- Explanatory soil-regolith models.
- Predictive soil-regolith models.

The descriptive soil-regolith process model shown in Figure 12 characterises relict (past geomorphological processes in development of deep weathering and erosion) and current saline, alkaline, sodic, sulfidic or sulfuric soil forming processes. Such models help to develop practical solutions for ameliorating soils at farm scale. The descriptive soil-regolith model is used as the precursor or framework for developing the explanatory soil-regolith model (3D) shown in Figures 13 and 14, which represents current soil salinity (hatching), salt groundwater flow (dark blue arrows) and freshwater flow (light blue arrows). If required, the explanatory soil-regolith model in turn is used to develop the predictive soil-regolith model (4D) shown in Figure 15. Consequently, the predictive soil-regolith model (4D) consists of a collage of figures, which illustrates several evolutionary cycles of soil-regolith events.

Descriptive soil-regolith models

To understand the lateral linkages and relationships between soil and landscape indicators (soil profile features), we have used the systematic structural approach to characterize soil-regolith features at different points along toposequences (Fritsch and Fitzpatrick 1994; Brouwer and Fitzpatrick 2002; Fitzpatrick *et al.* 2003a). Colour photographs of typical profiles at different parts down the toposequence are used (Figure 12). In summary, these authors identified and described in the field, by depth interval in all profiles along the toposequence, all relevant soil properties, including texture, coarse fragments, structure, matrix colour and mottling. In the laboratory, chemical and mineralogical properties were determined. Toposequence cross-sections were then drawn that identified similar layers that contain individual, or sometimes several, soil-regolith properties. Subsequently, boundaries were drawn around these layers. Each cross-section mapping unit or layer delineated is called a soil feature. A soil feature thus represents a limited range of one or more soil-regolith properties.

The key soil-regolith features that help recognise and explain soil formation and interactions between different parts of the toposequence were grouped into the same soil systems using concordant relationships, i.e. where there is a concordant relationship, spatial distributions and boundaries mostly coincide, and hydrological processes, geochemical processes and/or parent material will be the same or similar. Soil features were separated into different soil systems using discordant relationships; in such cases, spatial distributions show no or only partial overlap, boundaries do not coincide but abut or cut across each other, and processes and/or parent material will be different (Figure 12).

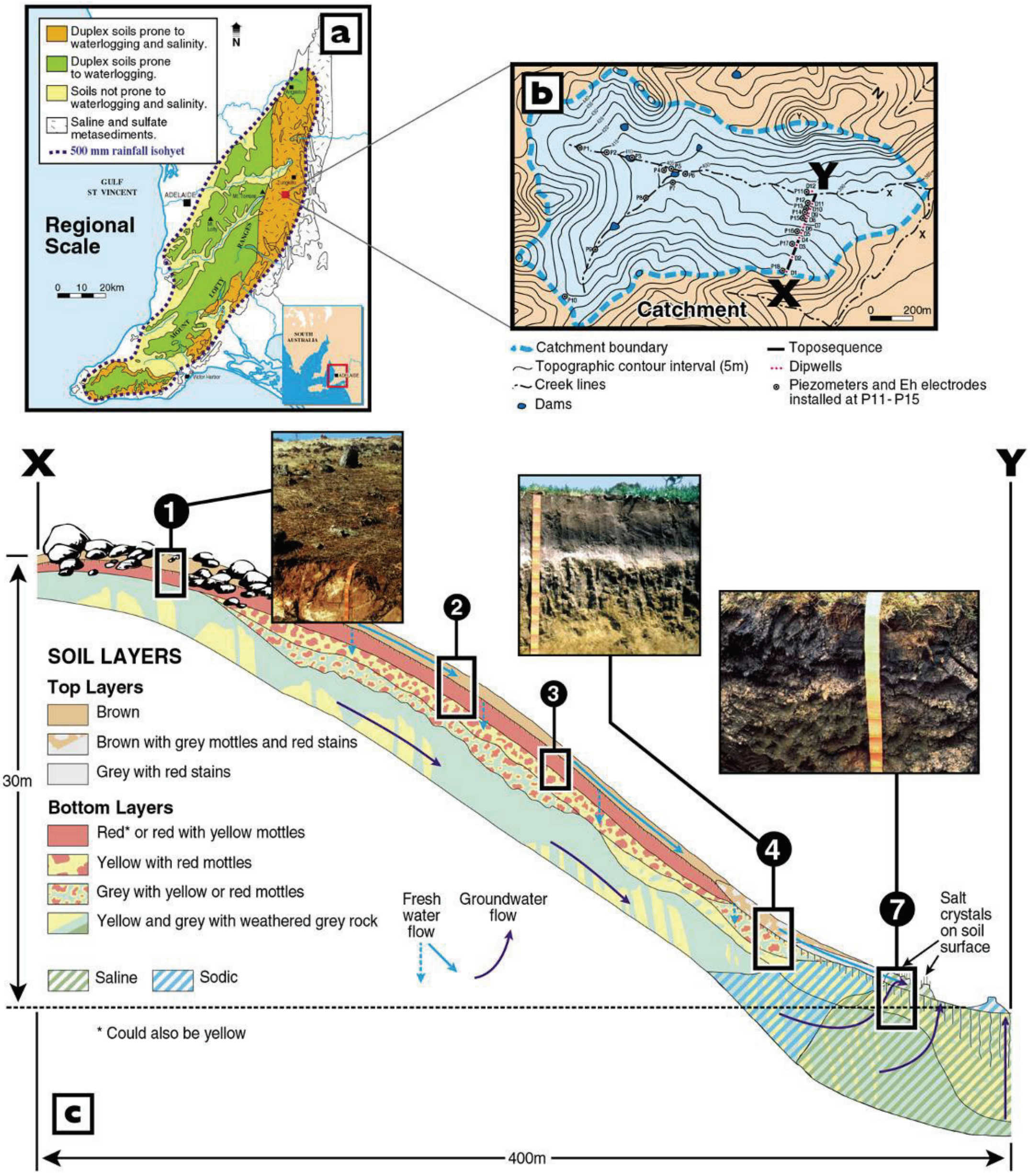


Figure 12. Descriptive soil-regolith model showing toposequences with three selected profiles, soil features (e.g., relict purple mottles and current very poorly drained saline soils with grey and red stains) and direction of perched fresh water flow and groundwater flow (after Fritsch and Fitzpatrick 1994; Fitzpatrick *et al*. 1996).

In summary, it was possible to group similar soil features into different soil layers, which were linked down the toposequence and mapped in cross-section (Figure 8). Each of these soil layers were linked to hydrological processes (water flow paths, salinity and sodicity) by using soil colour (together with other morphological, chemical and mineralogical indicators) and hydrology measurements (Cox *et al*. 1996; Fitzpatrick *et al*. 1996). This enabled the construction of 2D linkages that described water flow paths and the development of salinity in the Herrmann catchment in the Mount Lofty Ranges, SA (Figure 12).

Fitzpatrick and Skwarnecki (2005) explained how these descriptive process models can be used to characterise catchment-scale variability of relict (past geomorphological processes in development of deep weathering and erosion) and current (saline, sodic and acid sulfate soils) soil forming processes to develop practical solutions for ameliorating soils at farm scale, and for potential use in mineral exploration.

Explanatory soil-regolith models

Fitzpatrick *et al*. (1996) used the descriptive soil-regolith toposequence model (Figure 12) to construct an explanatory soil-landscape process model to explain contemporary geochemical dispersion and erosion processes present in the lower parts of a toposequence (Figure 13). This model explained the formation and degradation of acid sulfate soils in a single diagram that illustrates the pedological, geological, biogeochemical, mineralogical and hydrological processes occurring in the eastern Mount Lofty Ranges. Fitzpatrick *et al*. (1996) showed that a combination of: (i) saline groundwaters enriched in sulfate (with other elements sourced from mineralised zones e.g. Pb and Zn) seeping up through soils, (ii) anaerobic conditions and (iii) organic carbon in saturated soils, yielded sulfidic material containing pyrite framboids formed by anaerobic bacterial reduction of sulfate. Thus, when these sulfidic materials are eroded and exposed to air, pyrite is oxidised producing sulfuric acid, which dissolves soil minerals and leads to precipitation of a number of mineral combinations:

- sideronatrite, tamarugite, copiapite, halite and gypsum (Table 1) in sandy sulfuric materials with pH < 2.5,
- natrojarosite, jarosite and plumbojarosite (Table 1) in clay-rich sulfuric materials with pH 3.5-4,
- schwertmannite (orange; pH 4), ferrihydrite (reddish-brown; pH >6), akaganéite (reddish-orange) and white, poorly-crystalline Al oxyhydroxide precipitates (Table 1).

The formation of the complex suite of sulfate salts (of Fe, Al, Na, Pb, Ca, As, Zn), jarosite, oxyhydroxysulfates and Fe oxides are indicative of rapidly changing local environments and variations in Eh (redox), pH and availability of Fe, S and other elements (Skwarnecki and Fitzpatrick 2003).

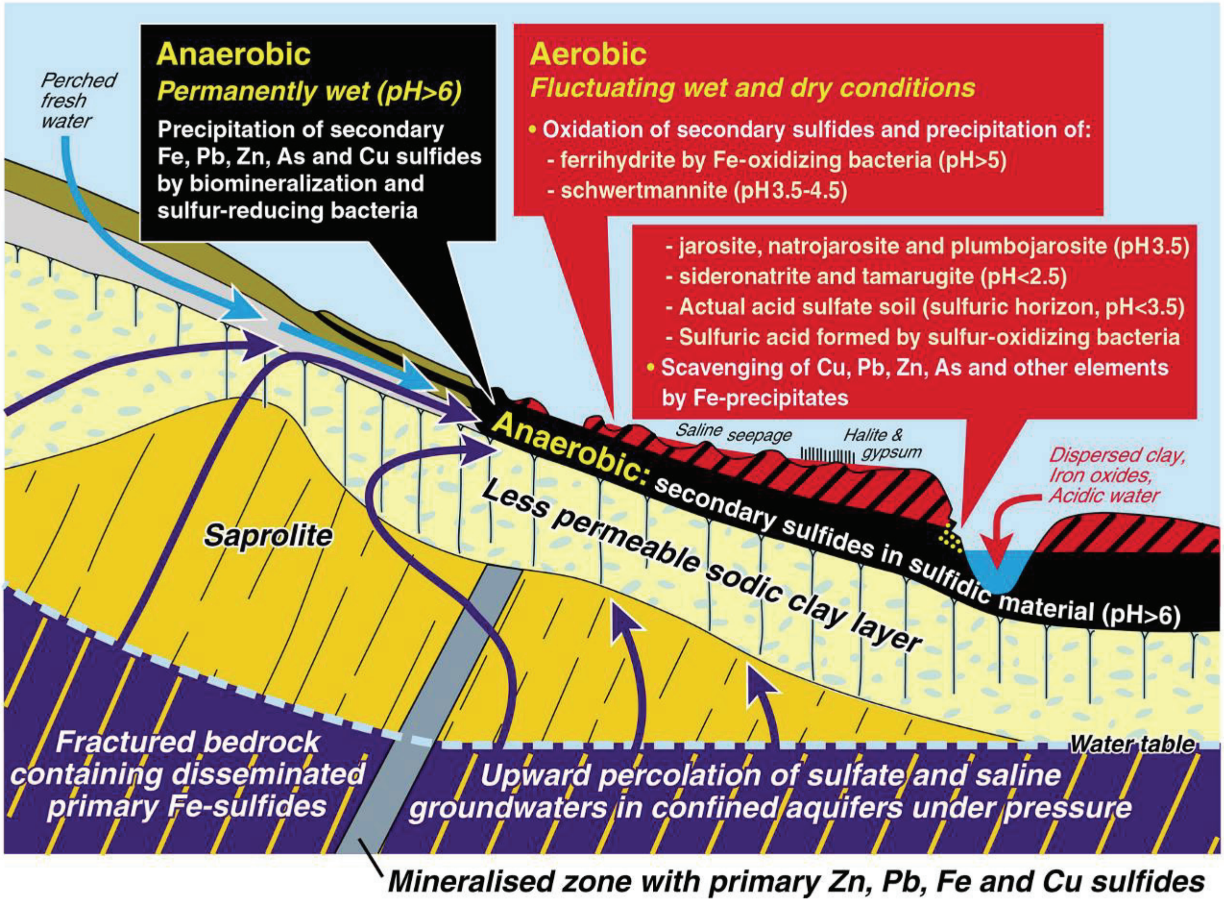


Figure 13. Explanatory soil-regolith model showing geochemical dispersion and erosion processes in saline seepages and formation of secondary sulfides in sulfidic material in a perched wetland and sulfuric materials along eroded drainage lines (after Fitzpatrick *et al*. 1996).

Regional sampling by Skwarnecki and Fitzpatrick (2003) showed that a range of materials (sulfidic materials, sulfuric horizons, salt efflorescences, and Fe- and Al-rich precipitates) are typically anomalously enriched in elements such as As, Bi, Cd, Cu, Pb, Tl and Zn, especially where they are spatially related to sulfide mineralisation (cf. elements likely to be present in gossans). Thus, the sulfidic/sulfuric material may carry indications of the presence of blind or concealed ore deposits, making these sediments a potential sampling medium for mineral exploration (Figures 13 and 14).

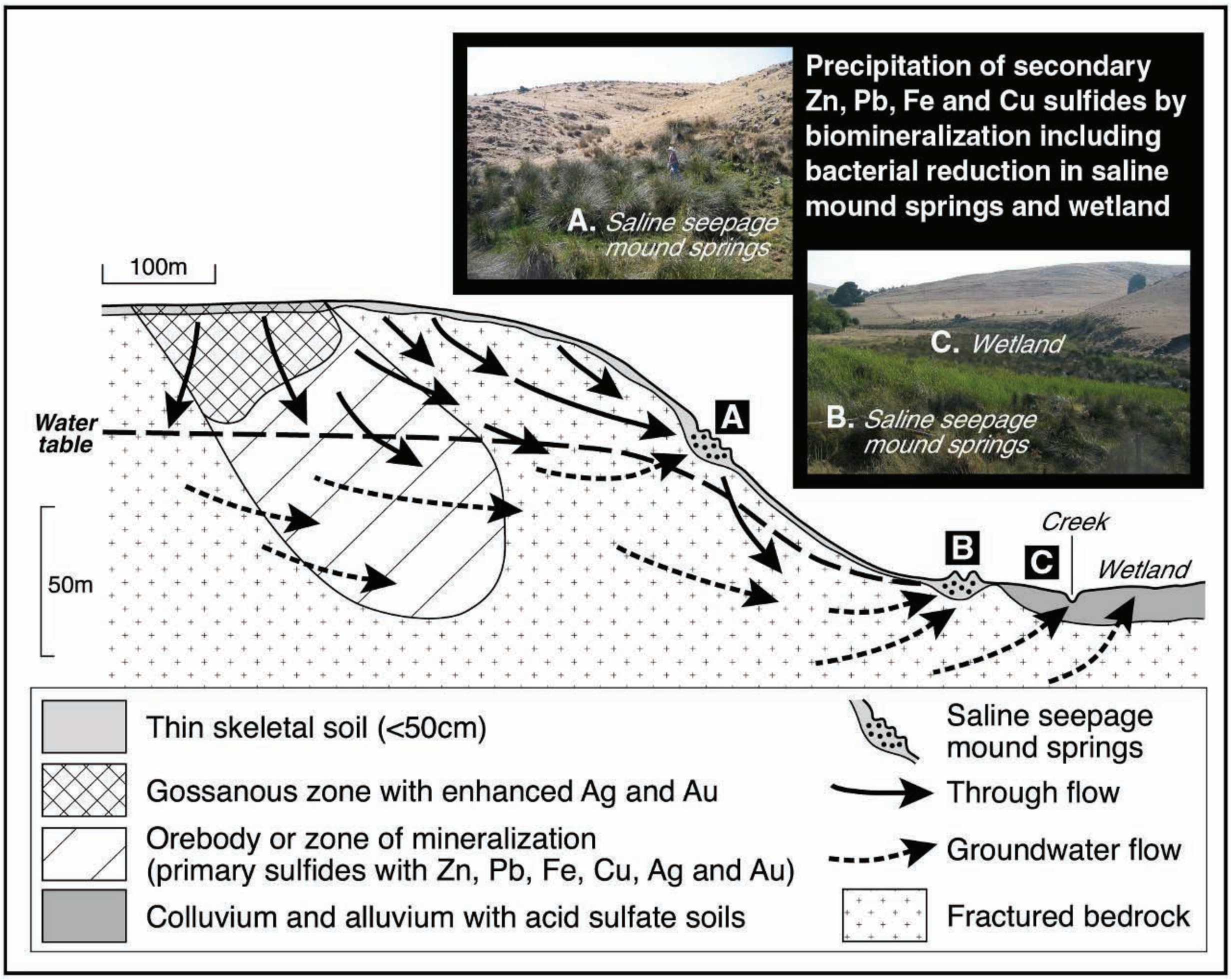


Figure 14. Explanatory soil-regolith model showing geochemical dispersion from mineralised zones in sulfidic/sulfuric materials from seeps, springs and wetlands, eastern Mount Lofty (after Skwarnecki and Fitzpatrick 2003)

Predictive soil-regolith models: landscape evolutionary processes

Fitzpatrick *et al*. (2000a) used the information contained in Figures 12-14 to construct a predictive soil model showing the hydrogeochemical processes that transform sulfidic material in a perched wetland to sulfuric material (Figure 15).

Stage 1: Saline groundwater enriched in sulfate (SO_4^{2-}) seeps up through the soil, along with other ions in solution such as Na^+, Ca^{2+}, Mg^{2+}, AsO_4^{2-}, I^- and Cl^-, and concentration by evaporation to form various mineral precipitates within and on top of the soil surface (Figure 15a). The combination of: (i) rising sulfate-rich groundwater, (ii) anaerobic conditions associated with saturated soils, (iii) agricultural activity and (iv) fractured rocks relatively enriched in Fe, S, Pb, Zn, etc. leads to the formation of sulfidic material and precipitation of anomalous concentrations of Pb and Zn. If the soil is wet and contains sufficient organic carbon, anaerobic bacteria use the oxygen associated with the sulfate (SO_4^{2-}) ions during the assimilation of carbon from organic matter. This process produces pyrite and forms sulfidic materials (Figure 15a) (Fitzpatrick and Skwarnecki 2005).

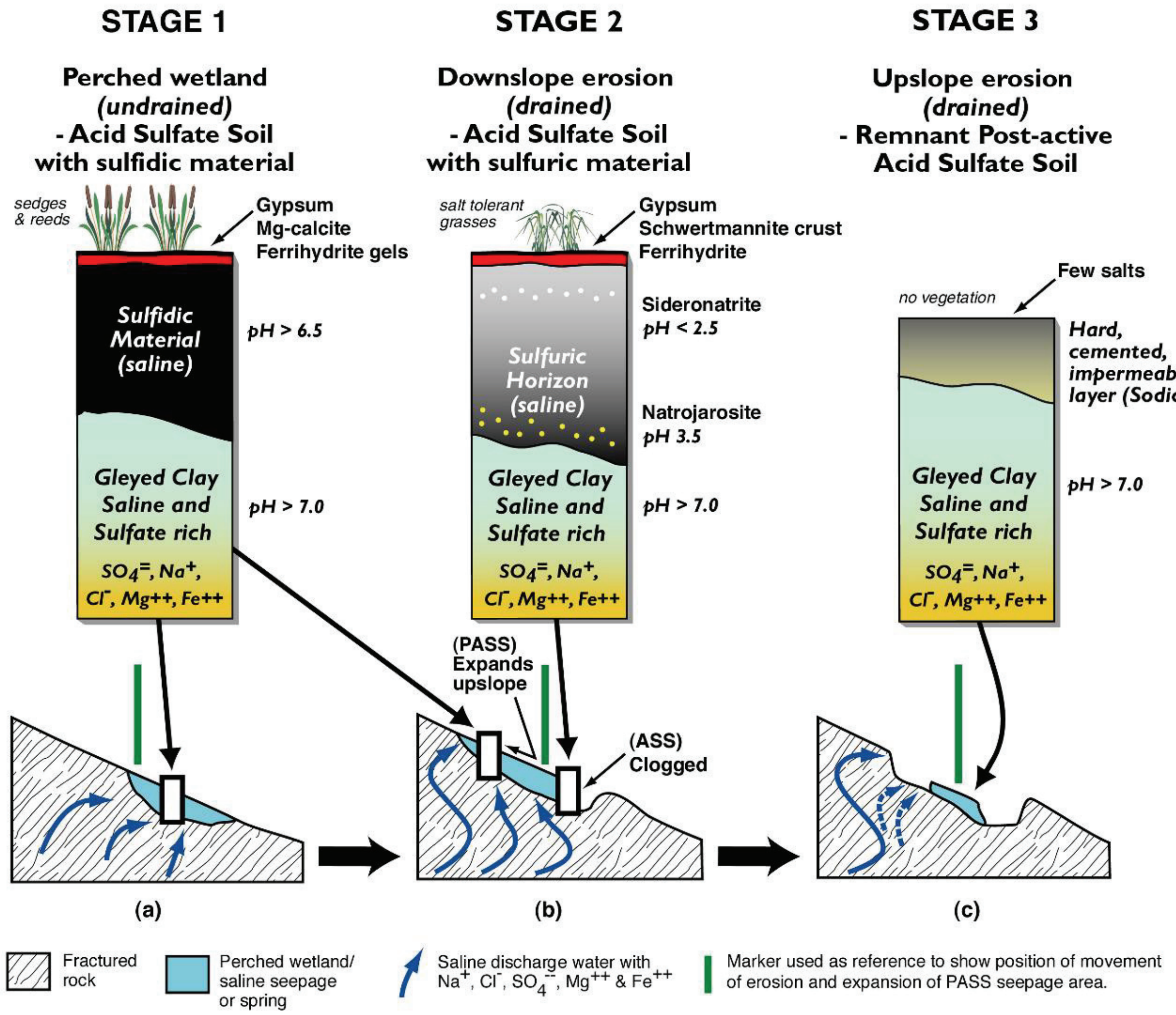


Figure 15. Predictive soil-regolith model showing the hydrogeochemical processes, which transform sulfidic material in a perched wetland to highly saline sulfuric material/horizon (after Fitzpatrick *et al*. 2000a).

Stage 2: Sulfuric materials result when pugging from animals, drainage works or other disruptions expose pyrite in previously saturated soils to oxygen in the air. Thus, pyrite is oxidised to sulfuric acid and various Fe sulfate-rich minerals, and sulfuric material forms (Figure 15b). When sulfuric acid forms, the soil pH can drop from ca. neutral pH 7 to below pH 4; locally, pH may decrease to as low as pH 2.5 to form a sulfuric horizon (Figure 15b). The sulfuric acid dissolves the clay particles in soil, causing base cations and associated anions (e.g. Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, SiO_4^{4-}), trace elements, and metal ions such as Fe^{3+} and Al^{3+} to be released into the soil and transported to stream waters. As the regolith structure degrades due to the accompanying sodicity, soils become clogged with dispersed clay and Fe precipitates and they lose their permeability and groundcover. This prevents the groundwater below from discharging and forces it to move transversely through the soil (Figure 15b). Soil around the clogged area eventually erodes, causing movement of acid, metal ions and salts into waterways and dams. An extended area with sulfidic material progresses upslope, or adjacent to the original area. If cattle or other activities continue to disturb the soil around the newly created sulfidic material, the area affected continues to expand (Figure 15b) (Fitzpatrick and Skwarnecki 2005).

Stage 3: If these processes become expressed on the surface of the soil, bare eroded saline scalds surrounding a core of lower permeability, highly saline, eroded sulfuric material may result (Figure 15c). These saline landscapes are characterised by slimy red or white ooze and scalds with impermeable Fe-rich crusts. As shown in Figure 15, when the sulfidic materials undergo change, different salt and Fe minerals form because of differences in pH, increases in salinity and differences is relative concentrations of salts. In the final stage of formation, a hard soil layer remains, with only few salts (Figure 15c). The acidification process accelerates the decomposition and formation of minerals in the soils and underlying rocks and can cause an increase in salinity and carbonate formation.

DESCRIPTIVE 3D WHOLE-OF-LANDSCAPE PROCESS MODELS

Fitzpatrick *et al.* (2003d) constructed a descriptive 3D whole-of-landscape process model (Figure 16) for a regionally representative upland hillslope near Jamestown, SA. The model characterises the catchment-scale variability of relict (past geomorphological processes in development of rock weathering and erosion) and current (saline, sodic and sulfidic soils) soil forming processes. The model also explains the contemporary geochemical dispersion and erosion mechanisms present in the lower parts (erosion gully) of the toposequence (Figure 16), and in particular, explains salt storage and salt mobilisation in this complex landscape dominated by both NAS and GAS (i.e. groundwater induced, occurring in the lowest part of the landscape in the erosion gully associated with stream salinity and underlying inland ASS-LSU 6: Figure 16). The model identifies a complex palaeovalley system containing alluvium, which provides new insights into the soil-regolith, geological and hydrological features associated with salt stores in both upland soil surface features and in low-lying valley-fill sediments. These observations are placed in a regional 3D regolith-landform evolution model derived from the interpretation of airborne magnetics and gamma-ray spectrometry, digital terrain analysis, airborne EM and drilling (Wilford 2004a).

Electromagnetic (EM-38, EM-31) and volume magnetic susceptibility (VMS) surveys were used to rapidly characterise complex landscape patterns (Thomas *et al.* 2008a, Fitzpatrick *et al.* 2003d). These survey methods in conjunction with terrain analysis and 3D GIS terrain visualisation showed strong promise for obtaining high intensity, non intrusive, spatially continuous soil information that revealed salt accumulation and other pedological processes. Using the combination of approaches, the authors: (i) produced maps showing the aerial extent of shallow NAS, and (ii), constructed a colour cross-sectional diagram or model to show the various saline and sodic soil horizons/layers and water flow pathways (Figure 16). Furthermore, the model was then used to underpin the development of GIS methods (upscaling) to predict and map the distribution of soil types and shallow NAS for the small region (2300 ha) surrounding the hillslope under study (Thomas *et al.* 2008b). These detailed toposequence descriptions and processes have the potential to be integrated into broader scale regolith-landscape models defined by airborne geophysical and terrain modelling techniques (Wilford 2004b).

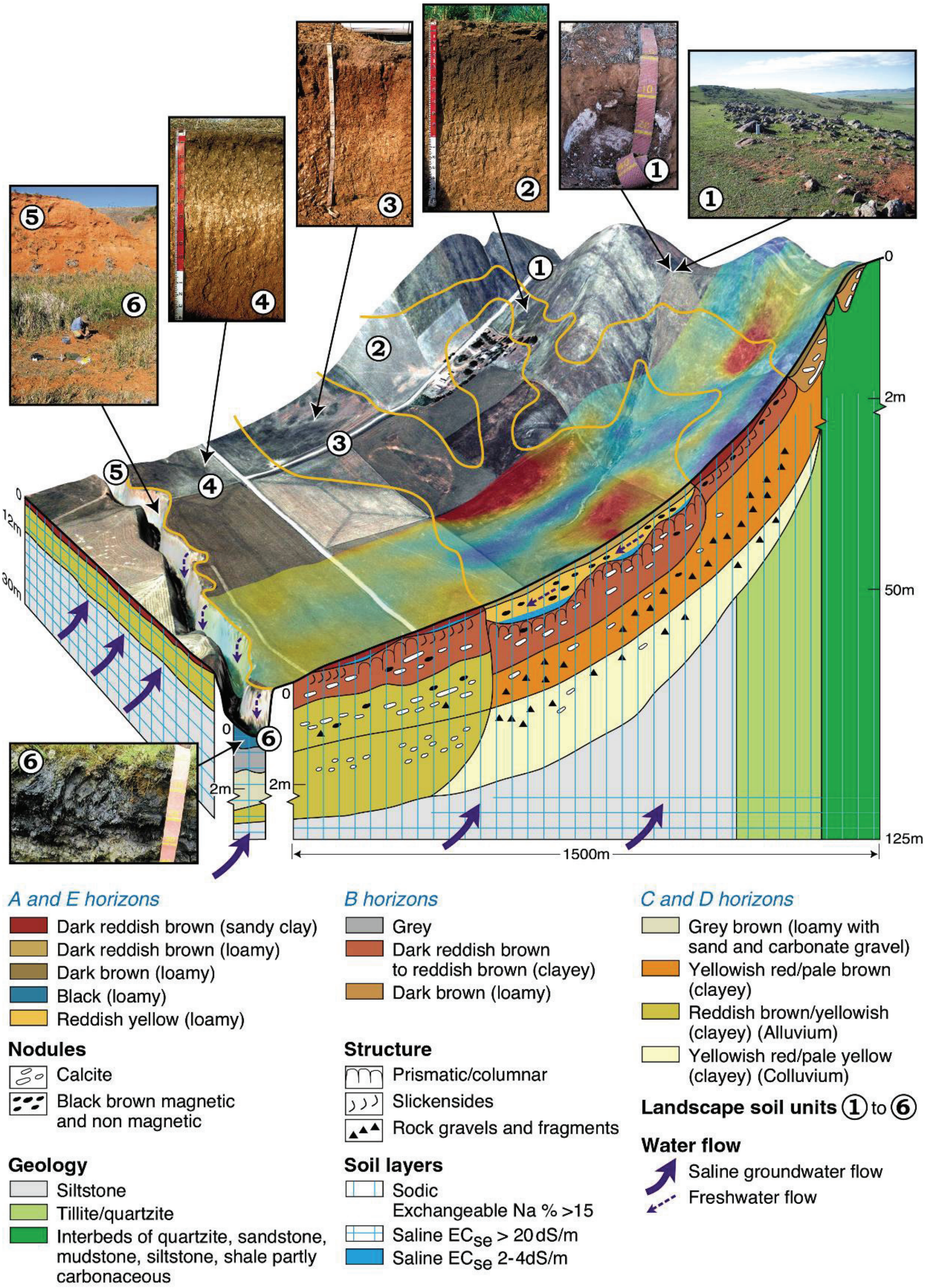


Figure 16. Whole-of-landscape 3D process model for Cootes case study area showing: (i) EM-38 map partly draped over the 3D aerial photograph drape of study area with boundaries of landscape-soil units (LSU), (ii) photographs of representative soil profiles for each LSU, inland ASS is dominant in LSU 6, (iii) geology, (iv) cross-section of typical toposequence showing the main morphological, saline and sodic soil-regolith features/layers and (v) groundwater and fresh surface water flow paths. The EM-38 map designates high conductivity values in red (subsoil expressed dry saline land), medium values in yellow-turquoise and low values in dark blue (after Fitzpatrick *et al*. 2003d)

PREDICTIVE SOIL-REGOLITH MODELS AND MAPS: TIME DEVELOPMENT SEQUENCES ILLUSTRATING FORMATION AND TRANSFORMATIONS OF SULFIDIC MATERIALS

The River Murray system (Figure 17) is a good example of a system which is not only highly stressed but has been highly managed for decades. The construction of locks, weirs and barrages (Figure 17) in the early part of the 20th Century to contain water flow has resulted in extensive agricultural development. However, the permanent inundation of the river, wetland and lake systems has had a significant impact on the formation of soils in these ecosystems because of loss of natural wetting-drying cycles so important to biodiversity and wetland functioning. This change has promoted the build-up of sulfide minerals (mostly iron pyrite) and sulfidic materials in these relatively newly formed subaqueous soils for over 50 years (Figures 18 to 20).

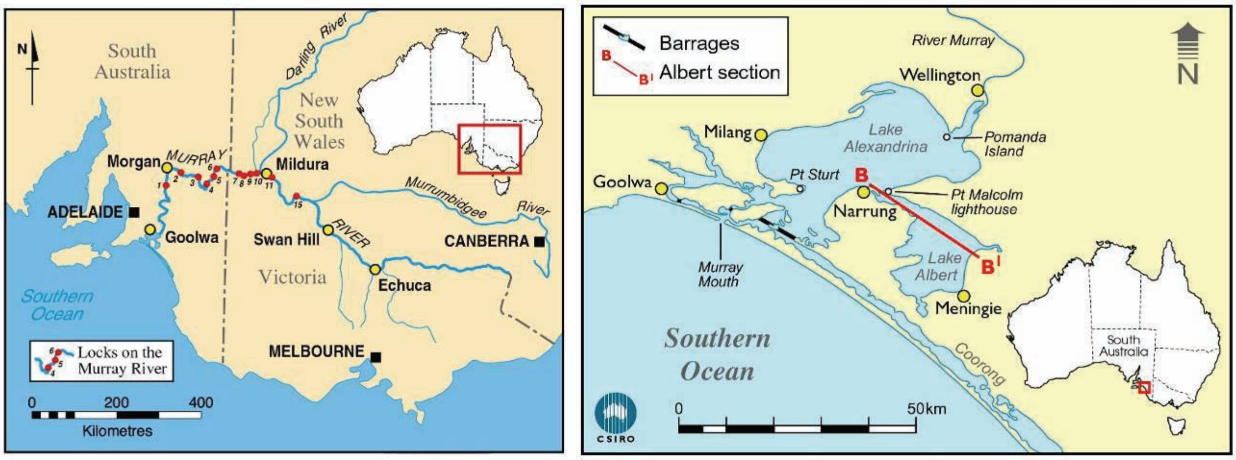


Figure 17. Locality maps showing part of the Murray-Darling River system in the Murray Darling Basin (MDB) along with locks on the River Murray (left map) and barrages, which were constructed to keep out sea water from the Lower Lakes (right map). Locality map also shows the generalised cross-section used in the construction of the eight conceptual models for Lake Albert (Figures 18 to 26)

However, prolonged extreme drought conditions in large parts of the MDB system (Figure 17) has caused water levels to recede in the river and wetland systems (including the freshwater Lower Lakes: Albert and Alexandrina), which have begun to dry, uncovering extensive areas of sulfidic material in the subaqueous soils (Fitzpatrick *et al*. 2008a,c,d). These soils are much more abundant in these riverine and lacustrine environments than previously recognised. Following drainage, sulfidic material in the anaerobic soils has oxidised and transformed to sulfuric material (pH <4), with consequent water quality, ecological and public health issues from metal/metalloid mobilization, de-oxygenation, noxious gas release and wind erosion.

A predictive soil-regolith model for Lake Albert: A chronosequence illustrating the formation and transformation of sulfidic materials

The newly formed anaerobic submerged and waterlogged soils in the floodplains, wetlands and tributaries below Lock 1 at Blanchetown and in the Lower Lakes of South Australia were ideal for the build-up of Fe sulfide minerals, which have been forming in these subaqueous soils since the construction of the locks, weirs and barrages over the past ca. 50 years (Figures 19 to 20). Under normal or natural wetting and drying cycles, build up of sulfidic materials may be minimised for some situations (Figure 18). The extreme drought conditions (2006 to 2008 and continuing into 2009), the worst on record, have led to a considerable drop in water levels in the Murray river channel below Lock 1, and the lower lakes and their tributaries (e.g. Currency Creek and Finniss river, Fitzpatrick *et al*. 2009). These low water levels exposed the accumulated sulfide minerals in the submerged or subaqueous soils to air for the first time (Figure 21) which in turn has led to the formation of sulfuric material (Figure 22 to 23) with pH levels dropping below 4 due to the formation of sulfuric acid (Fitzpatrick *et al*. 2008a,c,d). Dredging operations in both the lakes and River Murray have also exposed sulfides in the dredge spoils to oxygen, resulting in the formation sulfuric material.

Fitzpatrick *et al*. (2008c,d) have identified four sequential phases (or classes of ASS) that form depending on drainage conditions. Soils range from deep submerged sediments to subaqueous soils to waterlogged/saturated (all anaerobic) to unsaturated (aerobic) drained soils (Figure 11). Based on field investigations and historical/palaeo-pedological knowledge of the MDB, we have constructed a series of eight conceptual models that illustrate how various ASS materials in subaqueous, waterlogged (saturated) and dried conditions have sequentially changed, and will change over time with current predictions of lower water levels in the lower lakes. To illustrate these sequential changes, we have constructed the following series of conceptual models consisting of cross-sections across Lake Albert (Figure 17):

(i) Before 1880s (approximately 5,500 BC to 1880s period), Lake Albert cycled between natural wetting and flushing, and partial drying conditions
(ii) During the 1880s to 1930s period, when the river and lake systems were modified for irrigation purposes
(iii) During the 1930's, when Lake Albert was first managed using locks and barrages, to 2006
(iv) During the 2006 to 2007 period when partial drying of wetlands and beaches surrounding Lake Albert took place
(v) During the 2007 to 2008 period when large scale (unprecedented) drying of beaches surrounding Lake Albert and adjacent wetlands took place
(vi) During the 2008 to 2009 period, predicted if no pumping from Lake Alexandrina occurs and extreme drought conditions continue
(vii) During the 2008 period, as pumping water from Lake Alexandrina to Lake Albert is taking place to maintain water levels.

A similar series of conceptual models, comprising cross-sections, have been constructed for the River Murray below lock 1 to Wellington (Fitzpatrick *et al*. 2008d) and for Lake Alexandrina (Fitzpatrick *et al*. 2008f). Research has also progressed beyond studying the occurrence and processes of formation of the various sub types of acid sulfate soils to understanding the impacts on adjacent environments through the mobilization and transport of acidity and solutes (e.g. Fitzpatrick *et al*. 2008a,b,c; Simpson *et al*. 2008,. 2008-Ch3; Stauber *et al*. 2008). Such questions have involved harnessing skills in aqueous geochemistry, hydrodynamic modelling and ecological risk assessment. These investigations have been extended to determine the occurrence and impacts of inland acid sulfate soils across the entire MDB.

(i) Before the 1880s (5,500 BC to 1880s), Lake Albert cycled between natural wetting and flushing, and partial drying conditions in response to seasonal (i.e. winter/summer) and climatic (e.g. drought/wet) cycles occurring in the upper MDB (Figure 18).

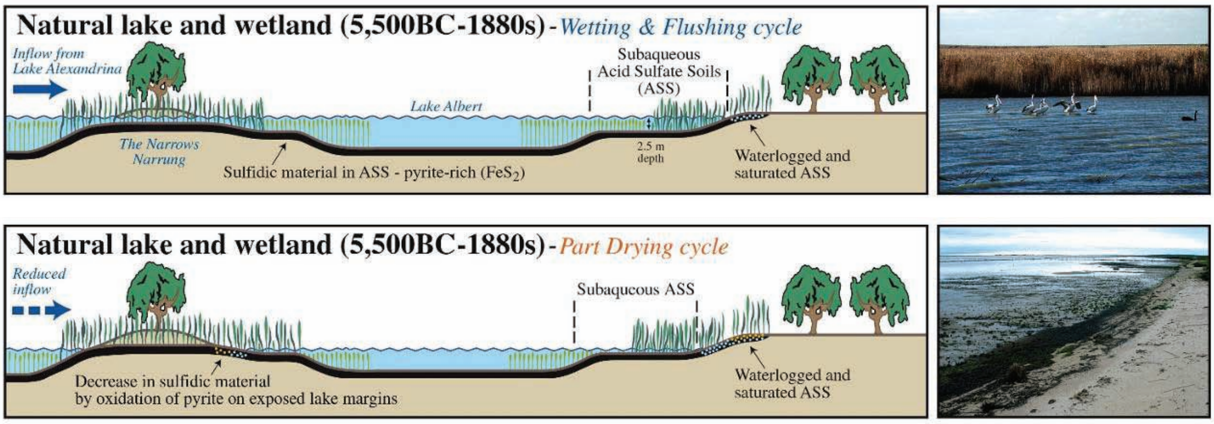


Figure 18. Generalised schematic cross section models for Lake Albert; illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycle conditions during the time prior to major pre-European development (5,000 BC - 1880s).

During wetter periods, Lake Albert underwent regular wetting and flushing cycles (Figure 18 - upper panel). Waters received by Lake Albert were transferred via channels, overland flow, and by infiltration. Lake Albert accumulated sulfidic materials from sulfate contained in surface waters and groundwaters. However, during dry periods such as droughts (Figure 18 - lower panel) when river flows were lower, Lake Albert and adjacent wetlands partially dried, causing oxidation of sulfidic materials, especially on the dry margins. Pyrite in the sulfidic material was oxidised with likely formation of sulfuric acid and potentially the formation of sulfuric materials. In wetter times and during floods, the acidic material was submerged in the water column, with dilution/neutralisation of acidity and the reformation of sulfidic material. The build-up of sulfidic materials in Lake Albert was regularly kept-in-check by oxidation and removal during scouring floods.

(ii) During the 1880s to 1930s period, European colonists moderated the flows of the River Murray and lower lakes to ensure reliable navigation and irrigation (Figure 19). During this period, Lake Albert was "managed for flood irrigation" (mainly dairy).

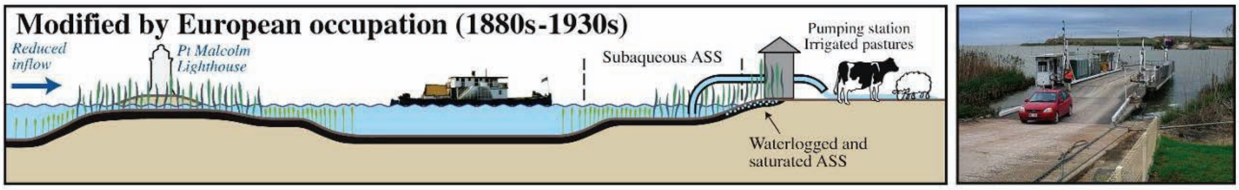


Figure 19. Generalised schematic cross section model for Lake Albert; illustrating modification of water flows by European occupation (1880s- 1930s).

(iii) During the 1930s to 2006 period, Lake Albert was managed using locks and barrages (Figure 20). The installation of locks and barrages allowed considerable build-up of sulfidic and MBO material in the lower lakes (subaqueous sulfidic materials) due to: (i) the evaporative concentration of sulfate containing nutrient/salt loads in stable pool levels and groundwater sources, (ii) the lack of scouring and seasonal flooding. Ultra-fine monosulfidic black ooze (MBO) material accumulated in low-flow backwaters and along the vegetated edges of the wetland (Figure 20.

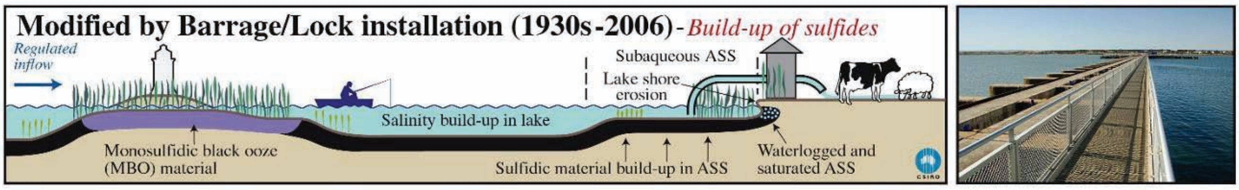


Figure 20. Generalised schematic cross section model for Lake Albert; illustrating modification of water flows by barrage (and lock) installations causing the build up of sulfides under continuous subaqueous ASS conditions from 1930s-2006.

(iv) During the 2006 to 2007 period, partial drying of wetlands and beaches surrounding Lake Albert took place (Figure 21), due to drought conditions, and the river and lake levels continued to decrease. During this period, subaqueous ASS transformed to waterlogged ASS (i.e. ASS that are wet or saturated long enough to produce periodically anaerobic conditions, thereby influencing the growth of plants: e.g. hydric soils with sulfidic material) and eventually to dried ASS.

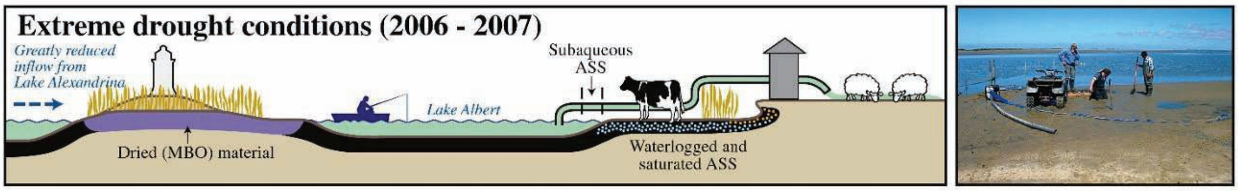


Figure 21. Generalised schematic cross section model for Lake Albert, illustrating extreme drought conditions in 2006 – 2007 where subaqueous ASS transform to waterlogged ASS (i.e. ASS that are wet or saturated long enough to produce periodically anaerobic conditions, thereby influencing the growth of plants: e.g. hydric soils with sulfidic material).

(v) During the 2007 to 2008 period, complete drying (unprecedented in recent history) of beaches surrounding Lake Albert and adjacent whole wetlands took place (Figure 22) because of the extreme drought conditions from 2006 to 2008, when the river and lake levels continued to lower. Most wetlands adjacent to Lake Albert effectively became hydraulically disconnected from the lake. This resulted in the formation of sulfuric material (pH less than 4 to depths up to 50cm). Under such low pH conditions, acid dissolution of the layer silicate soil minerals is likely to cause the release of Fe, Al, Mg, Si (and others) (Figure 22). These conditions have also permitted deepening of desiccation cracks (> 50cm), especially in areas that are organic-rich (>10 % organic carbon) and clayey (>35 % clay). The continued drying of Lake Albert and the adjacent wetlands has caused further desiccation, and the precipitation of sulfate-rich salt efflorescences in desiccation cracks and on the sandy beaches surrounding the lake. Areas with MBO continued to dry out, also causing desiccation cracks to develop in the fine textured material (Figure 22).

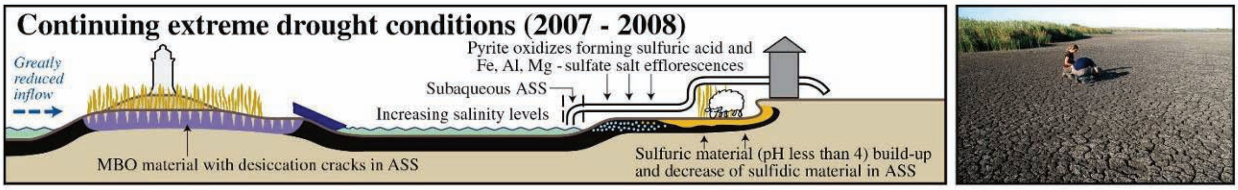


Figure 22. Generalised schematic cross section model for Lake Albert; illustrating the formation of: (i) sulfuric material (pH <4) by oxidation of sulfides present in sulfidic material, (ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued lowering of water levels under persistent extreme drought conditions during 2007 – 2008.

(vi) During the 2008 to 2009 period, if no pumping from Lake Alexandrina occurs to keep the soils under anaerobic conditions and extreme drought conditions continue, we predict that the whole of Lake Albert will be variously covered by: (i) sulfuric material, (ii) deep (> 1m) desiccation cracks, (iii) sulfate-rich salt efflorescences and (iv) localised areas with fine textured dried MBO material with micro desiccation cracks (Figure 23).

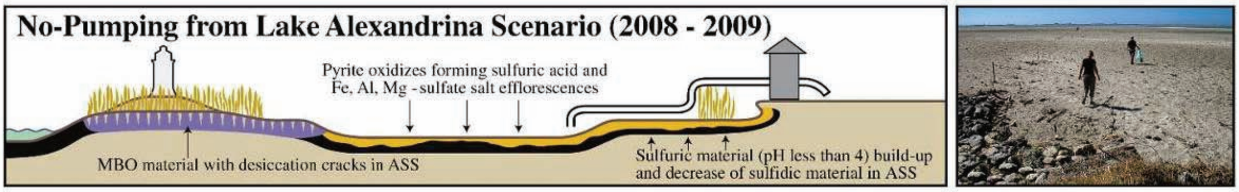


Figure 23. Generalised schematic cross section model predicted for Lake Albert under a no-management scenario (e.g. no water pumping from Lake Alexandrina); illustrating the widespread formation of: (i) sulfuric material (pH <4) by oxidation of sulfides in sulfidic material, (ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued lowering of water levels under persistent extreme drought conditions during 2008 – 2009.

Predictive acid sulfate soil maps for Lake Albert and Lake Alexandrina

Combined bathymetry, soil and vegetation mapping using GIS was used to help predict the distribution of the fourteen subtypes of ASS according to three predictive scenario maps (Fitzpatrick *et al*. 2008-Ch2; 2008a,c,d,f), which in Figures 24 and 25 depict sequential changes in ASS materials at different water levels in Lake Albert and Lake Alexandrina of +0.5 m AHD (pre-drought), -0.5 m (approximate level during early 2008), and for -1.5 m AHD (an extreme case, should lower lake inflows persist).

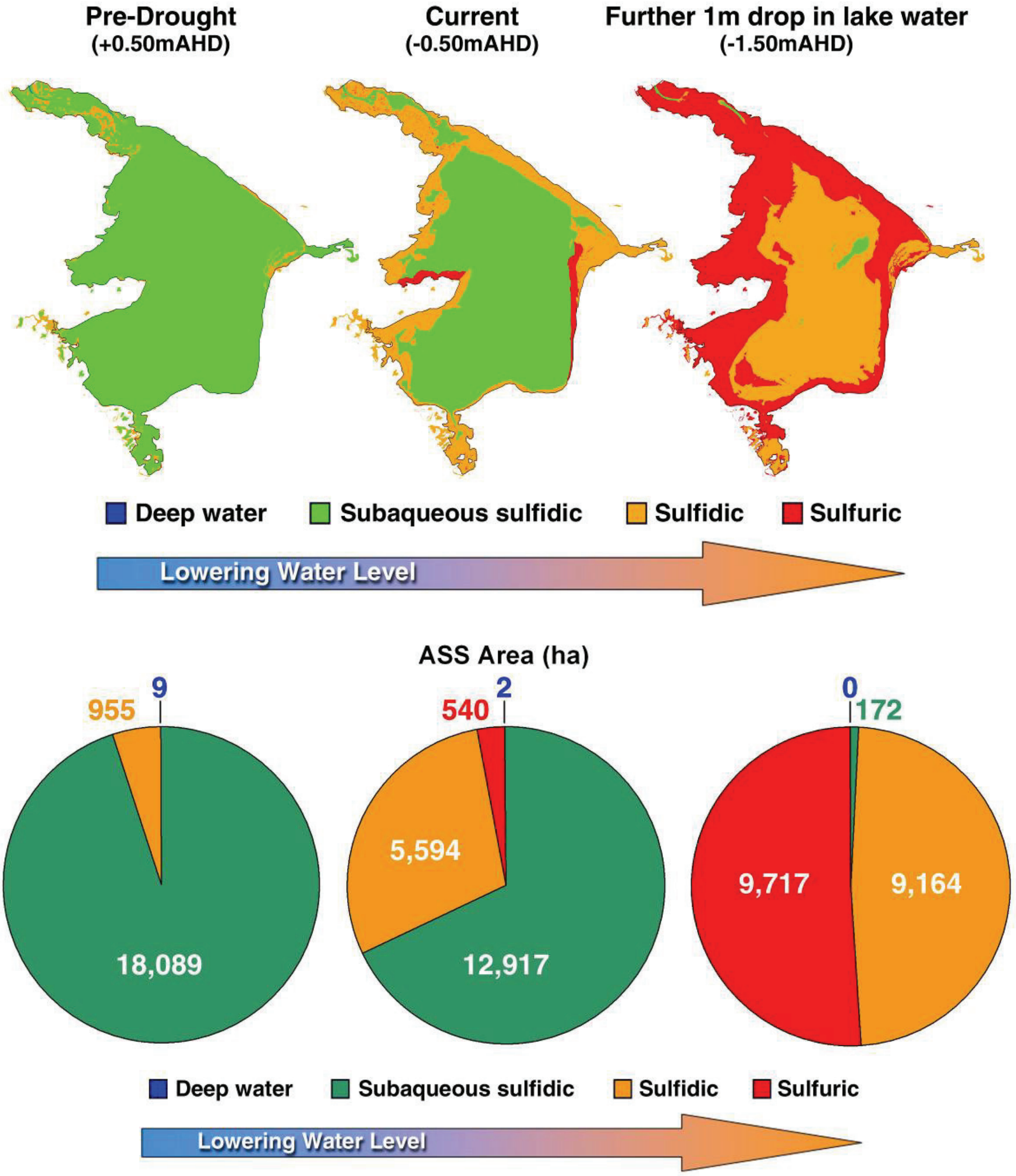


Figure 24. Predictive scenario maps and pie charts depicting changes in ASS materials at different water levels in Lake Albert (+0.5 m AHD, -0.5 m AHD and -1.5 m AHD). (From Fitzpatrick *et al.* 2008f)

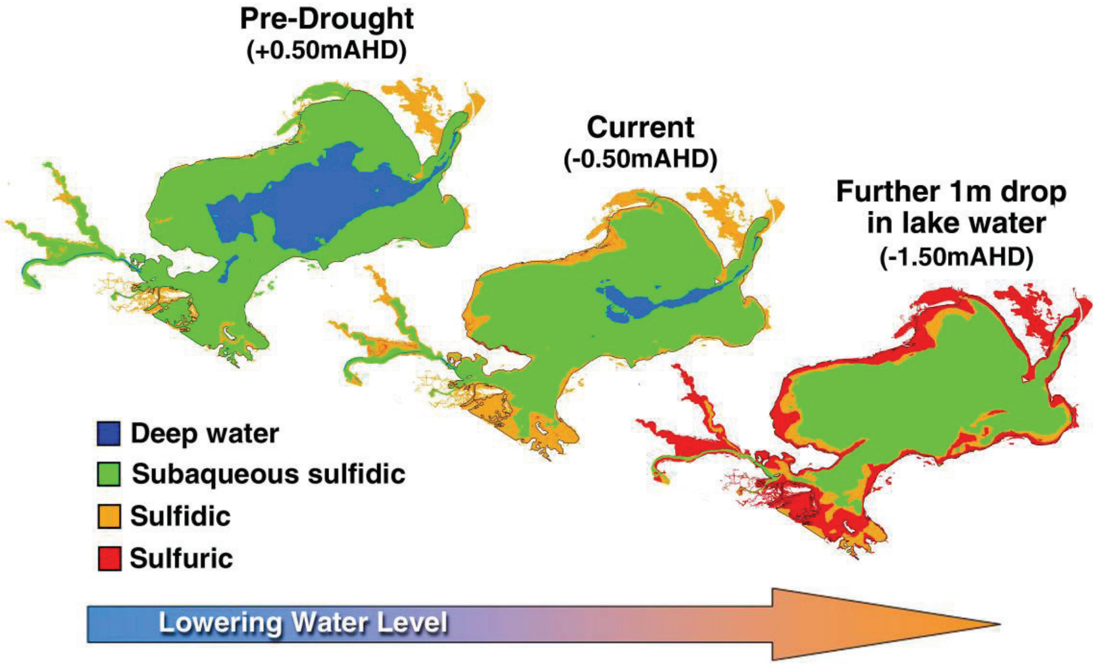


Figure 25. Predictive scenario maps depicting changes in ASS materials at different water levels in Lake Alexandrina for +0.5 m AHD (pre-drought), -0.5 m (approximate level during early 2008), and -1.5 m AHD (an extreme case, should lower lake inflows persist). (From Fitzpatrick et al. 2008a,c,d,f)

ACID SULFATE SOIL MANAGEMENT

Summary of principles

Environmental risks are present because draining river or wetland/lake systems involves the disturbance of material that has not been in contact with the oxygen in the atmosphere for some considerable time. During lowering water levels, sulfidic materials may be exposed. and sulfides within the subaqueous soil horizons will begin to oxidise once they are exposed to air (Figure 11). As discussed, this will produce sulfuric acid and potentially release toxic quantities of Fe, Al and heavy metals if the soils do not contain sufficient acid neutralising capacity to maintain a sufficiently high pH (> 5) (Simpson *et al*. 2008-Ch3).

The acid, metals (mainly Al), metalloids and non metals released can potentially leach into waterways, kill fish, other aquatic organisms and vegetation, and can even degrade concrete and steel pipes and structures to the point of failure. However, appropriate management of ASS during development can improve discharge water quality, increase agricultural productivity, and protect infrastructure and the environment. Such improvements can generally be achieved by applying low-cost land management strategies (e.g. Dear *et al*. 2002) based on the following general principals:

Identification and avoidance of ASS materials

Slowing or stopping the rate and extent of pyrite oxidation and hence avoidance of the formation of sulfuric materials. This can be achieved either by:

- Keeping sulfidic material anaerobic under saturated conditions to prevent the oxidation of pyrite in sulfidic materials (e.g. see case study below where water levels in Lake Albert have been maintained by pumping water from Lake Alexandrina to Albert).

- Rapid drying of sulfidic material to slow the biological processes which are responsible for the formation of acid.

Retaining existing acidity within the ASS landscape

Acidity and oxidation products that cannot be retained on-site may be managed by other techniques such as acidity barriers or constructed wetlands that intercept and treat contaminated water before discharge into rivers or estuaries.

Neutralization of acid in ASS

This can be achieved either by:

- Liming using fine agricultural lime ($CaCO_3$) to buffer the pH in the soil. The amount of lime required depends on acidity already produced, and potential for further production of acid. One of the issues with this option is the large amount of lime that is sometimes required and the effects it could have on biota. Liming, as a substitute for reflooding, and application to dry soils, also poses a problem as the lime would need to be mixed in with the soils. This would mean churning up wetland beds and disturbance of soils. However, surface application could effectively neutralize acid soil formed at the surface, which is most prone to erosion or to which animals and humans may be directly exposed.
- Bioremediation – applying mulched organic matter on top of a wetland bed so that as it breaks down the organic matter acts as a buffer to the acid in sulfuric materials.
- Controlled reflooding by sea water – where feasible, sea water can be used to neutralise acidity in sulfuric materials and dilute acidity, dissolved metals, metalloids and non-metals (e.g. from sulfate-rich salt efflorescences). Seawater contains alkalinity of about 140 mg/L as bicarbonate equivalent. However, the acids and any metals that would initially dissolve in the seawater should not be permitted to flush out to the ocean until removed by natural processes. If flushing is not possible, salinity and sulfides will progressively accumulate in such areas (e.g. lower lakes) over time. Note that flooding with sea water also helps the process of exclusion of oxygen, as mentioned above.

We emphasise that within the above management strategies there is still a degree of risk, and that some may not be suitable to a particular site. Management strategies other than those listed may be considered, provided sufficient information regarding their successful implementation, environmental impacts and scientific merit is provided.

Case studies for land management planning: Lower Lake and River Murray Systems

Several management options for mitigating the effects of sulfuric and MBO materials in ASS, which have formed because of the extreme drought conditions in the Lower Lakes and River Murray below Lock 1 regions are currently being considered, and in some cases being implemented by: (i) pumping water from Lake Alexandrina to Lake Albert to maintain water levels (Fitzpatrick et al. 2008c; Figure 26) and (ii) by retaining existing acidity, MBO material and mobilized metals within the ASS-affected wetlands (Fitzpatrick *et al*. 2008c; Figure 27).

Identification and avoidance of ASS materials

A management option for preventing more sulfidic material oxidising to form sulfuric material in ASS is currently being implemented by pumping water from Lake Alexandrina to Lake Albert to maintain water levels (Figure 26). This option is based on: (i) identification of abundant sulfuric and sulfidic materials on the edges of Lake Albert when water levels were -0.3 AHD and (ii) predicted formation of abundant sulfuric materials when water levels drop further (e.g. to -1.5 AHD) because of the extreme drought conditions in the Lower Lakes (See ASS maps, Figures 24 and 25).

(vii) Following recommendations from ASS studies in the Lower Lakes by Fitzpatrick *et al.* (2008 a,c,f), it was decided by the South Australian and Australian Federal governments to maintain water levels in Lake Albert at approximately -0.3 m AHD by pumping water at a rate of 400 ML/day (i.e. initial pumping rate) from Lake Alexandrina to Albert to prevent the water level in Lake Albert dropping below -0.6 m AHD (Figure 26) to minimise the risk of soil and water acidification. Hence, Lake Albert was disconnected from Lake Alexandrina after the construction of an earthen bank (see photograph in Figure 26) before pumping commenced in early 2008. During most of 2008, pumping water from Lake Alexandrina to Lake Albert has taken place to successfully maintain water levels (Figure 26).

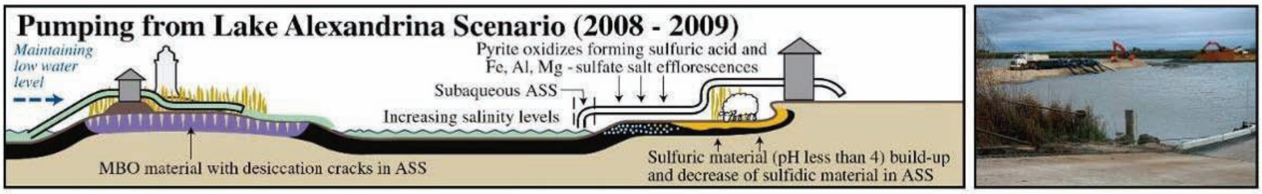


Figure 26. Generic conceptual model for Lake Albert showing: (i) the construction of an earthen bank between Lake Albert and Lake Alexandrina, which disconnects Lake Albert from Lake Alexandrina, before pumping commenced, (ii) previous formation of sulfuric materials on the edges of the lake and (iii) protection of sulfidic materials from oxidation due to partial water inundation.

Rapid drying of sulfidic material in the lower lakes region to slow the biological processes controlling the rate of acid formation will be difficult to achieve because of seiches (wind induced flow across the Lakes).

Finally, two field trials are being conducted north of Meningie (Figure 17) on the exposed dry-lake bed of Lake Albert using both fine agricultural lime to buffer the pH in sulfuric materials, and bioremediation. CSIRO Land and Water has conducted ASS soil testing to calculate lime requirements for these areas and have also developed protocols for sampling of ASS in the lower lakes and River Murray that may require dredging (e.g. water supply inlets or marina development). It is unknown how effective the bioremediation option is for ASS in this area.

Retaining existing acidity within the ASS landscape

Fitzpatrick *et al*. (2008d) described management options for wetlands adjacent to the River Murray between Lock 1 and Wellington, which included closing off selected wetlands with sluice gates to exclude or regulate water flow in wetlands from the main river channel to: (i) reduce evaporation losses and (ii) reduce the risk of saline, nutrient-laden and acidic-metal-rich water draining back into the river as river levels fall and/or rise.

The two scenarios presented are based on the availability of sufficient water for ASS management. Under the first scenario presented (upper panel, Figure 27), the river is maintained at before current drought levels in which the unmanaged wetlands and managed wetlands are once again sustained by sufficient water to maintain moderated flood and irrigation regimes. Under these conditions in the unmanaged wetland (upper panel, Figure 27), sulfuric material, MBO material and sulfate-rich salt efflorescences become diluted, mobilised, and once appropriate wetland/redox conditions resume, sulfidic materials reform, while metals bioaccumulate, or accumulate in the subaqueous soils. However, under this management scenario, there is little control of the distribution and eventual fate of sulfate, MBO and salts, the fates of which are controlled by natural – but moderated – river water flows and floods.

In order to address the fate of these materials on the river system, the second management scenario shown in the lower panel of Figure 27 involves the construction of sluice gates at the river inflows of the unmanaged wetlands. Management of these wetlands will involve carefully maintaining water levels by controlling in- and out-flows. Under this management scenario, sulfuric materials and metal salts will be contained in the wetland, thus allowing targeted and controlled management to occur to reinstate and maintain wetland quality. Such management options include bioremediation (such as organic mulching to help reform pyrite) and/or liming (to neutralise acidity). Clearly, however, such targeted management would not be possible on river banks, which would experience mobilisation of sulfuric materials (including MBO), although the volume of water in the river channel would provide considerable dilution to such materials.

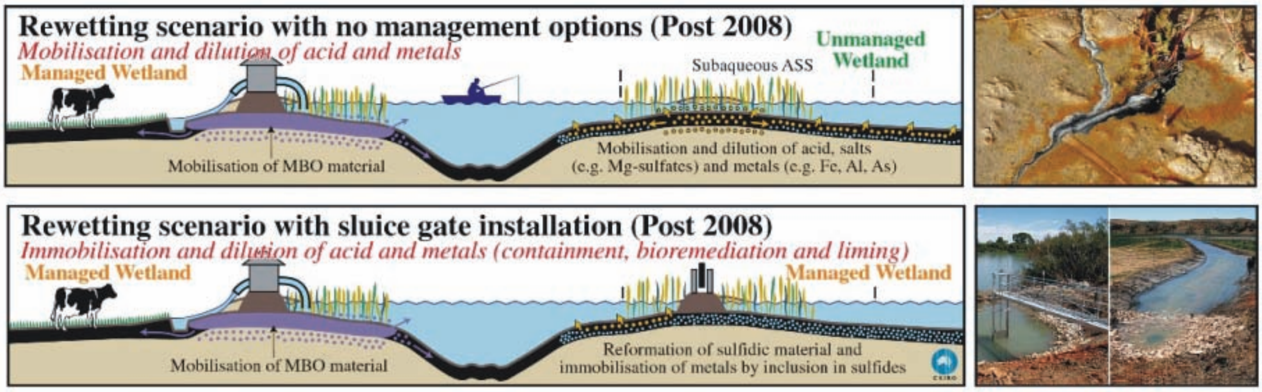


Figure 27. Generic conceptual model for lower-Murray River banks and wetlands; re-wetting management post-2008: no management scenario (upper panel) and management by sluice gate scenario (lower panel).

MINERAL FORMATION AND TRANSFORMATION: SULFIDES, OXYHYDROXYSULFATES, OXYHYDROXIDES AND SULFATE-RICH SALTS

This section provides a brief overview of the major Fe minerals, Al minerals and sulfate-rich rich salts occurring in earth surface environments where organisms are most likely to participate in mineral formation. Iron minerals, especially in the form of oxyhydroxides, hydroxides and oxides, are ubiquitous in almost all such environments, for example in soils, weathering zones, lakes, rivers and oceans (see Table 1 and Figure 2). In particular, Fe plays a fundamental role in many biological processes (e.g. Figure 1). Bacterial activity is frequently involved in both the degradation and formation of Fe sulfide phases, and indeed can be involved in all forms of secondary iron mineralisation from the transformation of Fe phases in ancient natural mineral sites to the mineralisation of iron in steel from modern times (e.g. corrosion). Depending on the specific environmental condition, the neoformed secondary Fe minerals (and Al minerals) are predominantly oxides, oxyhydroxides, sulfides, sulfates, carbonates and phosphates. Our discussions will concentrate mainly on the commonly occurring oxyhydroxides, hydroxides and oxide phases that occur in inland ASS; because of their common biological association (e.g. Schwertmann and Fitzpatrick 1992; Bigham *et al*. 1990, 1996, 2000, 2002). Table 1 lists the main minerals discussed, although it is by no means a comprehensive list of all the Fe phases that could be encounted.

During landuse changes and changes caused by extreme drought conditons, especially in the higher rainfall (> 600 mm per annum) Mediterranean soil environments of Australia where extreme changes in hydrology and geochemistry have occurred, many iron minerals form or transform relatively rapidly. The relative proportions of these secondary iron minerals that occur in soils depend critically on the soil solution chemistry conditions; in particular, Eh, pH and ionic concentrations. Colour, form, crystallite size and concentration of substituted cations in iron minerals can be used quantitatively as indicators of specific soil processes (e.g. Fitzpatrick 1988; Bigham *et al*. 2002).

Pyrite

Under conditions with decreasing redox potential (increasing effective "electron concentration") and decreasing pH the Fe^{2+} concentration in solution increases (Eqn 2). Once mobilized, the Fe^{2+} may be precipitated as secondary Fe^{2+}-containing minerals such as pyrite (Eqn 2 to 4) and other Fe^{2+} or mixed Fe^{2+}-Fe^{3+} sulfides (e.g. marcasite, greigite and mackinawite), siderite, vivianite and the so called green rusts (e.g. Schwertmann and Fitzpatrick 1992; Bigham *et al*. 2002). In their natural state, sulfidic materials are: (i) waterlogged, anaerobic materials that exist under reducing conditions at near-neutral pH with variable amounts of organic matter (e.g. up to 2.7 % organic C in the Herrmanns-Dairy Creek catchment in the Mount Lofty Ranges (Figure 28) and (ii) contain pyrite (typically framboidal; Figure 29; Fitzpatrick *et al*., 1996). They occur at the surface in wetlands or seeps, or are buried beneath alluvium (Figure 28). They consist of fine-grained quartz with variable amounts of pyrite, kaolinite/halloysite, albite, microcline, muscovite and monazite (Skwarnecki and Fitzpatrick 2003).

Figure 28. An exposure of black sulfidic material in buried acid sulfate soil in a bank section in Dairy Creek. The regolith sequence comprises relatively young sandy alluvium (with a thin soil horizon) overlying older relatively-clay-rich alluvium with thin gravel layers, which may contain fragments of bright yellow oxidised sulfidic materials containing sideronatrite and jarosite (pH <3.5). The sulfuric horizon overlies the black sulfidic materials and saprolite (derived from Tapanappa Formation lithologies). Note the white salt efflorescences (halite, gypsum) just above the water surface (from Skwarnecki and Fitzpatrick 2003).

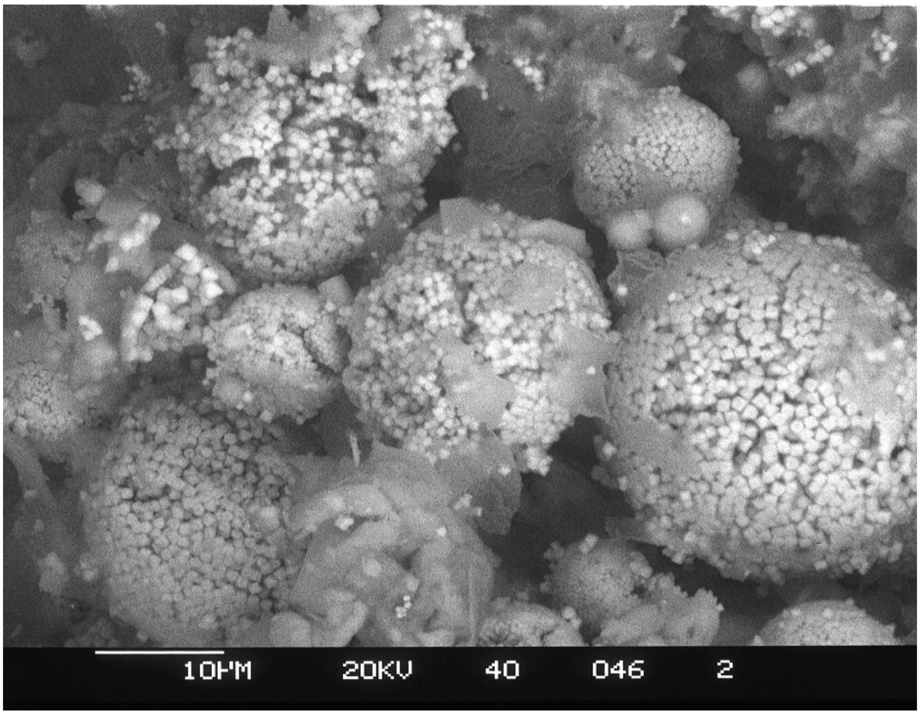


Figure 29. Back-scattered electron image (SEM) of sulfide framboids (spheroidal aggregates of pyrite crystals) in sulfidic material (i.e. pH 7-8) in the southern bank of Dairy Creek in the Mount Lofty Ranges shown in Figure 28 (from Skwarnecki and Fitzpatrick 2003).

Weathering of pyrite

The weathering of pyrite starts with exposure of pyrite to oxygen (in air) and water. Pyrite is usually stable if submerged in water under anaerobic conditions. In general, it is the exposure of fine grained pyritic framboids (Figure 29) to repeated wetting/drying cycles and the action of bacteria present at the soil surface that generates sulfuric acid. Some of the generalized chemical reactions used to describe the cycle of pyrite oxidation are described in Eqn 5. The complex details of the oxidation process are described by Fanning and Fanning (1989) and Fanning (2002). When sulfidic materials contain sulfides and low contents of neutralizing minerals (e.g. calcite) and are exposed to air by drainage or excavation, they become strongly acidic (pH <4) and are called sulfuric materials. Hence, the source of acid sulfate conditions is pyrite, which when oxidised generates sulfuric acid, thereby decreasing the pH to less than 4 therefore, unless the acid generated by these reactions is counteracted by a neutralizing agent, a serious acid-drainage problem may develop.

Jarosite group

Sulfuric materials generally have bright yellow or straw-coloured mottles of jarosite/natrojarosite (see Figures 30 to 32) and sideronatrite (Figures 34 to 41). In rare instances, e.g. associated with Pb-bearing mineral deposits, minerals such as plumbojarosite (Figure 33) and plumbogummite (Figure 32 and 33) may occur where they overlie mineralized zones in bedrock (e.g Skwarnecki and Fitzpatrick 2003). One occurrence of plumbojarosite was noted in the Dairy Creek gossan, where it is associated with cerussite and partially replaced by plumbogummite (Skwarnecki and Fitzpatrick 2003).

The chemical composition of jarosite group minerals is somewhat variable, even in the same sample, with varying proportions of Na and K. Lead is a significant component of some jarosites, with some compositions trending towards plumbojarosite. In general terms, jarosite appears to be dominant in most coastal ASS and natrojarosite is more dominant in inland ASS. Plumbojarosite appears to be relatively abundant in surface gossan exposures. Jarosite occurs disseminated in gossan and saprolite, as an weathering product of pyrite, and may occur associated with boxworks after pyrite (Figure 31) associated with plumbogummite. Less commonly, jarosite pseudomorphs after pyrite occur (Figure 32).

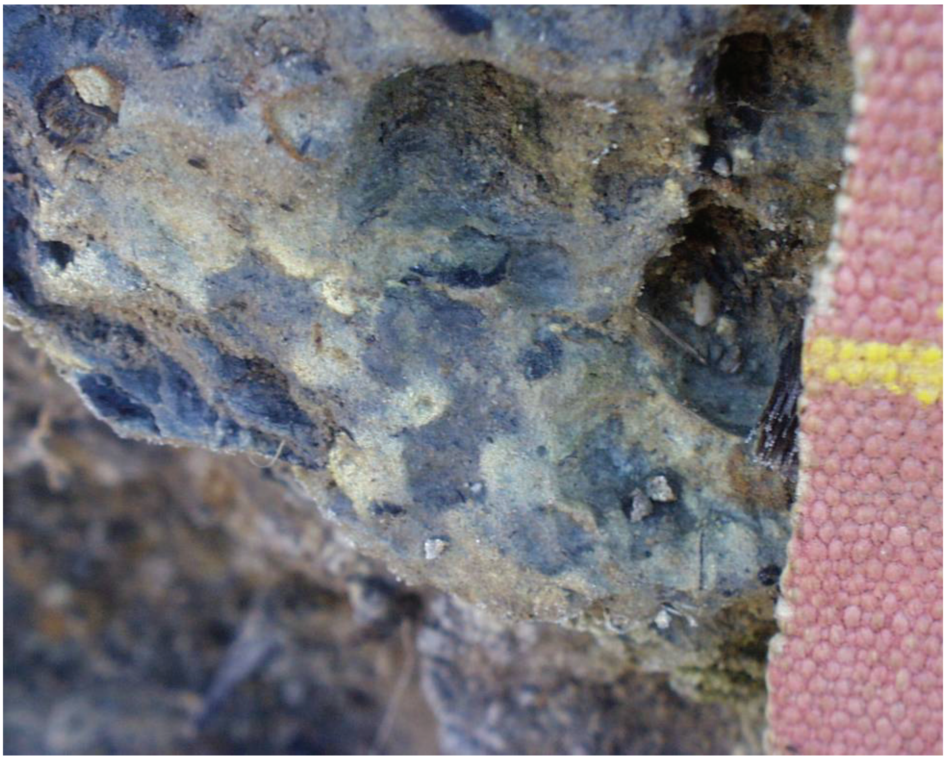


Figure 30. Pale yellow jarosite mottling (developed from the weathering of pyrite) in sulfuric material overlying sulfidic material, Dairy Creek. Profile N27 (see Figure 28). (from Skwarnecki and Fitzpatrick 2003)

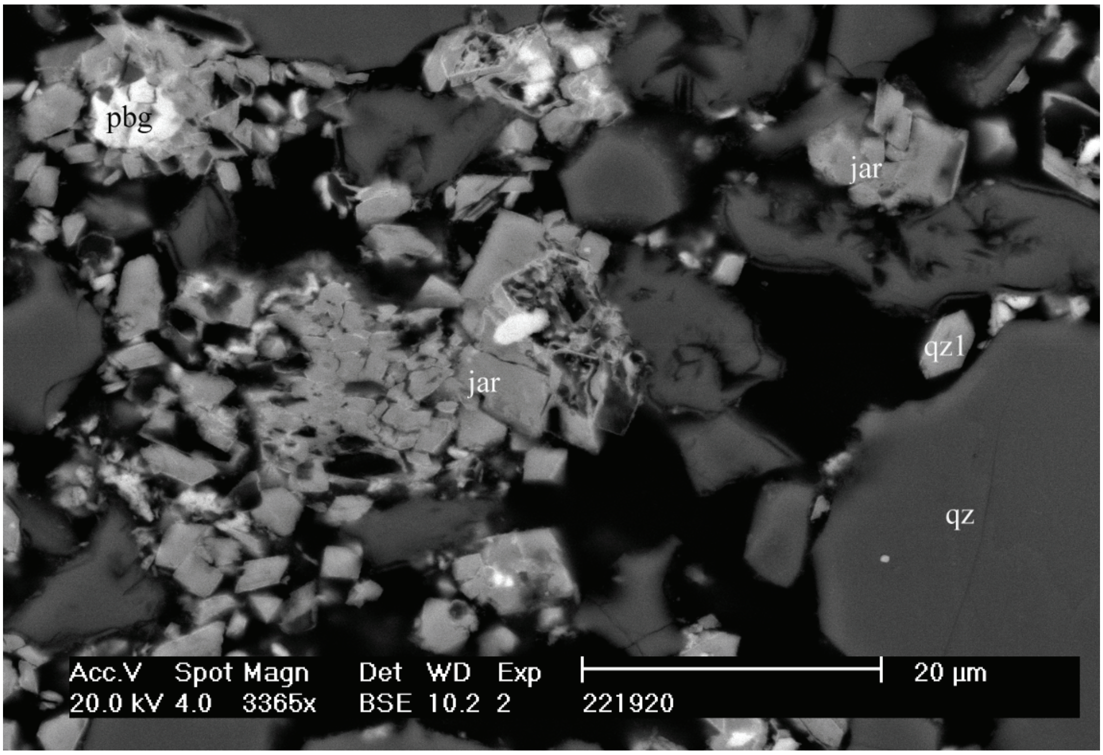


Figure 31. Jarosite (jar) grains associated with boxworks after pyrite and plumbogummite (pbg) and quartz grains (qz). The euhedral quartz grain (qz1) is coated by jarosite. Sample 221920, MTG4, 9.40 m depth. Back-scattered electron image (SEM). (from Skwarnecki and Fitzpatrick 2003)

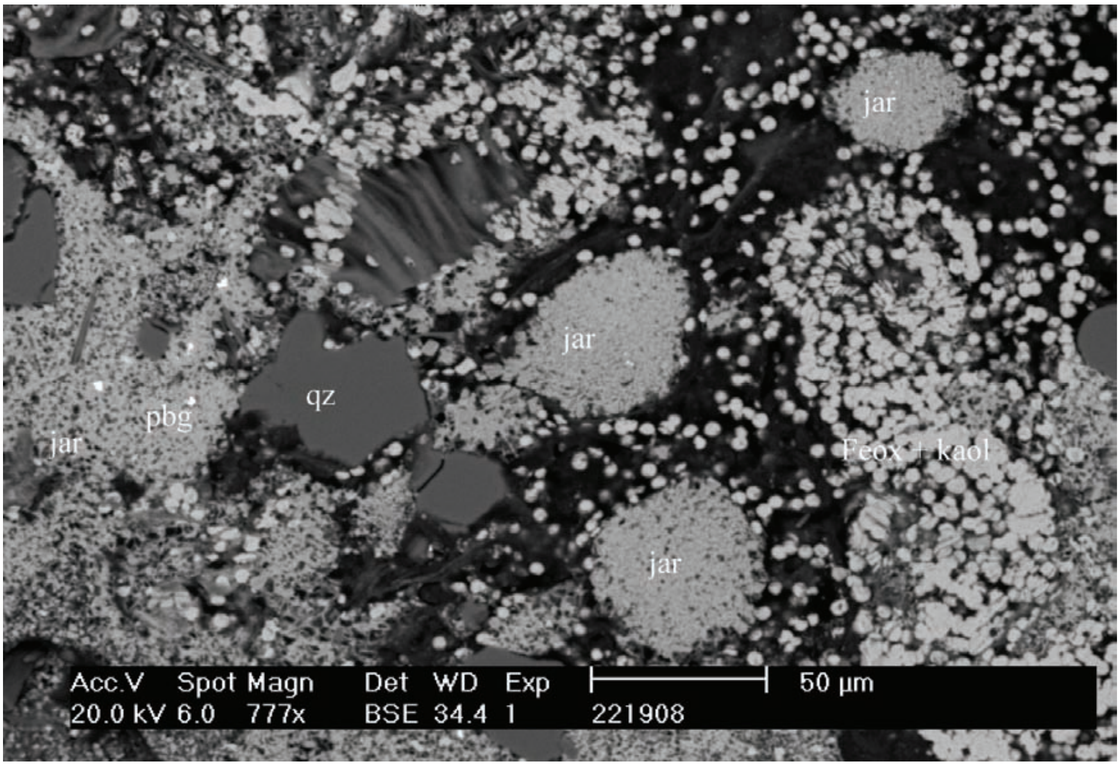


Figure 32. Jarosite (jar) pseudomorphs after pyrite framboids, associated with fine-grained disseminated plumbogummite (pbg), Fe oxides (Feox), kaolinite/halloysite (kaol), quartz (qz) and weathered biotite. Sample 221908, MTG3, 6.40 m depth. Back-scattered electron image (SEM). (from Skwarnecki and Fitzpatrick 2003)

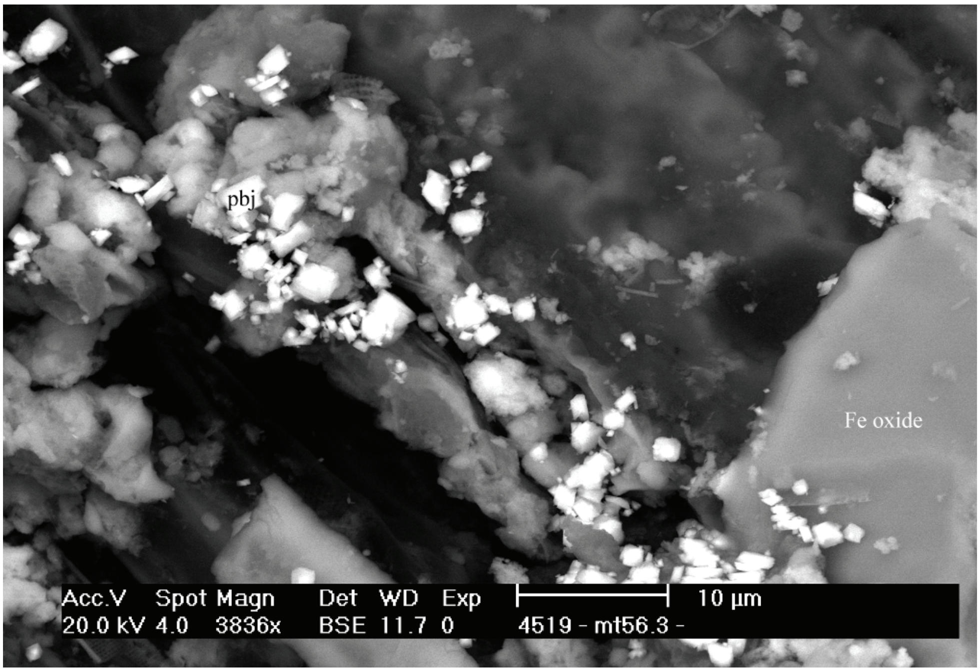


Figure 33. Plumbojarosite (pbj) crystals associated with Fe oxides in partially oxidised sulfidic material (sulfuric horizon), Herrmanns Creek. Sample MT056.3. Back-scattered electron image (SEM). (from Skwarnecki and Fitzpatrick 2003)

Figure 34. Acid Sulfate Soil in the clayey dry river-bed of the Finniss River, showing a soil pit with black sulfidic material (iron sulfides) at depth (> 60 cm) overlying sulfuric material. Light yellow or straw coloured mottles comprising mainly natrojarosite immediately overlies the sulfidic material between a depth of 30 to 60 cm, which in turn overlies a cracked surface layer (0 to 30 cm) with a pH ranging between 3 to 3.6 comprising mainly the bright orange mineral, schwertmannite. Pale yellow mottles (right hand side) can be seen surrounding old *Phragmites* root channels in a dark grey matrix. (from Fitzpatrick et al. 2009).

Iron - and Aluminium -rich surface precipitates

Most metals that behave as cations are generally more mobile at low pH (e.g. Nordstrom and Alpers, 1999; Bigham *et al*. 1990, 1996, 2000, 2002). If metals such as zinc and copper are available, they will tend to remain in solution as dissolved species at low pH. In sulfuric materials, the products of the chemical reactions that form pyrite and other sulfide minerals can: (i) remain as dissolved constituents of pore waters, (ii) form a range of secondary minerals in the form of salt efflorescences comprising sulfate-rich salts due to evaporation, (iii) undergo a series of hydrolysis reactions and precipitate new minerals such as iron oxyhydroxides and iron oxyhydroxysulfates (Table 1), and (iv) propagate pedogenic weathering cycles.

Because ferrous iron and sulfate are present as aqueous species (aq) as products of pyrite weathering, according to Nordstrom and Alpers (1999), melanterite commonly forms first as the solutions evaporate. Oxidation of ferrous to ferric iron can also lead to formation of mixed valence salts like copiapite. Other dissolved species can be incorporated in salts as major or trace constituents.

For example, the formation of solid halotrichite from aqueous species can be described by the reaction:

$$Fe^{2+}(aq) + 4\ SO_4^{2-}\ (aq) + 2Al^{3+}(aq) + 22\ H_2O \rightarrow FeAl_2(SO_4)_4 \bullet 22\ H_2O(s)$$

Melanterite, rozenite, copiapite, halotrichite with hexahydrite and epsomite are all soluble in water; once formed, they only persist if conditions remain relatively dry or if they are protected in some way (e.g. under jetties). Hence, they may or may not be present at a given site on a given day depending on weather conditions. Consequenly, these salts are important to recognize because they store acidity and metals that can subsequently generate extremely poor water quality. Several studies have shown that dissolution of salt accumulations along stream banks during a rainstorm temporarily lowers pH and increases metal loads in streams (e.g. Bigham *et al.* 1994). Such water-quality impacts can have damaging effects on aquatic ecosystems e.g., causing fish kills, and can complicate efforts to remediate acid drainage. Storm flooding can also flush salts leading to pulses of contaminated water flowing into streams.

Goethite and schwertmannite

Oxidation of ferrous iron (shown above) and subsequent hydrolysis can lead to the formation of goethite (Table 1) and additional acid:

$$Fe^{3+}\ (aq) + 2H_2O \rightarrow FeOOH + 3H^+$$

Goethite (α-FeOOH) is the most stable ferric oxide mineral commonly found in surficial deposits (e.g. Bigham *et al.* 1990, 1996, 2000, 2002). Goethite is the most common of the soil iron minerals (see Table 1; Figure 2); and is the first conversion product from ferrihydrite (Bigham *et al.* 2002). It is a yellow-brown mineral, forming as needle-shaped crystals about 1 µm long in synthetic preparations, but typically more equant in soils. Together with ferrihydrite, goethite imparts most of the brown colour to soils. The surface area of soil goethite ranges from 6-200 m^2/g, which can give goethite considerable adsorptive ability. Heavy metals such as Cu, Pb, and Zn are adsorbed to the extent of about 1µmol/m^2 (20µmol/g). Aluminium occurs in goethites substituting for Fe, up to 32 mole% from a wide range of weathering environment (Fitzpatrick and Schwertmann 1982). In soils, goethite is often present in hydromorphic environments, forming mottles and concretions, and ferricretes tend to have lower Al substitution (0-15 mole%), whereas freely drained regolith such as saprolites and bauxites have Al substitution ranging from 15-32 mole% (Figure 2; Fitzpatrick, 1988). Fitzpatrick and Schwertmann (1982) explain the difference as resulting from lower pH and therefore higher Al activity in the more freely drained regolith. Al substitution is readily estimated from the X-ray diffraction pattern of goethite; substitution of Al reduces the unit cell dimensions as well as reducing the mean crystalline dimension (shown by broader XRD peaks). Consequenly, future work is required on inland ASS to determine the range of Al substitution in goethites.

A wide variety of other ferric iron oxyhydroxide minerals, such as ferrihydrite, or iron hydroxysulfate minerals, such as schwertmannite, may form as precursors to goethite depending on the local chemical environment (e.g. Schwertmann and Fitzpatrick 1992; Bigham *et al.* 2002). These minerals often appear as reddish-brown rusty (e.g. ferrihydrite) or reddish-orange (schwertmannite) spots around pyrite or as crusts on completely weathered pyritic soil surfaces (e.g. Figures 35, 36, 38 and 39) in soils developing on weathering pyritic rock, and as muds that precipitate in puddles and streams affected by acid-rock drainage.

Schwertmannite is a poorly crystalline iron oxyhydroxysulfate mineral, with a variable chemical formula, $Fe_8O_8(OH)_822x(SO_4)x\ z\ nH_2O$ ($1 < x < 1.75$) or $Fe_8O_8(OH)_6SO_4$ that is a component of the orange-yellowish precipitates originally identified in many acid mine drainage waters (Bigham *et al*. 1990, 1996, 2000). However, schwertmannite was first sampled and identified in inland ASS in the Mount Lofty Ranges, South Australia in 1990 (see Figure 35(a) (b); Fitzpatrick *et al*. 1992; 1993; 1996; Fitzptrick and Self 1997).

Often, degraded agricultural areas in this region are conspicuous by the presence of ephemeral to semi-permanent saline seepages with surface accumulations of Fe oxyhydroxides and salts that overlie strongly reduced subsoil horizons containing pyrite formed by bacterial sulfate reduction. These soils are degraded by rising sulfate containing ground waters that percolate through rocks or sediments containing primary pyrite and stored salts. During wet winters, ferrihydrite, containing high levels of scavenged cations (e.g. As and Si) is the dominant Fe oxyhydroxide formed (Figure 35a). In summer, the seasonal changes in soil redox conditions strongly modify the geochemistry of the soil solution causing ferrihydrite to transform to goethite and schwertmannite in the presence of excess sulfate and chloride, usually in the form of cemented crusts (see Figure 35b). Schwertmannite is indicative of a weathering environment with soil solutions having a pH in the range 3 to 4 and sulfate concentrations between 1000 and 3000 µg/mL (Fitzpatrick *et al.* 1996).

Sideronatrite and Tamarugite

Mount Lofty Ranges region

The exposure of sulfidic material in stream banks caused by water erosion (Figure 36) may result in the exposure of the pyrite in previously buried swamp deposits and rapid weathering of pyrite. Exposure of fresh pyrite surfaces to air and water initiates a series of chemical and microbial reactions that form sulfuric acid. The sulfuric acid can dissolve a variety of layer silicate minerals in the newly exposed soil profile in the stream bank, mobilizing aluminium and trace metals. In addition to pyrite, the underlying rocks in this region contain sphalerite and traces of galena and other minerals that contain zinc, lead and arsenic (Figure 36). These elements are often concentrated in white and reddish seeps and puddles at the base of the eroded streamline (adjacent to Dairy Creek) and greatly exceed criteria for protection of fresh-water aquatic organisms. In addition, the seeps and soil leachate contain elevated concentrations of dissolved iron, aluminium, and sulfate. Soluble sulfate minerals (sideronatirite and tamarugite) crystallize on the bank face immobilizing the metals when these waters evaporate. However, during rain events, these minerals readily dissolve releasing the stored acidity and metals to runoff and infiltrating stream water. The cycle of salt formation and dissolution contributes to acid-drainage from the site as long as sulfidic material remains exposed to air but is also kept moist.

The acid leachate from sulfuric materials shown in Figure 36 dissolves clay minerals and oxidises Fe sulfides to produce hydrated white and red-brown precipitates via biogeochemical reactions (Fitzpatrick *et al*. 1992) depending upon pH (Figure 36 and 37). The white precipitate in Figure 36 is composed dominantly of Al_2O_3 (42 %), SiO_2 (8.28 %), SO_3 (7.16 %), As (<5 ppm) and Na_2O (1.07 %). Transmission electron analyses (TEM) and XRD suggest that it is an amorphous hydrated aluminium oxyhydroxide (with some evidence for pseudoboehmite-like characteristics). The red-brown precipitates (ferrihydrite, goethite and schwertmannite) are rich in Fe (35.6 %), Mn (0.5 %) and As (135 ppm). It appears that As is preferentially scavenged by iron oxides.

(a)

(b)

Figure 35. Photographs of the Gutheries site near Mt Torrens in the Mt. Lofty Ranges in South Australia in:
(a) July 1990 when the perched and ground water table levels were relatively high with a gelatinous reddish-brown precipitate layer, which overlies black sulfidic material (see Fitzpatrick 1991) – Drs Peter Self (left) and Rob Fitzpatrick (right). The site was also sampled in January 1991 when the perched and ground water table levels were relatively low leaving an essentially moist to almost dry surface with a thin friable reddish/orange-brown crust (2 to 5 mm) that is weakly cemented. The reddish-brown gelatinous precipitates contained ferrihydrite with minor amounts of goethite. The reddish/orange-brown thin friable crusts contained schwertmannite and goethite (Fitzpatrick *et al*. 1992; Fitzpatrick *et al*. 1996; Fitzpatrick and Self 1997).
(b) August 1993 showing Professor Udo Schwertmann (right – after whom the mineral schwertmannite is named) and Dr Rob Fitzpatrick (left) both pointing to the thin friable crust where schwertmannite was first identified in a natural soil (i.e. Alfic Sodic Sulfaquent).

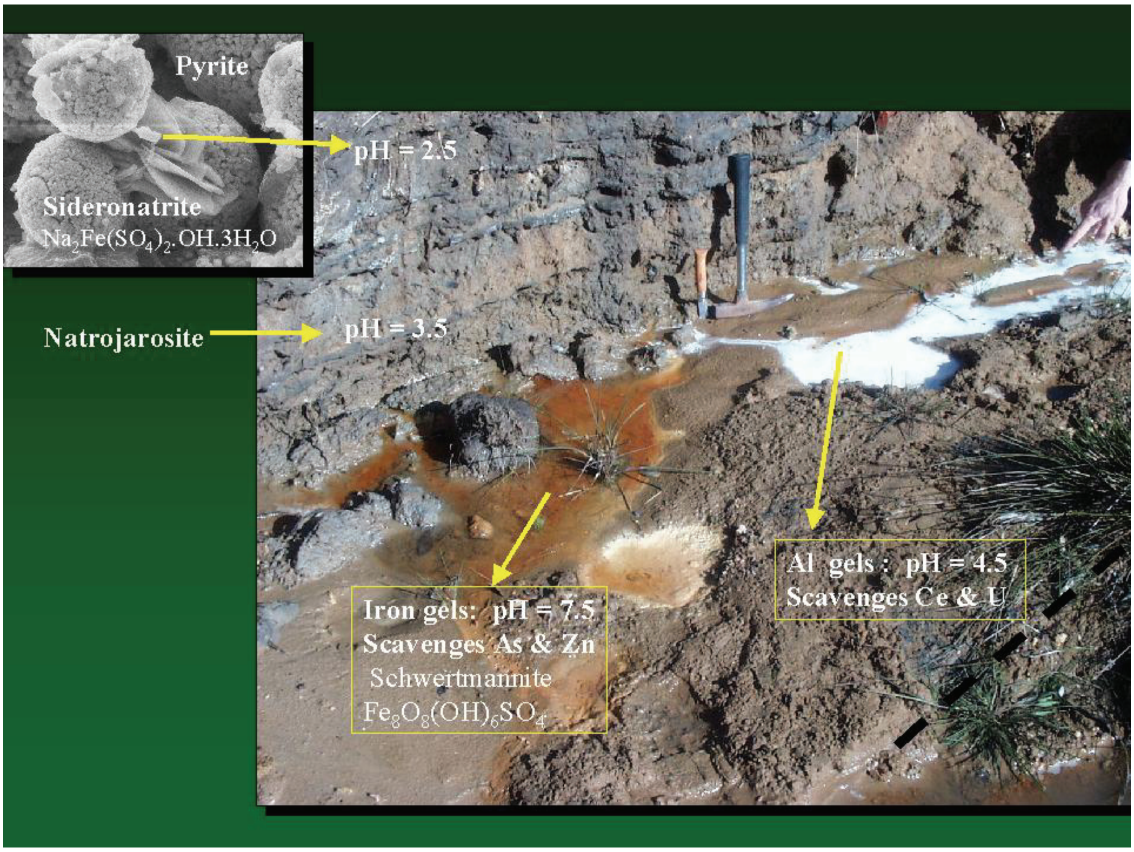


Figure 36 A highly saline acid sulfate soil with sulfuric material (pH 2.5-3.5) exposed in the stream bank by recent water erosion in the upper catchment of Dairy Creek. Sulfidic material (pH 7-8) occurs in the waterloggeed zone below the exposed sulfuric material. The white precipitate is Al-rich and preferentially forms in sandy layers (pH 4.5), whereas the red-brown precipitates are Fe-rich and preferentially form in clay-rich materials (pH 7.5). The inset shows a SEM image of large platelets of sideronatrite ($Na_2Fe(SO_4)_2.OH.H_2O$) derived from the oxidation and dissolution of the adjacent pyrite framboids in an acid sulfate soil (See Fitzpatrick *et al.* 2000b). Adjacent to profile N27 (see from Skwarnecki and Fitzpatrick 2003).

Figure 37. A highly saline sulfuric material (pH 2.5-3.5) exposed along upper Dairy Creek, showing green crystals of sideronatrite ($Na_2Fe(SO_4)_2.OH.H_2O$) formed in sandy layers and derived from the oxidation and dissolution of the pyrite framboids. Profile N25 (see Figure 28).

Lower lakes region of the River Murray

The widespread occurrences of bright yellowish-green, 2 to 5 mm thick, sandy friable crusts can be observed at a range of scales in Figures 38 and 39. These contain mainly precipitates of the mineral sideronatrite (Table 1), which occur as rosettes and platelets (see Figure 40) within sulfuric material (< pH 2.5) on the soil surface. Sideronatrite is derived from the oxidation and dissolution of pyrite framboids, which occur mainly in the form of spheroidal aggregates of pyrite crystals (Figure 40). Sideronatrite in the yellowish-green crusts dissolves and re-precipitates as schwertmannite (Figure 31) in immediately adjacent zones where the pH is slightly higher, to display distinct orange patches or areas on the soil surface and orange mottles to a depth of 2 to 10 cm (Figures 38 and 39). This process occurs during winter rainfall cyclic wetting and drying events, which causes water to dissolve sideronatrite and transport ferrous Fe and sulfate ions to adjacent “micro-ponds” where schwertmannite rapidly crystallises. We have been able to simulate this process in the laboratory by adding rain water to samples of the yellowish-green sideronatrite-rich crusts and synthetic sideronatrite prepared our laboratory. A remarkably similar dissolution and precipitation mechanism was previously observed by Fitzpatrick *et al*. (2000b). These workers were the first to identify the formation of sideronatrite from oxidation of sulfide framboids in sandy sulfuric materials in the Mount Lofty Ranges (see Figures 36 and 37). They also observed dissolution of sideronatrite (and tamarugite) in sulfuric materials on eroded stream banks and the subsequent formation of schwertmannite in immediately adjacent stream waters (Figure 36). The formation of these minerals is indicative of rapidly changing local geochemical environments and variations in pH and rates of Fe, S and Na mineralisation.

The data we have gained indicates that these salts are seasonal or wet/dry period pedogenic products and result from the evaporation of saline sulfatic soil water produced from the oxidation of sulfidic material at depth (i.e. sulfidic subaqueous clayey or organic soil).

The significance of the minerals found in these salt efflorescences is that they appear each summer, or in dry periods, and are environmental indicators. A change in the minerals present may also indicate a change in the nature of the salts entering the system from surface or ground waters. Hence, more monitoring work should be undertaken to confirm seasonal/wet-dry period changes in mineralogical composition.

Figure 38. ASS surface within sulfuric material in the dry lake-bed of Lake Alexandrina near Point Sturt. Upper left and right images show surface crusts comprising the following various coloured salt efflorescences: (i) white coloured fluffy efflorescences on slightly elevated surfaces (A), (ii) adjacent bright yellowish-green colours on slightly lower surfaces (B), and (iii) orange patches occurring on the edges of the elevated surfaces (C) and (iv) grey sand (D). Bottom: Light microscope compiled image (field width = 2 mm) of the yellowish-green area (B) in the AA 29 profile showing: (i) whitish, elongated, acicular crystals (50 to 100 µm) of pickeringite-halotrichite (XRD evidence) and redingtonite (XRD + SEM/EDX data), (ii) yellowish coatings of sideronatrite and copiapite-botryogen (XRD and SEM/EDX) (B) and (iii) rounded quartz grains (D) (modified from Fitzpatrick *et al*. 2008c).

Figure 39. Aerial photograph (above) showing of the exposed sandy dry lake-bed of Lake Alexandrina acid sulfate soil near Poltalloch Station, Narrung area, showing a soil pit (lower left) with black sulfidic material (iron sulfides) overlying sulfuric material with distinct yellow patches comprising mainly the bright yellow mineral, sideronatrite, with a pH ranging between 1.3 to 1.6. (from Fitzpatrick *et al.* 2008f)

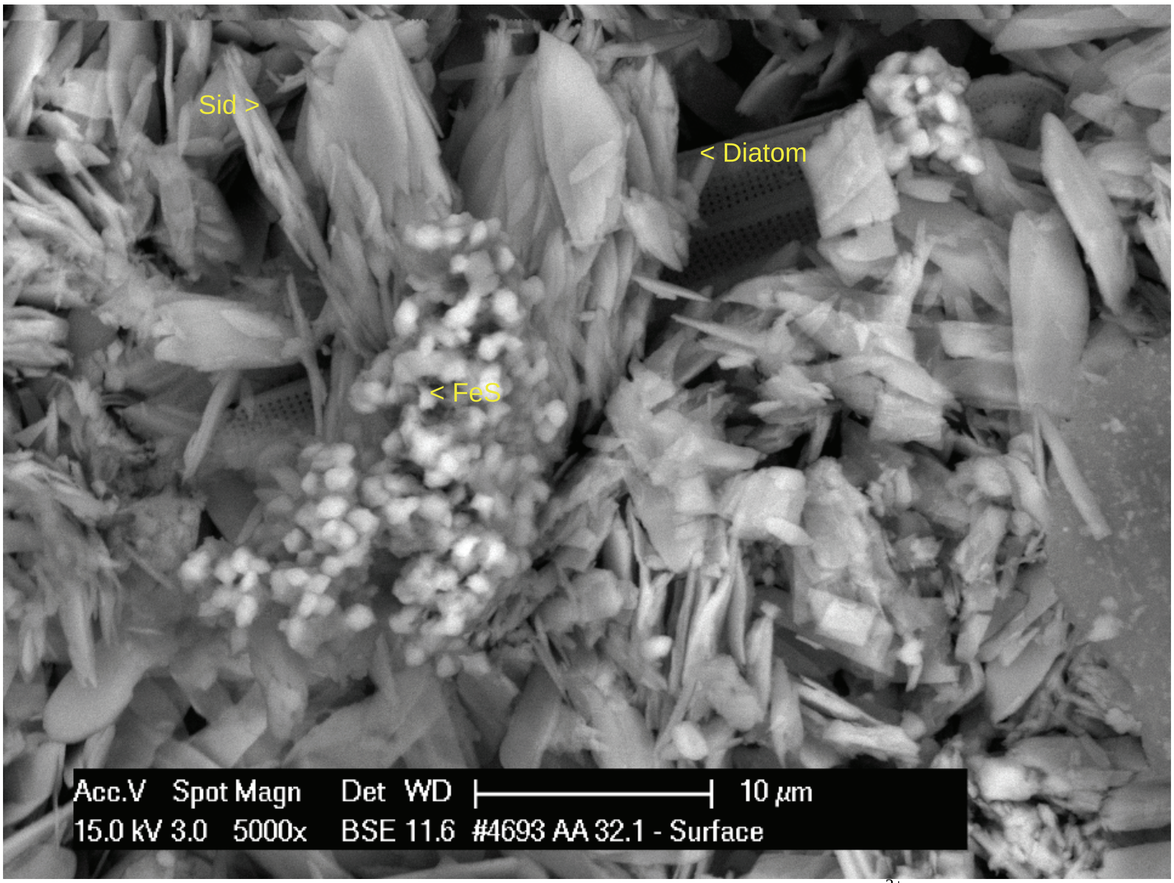


Figure 40. Scanning electron micrograph, of bladed sideronatrite (Sid) crystals ($Na_2Fe^{3+}(SO_4)_2(OH)\cdot 3H_2O$), weathered iron sulfide (FeS), and diatom. The image was taken in the backscattered electron imaging mode, using a Phillips XL30 SEM, at a magnification of x 5k (from Fitzpatrick *et al.* 2008f)

Metavoltine and alunogen

The salt efflorescence or evaporite deposits sampled in sulfuric materials at Swanport and Ukee proved to be an assemblage of sulfate-containing minerals (as detected by X-ray diffraction and by scanning electron microscopy; Fizpatrick *et al.* 2008d). Movement and accumulation of such soluble salts is typical of drained soils under extremely acidic conditions (i.e. pH <3.5). In surface samples at Swanport and Ukee wetlands, these salt efflorescences consist of salts with a yellowish brown (golden) mineral called metavoltine ($Na_6K_2FeFe_6(SO_4)_{12}O_2.18H_2O$), which forms botryoidal encrustations on the edges of cracks (Figure 41) forming as an alteration product of weathered pyrite in the sulfidic material. This mineral was first identified in the Swanport wetland and documents the first occurrence of metavoltine in Australia and possibly the first ever occurrence associated with Acid Sulfate Soils. White crystals of alunogen ($Al_2(SO_4)_3$ $17H_2O$) were identified and also formed as a result of aqueous, acidic (pH < 2.5), sulfate bearing solutions that have percolated through the soil and reacted with layer silicates in the soils. These localised solutions were rich in ferrous and ferric iron and also contained dissolved potassium and *sodium. Metavoltine and alunogen are presumed to be the last minerals to form in areas of intense evaporation. The sulfuric material, which also contains natrojarosite, hexahydrite and gypsum developed after drainage as watertable levels dropped below 40 cm in June 2007 and below 90 cm in November 2007.

Figure 41 Photograph of Swanport wetland showing: Acid Sulfate Soil with sulfuric material in drained wetlands adjacent to the River Murray (left), which shows extensive cracking and accumulation of scale-like, bright golden yellow crystals of metavoltine ($K_2Na_6Fe^{2+}Fe^{3+}_6$ $(SO_4)_{12}O_2$ $18H_2O$) and white crystals of alunogen ($Al_2(SO_4)_3$ $17H_2O$), which have formed as a result of aqueous, acidic ($pH < 2.5$), sulfate bearing solutions that have percolated through the soil and attacked layer silicates. These localised solutions were rich in ferrous and ferric iron and also contained leached potassium and sodium. Metavoltine and alunogen are presumed to be the latest minerals to form. The sulfuric material, which also contains natrojarosite, hexahydrite and gypsum developed after drainage when watertable levels had dropped below 40 cm in June 2007 and below 90 cm in November 2007, due to the severe drought conditions, exposing large sections of riverbank and wetlands that once contained high levels of un-oxidized iron sulfide (pyrite). Sulfidic material ($pH>4$), which contains un-oxidized pyrite, occurs below the water table. (From Fitzpatrick *et al.* 2008a).

Ferrihydrite

Ferrihydrite has an approximate composition $5Fe_2O_3.9H_2O$. Ferrihydrite is the brown rusty scum or 'oil slick' visible on the surface water overlying most wetlands or swamps with subaqueous and waterlogged ASS (Figure 35a). Ferrihydrite is commonly found in such surface environments where waters are rich in Fe^{2+} are exposed to rapid oxidation in the presence of compounds such as organic matter that block crystal growth (Bigham *et al.* 2002). Thus, it may be expected to occur in ASS formed in zones where groundwaters and surface waters fluctuate seasonally. Ferrihydrite is metastable under most conditions and is often associated with goethite or lepidocrocite (Table 1).

Most ferrihydrite is associated with bacteria (*Gallionella* and *Lepthotrix*), which gain their energy from the oxidation reaction $Fe^{2+} \rightarrow Fe^{3+} + e^-$. Ferrihydrite also precipitates from ferric iron solution as pH increases. Ferric iron is soluble at pH 2, becoming less so with increasing pH. However, at pH 4 it is much less soluble (about 1 in 10 million). Very acid pore waters in sulfuric materials can hold appreciable ferric iron in solution, which precipitates as ferrihydrite as the pH increases, e.g. during input of alkaline water. Soils derived from the oxidation of pyrite-rich sulfidic materials are commonly acid enough to mobilize iron, from whence it may rise to the surface and precipitate through dilution or oxidation. Ferrihydrite crystals range from about 2 nm in diameter to 7.5 nm. The degree of organization of these particles is low, and the X-ray pattern is usually weak with broad lines. Much ferrihydrite in inland ASS is not detected because it does not yield a marked diffraction pattern. The surface area of ferrihydrite crystals ranges from 200-800 m^2/g. Ferrihydrite is a strong adsorber of phosphate, silica, organic molecules and heavy metals. In the laboratory, ferrihydrite transforms to a more stable oxide-hydroxide (usually goethite) over a period of a few years. In the soil, it probably passes in and out of solution seasonally. Ferrihydrite is of the order of 100 times more soluble in normal ground water than the other Fe oxides or oxyhydroxides (Table 1).

Sulfate-rich salt efflorescences

Fitzpatrick *et al.* (2008c,d) have identified a wide range of highly soluble whitish coloured sulfate-containing evaporite minerals (e.g. pickeringite-halotrichite, redingtonite, hexahydrite and epsomite) that crystallise in micron thick layers on the exposed sandy soil surfaces of sulfuric materials of lake Alexandrina (Figure 38) and lake Albert during the winter rainfall cyclic wetting and drying events.

Soil-surface salt accumulations are unique in the region, which results from a combination of the characteristic Mediterranean type climate, hydrogeology, saline seepages, and salt crusting formed above sulfidic materials. The salt efflorescences are dominated by a large number of soluble minerals, including halite (NaCl), gypsum ($CaSO_4.2H_2O$), thenardite (Na_2SO_4), hexahydrite and epsomite, and range in morphology from thin, powdery, very transient efflorescences to thicker, more persistent, soil-cementing crusts. The salt crusts form by the upward wicking of Na, Mg-, Cl and SO_4 containing groundwaters and their subsequent surface evaporation. As such, these accumulated salt minerals are indicators of soil-water sub-surface processes operating in these landscapes (Fitzpatrick *et al.* 1996; Fritsch and Fitzpatrick 1994).

Carbonates

In this region of Australia, rising saline groundwaters, and the acidification of soils, accelerates both the formation and the dissolution of carbonates. Mg-substituted calcite forms from the accelerated weathering of rocks caused by rising acidified groundwaters (containing high levels of Ca and Mg). This process represents a sink of CO_2 from the atmosphere. In contrast, carbonate is dissolved in soils occurring immediately adjacent to acid sulfate soils and from soil acidification caused by intensification of agriculture in the absence of liming (acids produced in the nitrogen and carbon cycles of dryland agricultural systems). This represents a net gain of atmospheric CO_2 (Fitzpatrick and Merry 1999).

PICTORIAL MANUALS FOR LAND MANAGEMENT PLANNING

A sequence of steps used to develop easy-to-follow pictorial manuals for identifying soil indicators, land use options and best management practices are shown in Figure 42. Steps 1-5 describe soil layers and construct them in toposequences (descriptive, explanatory or predictive models), which have been used to help map soil types in areas with variable geochemistry (Fitzpatrick *et al*. 2003b).

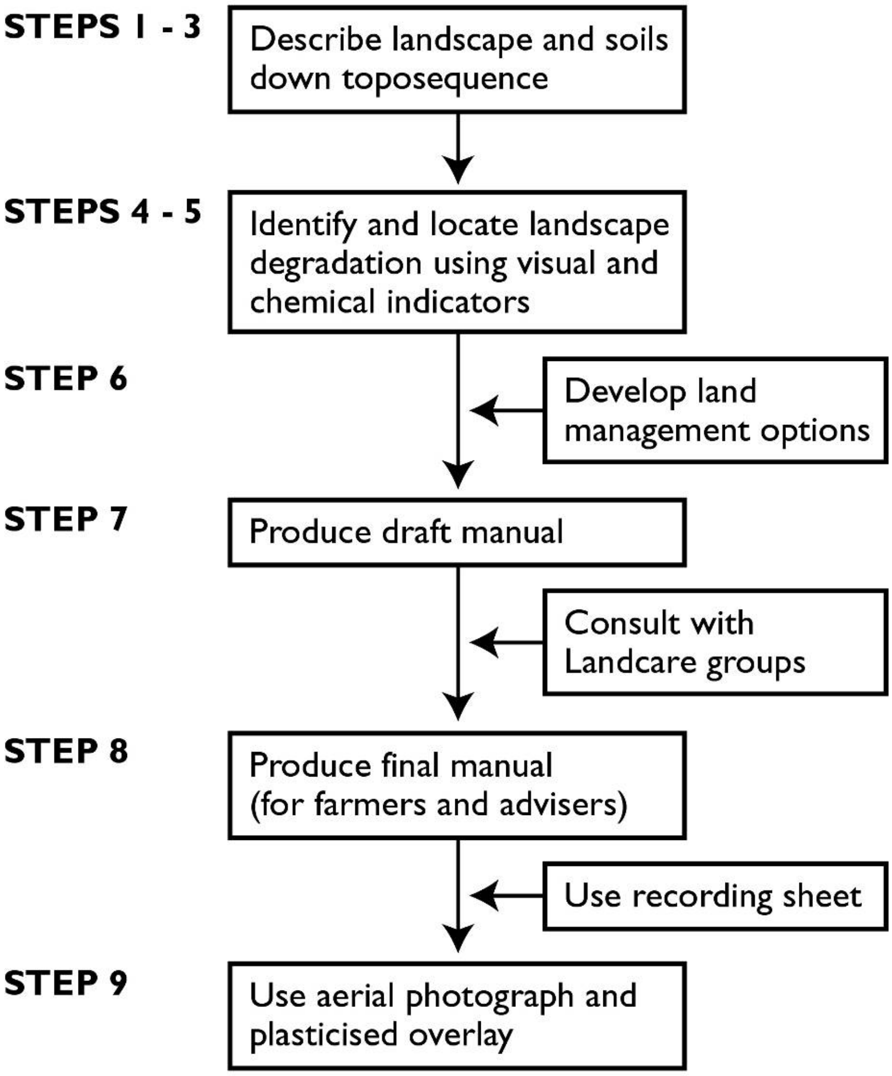


Figure 42. Flow diagram showing steps involved in developing manuals for land management (after Fitzpatrick *et al*. 2003b).

Steps 6-9 involve the participation of local communities in developing the manual by integration and adoption, where knowledge of the hydrological and soil-regolith processes models (bottom half of Figure 43) and production systems are bought together in recommendations for appropriate best management practices (top half of Figure 43). Several case studies from geochemically variable inland Acid Sulfate Soil environments are listed in Table 4. For example, in the Mount Lofty Ranges in South Australia (Fitzpatrick *et al*. 1997; 2003b) and Woorndoo region in Victoria (Figure 43; Fitzpatrick *et al*. 1997; 2003b; Cox *et al*. 1999) fencing protected saline-sulfidic wetlands from physical disturbance (e.g. pugging by cattle) and has:

- Allowed rapid recovery of wetland vegetation
- Prevented physical erosion of the A horizon
- Facilitated the reestablishment of more reducing soil conditions in the A horizon
- Decreased the amount of pyrite oxidation
- Allowed a return to neutral pH (pH = 6.5 to 7)

SOIL TYPE No.	❺	❼
SUMMARY OF MAJOR MANAGEMENT OPTIONS	● Fence off ● Plant salt tolerant grasses ● Exclude stock throughout winter ● Salt tolerant trees ● Consider subsurface drains	● Fence off ● Plant salt tolerant grasses ● Exclude stock throughout winter ● Stabilise bare eroded areas with salt tolerant trees, shrubs and native grasses ● Add lime to areas that are strongly sulfidic to prevent acid conditions ● Do not drain strongly sulfidic areas
SOIL & WATER PROBLEMS	Strongly waterlogged saline and sodic	Strongly waterlogged and saline sulfidic
SOIL DESCRIPTION	Poorly drained grey saline and sodic soil	Very poorly drained black saline sulfidic soil

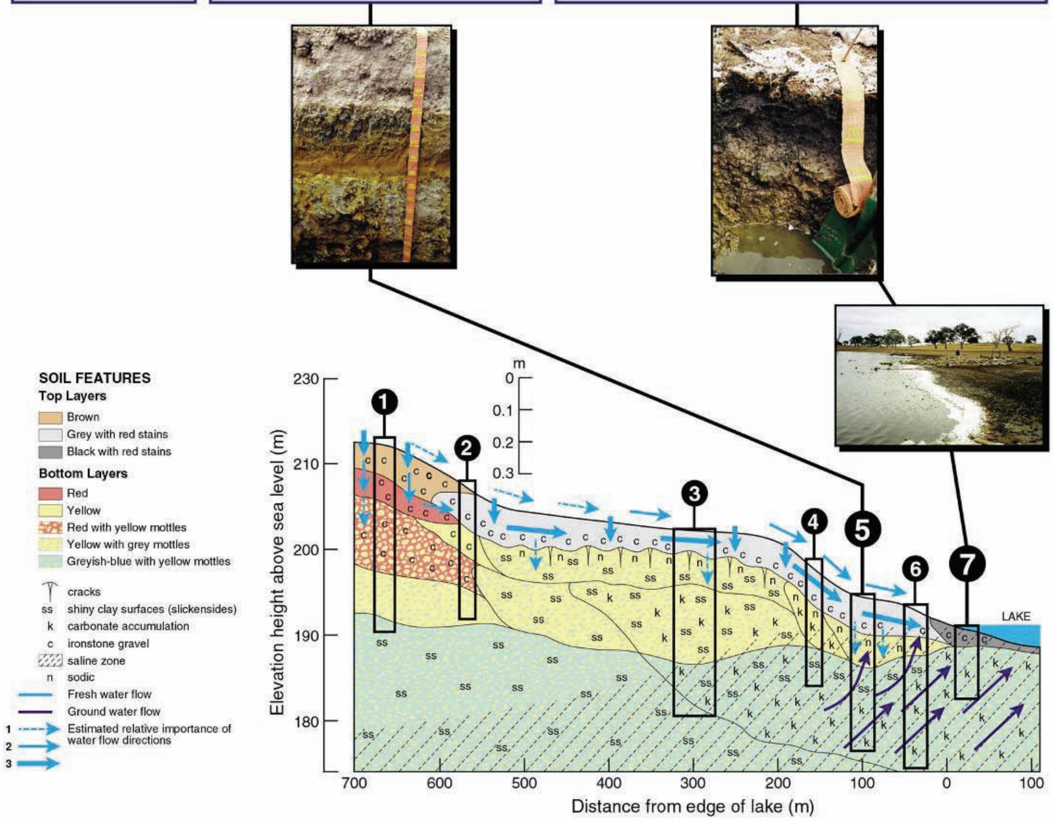


Figure 43. Sequence of soils down a slope (two of the seven soils are illustrated) linked to a 3D mechanistic model of soil and water processes with summaries of management options associated with each soil type from Woorndoo (Table 4; after Fitzpatrick *et al*. 2003b).

CONCLUSIONS, OUTCOMES AND FUTURE WORK

Sulfidic materials form and build-up in inland ASS under fresh water conditions where: (i) contemporary clearing of native vegetation has caused the rising of local water tables and excess discharge of saline-sulfatic groundwater and (ii) ponding of wetlands, lakes and disposal ponds following construction of barrages and locks. For example, changes to the hydrology in regulated sections of the Murray-Darling Basin (MDB) system (due to higher weir pool levels), and the chemistry of rivers and wetlands have caused significant accumulation of sulfidic material in sub-aqueous and margin soils. If left undisturbed and covered with water, sulfidic materials pose little or no threat of acidification. However, when sulfidic material is exposed to the air, the sulfides react with oxygen to form sulfuric acid (i.e. sulfuric materials with $pH < 4$). When these sulfuric materials are subsequently covered with water, significant amounts of acidity can be released into the water.

Other risks associated with acid sulfate soils include: (i) mobilisation of metals, metalloids and non-metals, (ii) decrease in oxygen in the water column when monosulfidic materials are mobilised into the overlying water column, and (iii) production of noxious gases. These risks can potentially lead to severe degradation to the environment and have wide ranging impacts on water quality and potentially to human and livestock health.

This chapter has outlined the “descriptive, explanatory and predictive conceptual models” (e.g. pedological hydrological and biogeochemical) that have been applied to validate and refine soil-regolith models for the formation of inland acid sulfate soils. These refined models were used to help explain the complex pedological, hydrological and biogeochemical interactions that occur in the regolith environment. This increased understanding of environmental degradation processes has also aided in mineral exploration in the eastern Mt Lofty Ranges.

These conceptual models showed that physical disturbance (e.g. pugging by cattle) resulted in:

- Degradation of wetland vegetation
- Disturbance and oxidation of pyrite in the O and A horizons.
- Production of sulfuric acid and development of low pH (i.e. $pH < 5$) conditions
- Dissolution of soil minerals and the precipitation, accumulation and oxidation of iron- and sulfur-rich precipitates.

These processes have caused less permeable, Fe-rich surface layers to form in discharge areas, which lead to degraded soils, erosion and poor stream water quality.

Record low inflows and river levels in recent years have led to the drying of many wetlands in the MDB, resulting in the exposure of sulfidic material in ASS, and soil acidification in many wetlands. The extent of the threat posed by ASS has required urgent assessment by CSIRO and others from June 2007 to the present. Despite decades of scientific investigation of the ecological (e.g. Living Murray Icon Site Environmental Management Plan: MDBC, 2006a,b), hydrological (salinity), water quality and geological features of wetlands in the MDB, we have only recently advanced far enough to appreciate the wide spectrum of inland ASS subtypes and processes that are operating in these contemporary environmental settings, especially from continued lowering of water levels (e.g. Fitzpatrick *et al.* 2008a,b,d,e;f; Shand *et al.* 2008a,b; Simpson *et al.* 2008; Lamontagne *et al.* 2006). Several catchments with inland ASS in the MDB appear to behave in a nonlinear, hysteretic manner, exhibiting collapses that are not easily reversed. However, relatively little research has been undertaken on ASS processes causing irreversible changes. We argue here that the hysteretic nature of inland acid sulfate soil systems means that reliable information is of fundamental importance to improved environmental outcomes. Hence, the MDB Ministerial Council at its meeting in March 2008 directed the Murray-Darling Basin Commission (MDBC) to undertake an assessment of ASS risk at all wetlands on the Murray River affected by regulated flow, including Ramsar wetlands and other key environmental sites in the MDB.

The Murray Darling Basin Authority (MDBA), in partnership with its Partner Governments and scientists, has designed a project in the MDB to: (i) identify the extent of various ASS materials, (ii) quantify the level of risk, and (iii) provide management and mitigation options. The project established a list of more than 10,000 wetlands that were then assessed against a number of criteria aimed at identifying those that had potential for ASS occurrence. A new systematic approach was used to improve acquisition, collation, integration and communication of diverse inland ASS data.

Although some ASS risk mapping has taken place in Australia, large gaps remain from a national perspective, especially with regard to inland ASS (e.g. Murray Darling Basin, Corangamite and Gippsland in Victoria, Eyre Peninsulas and York Peninsulas in South Australia, Tasmania, Northern Territory, Western Australian Wheatbelt and in several parts of NSW and Queensland). The fate and effects of heavy metals, metalloids and non-metals, which are mobilised when ASS materials (sulfidic, sulfuric and monosulfidic) are disturbed, remains poorly understood. Their interactions with organic and inorganic colloids, transformations following sedimentary burial and fluxes to the water column are largely unknown, particularly in inland environments (e.g. Lower Lakes of the MDB, in drains and salinised wetlands). The response of disturbed systems to different management options is currently poorly tested and understood.

There is a need to:

- Develop a more robust approach (using a new philosophy) to risk assessment of ASS for inland systems by integrating information from the Atlas of Australian ASS mapping program, acid-base accounting and new information on metal contaminants/mobility with respect to the different types of acid sulfate soil materials (i.e. sulfidic, sulfuric and MBO)
- Develop an improved understanding of the processes that control the amount and distribution of reduced sulfur in inland environments. Currently, there are various methods and philosophies used for determining ASS risk that rely on acid-base accounting, but which are probably outdated and in need of review
- Develop toolkits, which should include an improved classification of ASS with clear definitions and methods for national ASS assessment, environment protection and a State and regional policy and planning tool
- Continue to develop, refine and expand the Australian Atlas for Acid Sulfate Soils, which incorporates the Australian Soil Resource Information System (ASRIS) and CSIRO National Soil Archive. This will incorporate the following new information:
    - Regional baselines and advice on ASS condition (pedological, geochemical and mineralogical) and seasonal/drought predictions of processes causing changes in ASS materials across the nation by 2015 (e.g. sulfidic to sulfuric material transformations when drying; and sulfuric to sulfidic materials on reflooding).
    - Geochemistry, mobility of elements and mineralogy.
    - National collection of reference ASS as part of the CSIRO National Soil Archive.
    - Online access to primary data and conceptual ASS models on the functional properties of Australia's ASS.
    - Understanding of acid and metal fluxes to major waterways and impacts on surrounding ecosystems.
- Develop better, user-friendly methodologies and approaches for consultants and land managers to identify and manage ASS and publish them as a manual and CD set. Provide advice on ASS regulatory issues, management and guidelines for land managers to minimise land and water degradation and contamination from sulfidic soil issues in both coastal and inland areas of Australia, south-east Asia and worldwide.
- Publish a comprehensive book on "Inland Acid Sulfate Soils" by 2010 incorporating more descriptive soil information that is pictorially integrated along toposequences and hydrosequences (i.e. using coloured cross-sectional diagrams and photographs of soils) and applied to identify soil and hydrological features to overcome some of the perceived barriers to adoption of best management practices. In this way, complex scientific processes and terminology are more easily communicated to community groups.
- Develop tools to spatially and temporally predict changes in ASS properties in landscapes at a range of scales.

ACKNOWEDGEMENTS

We would especially like to thank the Acid Sulfate Soil team in CSIRO Land and Water (Richard Merry, Mark Raven, Steve Marvanek, Warren Hicks, Stuart McClure, Brett Thomas, Mark Thomas, Nathan Creeper, Andrew Baker, Stuart Simpson, Peter Self and Nilmini Jayalath) for assistance over several decades. Professor Bob Bourman for directing the senior author to the book by Ernestine Hill entitled “Water Into Gold” when observations were made in 1841 of the possible formation of sulfuric material in Lake Bonney when it was dry (Box 1). We are exteremely grateful to Jock Churchman for a through review of the chapter. In addition, we also thank all members of the National Committee for Acid Sulfate Soils (NatCASS) for their help and assistance.

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CHAPTER 2

ATLAS OF AUSTRALIAN ACID SULFATE SOILS

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SUMMARY

The Atlas of Australian Acid Sulfate Soils (ASS) is a new web-based hazard assessment tool with a nationally consistent legend, which provides information about the distribution and properties of ASS across Australia. This tool is available on ASRIS (Australian Soil Resource Information System: www.asris.gov.au) and every polygon or mapping unit is attributed with information pertaining to: (i) 4 classes of "probability of occurrence", (ii) 4 levels of confidence relating to the quality of data source, and (iii) 10 additional descriptors such as desiccation cracks. The Atlas is a constantly evolving national map of available ASS information, which also includes priority case studies at a range of localities across Australia. (e.g. http://www.clw.csiro.au/acidsulfatesoils/index.html).

In Australia, ASS occupy an estimated 215,000 km^2 of which 58,000 km^2 is coastal ASS and 157,000 km^2 is inland ASS. In the coastal zone 41,000 km^2 are exposed at some point during the tidal cycle with the remaining 17,000 km^2 being permanently subaqueous. Finally, 126 km^2 of ASS with sulfuric material has been mapped.

The Atlas of Australian ASS has been utilised as a basis to:

- Assist in the development a robust national framework to estimate and predict occurrence of inland and coastal ASS in Australia
- Support and enhance implementation of the National ASS Management Strategy (www.deh.gov.au/coasts/cass/index.html, which aims to avoid disturbance of all types of ASS
- Assist the successful adoption of land and water management options
- Assist the development of a nationally consistent ASS policy framework across Australia

HOW THE ATLAS OF AUSTRALIAN ASS WAS PUT TOGETHER

The Atlas of Australian ASS project was developed under the auspices of the National Committee for Acid Sulfate Soils (NatCASS) and completed by CSIRO Land and Water with assistance from staff in all states throughout Australia. The ASS qualification was inferred from surrogate datasets. The ASS Atlas was put together in two parts using two different methodologies and classification paths. First the Atlas of "Coastal" ASS was compiled using existing state ASS mapping and other datasets that mapped landscape indicators of ASS environments, e.g. coastal vegetation mapping. At a later stage, the interior of the Australian continent was back-filled with "Inland" ASS mapping, inferred from broader and coarser scale national soil and hydrography mapping. The result of these two exercises were combined to form the current Australian ASS Atlas.

The "Coastal" ASS component

Existing Coastal Acid Sulfate Soil mapping from states were received and processed to varying degrees to conform to the Atlas of Australian ASS classification system (see Appendix A). Classification of state mapping polygons to the NatCASS classification system was as follows: In the case of SA, NSW, Qld and WA the original state ASS classifications were directly translated to the Atlas of Australian ASS classification. These translations were undertaken by the creators of the state data and other experts within the respective states.

Due to the more broad classifications of the original Victoria and Tasmania ASS mapping, polygons for these two states were initially translated to a broad Atlas of Australian ASS classification group (e.g. Tidal, Non-tidal) by the data custodians then subsequently differentiated further through intersecting with other layers. These included the 3 second SRTM DEM and North Coast Mangrove mapping GIS datasets. The former being used to differentiate within the Non-Tidal zones (i.e. classes Ae-j and Be-j) and the latter used to differentiate the Tidal zones (i.e. Ab-d, Bb-d).

Mapping of the Tidal-Zone classes was augmented for all states except SA and NSW with 1:100K Coastal Waterways Geomorphic Habitat Mapping (Geoscience Australia). This dataset was used to infer additional areas of subaqueous material in subtidal wetland (class Aa & Ba) and Intertidal Flats (class Ab & Bb).

The "Inland" ASS component

Provisional inland ASS classifications were derived from National and (in the case of Tasmania) state soil classification coverages combined with 1:250K series 3 Hydrography and Multiresolution Valley Bottom Floor Index (MrVBF). A matrix devised to translate combinations of Soil Order (Isbell 1996) and landscape "wetness" to NatCASS inland ASS codes. The foundation for the inland component is very coarse, being underpinned by the Atlas of Australian Soils (1:2M scale) with "wetness" inferred from 1:250K topographic hydrography (see Appendix 2).

With ongoing field investigations and acquisition of more detailed local spatial data sets, the resolution and accuracy of the inland ASS component is being continually improved from its current, first cut "broad brush" depiction.

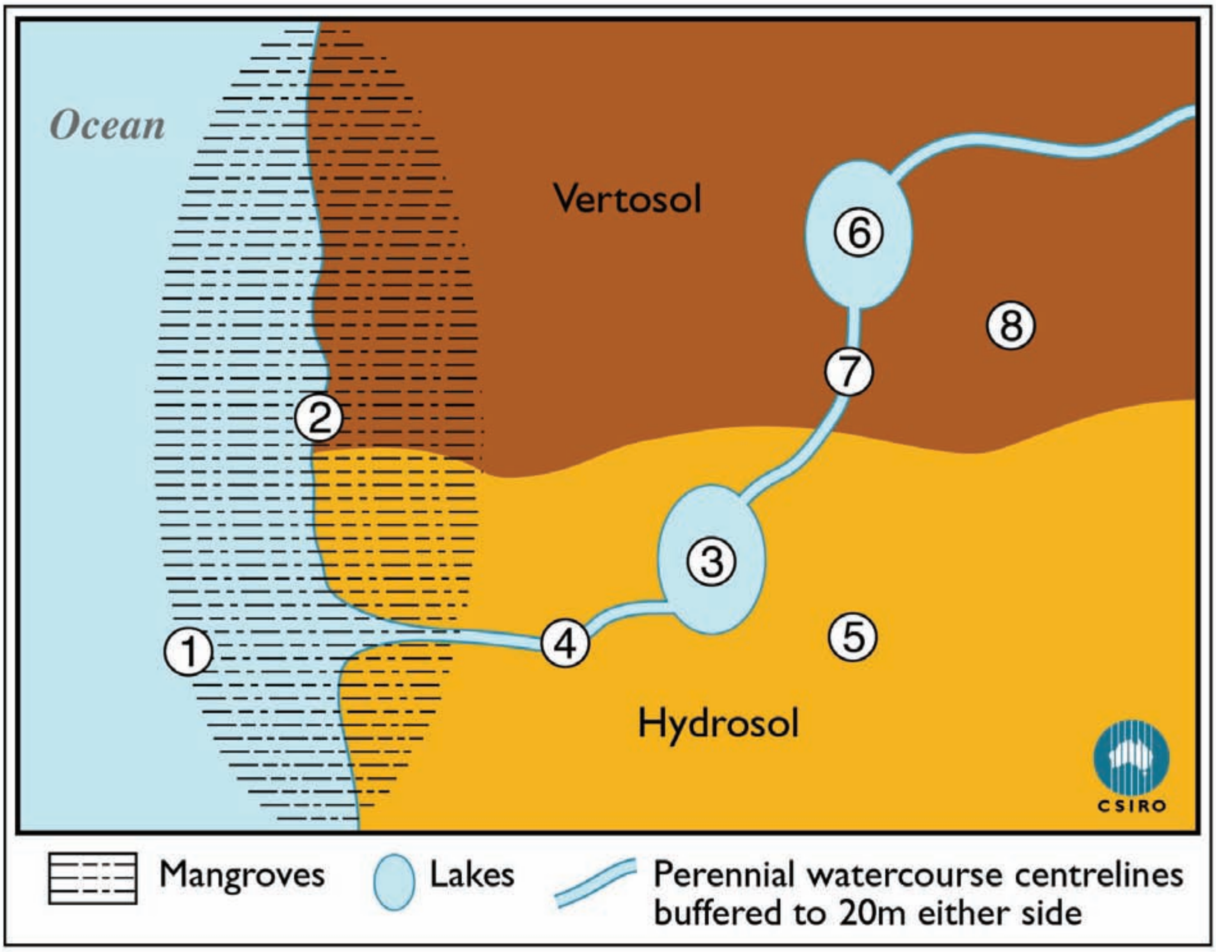

Figure 1. Examples of occurrences of different ASS. See Table 1 for explanations for map.

Table 1. Explanation of example ASS settings (from Fig 1) and how they relate to legend and areal calculations

Setting	Chance of ASS occurrence in map unit	Legend probability class	Typical extent within setting if ASS present	Map unit polygon area scaling factor
1 Subaqueous marine soils	>70%	A	100%	1.0
2 Intertidal flats	>70%	A	100%	1.0
3 Hydrosols under lakes	>70%	A	80%	0.8
4 Riparian zone hydrosols	>70%	A	10%	0.1
5 Hydrosols	>70%	A	5%	0.05
6 Vertosols under lakes	>70%	A	50%	0.5
7 Riparian zone Vertosols	5 - 70%	B	5%	0.05
8 Vertosols	<5%	C	5%	0.05

FEATURES OF THE ATLAS OF AUSTRALIAN ASS

The Australian ASS mapping project seeks to make accessible, all currently available ASS mapping and information across the whole continent presented in a uniform, highly descriptive and systematic classification system (the “Legend” - See Appendix 1). Consequently the component ASS mapping in descriptions are from disparate sources and of varying quality, accuracy and mapping scales. A principle feature of the ASS Atlas is that every polygon is attributed with information pertaining the quality of its source, confidence in the ASS classification code and scale of the mapping (Appendix 1). The Atlas has enabled estimates of the area of ASS extent to be calculated across Australia (Table 1).

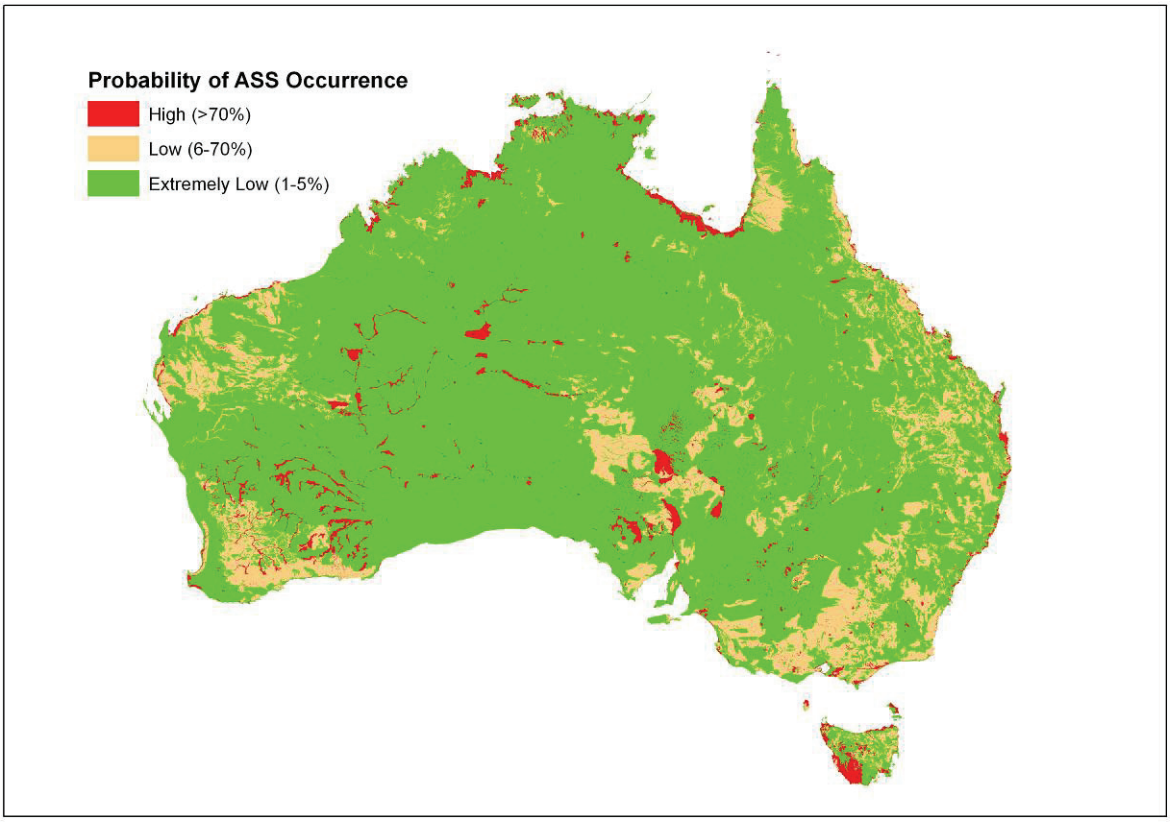

Figure 2. Map of Australian ASS. The latest mapping is disseminated live via Web served GIS facility at www.asris.csiro.au.

Of the 7,693,111 km^2 of the Australian land and offshore assessed ASS 300,528 km^2 is deemed to have a high probability of ASS occurrence and 1,106,786 km^2 deemed to have a low probability of occurrence. The remaining 6,285,797 km^2 of land and near offshore soils is rated as extremely low probability of occurrence. Scaling factors are applied to these total areas to estimate the actual extent of ASS within these landscapes. With the area scaling factors applied, there is estimated to be 154,269 km^2 of High Probability ASS and 65,771 km^2 of Low Probability ASS (Figure 2). The landscape settings where ASS is found within these High and Low Probability extents are broken down in Table 2 below.

Table 2. Area (km^2) of ASS classes in Australian landscapes with high or low probability of ASS occurrence

ASS setting	**Area (km^2)**
Subaqueous ASS (Marine setting)	16,930
Tidal zones	23,972
Floodplain in coastal settings	6,667
Sandplains & dunes in coastal settings	9,681
Other coastal settings	206
ASS in inland settings	157,031
Disturbed ASS	853
Within the above categories:	
Observed ASS with sulfuric material (pH <4)	126
Observed MBO (Monosulfidic black ooze)	81

APPLICATION OF ATLAS FOR AUSTRALIAN ASS LEGEND TO THE MAPPING OF ASS IN THE LOWER LAKES OF THE RIVER MURRAY

The lower lakes (Lakes Alexandrina and Albert) are two lakes totalling approximately 81,000ha in area located at the terminus of the Murray River. Once estuarine systems, they are now freshwater lakes due to the installation of seawater exclusion barrages in the 1930's. (Figure 3).

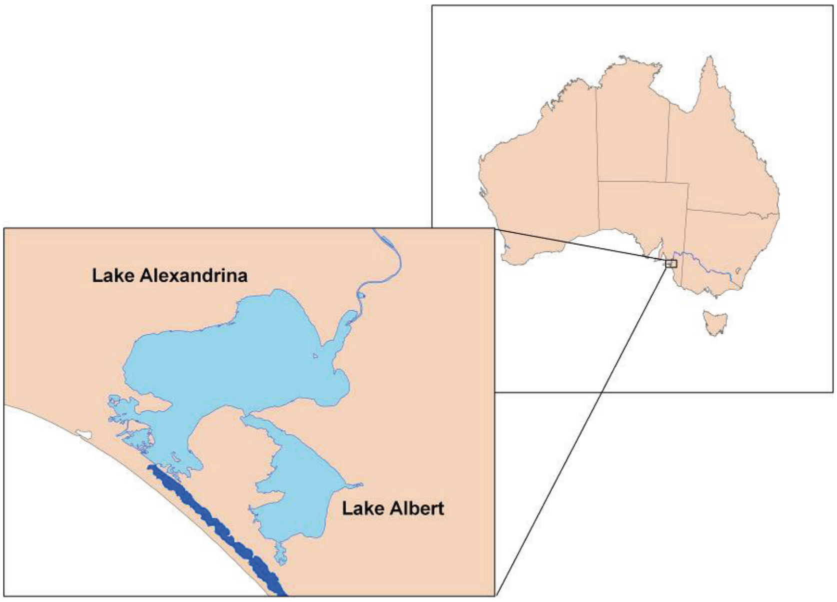

Figure 3. Lower Lakes location map

Sulfidic material containing iron pyrite forms naturally in freshwater and marine settings as a result of the depositing of large amounts of organic matter, such as decaying vegetation, in saturated and anaerobic wetland areas. With sufficient sources of iron and sulfate such anaerobic environments are ideal for the build-up of iron sulfide minerals. In the Lower Murray region's waterways iron sulfides have been accumulating in submerged and waterlogged soils since the construction of locks, weirs and barrages over 50 years ago, and have led to the retention of water in the river system.

The current drought conditions (worst on record), however, has dropped water levels in the River Murray, particularly between Lock 1 (at Blanchetown) and the Lower Lakes (Alexandrina and Albert). These low water levels have exposed submerged or subaqueous soils, wetlands, areas of riverbank and parts of the lower lakes that contain high levels of pyrite. This has resulted in the artificially thick layers of accumulated sulfide minerals being exposed to air for the first time leading to the development of sulfuric material with pH levels dropping below 4 because of the formation of sulfuric acid. Dredging operations have also exposed sulfides to oxygen, resulting in the formation sulfuric material.

We have identified four sequential phases (Classes of ASS) that occur when these soils dewater as water levels drop. The four broad Classes of acid sulfate soils form depending on drainage conditions, which range from submerged or subaqueous soils to saturated and unsaturated drained soils (Figure 4).

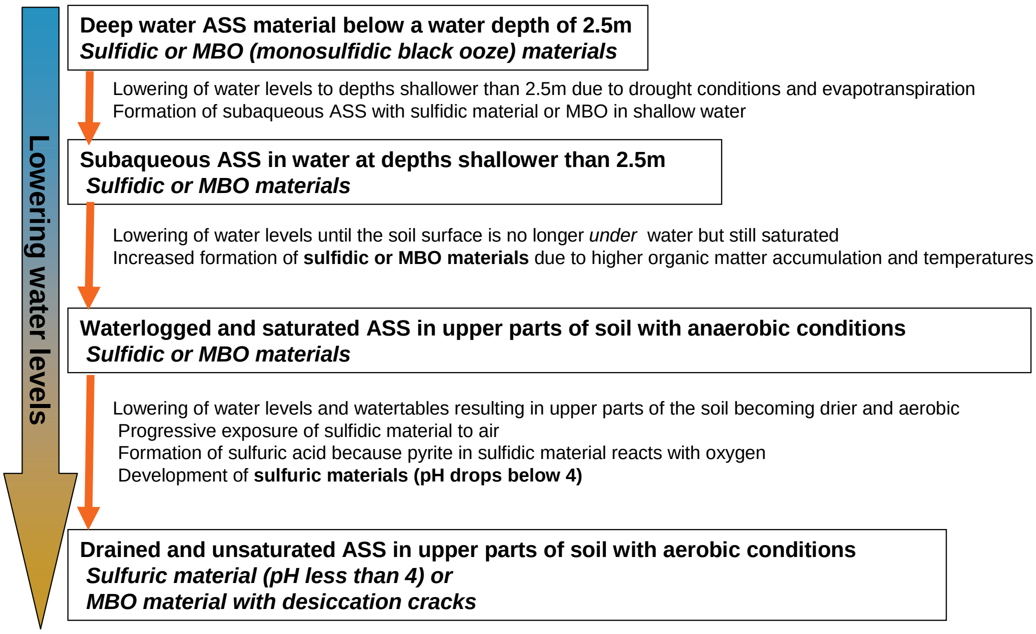

Figure 4. Generalised conceptual model showing the sequential transformation of four Classes of ASS due to lowering of water levels from “Deep water ASS” → “Subaqueous ASS” → “Waterlogged and saturated ASS” (all containing sulfidic material with high sulfide concentrations and pH>4) to → “Drained and unsaturated ASS” containing sulfuric material (pH<4) in the upper soil layers. A wide range of ASS Subtypes containing organic materials/peat, clays and sands have been identified in the ASS classes (definitions in detailed map Legend in Table 2) and in ASS maps (see accompanying ASS maps). (From Fitzpatrick *et al*. 2008a,b,c,d).

Some areas also contain substantial ‘monosulfidic black ooze’ (MBO) material, which causes rapid oxygen depletion of lake and drainage waters when the ooze is mixed with oxygenated waters during disturbance. Unpleasant odours have been experienced in some areas of exposed soils with desiccation cracks when water levels are extremely low or allowed to evaporate to dryness due to rotting vegetable matter and release of sulfidic gases (e.g. ‘rotten egg smell’).

Field observations and chemical analysis confirm the generalised conceptual model in Figure 4, which illustrates the four sequential phases (broad classes of ASS) that occur when the soil classes progressively dewater as water levels drop from pre-drought water levels (approximately plus 0.5 mAHD) to current levels (close to minus 0.5m AHD). The conceptual model, the detailed field survey and laboratory data (e.g. chemistry and texture), and the subtypes of ASS were used to construct the final map legend for the ASS maps of the River Murray below Blanchetown (Lock 1) and Lakes Alexandrina and Albert when water levels were at pre- drought and current drought conditions (Fitzpatrick *et al* 2008 a,c,d). To easily identify types and subtypes of ASS (Table 3) a “Soil Identification Key”, was developed for ASS in the River Murray and Lower Lakes systems to easily identify and classify the fourteen Subtypes of ASS and non-ASS (Fitzpatrick *et al* 2008 a,c,d). The key uses a collection of plain language names for ASS types and subtypes in accordance with the legend for the Atlas of Australian ASS (Appendix 1), which is designed for people who are not experts in soil classification systems such as the Australian Soil Classification (Isbell 1996). Attributes include water inundation (subaqueous soils), organic material, cracks or structure, texture, colour, features indicating waterlogging (hydric conditions) and ‘acid’ status – already acidified, i.e. sulfuric material, or with the potential to acidify, i.e. sulfidic material (Isbell 1996).

DEVELOPMENT OF PRIORITY (HOTSPOT) REGIONS/AREAS AND SITES ACROSS AUSTRALIA

Part of the Atlas of Australian ASS website establishes a national database for storage and display of ASS data was established for several key priority regions across Australia. A national protocol for showcasing priority/hotspot areas via the Atlas of Australian ASS on the ASRIS website was developed. This involved the development of a standard presentation format document for each region, area or site across Australia, which has been hotlinked to a national map of Priority areas in ASRIS. More specifically, the database of representative priority case studies around Australia (with images appropriate to each case) has detailed information on the following:

- Soil data (e.g. morphological, chemical, physical, soil classification)
- Coastal (estuary) hydrology, geology and geomorphology
- Climate, land use, vegetation, etc
- Environmental hazard assessment such as pollution hazard rating, infrastructure impact rating (e.g. subsidence, corrosion), environmental sensitivity rating (e.g. proximity to Ramsar designated wetlands).
- Major cause of oxidation or increased anaerobic conditions of ASS.
- Off-site impacts.
- Available options for amelioration and management.
- Estimates of the increase (or decrease) in area of acidified ASS or increased anaerobic condition of ASS.

As further information on hotspot areas is uploaded progressively across the country, web browsers will be able to view a map of Priority regions/areas/sites on the web and access information about them via a hyperlink by clicking on the map. South Australian examples of priority (hotspot) regions/areas and sites have been developed and published as a series of CSIRO Land and Water Science Reports (in PDF format with ASS data that reside on the CSIRO Land and Water ASS website and are hotlinked from ASRIS). Several similar examples have been developed for all the other States as PDF documents, which reside on the respective State-based websites.

An example of a case study is the Gulf of St Vincent (GSV) and Barker Inlet “Priority Region.” This is a priority or hotspot region site linked to the “Atlas of Australian Acid Sulfate Soils” website via the Australian Soil Resources Information System - ASRIS) report (CSIRO Land and Water Science Report No. 35/08: Fitzpatrick *et al* 2008b). The website summarises factors associated with formation of pyrite and sulfuric acid across the wide range of ASS types that occur and the key impacts this has on coastal, estuarine and mangrove swamp environments that fringe the shoreline of the GSV. This report also provides the following critical database information on coastal ASS:

- Properties (descriptions of 6 major types of ASS materials that commonly occur as layers in soil profiles)
- Conceptual process models (schematic soil-landscape cross sections)
- Australian and international soil classification systems (Types of ASS based on the legend used in the Atlas of Australian Acid Sulfate Soils, Australian Soil Classification, Soil Taxonomy and World Reference Base)
- Distribution (ASS map and aerial extent in hectares for GSV and Barker Inlet)
- Impacts (Land and water degradation; noxious odours; climate change and greenhouse gas emissions)
- Management and remediation options (brief overview of general principles)

Similar priority or hotspot case studies across Australia have been developed and are either published or in the process of being published, with a view to being accessible via the National ASS Atlas website.

ACKNOWLEDGMENTS

David Jacquier (CSIRO), Leigh Sullivan (Southern Cross University), John Williams (DIPNR), Glenn Atkinson (DIPNR), Mitch Tulau (DIPNR), Greg Chapman (DIPNR), Jason Hill (Dept Natural Resources, Environment & Arts, NT) Brad Degens, Steve Appleyard and Steve Wong (Dept of Environment & Conservation, WA), Doug Fotheringham (DEH, SA), Tim Noyce (DEH, SA), Brett Thomas (CSIRO), Doug Crawford (DPI) Austin Brown (DPI), Don Malcolm (QNRM), Rob Moreton and Ken Bird (Dept Primary Industry, Water and Environment, TAS). In part funding from the National Acid Sulfate Soil Knowledge Project, NAP 2.

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Table 3: Explanation of ASS Map Legend for Lower Lakes and River Murray below Lock 1

Deep water ASS material below a water depth of 2.5m	**Subaqueous ASS in shallow water (<2.5m depth)**		**Waterlogged and saturated ASS in upper part of soil with anaerobic conditions**		**Drained and unsaturated ASS in upper part of soil with aerobic conditions**	
	Subtype of ASS	[1]Map code	Subtype of ASS	[1]Map code	Subtype of ASS	[1]Map code
	Sulfidic subaqueous organic soils	Ak(p2)o	Sulfidic organic soils	Al(p2)	Sulfuric organic soils	Al(a1)
	Sulfidic subaqueous clayey soils	Ak(p2)c	Sulfidic vertosols (clayey)	Bo(p2)	Sulfuric vertosols (clayey)	Ao(a1)d
	Sulfidic subaqueous sandy soils	Ak(p2)s	Sulfidic hydrosols (sandy)	Am(p2)	Sulfuric hydrosols (sandy)	Am(a1)
	Sulfidic subaqueous soils	Ak(p2)	Sulfidic hydrosols (sandy)	Bm(p2)		
	[2]MBO subaqueous soils	Ak(m2)	[2]MBO Sulfidic hydrosols	Am(m2)	[2]MBO hydrosols (Desiccation cracks)	Am(m2)d

[1] Map code: Map Legend codes (see below); [2]MBO: Monosulfidic Black Ooze subaqueous soils

Symbols in map code: A, B, C or D; k, l, m, o (a, p, m 1,2 or 3) o, c, s, d

Probability of Occurrence of Acid Sulfate Soils:

A - High probability of occurrence (> 70% of mapping unit)

B - Low probability of occurrence (6-70% of mapping unit)

C - Extreme low probability of occurrence (1-5% of mapping unit) with occurrences in small localised areas.

D - No probability of occurrence <1% of mapping unit (e.g. outcrops of hard calcrete).

Codes:

k - Subaqueous soils (in shallow water <2.5 m depth)

l - Organosols (organic or peaty soils)m - Hydrosols (Saturated in upper part to develop anaerobic conditions)

o - Vertosols (cracking clay soils with slickensides)

Subscripts to codes:

(a) - Sulfuric material (pH < 4)

(m) - Monosulfidic Black Ooze (MBO) material

(p) - Sulfidic material (pH > 4 but on aging pH drops below 4)

Confidence levels: Map polygon contains ASS, and:

(1) - All necessary analytical and morphological data are available

(2) - Analytical data are incomplete but are sufficient to classify the soil with a reasonable degree of confidence.

(3) - No necessary analytical data are available but confidence is fair, based on a knowledge of similar soils in similar environments.

(4) No necessary analytical data are available and classifier has little knowledge or experience with ASS, hence classification is provisional.

Descriptors: used where more information is available

o - Organic material (sapric and hemic material)

c - Clayey material (> 35 % clay; light, medium and heavy clay)

s - Sandy materials (= sand, loamy sand, clayey sand texture groups)

d - Desiccation cracks.

AHD = Australian Height Datum, which approximates mean sea level

APPENDIX 1

LEGEND for Australian Atlas of Acid Sulfate Soils[1] (ASS) map. Developed by Rob Fitzpatrick (CSIRO/ NatCASS), Steve Marvanek (CSIRO) and Bernie Powell (QNRW/ NatCASS) with input from several workers across Australia and overseas (2nd June, 2008)

Code and Map Unit	Distinguishing soil/sediment properties, vegetation, landforms, or other characteristics
PROBABILITY OF OCCURRENCE OF ASS[1]	
A High Probability of occurrence	>70% chance of occurrence in mapping unit
B Low Probability of occurrence	6-70% chance of occurrence in mapping unit
C Extremely low probability of occurrence	1-5% chance of occurrence in mapping unit with any occurrences in small localised areas
D No probability of occurrence	<1% chance of occurrence in mapping unit (e.g. thick outcrops of hard rock, ferricrete, calcrete, silcrete)
MAP UNIT (area scaling factor)	
PROFOUNDLY DISTURBED	
x Disturbed ASS[1] terrain (1.0)	ASS[1] material present below urban development, or present in former tidal zones inside bund walls (e.g. dredge spoil, ponds, major excavations) or as anthropic[5] ASS or fill material > 0.3 m thick.
SUBTIDAL ZONE[7] SUBAQUEOUS MATERIALS[6]	
a Subaqueous material in subtidal wetland[7] (1.0)	PASS[2] material and/or MBO[4]. Often seagrasses.
TIDAL ZONES[8]	
b Intertidal[9] flats (1.0)	PASS[2] generally within upper 1 m. Often with mangroves.
c Supratidal[10] flats (1.0)	ASS[1] generally within upper 1 m. Halophytes (mainly samphire), salt marsh, salt pans.
d Extratidal[11] flats (0.8)	ASS[1] generally within upper 1 m.
NON-TIDAL ZONES Floodplains	
e Floodplains < 2 m AHD[12] (0.8)	ASS[1], generally within upper 1 m. Grasslands, reedlands and wetland forests (e.g. Melaleuca, Casuarina). Includes backplains, backswamps and interbarrier swamps.
f Floodplains 2 - 4 m AHD[12] (0.7)	ASS[1], generally below 1 m from the surface. Generally wetland forests (e.g. Melaleuca, Casuarina). Includes plains and levees.
g Floodplains > 4 m AHD[12] (0.7)	ASS[6], generally below 3 m from the surface. Generally forests. Includes plains and levees.
NON-TIDAL ZONES Sandplains and dunes in coastal[15] landscapes	
h Sandplains and dunes <2 m AHD[12]	ASS[1], generally within 1 m of the surface. Often wet heath. Holocene or Pleistocene.

(0.7)	
i Sandplains and dunes, 2 - 10 m AHD[12] (0.7)	ASS[1], generally below 1 m from the surface. Heath, forests. Holocene or Pleistocene.
j Sandplains and dunes, > 10 m AHD[12] (0.7)	ASS[1], generally below 1 m from the surface. Heath, forests. Mainly Pleistocene.
Inland (i.e. not coastal[15]) landscapes (> 10 m AHD[12]) in wet / riparian areas[13] associated with:	
k Subaqueous material in lakes[14] (1.0)	ASS[1] material and/or MBO[4]
l Organosols (0.8/0.05)	ASS[1] generally within upper 1 m in wet / riparian areas with Organosols (Isbell 1996)
m Hydrosols (0.8/0.1/0.05)	ASS[1] generally within upper 1 m in wet / riparian areas with Hydrosols (Isbell 1996)
n Sodosols, Chromosols and Dermosols (0.5/0.05)	ASS[1] generally within upper 1 m in wet / riparian areas with Sodosols, Chromosols and Dermosols (Isbell 1996)
o Vertosols (0.5/0.05)	ASS[1] generally within upper 1 m in wet / riparian areas with Vertosols (Isbell 1996)
p Calcarosols (0.5/0.05)	ASS[1] generally within upper 1 m in wet / riparian areas with Calcarosols (Isbell 1996)
q Kandosols, Ferrosols, Tenosols, Rudosols, Podosols and Kurosols (0.5/0.05)	ASS[1] generally within upper 1 m in wet / riparian areas with Kandosols, Ferrosols, Tenosols, Rudosols and Podosols (Isbell 1996)
SUBSCRIPTS TO CODES	
(a) Actual ASS (AASS)[3]	Actual acid sulfate soil (AASS) = sulfuric material (Isbell 1996, p.122.)
(p) Potential ASS (PASS[2])	Potential acid sulfate soil (PASS) = sulfidic material (Isbell 1996, pp. 121-122)
(m) MBO[4], significant occurrence	Monosulfidic Black Ooze (MBO) is organic ooze enriched by iron monosulfides (Bush *et al*. 2004).
CONFIDENCE LEVELS (after Isbell 1996) Map polygon contains ASS, and:	
(1) All necessary analytical and morphological data are available	
(2) Analytical data are incomplete but are sufficient to classify the soil with a reasonable degree of confidence	
(3) No necessary analytical data are available but confidence is fair, based on a knowledge of similar soils in similar environments	
(4) No necessary analytical data are available and classifier has little knowledge or experience with ASS, hence classification is provisional	
OPTIONAL DESCRIPTORS	
f Fill materials	Undifferentiated fill material between 0.5m and 3 m thick, overlays ASS materials
h Hypersaline or gypseous horizons generally within 10 cm of the surface	Hypersaline is equivalent to hypersalic as defined by Isbell (1996, p 47). Saltpans are common, average annual rainfall is generally < 400 mm, and the vegetation is dominated by halophytes (samphire, salt bush, blue bush) Gypseous is equivalent to gypsic as defined by Isbell (1996, p 114).
o Organic material	Organic, as for organic materials defined by Isbell (1996, p 116; including sapric, and hemic material). Average annual rainfall is generally > 400 mm, and the vegetation is mainly grassland (e.g. saltwater couch, Phragmites)
n Self neutralising sulfidic material	Self neutralising sulfidic material (PASS material) confirmed by field observation, sampling and laboratory analyses (commonly carbonate rich).
D Deep variant ASS	ASS generally deeper than the depth specified in the legend
P Pleistocene	Based on dating or stratigraphic evidence
e Excavation feature	Excavated drains, canals, lakes, dams and other water accumulating structures within which modern ASS forms.
d Desiccation cracks	Desiccation cracks usually expressed as irreversible trans-horizon polygonal cracks, often with coarse columnar ped structures,

	which usually forms as a result of desiccation and dewatering of clayey or peaty subaqueous soils and sediments during drying and wetting cycles.
c Clayey material	Clayey material (>35% clay; light, medium and heavy clay)
s Sandy material	Sandy materials (sand, loamy, sand, clayey sand texture groups)

Examples (i): Ae (p1) h Polygon with high probability of ASS occurrence in a floodplain < 2 m AHD, with potential ASS confirmed by analytical and morphological data, that also contains a hypersaline and gypsic horizons.
(ii): Bx (a2) f - Polygon with low probability of ASS occurrence in a disturbed environment with actual ASS. Analytical data are incomplete but are sufficient to classify the soil with a reasonable degree of confidence. The actual ASS is now covered by 0.5 to 3 m of undifferentiated fill material.

[1] Acid Sulfate Soils (ASS) are all those soils in which sulfuric acid may be produced, is being produced, or has been produced in amounts that have a lasting effect on main soil characteristics (Pons 1973). This general definition includes: (i) potential, (ii) actual (or active), and (iii) post-active ASS, three broad genetic soil types that continue to be recognized (e.g. Fanning 2002). ASS form in coastal, estuarine, mangrove swamp and marsh environments because these waterlogged or highly reducing environments are ideal for the formation of sulfide minerals, predominantly iron pyrite (FeS_2). Soil horizons that contain sulfides are called sulfidic materials (Isbell 1996; Soil Survey Staff 2003) and can be environmentally damaging if exposed to air by disturbance. Exposure results in the oxidation of pyrite, with each mole of pyrite yielding 4 moles of acidity (i.e. 2 moles of sulfuric acid). This process transforms sulfidic material to sulfuric material when, on oxidation, the material develops a pH of 4 or less (Isbell 1996); note that a sulfuric horizon has a pH of 3.5 or less according to Soil Survey Staff (2003).

1. Acid sulfate soil (ASS) may include PASS or AASS + PASS.

2. Potential acid sulfate soil (PASS) = sulfidic material (Isbell 1996, pp. 121-122)

3 Actual acid sulfate soil (AASS) = sulfuric material (Isbell 1996, p.122.)

4. Monosulfidic Black Ooze (MBO) is organic ooze enriched by iron monosulfides (Sullivan *et al*. 2002).

5. Anthropic material is profoundly modified soil material, the term being derived from the soil order Anthroposol as defined by Isbell (1996, p 18).

6. Subaqueous materials: Soil materials that form in sediment found in shallow permanently flooded environments. Excluded from the definition of these soils are any areas “permanently covered by water too deep (typically greater than 2.5m) for the growth of rooted plants (Stolt 2006).

7. Subtidal wetlands: Permanently inundated areas within estuaries dominated by subaqueous soils and submerged aquatic vegetation. Subtidal: (adjective) continuous submergence of substrate in an estuarine or marine ecosystem; these areas are below the mean low tide (Stolt 2006).

8. Tidal zone or flat: An extensive, nearly horizontal, barren or sparsely vegetated tract of land that is alternately covered and uncovered by the tide, and consists of unconsolidated sediment (mostly clays, silts and/or sand, and organic materials) (Stolt 2006).

9. Intertidal zone is that between mean lower low water (MLLW) and mean higher high water (MHHW) (see MHL).

10. Supratidal zone is that above mean higher high water (MHHW), but below the extratidal zone. Spring tides will reach the lower part of the supratidal zone, the average spring tidal level being that known as mean high water springs (MHWS). See Isbell (1996, p 47) and MHL

11. Extratidal zone and the supratidal zone boundary is defined by vegetation community, i.e. grassland v saltmarsh (see Isbell 1996, p 47).

12. Australian Height Datum (AHD) approximates mean sea level. AHD is a surface based on mean sea level adopted in 1971, and described in Special Publication 10 -Australian Geodetic Datum Technical Manual, Division of National Mapping, for the National Mapping Council.

13. Riparian/wet zones: integration of topographic wetness index (TWI), which defines the "riparian/wet" zones and the "deposition/sedimentary" zones through Multiresolution Valley Bottom Floor Index (MrVBF) (Gallant and Dowling, 2003). MrVBF data from Dr John Gallant (CSIRO) for national MrVBF and TWI coverage (250 m cell size).

14. Lakes: Waterbodies from GEODATA TOPO 250K Series 2 Topographic Data, Hydrography Theme, Geoscience Australia http://www.ga.gov.au/meta/ANZCW0703005458.html.

15. Coastal zone: Includes coastal waters and those areas landwards of the coastal waters where there are processes or activities that affect the coast and its values. Natural Resource Management Ministerial Council (2006) – Glossary of terms Page 50. Commonwealth of Australia Department of the Environment and Heritage, Canberra, ACT. . National Cooperative Approach to Integrated Coastal Zone Management: Framework Implementation Plan. ISBN 0642550514.

APPENDIX 2

Legend classification matrix used for inland Acid Sulfate Soils

	Legend Probability and Map Unit (polygon area scaling factor)		
ASC Soil Order Isbell (1996)	Under Lake	Adjacent to watercourse	Away from lakes & water courses
Anthroposols	A (0.5)	A (0.05)	B (0.05)
Calcarosols	A p (0.5)	A p (0.05)	C p (0.05)
Chromosols	A n (0.5)	B n (0.05)	C n (0.05)
Dermosols	A n (0.5)	B n (0.05)	B n (0.05)
Ferrosols	A q (0.5)	B q (0.05)	C q (0.05)
Hydrosols	A m (0.8)	A m (0.1)	A m (0.05)
Kandosols	A q (0.5)	B q (0.05)	C q (0.05)
Kurosols	A q (0.5)	B q (0.05)	C q (0.05)
Organosols	A l (0.8)	A l (0.05)	A l (0.05)
Podosols	A q (0.5)	B q (0.05)	C q (0.05)
Rudosols	A q (0.5)	B q (0.05)	C q (0.05)
Sodosols	A n (0.5)	A n (0.05)	B n (0.05)
Tenosols	A q (0.5)	B q (0.05)	C q (0.05)
Vertosols	A o (0.5)	B o (0.05)	C o (0.05)
Lakes	A k (1.0)	N/A	N/A

Simpson Stuart, Rob Fitzpatrick, Paul Shand, Brad Angel, David Spadaro, Richard Merry and Mark Thomas. 2008. Acid and Metal Mobilisation Following Rewetting of Acid Sulfate Soils from the River Murray, South Australia: A Rapid Laboratory Method. In *Inland Acid Sulfate Soil Systems Across Australia* (Eds. Rob Fitzpatrick and Paul Shand). pp 90-97. CRC LEME Open File Report No. 249. (Thematic Volume) CRC LEME, Perth, Australia.

CHAPTER 3

ACID AND METAL MOBILISATION FOLLOWING REWETTING OF ACID SULFATE SOILS FROM THE RIVER MURRAY, SOUTH AUSTRALIA: A RAPID LABORATORY METHOD

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ABSTRACT

Soils in the River Murray system of South Australia are being impacted by a combination of low water levels and the presence of acid sulfate soils (ASS). As water levels recede in the river channel and surrounding wetlands, the exposed ASS may dry, causing oxidation of soil constituents (e.g. sulfide) which release acidity and cause significant decreases in soil pH. One hundred and fifty soils samples were collected from the lower River Murray and Lakes region of South Australia to assess the potential for the mobilisation of acid and metals following the rewetting of the soils. The soils and ASS subtypes were classified as; (i) 29 sulfuric materials (pH <4), (ii) 73 sulfidic materials (high sulfide concentrations and potential to develop pH<4), (iii) mono-sulfidic black ooze materials (MBO), and (iv) 13 clays, 32 sands and 1 organic material, all containing some sulfides. Trace metal concentrations in the soils were low and generally well below the guideline concentrations for sediment/soil quality. Upon wetting of the soils with River Murray water using a rapid laboratory testing method, the water was effectively buffered to the pH of the soil; 9% had pH <3, 19% had pH <4, 30% had pH <5, 43% had pH <6, 58% had pH <7, and 87% had pH <9. The metal release from the soils was rapid. After 24-h mixing of soils with River Murray water, the concentrations of dissolved metals were (mean/maximum, in mg/L): Al 49/460, Fe 39/230, Mn 0.45/60, As 0.008/0.05 As, Cd 002/0.02, Co 0.28/4.4, Cr 0.01/0.12, Cu 0.035/0.22, Ni 0.41/6.9, Pb 0.002/0.017, V 0.07/1.1, and Zn 0.65/140. The water quality guideline (WQG) concentrations for these metals (in mg/L) are Al 0.055, As 0.013, Cd 0.0002, Co 0.02, Cr 0.001, Cu 0.0014, Ni 0.011, Pb 0.0034, V 0.006 and Zn 0.008. The metals which most often exceeded the WQGs were Cu (87% of 47 samples tested), Zn (68%), Ni (64%), Co (60%), Cd (51%), Mn (51%) and Al (>49%). For Al, Cu, and Zn, concentrations were often greater than 100×WQGs. The release of Al, Fe, Cr Cu, V and Zn increased as pH decreased and was adequately modelled using power functions. The mixing of acidic (pH 2.5) metal-spiked water with River Murray water (pH 7, 40 mg/L $CaCO_3$ alkalinity) indicated that at a 100-fold dilution the pH should increase to pH>6.5 and 30 to 99% of the trace metals may be removed through co-precipitation and adsorption to freshly forming aluminium and iron oxyhydroxide phases. However, although metals may be removed from the dissolved phase, the flocculation of aluminium may cause toxicity to a range of aquatic fish, and the trace metal-enriched precipitates may be toxic to a variety of filter feeding or benthic organisms. The soil re-wetting experiments and relationships between pH and metal release indicated that exceedances of WQGs in the River Murray system are likely if the mixed waters have pH 5, but possible at pH 6 if attenuation processes are inadequate. Higher pH, alkalinity and suspended solid concentrations in the mixed waters are expected to increase the rate of removal of dissolved metals. This study indicated metal releases from all of the sulfuric (19% of total) and sulfidic soil samples (53%) may cause significant ecological effects in the River Murray system. The duration for which dissolved metal concentrations exceed WQGs is likely to greatly influence whether ecological effects occur. To adequately quantify the risk of ecological effects occurring, greater understanding of the rate of metal release and attenuation processes is required.

INTRODUCTION

Soils in the River Murray system of South Australia are being impacted by a combination of low water levels and the presence of acid sulfate soils (ASS). As water levels recede in the river channel and surrounding wetlands, the exposed ASS may dry, causing oxidation of soil constituents (e.g. sulfide) which release acidity and cause significant decreases in soil pH (Fitzpatrick *et al.* 2008). This summary paper is based on a study conducted by Simpson *et al* (2008) to assess the potential for the mobilisation of acid and metals following the rewetting of a wide range of dried ASS subtypes in the lower River Murray and Lakes region (Figure 1).

Soil and water samples were collected from areas that were, or potentially will be exposed to the atmosphere before mid-2009 (+0.7 to -1.5 m AHD areas). The samples comprised both water logged (hydrosols), submerged sediments (subaqueous soils) and air-exposed dry or semi-dry soils (Fitzpatrick *et al.* 2008). The depth to which samples were collected (through the profile) was determined from a detailed assessment of soil horizons, and varied from site to site. Water samples for baseline characterisation were collected from the River Murray, adjacent wetlands, and Lakes Albert and Alexandrina.

METHODS

Approximately 150 samples of ASS and were selected from 63 sites below lock 1 at Blanchetown and comprised 11 River Murray sites (29 samples), 5 Wellington Weir sites (10 samples), 16 Lake Albert sites (44 samples), 19 Lake Alexandrina sites (31 samples), and 12 wetland sites (36 samples) (Figure 1). The samples were collected by wading and using a range of implements. Soil profiles were sampled from up to five soil depths (horizons, layers) to a maximum of about 60 cm depth. The ASS samples were photographed, described and characterised by physical and chemical analyses (e.g. pH, metals, acid-base accounting, organic carbon, particle size) using the methods described in Ahern *et al* (2004). Greater details of procedures for the collection and analyses of the soil samples are described in Fitzpatrick *et al.* (2008). The background water samples from seven locations were collected and handled using strict protocols to avoid sample contamination (Ahlers *et al* 1990) (Figure 1).

Soils, whether they were dry, moist or saturated when collected, were air-dried at 40ºC in a non fan-forced oven for five days before use in the mobilisation tests. The rapid remobilisation of acid (H^+) and metals was evaluated by resuspending 24 g of air-dried soil in 240 mL of oxygenated, unfiltered River Murray water for 24 h (100 g/L, 250 mL low density polyethylene bottle (Nalgene) rolled at 50 rpm on a bottle roller). After 24 h, a filtered (<0.45 µm) water sample was taken for analyses of alkalinity, major ions (Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}) and the trace metals and metalloids (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn). The pH, redox potential (Eh), specific electrical conductivity (EC) and dissolved oxygen concentration of the water were measured at the start and finish of all tests. Acid mobilisation tests were made on 135 samples and metal mobilisation tests on 47 samples.

The amount of metal released for soils shaken in water may increase with increasing total suspended solids (TSS, g/L) concentration. For metals that are present as salts (e.g. $MgSO_4$), the concentrations may continue to increase with increasing TSS concentration, until saturation is reached. However, for many metals, the relationship between metal release and TSS is usually non-linear and becomes independent of further increases in the TSS concentration at ~100 g/L. The kinetics of metal mobilisation was investigated for six soils at time-periods of 0.1, 6, 1, 3, 6, and 24 h. The kinetics tests indicated that metal release was initially very rapid, with >50% of the metal released after 24 h generally occurring in the first 6 h and a plateau forming by 24 h. These observations were the basis for selecting 100 g TSS/L and 24 h resuspension time for the rapid release tests.

The ability of the River Murray water to buffer inputs of ‘mobilised acidity and metals’ was assessed using mixing experiments. River Murray water (pH 7, 40 mg/L $CaCO_3$ alkalinity) and acidic metal-spiked water (pH 2.5; containing 0.2 mg/L As, Cd, Co, Cr, Cu, Ni, Pb, Se, V, Zn and 2 mg/L for Al, Fe and Mn) were mixed at ratio's of 1:10, 1:25 and 1:100 for 3 h, then changes in pH and dissolved metal concentrations measured. The experiments were made on River Murray water containing eight different non-acidic soils at TSS concentrations of 10 and 100 g/L.

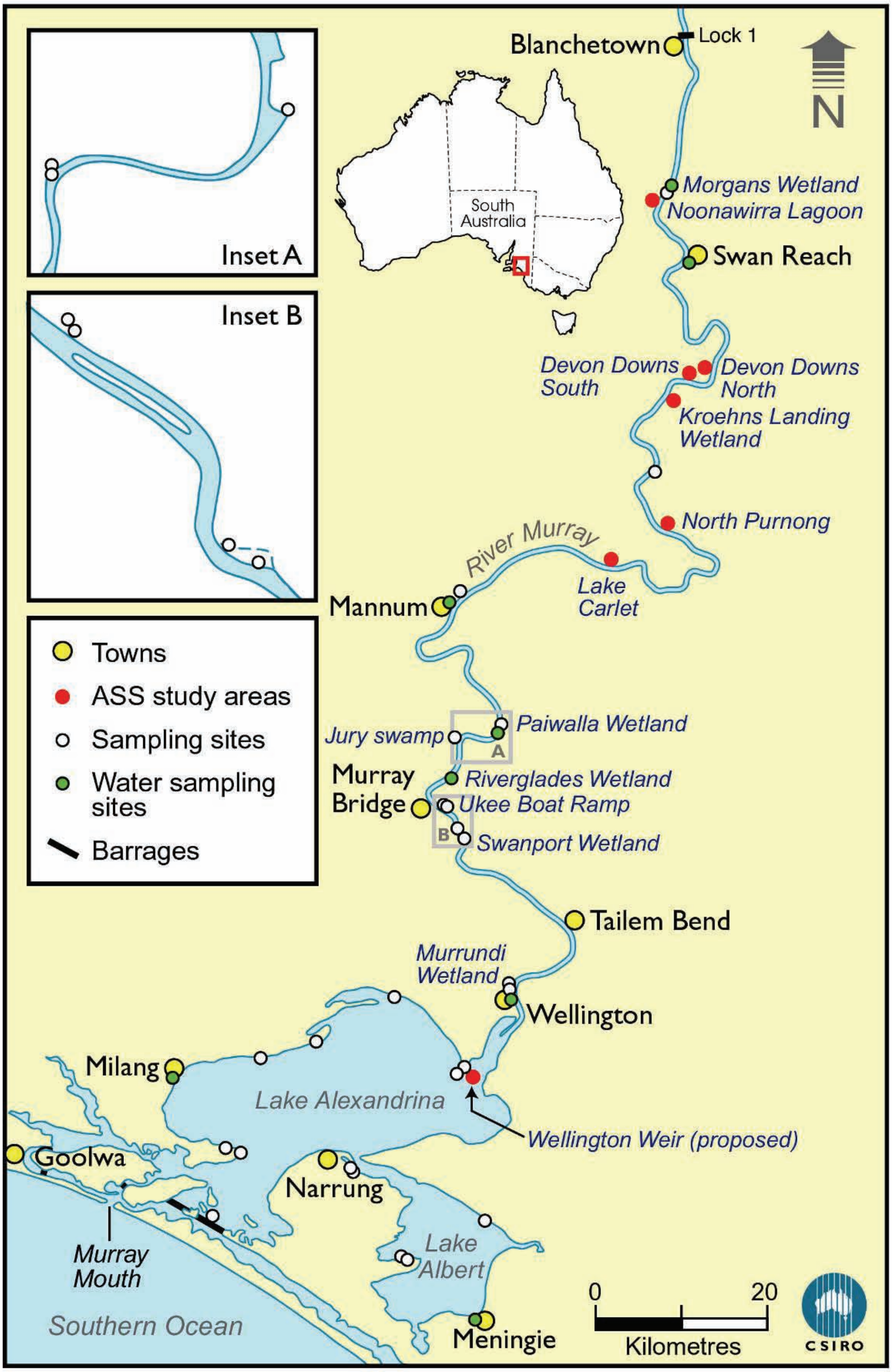

Figure 1. Water and soil sampling sites within the River Murray study area. At each soil sampling site depicted (○), up to four soil samples were collected from various soils depths.

Results

Soils: The 150 soil samples were identified in the ASS subtypes as: 29 sulfuric materials, 73 sulfidic materials, 2 MBO materials, 13 sulfide-rich clays, 32 sulfide-rich sands and sulfide-rich organic materials (Chapter 3). The moisture content (% water) of the soils ranged from 1% (dry) to 86% (water-logged). In total, 102 of the 150 samples (68%) were classified as either sulfuric (pH<4) or sulfidic (would go to pH<4 if suitable conditions existed). The pH of the soils ranged from pH 2.1 to 9.3: 9% were pH<3, 19% were pH<4, 30% were pH<5, 43% were pH<6, 58% were pH<7, and 87% were pH<9. The air-drying of the soils at 40ºC for 5 days did not result in sufficient oxidation of the soils to significantly lower the soil pH ($pH_{before\text{-}drying} = 1.00 \times pH_{after\text{-}drying}$, $r^2 = 0.92$), i.e. the sulfidic samples did not become sulfuric.

The particulate metal concentrations of the soils were low and below guideline concentrations for sediment and soil quality in waterways (ANZECC/ARMCANZ 2000). The wetlands generally had higher trace metal concentrations (e.g. Cr, Cu, Ni, Pb, V, Zn) than the River Murray and Lakes sites. For the River Murray (main channel) and Wellington Weir soils, none of the studied sites showed significant trends of particulate metals with soil depth, i.e. particulate metal concentrations did not consistently increase or decrease with soil depth. For some of the Lakes and wetlands sites, there were significant depth profiles for some metals, for example, one Ukee soil had particulate copper concentrations of 458, 537, 111, 83, and 11 mg/kg for soils at depths 0-0.5, 0.5-1, 1-8, 8-12, 12-20 cm.

Waters: The River Murray water used for the remobilisation tests had a pH of 7.4, conductivity of 450 µS/cm, 40 mg/L $CaCO_3$ alkalinity and concentrations of major ions were (in mg/L) 71 (Na^+), 4.5 (K^+), 14 (Ca^{2+}), 13 (Mg^{2+}), 26 (SO_4^{2-}) and 135 (Cl^-). Of all the water samples (Figure 1), the wetland at Meningie had the highest pH (8.7) and alkalinity (230 mg/L) and the wetland at Riverglades had the lowest pH (6.5) and had a small amount of acidity (5 mg/L as $CaCO_3$). The Meningie site had the highest concentrations of dissolved Al (0.5 mg/L) and Fe (0.6 mg/L) and these elevated dissolved concentrations are most likely to be a result of the high dissolved organic carbon concentration (25 mg/L) of this water.

The concentrations of trace metals in the waters were generally low, with the exception of the wetlands at Meningie, Paiwalla, and Riverglades waters (Table 1). The dissolved manganese concentration at the Riverglades site was 16 mg/L, the vanadium concentration at the Meningie site was 28 µg/L, and the zinc concentration at the Paiwalla and Riverglades sites were 60 and 85 µg/L, respectively. There were exceedances of water quality guideline concentrations (WQGs) for Ag, Cr, Zn at Paiwalla, for Ag, Cd, Co, Mn and Zn at Riverglades, and Ag and Cu at Meningie (Table 1). Dissolved metal concentrations at Swan Reach, Mannum, Wellington and Milang were low and below guideline concentrations (data not shown). Cd, Pb and Se concentrations were below detection limits of 0.05, 0.1 and 0.2 µg/L, respectively, for all samples, except Pb at Mennigie (1.1 µg/L versus WQG of 3.4 µg/L) and Cd at Riverglades (0.37 µg/L versus WQG of 0.2 µg/L). Silver concentrations were less than 0.2 µg/L in all waters, but above the WQG of 0.05 µg/L in half of the water samples.

Table 1. Comparison of dissolved metal concentrations to water quality guidelines

Site	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Mn µg/L	Ni µg/L	V µg/L	Zn µg/L
River Murray	0.6	<0.05	<0.1	<0.1	0.8	2	0.6	0.5	4.5
Paiwalla	1.9	<0.05	0.4	1.1	<0.2	<1	<0.1	1.9	58
Riverglades	1.4	0.37	86	0.2	0.8	16300	54	0.4	87
Meningie	3.1	<0.05	0.6	0.8	2.5	38	3.1	5.6	2.8
WQG (95% PC) [a]	13	0.2	1.4	1.0	1.4	1900	11	6	8.0

[a] Water quality guideline, 95% level of ecosystem protection (without hardness corrections etc) in ANZECC/ARMCANZ (2000). The WQG for As assumes all is as As(V), which is less toxic than As(III) (WGQ = 24 µg/L). The WQG for Cr assumes all is as Cr(VI). The WQG for Co and V are low reliability values. Exceedances of guidelines are in bold.

Acid and metal mobilisation from soils: The mobilisation of acid from soils was tested on 135 of the 150 soil samples. At the end of the 24-h mobilisation period, 6% had pH <3, 18% had pH <4, 25% had pH <5, 33% had pH <6, 67% had pH <7, and 95% had pH <8. There were significant positive relationships between the soil pH and the pH measured in the test water in which the soils were resuspended ($pH_{Water\,(24\text{-}h)} = 1.02 \times pH_{after\text{-}drying}$, $r^2 = 0.89$).

The 47 soils that resulted in the River Murray water becoming pH 6 or less were used for metal remobilisation tests. The metal release was demonstrated to be rapid, with >50% of the metal released after 24 h generally occurring in the first 6 h and a plateau forming by 24 h. The initial rapid metal release may have involved significant amounts of re-dissolution of metal salts that had formed relatively recently at the soil surface through the re-precipitation of metals that had been from the soil matrix as the soils acidified over much longer time periods. Beyond the 24-h time period there may be some ongoing release of metals, such as occurs due to oxidation of sulfides, but this will occur much more slowly and was expected to comprise a less significant portion (e.g. <20%) of the total metal release.

The concentrations of metals released from the different soils varied over several orders of magnitude (Table 2). There were exceedances of the water quality guidelines (WQGs) for all metals for which WQGs exist. The metals that most often exceeded the WQGs were Cu (87% of 47 samples), Zn (68%), Ni (64%), Co (60%), Cd (51%), and Mn (51%). Concentrations of dissolved Ag were <0.02 µg/L in all test waters. Lead concentrations were in the low ppb range and below WQG of 3.4 µg/L in most test waters. Selenium concentrations were below the WQG of 11 µg/L in all test waters. For aluminium, the limit of reporting (LOR) was 100 µg/L and above the WQG of 55 µg/L. It is possible that all (100%) of the mobilisation waters exceeded the WQG for aluminium (49% of samples definitely exceeded the WQG). The number of WQG exceedances after applying a dilution factor (10×, 100×, 1000×), expected for these waters mixing with river or lake water, was also calculated. Based on the maximum dissolved concentrations following dilution, the metals most greatly exceeding the WQGs by 10× were Ni (47% of 47 samples), Zn (43%), Cu (38%), and Al (34%). The metals exceeding the WQGs by 100× were Al (34% of 47 samples), Cu (11%), and Zn (11%). The metals exceeding the WQGs by 1000× were Al (4% of 47 samples) and Zn (2%).

Table 2. Concentrations of dissolved metals mobilised from soils for each sampling area.

	n	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Mn µg/L	Ni µg/L	V µg/L	Zn µg/L	Al mg/L	Fe mg/L
Maximum (All)	47	51	20	4400	120	220	60000	6900	1130	14000	460	230
Mean (All soils)	47	7.8	1.7	280	9.5	35	4530	410	71	650	49	39
SD (All soils)	47	11	3.9	760	21	57	10400	1200	190	2300	110	55
Murray River	11	3.6	0.52	80	4.0	34	2090	120	23	110	8.7	32
Wellington Weir	4	1.6	0.05	5.6	1.1	3.3	1000	7.1	3.5	11	<0.1	<0.1
Lake Albert	8	7.9	1.1	240	1.1	13	2600	250	1.8	140	13	8.1
Lake Alexandrina	8	9.0	1.7	150	5.4	45	2700	190	45	230	18	14
Ukee	10	15	5.2	880	32	84	14000	1360	280	2600	120	85
Jury Swamp	5	8.0	1.1	140	20	37	3700	190	150	476	33	68
Murrinda	6	1.6	0.05	8.0	0.4	2.9	380	7.0	3.4	11	0.48	<0.3
Paiwailla	1	4.7	0.05	6.6	0.4	4.3	180	5.3	15	2	<0.1	<0.1
Swanport	3	12	2.5	330	11	28	3700	520	67	350	12	17.4
WQG (95% PC) [b]		13	0.2	20	1.0	1.4	1900	11	6	8.0	0.055	NA

[a]SD = Standard deviation. [b]WQG, 95% level of protection (without hardness corrections etc). The WQG for As assumes all is As(V), which is more toxic the As(III) (WGQ = 24 µg/L). The WQG for Cr assumes all is as Cr(VI). The WQGs for Co and V are a low reliability values. Exceedances of guidelines are in bold. Concentrations of Ag and Sb were <0.02 and <0.5 µg/L, respectively.

Dissolved Metal - pH Relationships: Over the entire study area, there was no significant relationship between the soil depth and soil pH. However, there were significant relationships between the soil pH and (i) the final pH of the River Murray water in which the soil was resuspended, and (ii) the amount of release for many of the trace metals. The concentration-pH relationships were strong for Al, Cr, Cu, Ni, V, and Zn, but poor for Co and Mn (Figure 2). The significant relationships were non-linear over the pH range of the soils and indicated that a number of different processes are affecting the metal-release as a function of pH (Jenne, 1995). This is not surprising as the soils had varying properties (depending on site locations), and represented a range of soil depths and degrees of drying and oxidation.

Based on the relationships between soil pH and the dissolved metal release, for soils with pH <5 the associated waters are expected to have pH<5, and in the absence of processes that attenuate metal release, the WQGs are expected to be exceeded for at least one of the metals Al, Fe Cu, Ni, V or Zn.

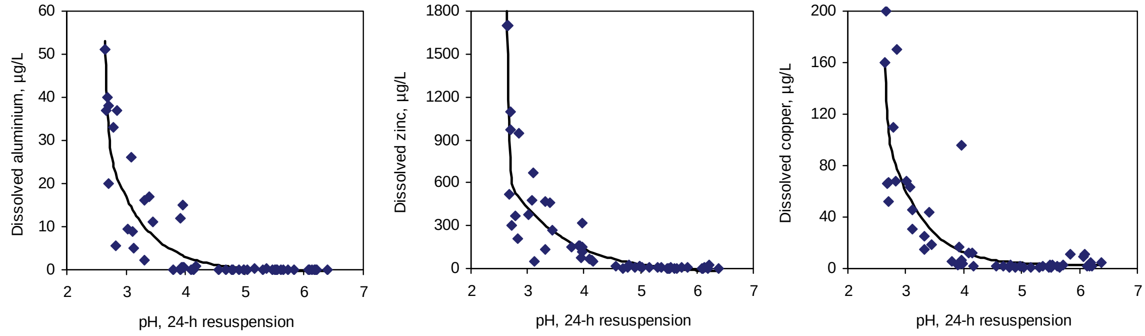

Figure 2. Released dissolved Al, Zn, and Cu as a function of pH. The model lines are:
Dissolved metal (µg/L) = y0 + A1*exp(-(pH-B1)/C1) + A2*exp(-(pH-B1)/C2) + A3*exp(-(pH-B1)/C3)

Precipitation and adsorption of trace metals through dilution with turbid waters: The metals mobilised from the soils may be transported either through soils (sub-surface) or transported into the surface waters. During sub-surface transport, the water can effectively be considered as groundwater and will interact with a range of different soil materials which may neutralise the acidity and adsorb many of the substances that were mobilised during re-wetting. During transport into surface waters, the mixing with waters of differing pH, alkalinity and concentration of TSS, may also result in neutralising of acidify and precipitation or adsorption of metals.

The mixing of 1-part acidic, metal-spiked water with 100-parts River Murray water (pH 7, 40 mg/L $CaCO_3$ alkalinity) was sufficient to raise the pH from 2.5 to 6.4-6.5, or to pH 6.6-7.2 for River Murray water containing 10 g/L soil TSS (depending on the soil). The presence of additional TSS generally resulted in little change in water alkalinity, although 10 g/L of a soil from the Paiwalla wetland resulted in a doubling of alkalinity to 80 mg/L $CaCO_3$). The pH increase in the mixed waters resulted in considerably lower dissolved metal concentrations: <1% (of total) for Al, Fe and Pb, <15% for As, Cr and Cu, <40% for Se and Zn, <60% for Cd, but less than 70% for Ag, Co, Mn, Ni and V. These results reflect the precipitation of Al, Fe and Mn (oxy)hydroxide phases (e.g. $Al(OH)_3$, FeOOH, MnOOH) as the pH increased, and the co-precipitation and adsorptive losses of trace metals that have low solubility or have a preference for adsorption to the iron and aluminium solid phases.

The effectiveness of the TSS (added as air-dried soils) in removing metals was different for the different TSS types. Some soils released significant amounts of dissolved Al and Fe (which is likely to be colloidal or complexed by dissolved organic matter (DOC) to remain in solution at this pH) and appeared to increase the removal of some trace metals (e.g. As, Cd, Ni, and Pb). For those soils, the magnitude of the removal of dissolved metals increased significantly (almost in proportion) as the TSS concentration increased. At 100-fold (as above), 25-fold and 10-fold dilutions of the acidic, metal-spiked water with River Murray the final pH was pH ~6.7, ~5.8 and ~4, respectively. The final dissolved metal concentrations reflected the final pH of the water, with much greater concentrations remaining in solution phase at the lower pH.

Toxicity and remobilisation of metal associated with precipitates

Although metals may be removed from the dissolved phase, it is well known that flocculation of aluminium at high concentrations is likely to cause toxicity to a range of aquatic aquatic fish, particularly for waters in the pH 5-6 range (Sparling *et al*. 1997). The precipitated Al, Fe and Mn oxyhydroxide phases are likely to be greatly enriched with trace metals through adsorption/co-precipitation. These precipitates may be toxic to a variety of organisms, e.g. aquatic organisms exposed to suspended solids through filter feeding or benthic organisms that graze on materials at the sediment-water interface (Simpson and Batley 2007). The metals associated with the iron and manganese precipitates may also be easily remobilised to the dissolved phase if these phases undergo reductive dissolution to form Fe(II) and Mn(II), which is likely to commence shortly after the precipitated materials are deposited as sediments. Although in reducing environments (low dissolved oxygen), the bacterially-mediated reduction of sulfate to sulfide may result in the formation of relative insoluble metal-sulfide phases, these phases may be re-oxidised with water conditions change, resulting in re-release of the metals to the water column. The ongoing oxidative-precipitation and reductive-dissolution reactions may result in the metal remaining labile and highly bioavailable for long periods of time (following the initial mobilisation).

CONCLUSIONS

Acid sulfate soils exist in the River Murray system, which are progressively becoming acidic as a result of air exposure caused by lower water levels. The re-wetting of these soils has been demonstrated to mobilise significant quantities of acid and trace metals. For Al, Cu, and Zn, the concentrations released were often greater than 100× the water quality guideline (WQG) concentrations. There were strong concentration-pH relationships for Al, Fe Cu, Ni, V and Zn. The mixing of these acidic metal-rich waters with River Murray water is likely to result in the removal of 30 to 99% of the trace metals through co-precipitation and adsorption to freshly forming Al, Fe and Mn oxyhydroxide phases. However, although metals may be removed from the dissolved phase, the flocculation of aluminium may cause toxicity to a range of aquatic fish, and the trace metal-enriched precipitates may be toxic to a variety of filter feeding or benthic organisms. The soil re-wetting experiments and relationships between pH and metal release indicated that exceedances of WQGs in the River Murray system are likely if the mixed waters have pH 5, but WQG exceedances may occur even at pH 6 if attenuation processes are inadequate. Higher pH, alkalinity and suspended solid concentrations in the mixed waters are expected to increase the rate of removal of dissolved metals. The study indicated metal releases from all of the sulfuric (19% of total) and sulfidic soil samples (53%) may cause significant ecological effects in the River Murray system. The duration for which dissolved metal concentrations exceed WQGs is likely to greatly influence whether ecological effects occur. To adequately quantify the risk of ecological effects occurring, greater understanding of the rate of metal release and attenuation processes is required.

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CHAPTER 4

GEOCHEMICAL DISPERSION IN ACID SULFATE SOILS: IMPLICATIONS FOR MINERAL EXPLORATION IN THE MOUNT TORRENS-STRATHALBYN AREA, SOUTH AUSTRALIA

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ABSTRACT

Acid sulfate soils (ASS) from creeks, dams, seeps, springs and wetlands were sampled in an area 25 km wide and 40 km long in the eastern Mt Lofty Ranges, between Mt Torrens in the north and Strathalbyn in the south. Acid sulfate soils are most common in landscapes with relief and can occur in seeps or springs (on mid to upper slopes of valleys) or in creeks and wetlands, typically in narrow valleys. Acid sulfate soils contain sulfidic material (Fe and other sulfides; pH >4), which may form continuous layers (up to at least 30 cm thick), or consist of a series of discontinuous layers, normally below water level, associated with decaying vegetation and algae. Acid sulfate soils appear to be absent from broad valleys with relatively thick accumulations of alluvium and where drainages may be dry.

Sulfidic material may contain two types of iron sulfide: pyrite and monosulfides (such as greigite or mackinawite). The matrix to the sulfides is dominantly quartz, with variable minor amounts of mica, plagioclase, potash feldspar, calcite and kaolinite. In drained or disturbed ASS, several rare to accessory phases such as gypsum, halite, jarosites, ferrihydrite and/or schwertmannite and Fe oxides occur in sulfuric horizons (pH <4). However, in the vicinity of mineralised zones in bedrock, sulfidic materials may also contain sphalerite, galena, chalcopyrite, native gold, barite and Mn oxides (with minor Co, Zn and I). These minerals tend to be intimately associated with, and incorporated in, organic matter. In particular, sphalerite and galena tend to occur in very fine (<1 μm diameter) spherical grains and have been precipitated as a result of biomineralisation. The compositions of the sphalerites in sulfidic material are relatively Fe-poor, in contrast to those from the mineralised zones (significantly richer in Fe).

Acid sulfate soils proximal to mineralised zones in bedrock are anomalous in a range of elements, including Ag, As, Au, Bi, Cd, Co, Cu, Hg, In, Ni, Mo, Pb, Sb, Se, Tl and Zn, for example, at Wheal Ellen, Glenalbyn, the Mt Torrens and Monarto prospects, and in the Kanmantoo area. Several anomalies also occur in locations not associated with known mineralisation. These materials may also record geochemical differences in parent bedrock, such as the distribution of Na and K on either side of the Bremer Fault. To the west of the fault, Na and K are positively correlated, whereas to the east, Na and K are negatively correlated and Na contents are greater. These differences may relate to regional fluid flows, possibly related to the relatively intense mineralising event to the west of the fault, or to regional metamorphism, or to granitoid intrusion in the east. A soil-landscape conceptual model has been developed for the soil, regolith and hydrogeochemical processes and explains geochemical dispersion from mineralised zones into acid sulfate soil seeps.

The principal conclusions of this study confirm that various materials associated with acid sulfate soils are a new and valid sampling medium for mineral exploration.

INTRODUCTION

Acid sulfate soils in saline seeps occur naturally in the Mount Lofty Ranges, but are expanding in response to land clearing, rising water tables and soil disturbance (such as drainage, or pugging by grazing animals). The seeps can form unsightly discharge areas, with eroded “iron ochre scalds” and swampy saline sulfidic soils, which continue to creep up slopes in high rainfall (>500mm) catchments. Recent investigations have found that accumulation and oxidation of iron and sulfur in seasonally rising ground and surface water are causing less permeable soil layers to form in discharge areas (Fitzpatrick *et al* 1996). Data on the composition of the iron oxide precipitates forming in the saline sulfidic soils indicates that they commonly have elevated levels of indicator elements, for which the iron oxides have a high sorptive capacity (Skwarnecki *et al* 2002a, b). These scalds and associated iron oxide precipitates thus have potential as a geochemical sampling medium for the detection of mineral deposits. Consequently, this information has potential to be used to assist in understanding the underlying regolith and develop new tools for mineral exploration. In particular, they have potential to give, or at least enhance, surface expressions of otherwise buried and blind deposits.

In several catchments in the Mount Lofty Ranges, saline groundwater, enriched in sulfate (SO_4^{2-}) and ions such as Na^+, Mg^{2+}, AsO_4^{3-}, I^- and Cl^-, can seep up through the soil and concentrate by evaporation, forming various mineral precipitates within and on top of the soil. The combination of rising sulfate-rich groundwater tables, waterlogging, agricultural activity and fractured lithologies rich in Fe and S can lead to the formation of saline soils with potential and actual acid sulfate (AASS) soil conditions (Fitzpatrick *et al* 1996, 2000). If the soil is waterlogged, anaerobic bacteria use the sulfate to promote the degradation of organic matter. This process produces pyrite (FeS_2) and forms sulfidic material (Isbell 1996). This pyrite-enriched soil material is termed “potential” acid sulfate soil material (PASS material) because they have all the ingredients necessary to produce sulfuric material or actual acid sulfate soil material (AASS-materials). Sulfuric material (AASS material) result when cattle, drainage works or other disruptions expose the pyrite within waterlogged soils to air. When this happens, pyrite is oxidised to sulfuric acid and various iron sulfate-rich minerals precipitate, and sulfuric material or "actual" ASS forms. When sulfuric acid forms, the soil pH can drop from neutral (pH 7) to below 4, with values as low as 2, to form sulfuric material ("sulfuric horizon" according US Soil Taxonomy). The sulfuric acid dissolves layer-silicate minerals within the soil, causing ions (e.g, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cl^-, SO_4^{2-}, SiO_4^{4-}) to be mobilised on the soil surface and in stream waters.

An orientation study at the Mount Torrens Pb-Zn prospect (Skwarnecki *et al* 2002a, b) indicated that saline acid sulfate seeps and soils can be used as exploration sampling media. Sulfidic materials contain anomalous concentrations of As, Ba, Bi, Cd, Cu, P, Pb, Sn, Tl and Zn along the strike of the mineralized zone. The study concluded that these sulfidic material and associated iron oxide precipitates were a geochemical sampling medium for the detection of mineral deposits. The next stage of the project, involved the systematic regional sampling of seeps (Skwarnecki and Fitzpatrick 2003a, b) constrained by catchments and areas of known mineralisation, together with background areas with no known mineralisation, to provide a robust evaluation of the technique. This summary paper is based on several studies (Skwarnecki *et al* 2002a, b; Skwarnecki and Fitzpatrick 2003a, b; Fitzpatrick *et al* 1992, 1996, 2000, 2002; Fitzpatrick and Skwarnecki 2005) to assess the potential for acid sulfate soils to be used as sampling medium for mineral exploration.

LOCATION, LANDSCAPE, CLIMATE AND LAND USE

Samples were collected in the eastern Mt Lofty Ranges (Figure 1) from an area up to 25 km wide and 40 km long, between Mt Torrens (34°53’S 138°58’E) and Palmer (34°51’S 139°09’E) in the north and Strathalbyn (35°16’S 138°54’E) in the south.

The landscape is undulating low hills with altitudes between 400 to 500m and local relief of about 30 to 50m. The climate of the area is Mediterranean, with a pronounced maximum of rainfall in winter (May to August) and hot, dry summers (December to February). Annual rainfall is topographically controlled, with a mean average annual rainfall of 680 mm. Average annual rainfall varies from about 800 mm at Mt Torrens and Mt Barker (in the northwest), to about 500 mm at Strathalbyn, 420 mm at Palmer, and to 400 mm and less south-east of Callington (in the southeast). During the sampling period (July-August, 2002), rainfall was significantly below average (97 mm at Mt Torrens (average 150 mm) and 76 mm at Strathalbyn (average 104 mm)).

The land cover of the area is predominantly pasture, with most native tree vegetation having been cleared by the end of the 19th century. The remaining areas of remnant vegetation are associated mainly with topographic high points, roadways and watercourses. Land use is predominantly pastures grazed by sheep or cattle. Increasingly, land is being used for more intensive purposes such as viticulture, commercial forestry and some cereal cropping. The catchments drain to the east and into the Murray River system. Stream channels have a normal tributary pattern and are mostly eroding soils, bedrock or the alluvial soils and sediments of valley floors, locally to depths of two to three metres.

Regional geology

The Kanmantoo Group (Figure 2; Belperio et al 1998; Toteff 1999) occurs in a fault-controlled basin that developed in the early Cambrian by extensional tectonism along the southeastern flank of the Neoproterozoic Adelaide Geosyncline, following initial stable platform carbonate sedimentation (Normanville Group). The marine clastic flyschoid sediments of the basin (together with the Neoproterozoic succession to the west) were deformed, metamorphosed and intruded by granites during the Delamerian Orogeny (middle to late Cambrian), and are now exposed in an arcuate zone over 300 km in length in the eastern and southern Mount Lofty Ranges. At least two main phases of deformation have been recognised. Metamorphism at low pressure and high temperature locally attained amphibolite facies, and appears to have coincided with a major period of granite emplacement.

The apparent thickness of the Kanmantoo Group is up to 15 km, and may consist of a stack of thrust sheets. The main rock types are sandstones, siltstones and phyllites, with intercalated pelites and minor carbonates. The lowermost sequence comprises muddy sandstone and siltstone (Carrickalinga Head Formation), which passes up into cleaner, cross-bedded, feldspathic sandstone (Backstairs Passage Formation). A disconformity separates the Backstairs Passage Formation from the overlying upper parts of the sequence, which comprises interbedded muddy sandstone and siltstone (Tapanappa and Balquhidder Formations), and dominantly fine-grained clastic rocks of the Talisker Calc-siltstone, and Tunkalilla Formation.

Most of the significant base-metal syn-sedimentary mineralisation in the Kanmantoo Group is confined to the Tapanappa Formation. It may be spatially associated with exhalites, such as garnetiferous lithologies (including BIF) and gahnite-bearing rocks, and unusual metamorphic mineral assemblages interpreted to be metamorphosed alteration zones. Sulfide mineralisation has been classified into four commodity-based categories:

(i) Cu±Au (e.g., Kanmantoo (Both, 1990), Breadalbane, Bremer (Spry 1976; Both 1990));
(ii) Pb-Zn-Ag±Au (e.g., Aclare (Askins 1968), Wheal Ellen (Wade & Cochrane 1952; Spry 1976));
(iii) Cu-As±Au (e.g., Preamimma (Anon 1924), Glenalbyn (Brown 1908));
(iv) Fe (pyrite, pyrrhotite) at various stratigraphic levels (e.g., Brukunga (George, 1967)).

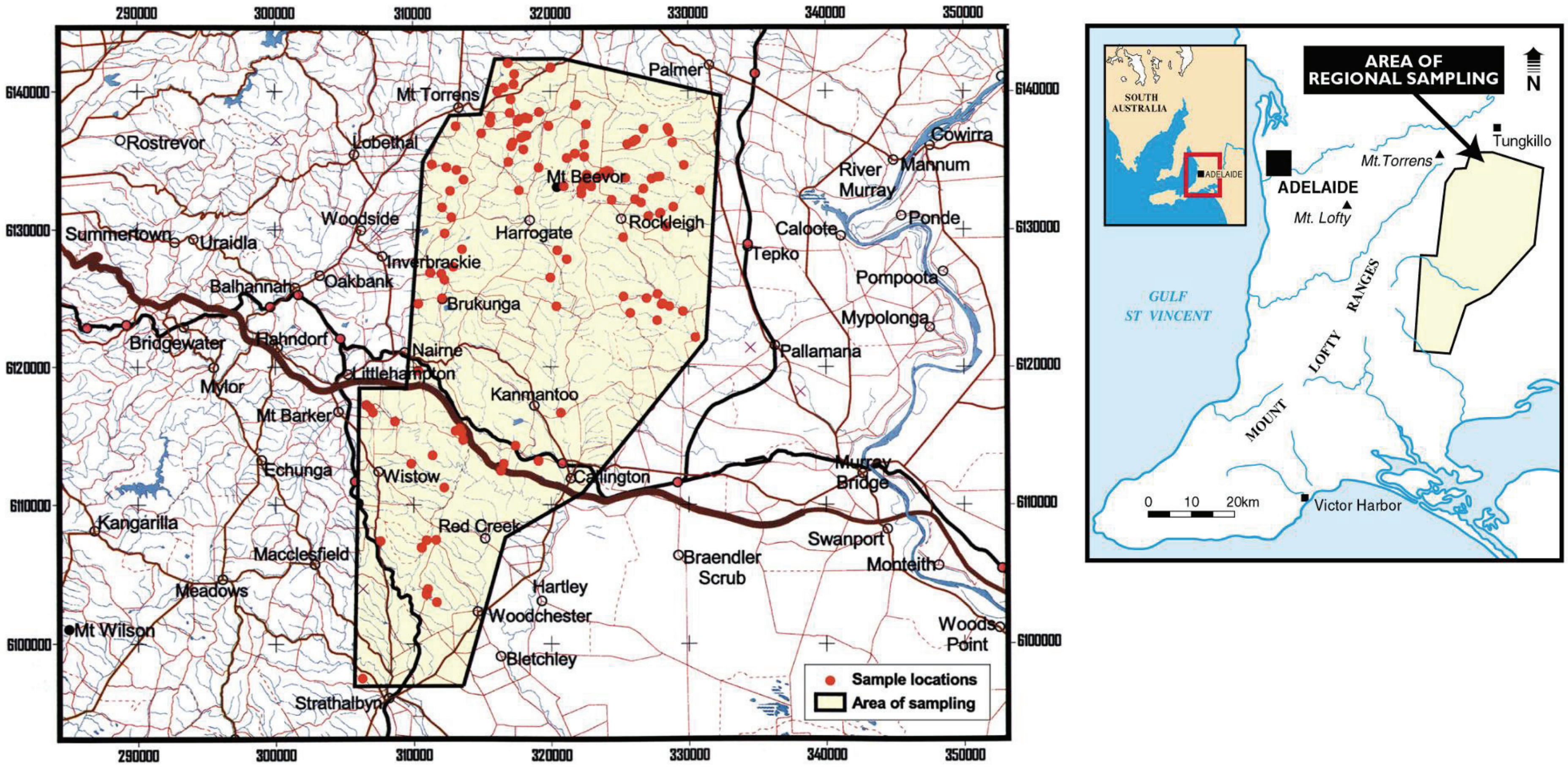

Figure 1. Location of the samples collected in the eastern Mt Lofty Ranges, South Australia.

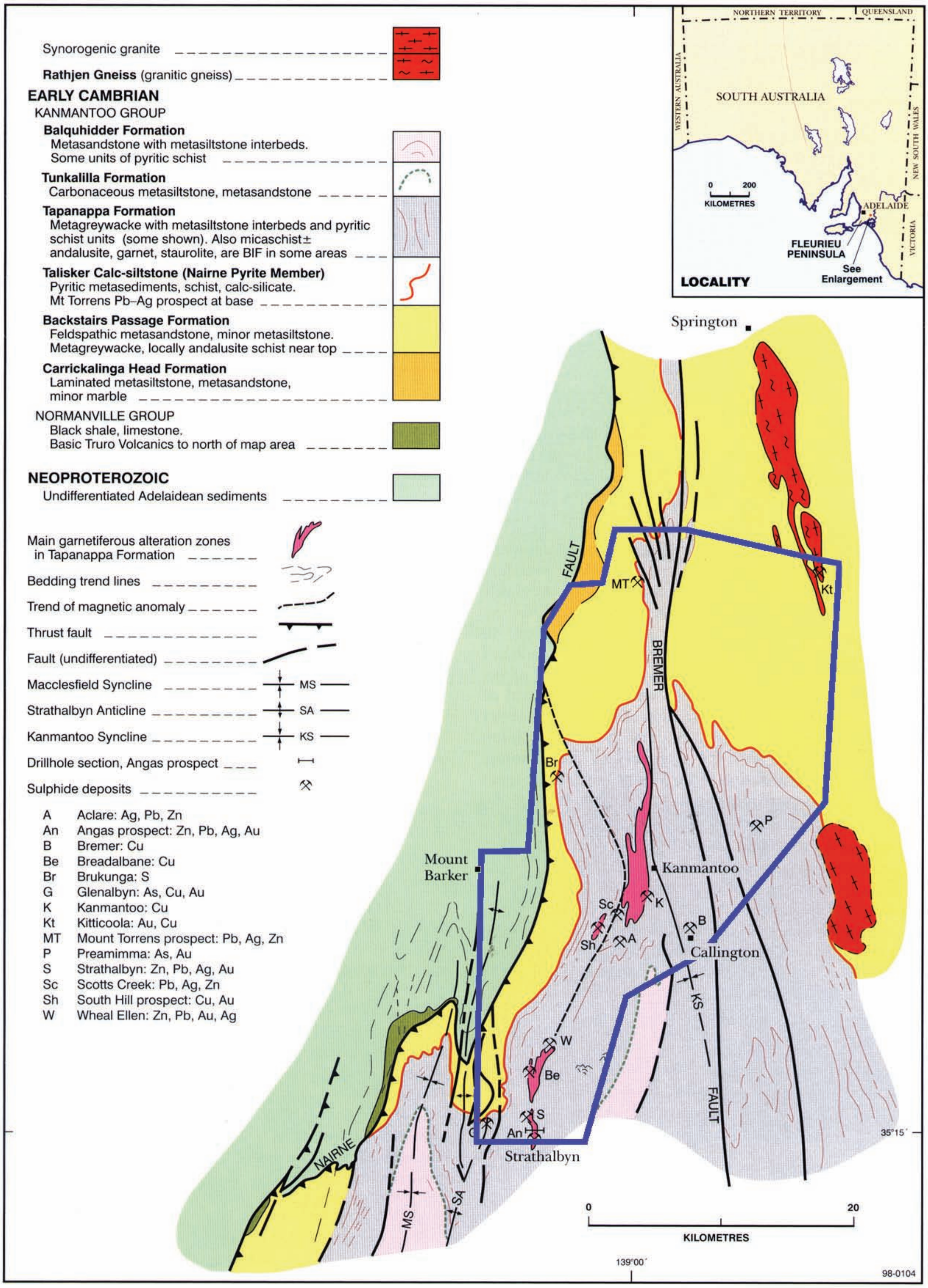

Figure 2. Regional geological setting of mineral deposits in the Kanmantoo Group (from Toteff, 1999). The blue polygon indicates the area of study.

METHODOLOGY

The main part of the regional sampling programme was carried out between late June and early September, 2002, during a relatively dry winter. Previous samples from acid sulfate seeps at the Mt Torrens prospect (Skwarnecki et al 2002a) were incorporated into this study.

One hundred and fifty samples of ASS materials were collected (Figure 1), of which 125 were sulfidic, and 25 were oxidised:
(i) 35 samples from seeps (8 oxidised)
(ii) 71 samples from creeks (9 oxidised)
(iii) 7 samples from wetlands (3 oxidised)
(iv) 6 samples from springs (1 oxidised)
(v) 6 samples from dams
(vi) 4 samples from creek banks
(vii) 2 (oxidised) samples from scalds
(viii) 2 (oxidised) samples from water-filled depressions.

Samples were oven-dried (at 40^{o}C), a 250g aliquot of sample was crushed in a jaw crusher (core and samples from outcrop), and about 100 g was milled in a Cr-free disc mill to a nominal 90% passing through 106 μm.

The milled aliquots were analysed by atomic absorption spectrophotometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma spectrometry (ICP-MS) by AMDEL in Adelaide. The digestions, methods and respective element suites were:
(i) Au – aqua regia digest (a mixture of nitric and hydrochloric acids) of sample (up to 50 g), extraction into di-isobutyl ketone (DIBK), and analysis on a graphite furnace AAS
(ii) ICP-OES suite (Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Nb, Ni, P, Pb, S, Ti, V, Zn); sample digestion with hydrochloric, nitric and hydrofluoric acids, with a final dissolution in hydrochloric acid (mixed acid digest)
(iii) ICP-MS suite (Ag, As, Bi, Cd, Co, Cs, Ga, In, Mo, Rb, Sb, Se, Sn, Sr, Te, Th, Tl, U, W, Y, Hf, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb); mixed acid digest
(iv) Hg – aqua regia digest followed by generation of cold vapour and analysis by AAS.

The samples were also analysed by X-ray fluorescence spectrometry (XRF) at CSIRO for SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, Cl and Zr on fused borate glass discs.

Scanning electron microscope (SEM) analyses were carried out on a Philips XL30 (FEG-SEM) using an EDAX DX4 energy-dispersive X-ray analyser at the Centre of Electron Microscopy and Microanalysis South Australia (CEMMSA), University of Adelaide. Polished thin sections and polished blocks were coated with a 20 nm film of carbon. Analyses were standardless using ZAF corrections on an accelerating voltage of 20 kV. The main purpose of using the SEM was to acquire high-quality back-scattered electron images.

ACID SULFATE SOILS

Occurrence

Soils with acid sulfate features (such as Fe sulfide-rich material, sulfidic material and sulfuric material) occur in creeks, seeps, wetlands, springs and dams. With the exception of springs, acid sulfate soils tend to occur in those environments affected by salinity, such as: degraded agricultural land, commonly with tall wheat grass or sea-barley grass, adjacent to drainages; scalded ground, generally devoid of vegetation and dissected by erosion gullies; white salt encrustations along creek banks; or clear waters in creeks and dams (due to suppression of clay flocculation). Springs can occur in both saline and non-saline environments.

Acid sulfate soils are most common in landscapes with relief, and can occur along creeks (Figure 3a) on the sides of valley slopes (in seeps or springs; Figure 3b-c) and in wetlands, typically where drainages are narrow, where there is abundant outcrop (i.e., in erosional terrains), and where drainages are flowing (such as Loxton Creek). In creeks, acid sulfate soils generally occur below water level, in upper parts of the stream sediment. The sulfidic horizons (continuous layers or as series of discontinuous layers and streaks) may in rare instances exceed 30 cm in thickness, and are commonly associated with decaying vegetation and green/pink algae, typically in stagnant pools.

Figure 3a. Subsurface acid sulfate soil (grey to black) in stream sediment. Note that the sulfidic material occurs beneath a veneer of sand and the partial oxidation (orange-brown). Sample site KRS59.

Figure 3b. Acid sulfate soil in a natural spring associated with wetland vegetation. Sample site KRS142.

Figure 3c. Acid sulfate soil in a seep in pasture. Sample site KRS135.

Figure 4a. Ferrihydrite (orange-brown) weeps in stream sediment indicating the presence of sulfidic material beneath a veneer of sand. Sample site KRS68.

Figure 4b. Ferrihydrite-rich layer (orange-brown) overlying sulfidic material. Sample site KRS63.

The presence of sulfidic materials in stream sediment may be indicated by ferrihydrite weeps (Figure 4a), or, in extreme cases, by a layer several millimetres thick of ferrihydrite and orange algae (Figures 4b). In contrast, acid sulfate soil features were not found where drainages are dry or along broad valleys with relatively thick alluvium (i.e., in depositional terrains), as in the area between Harrogate and Callington.

In a few instances, acid sulfate soil materials were found in dried-out, sandy creek beds, in damp depressions or below decaying algal mats, several centimetres below surface associated with subsurface water. Where desiccation was complete, the sulfidic material in the acid sulfate soil had been oxidised to red-brown/orange-brown Fe oxides (mainly ferrihydrite, schwertmannite or goethite; Figure 4a,b) and occurred as layers mimicking the original sulfidic material in the acid soil layer.

There are two end-member types of sulfidic materials in acid sulfate soils, based on iron sulfide mineralogy: (a) pyrite-bearing material; and (b) monosulfide-bearing material, with iron sulfides such as greigite or mackinawite (Bush and Sullivan 1997). However, in practice, most, if not all, samples collected contain both. The two types can be distinguished in the field by smell (monosulfide-bearing varieties tend to be malodorous), colour (monosulfide-rich varieties are black and gelatinous, pyrite-rich varieties tend to be brown), and chemical reaction with HCl (monosulfides react to produce H_2S, pyrite is unreactive).

MINERALOGY

Acid sulfate soils are quartz-rich, with variable minor amounts of muscovite, plagioclase, orthoclase, microcline, calcite, sulfides (pyrite and/or monosulfides) and kaolinite, and lesser to accessory halite, bassanite ($CaSO_4.{}^1/_2H_2O$), gypsum, jarosite, natrojarosite, bischofite ($MgCl_2.6H_2O$), ferrihydrite and/or schwertmannite, hematite, goethite, aragonite, montmorillonite, illite, halloysite, beidellite, zircon, anatase and/or rutile, monazite, xenotime, ilmenite, actinolite, biotite and chlorite. In one sample, one grain of $CdCl_2$ was associated with halite, within a ferrihydrite precipitate.

Adjacent to mineralised zones in bedrock, acid sulfate soil materials may contain sulfides other than pyrite and monosulfides, such as sphalerite, galena and chalcopyrite, sulfates such as barite and plumbojarosite (see Skwarnecki et al 2002a), native gold and Mn oxides (with minor Co, Zn and I). The presence of these minerals corresponds to anomalous accumulations of Cu, Pb, Zn, Au and other elements.

SULFIDES

Pyrite

Pyrite is the most common sulfide. It occurs as:

(i) disseminated euhedral cubes, typically associated with organic matter (Figure 5a)
(ii) as coatings on Mn oxides (Figure 5b)
(iii) individual framboids (Figure 5c), or clusters of framboids (Figure 5d), associated with disseminated pyrite. Three types of framboids have been recognised:
    (a) the most common, comprising aggregates of cubes (Figure 6a)
    (b) aggregates of pyritohedra (Figure 6b)
    (c) aggregates of rounded grains (Figure 6c).
(iv) disseminated, in calcite nodules.

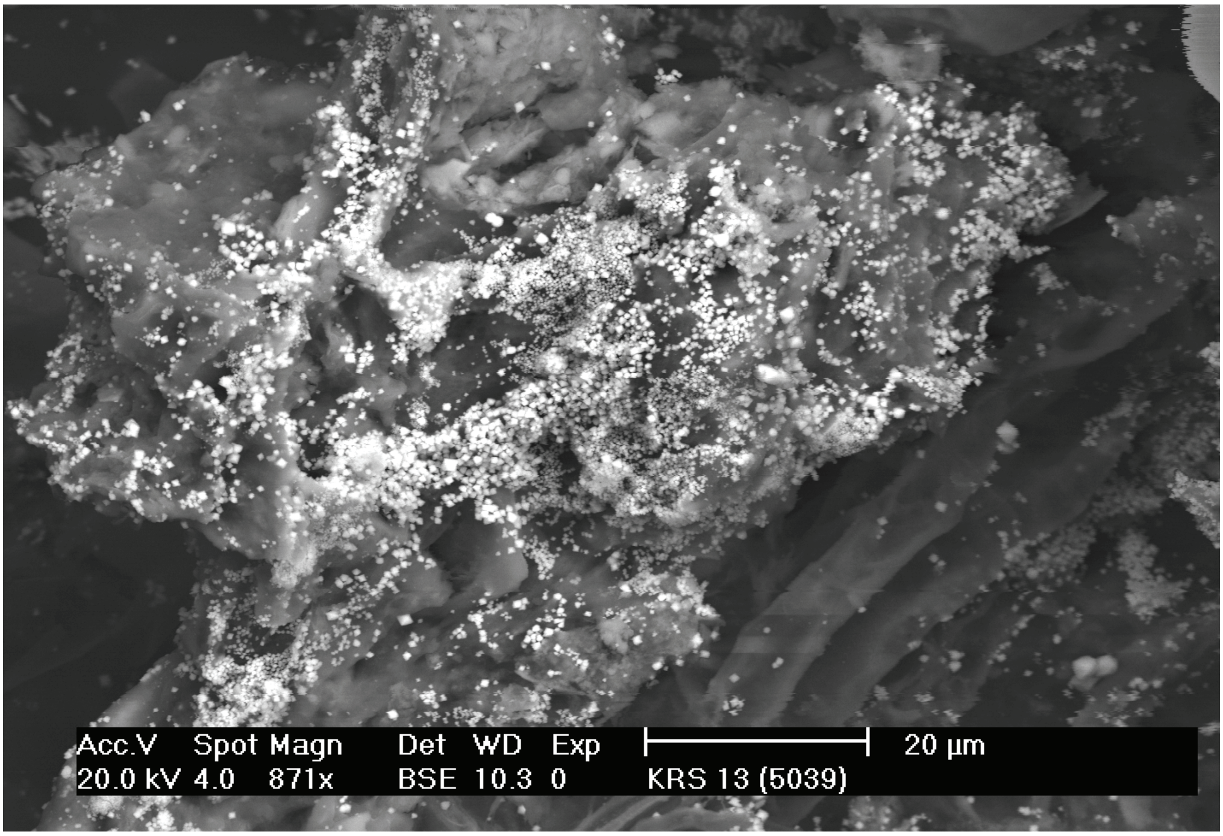

Figure 5a. Fine-grained, disseminated pyrite grains on organic matter. Sample KRS13, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

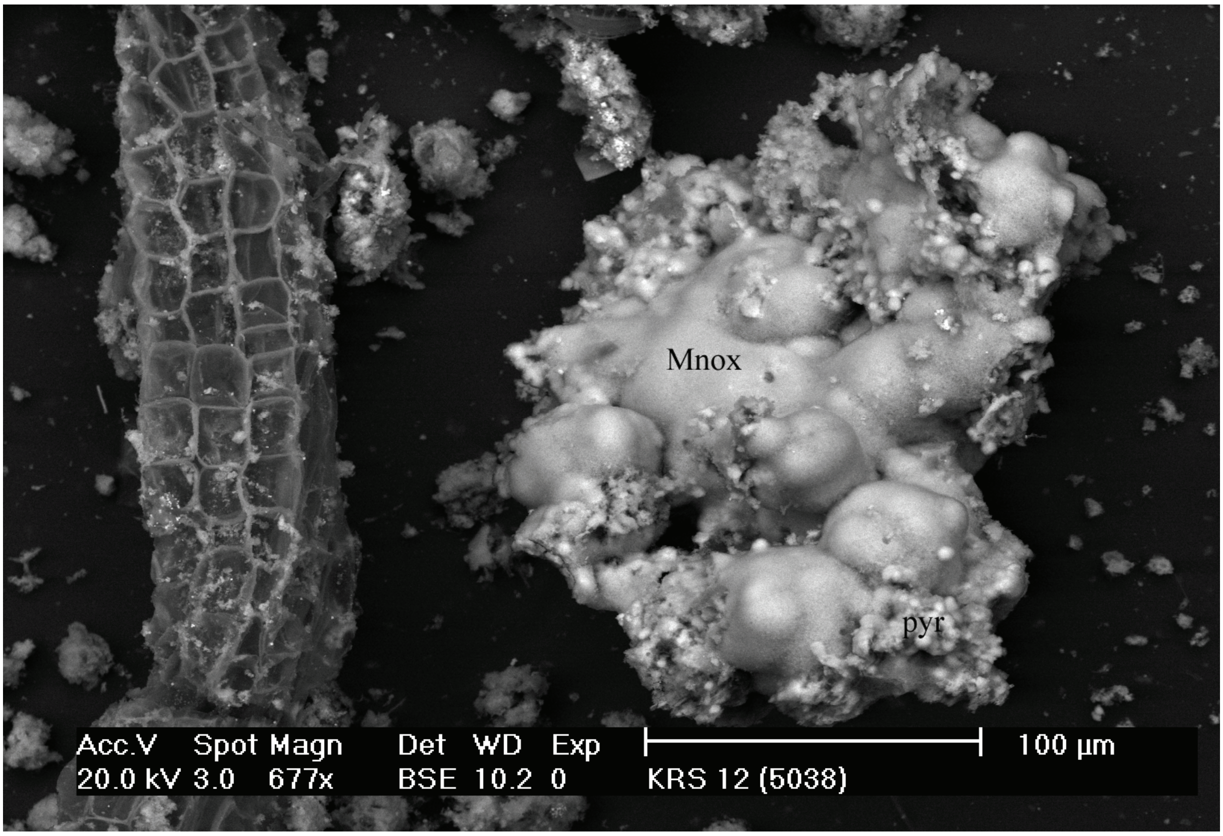

Figure 5b. Pyrite (pyr) aggregates encrusting a botryoidal aggregate of cobaltian Mn oxides (Mnox) associated with plant material. Sample KRS12, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

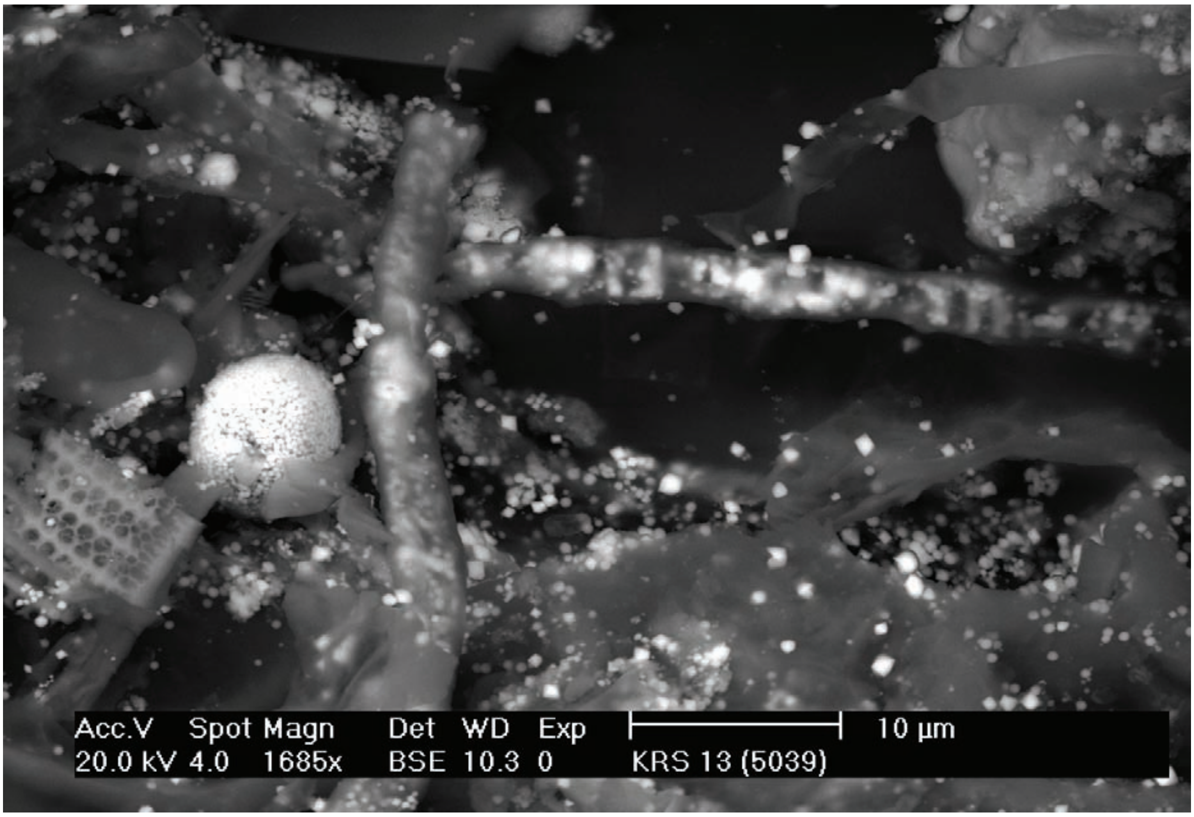

Figure 5c. Pyrite framboid associated with a diatom fragment. The rootlets contain anhedral sphalerite grains. Sample KRS13, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

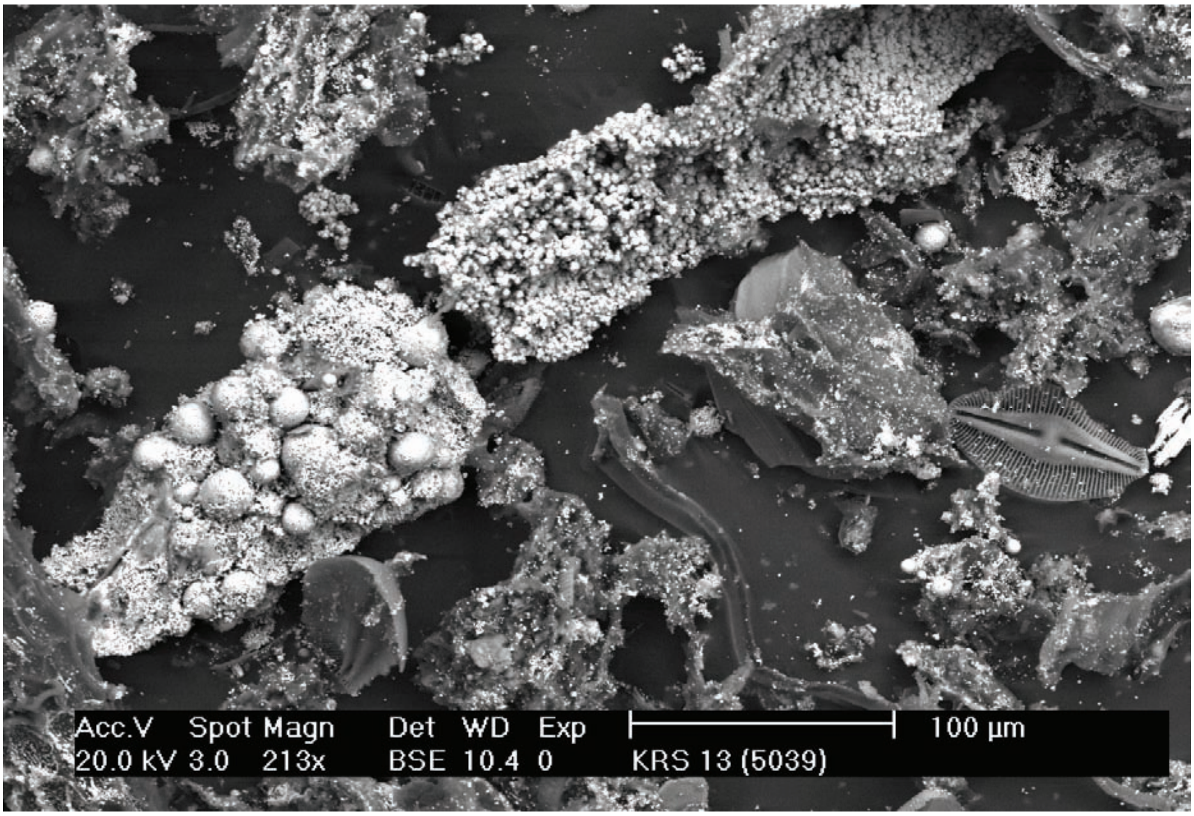

Figure 5d. Aggregates of pyrite framboids and individual grains encrusting a rootlet. Individual framboids, disseminated pyrite cubes and rare diatoms occur in the matrix. Sample KRS13, mound springs, Wheal Ellen. Back-scattered electron image (SEM).

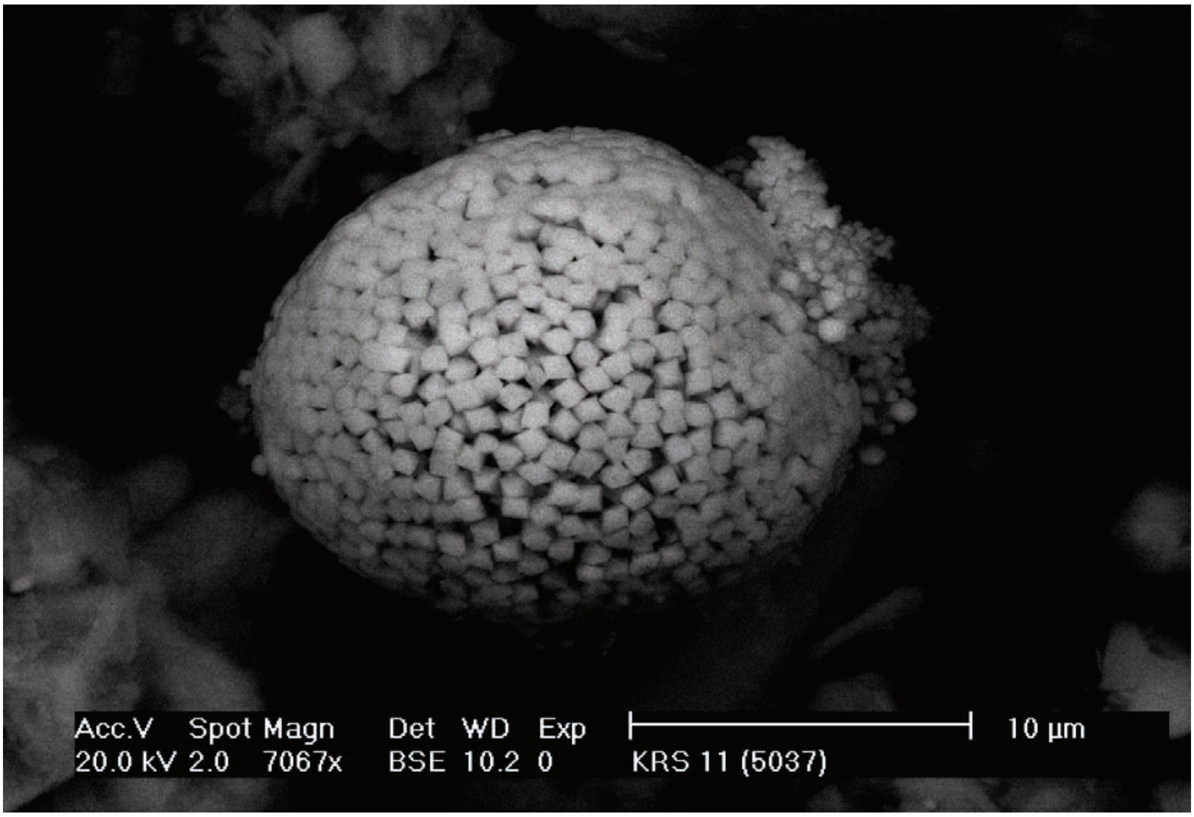

Figure 6a. Pyrite framboid composed of cubes. Sample KRS11, Glenalbyn mine. Back-scattered electron image (SEM).

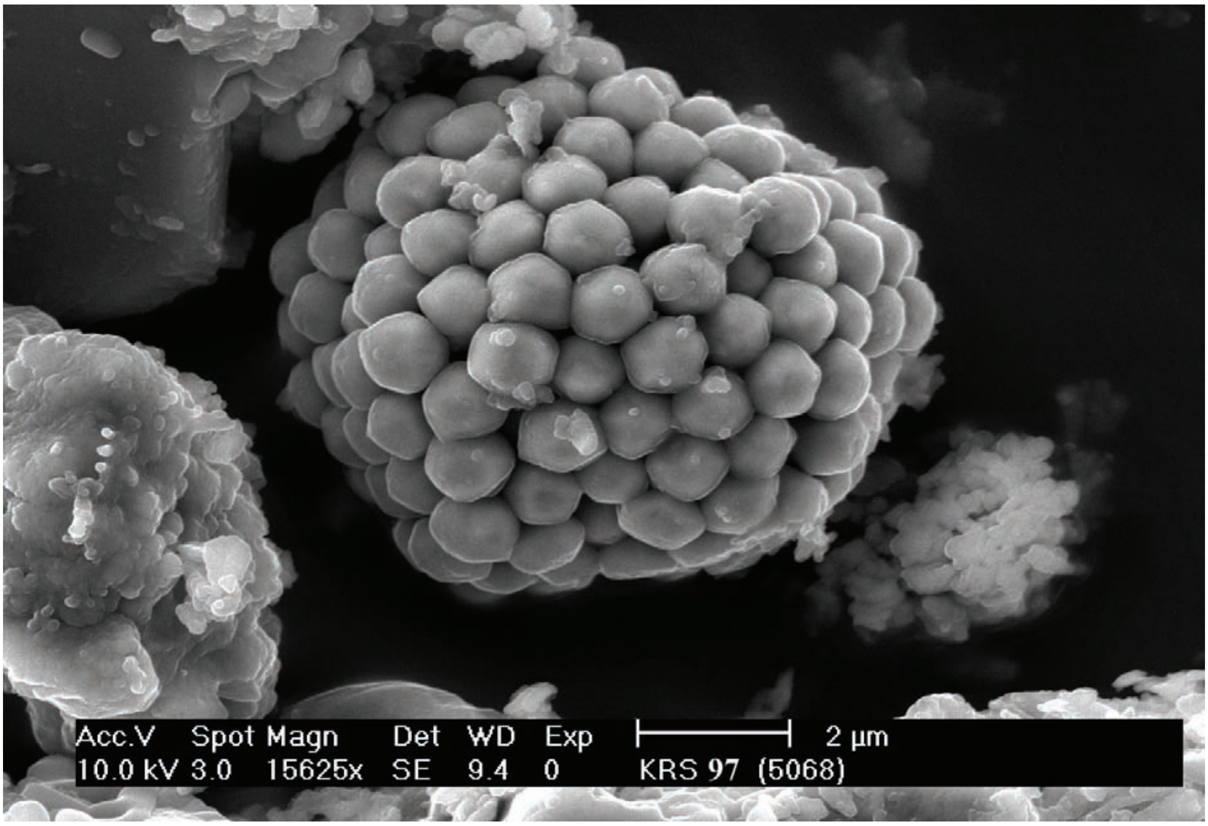

Figure 6b. Pyrite framboid composed of pyritohedra. Sample KRS97. Back-scattered electon image (SEM).

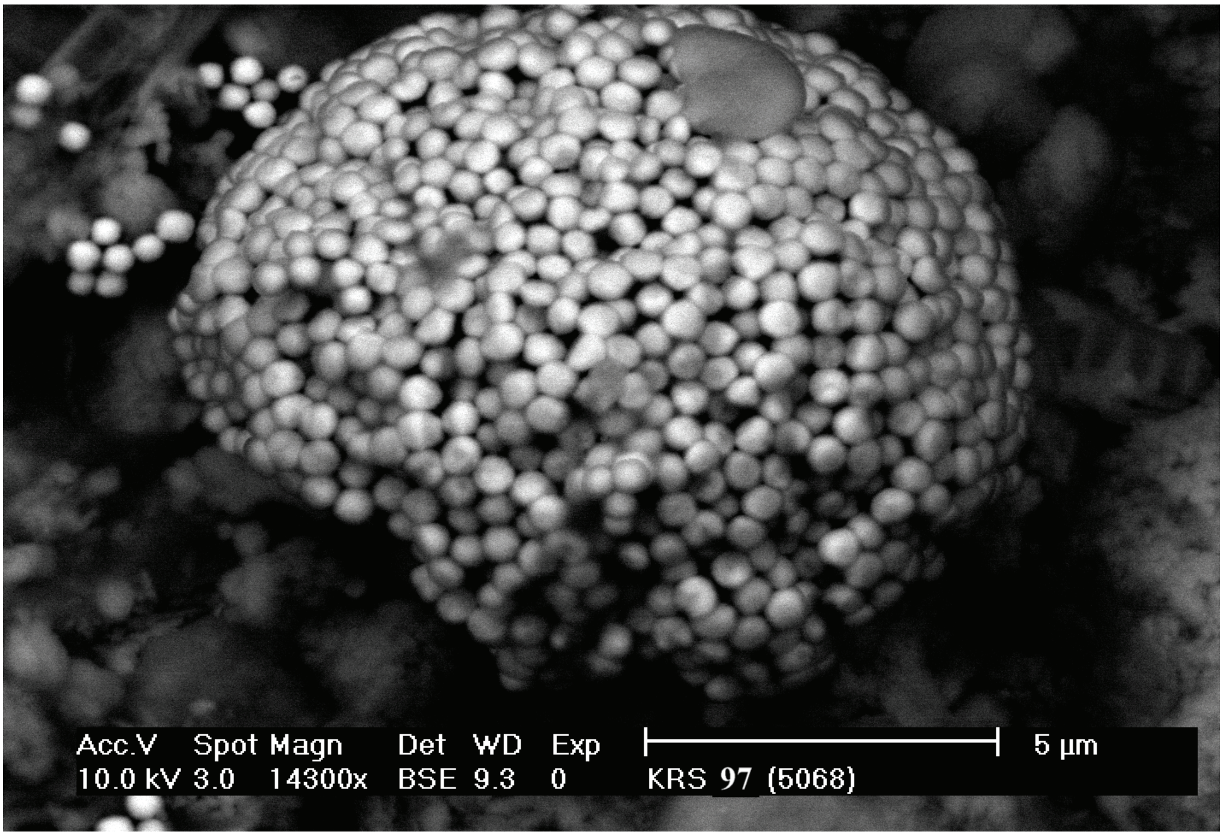

Figure 6c. Pyrite framboid, with minor organic coatings, formed of rounded grains. Sample KRS97. Back-scattered electron image (SEM).

Monosulfides

Monosulfide grains (possibly greigite), with compositions ranging between $FeS_{1.18}$ and $FeS_{1.22}$, appear to be relatively rare, although field observations (colour, reaction with hydrochloric acid, smell) suggest that monosulphides should be more common than observed under the SEM. The reasons for this are unclear, but it is possible that most of the monosulfide is very fine-grained (<<1 µm in diameter) and is unstable as soon as samples are freeze-dried. Monosulphide grains occur in pyritic materials as subhedra associated with Fe-Mn oxides (Figure 7a), as corroded grains, or as irregular aggregates on organic matter (Figure 7b).

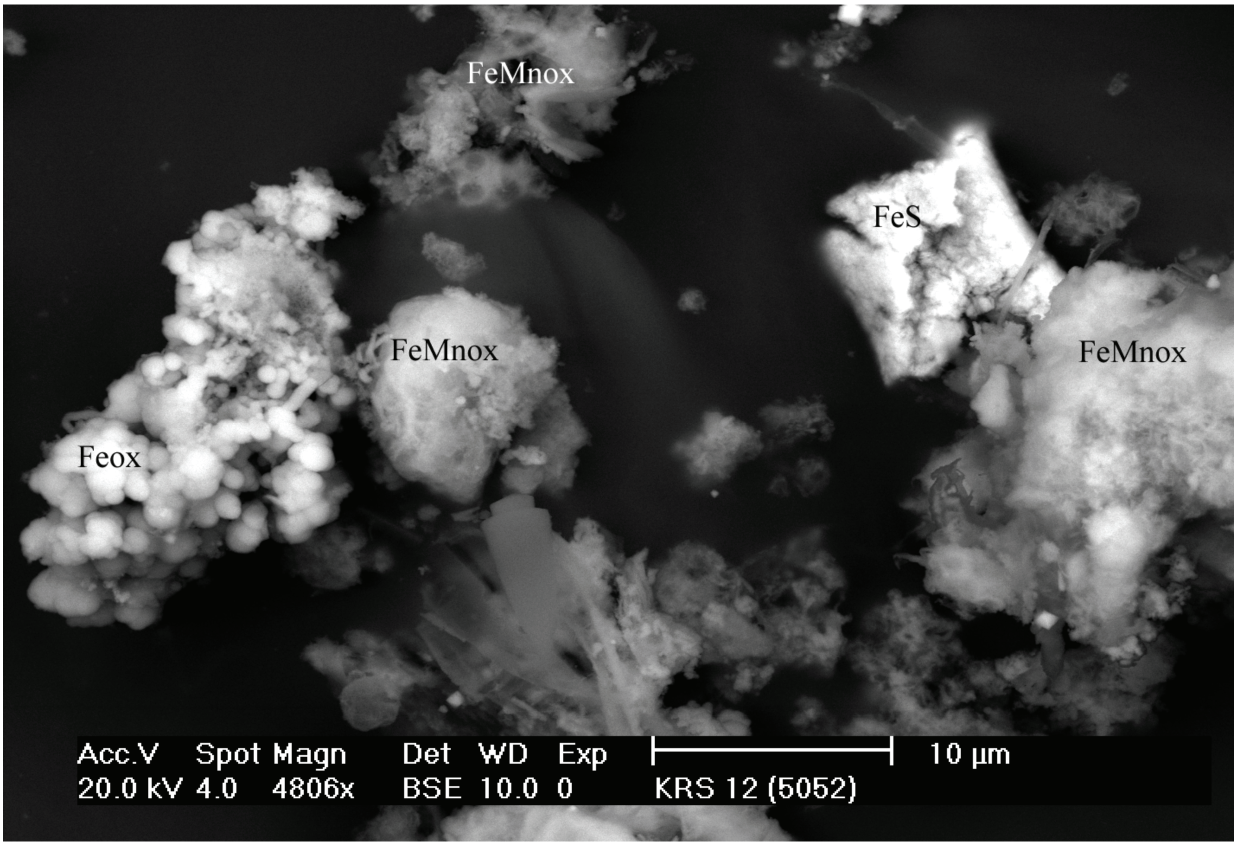

Figure 7a. Subhedral grain of monosulfide (FeS) associated with Fe-Mn oxide aggregates (FeMnox) and Fe oxides (Feox). Sample KRS12, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

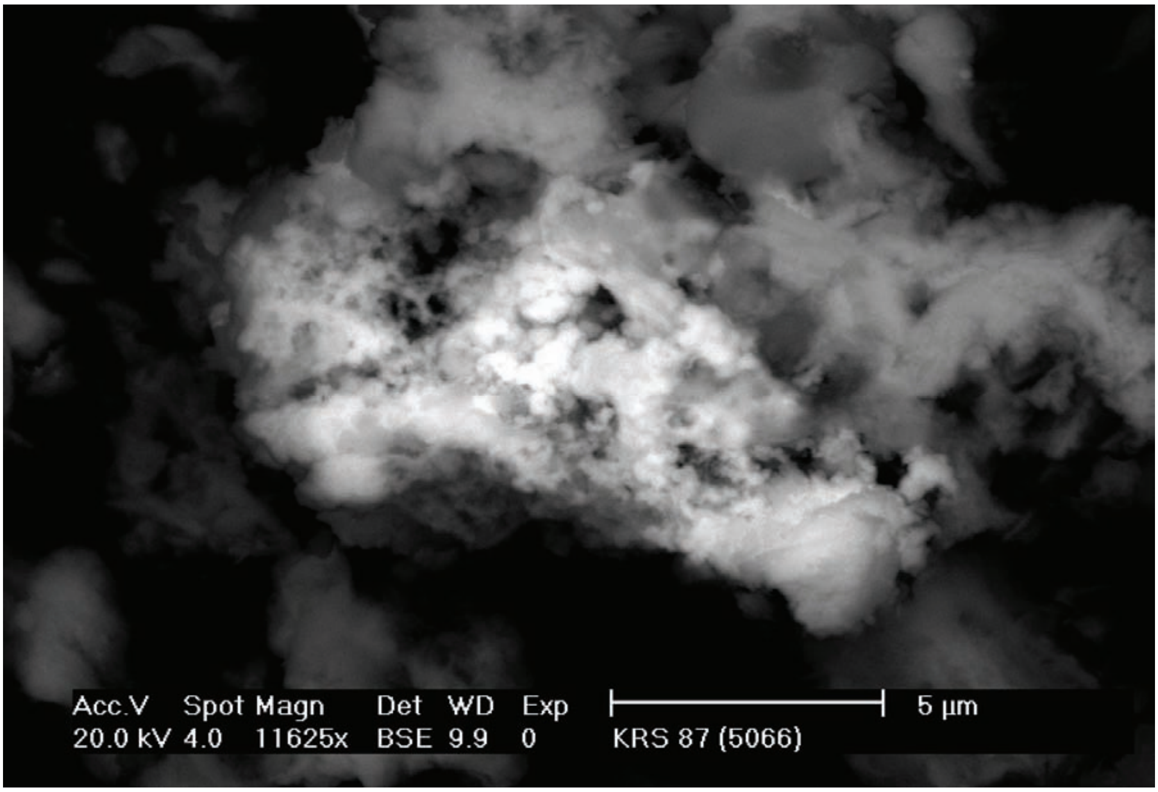

Figure 7b. Aggregate of anhedral monosulfide grains associated with kaolin and minor calcite. Sample KRS87. Back-scattered electron image (SEM).

Sphalerite

Sphalerite occurs in acid sulfate soils from mound springs at Wheal Ellen, the wetland along Rodwell Creek to the south of Wheal Ellen, and in a seep near an unnamed Cu-Au-Ag mine, south-east of Wheal Ellen. It is typically associated with pyrite, zincian Mn oxides and organic matter. The composition of sphalerite from the springs differs from that in the mineralised zones (Figure 8), in that sphalerite from the springs contains significantly less Fe.

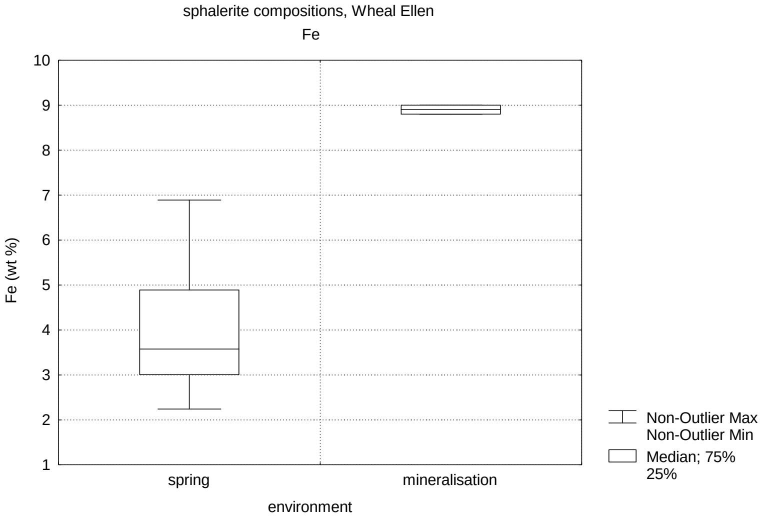

Figure 8. Box plots showing compositional ranges for Fe and Mn in sphalerites from the mound springs and from the mineralised zone at Wheal Ellen. Data for sphalerite from mineralisation taken from Spry (1976).

The most common forms of sphalerite are:

(i) spheres (up to 1 μm in diameter), generally as clusters on the surface of organic matter (Figure 9a) or lining cell walls in plant material (Figure 9b); the size of these spheres suggests that bacterial processes may have played an important role in their formation

(ii) irregular flakes, with dissolution pits (Figure 9c)

(iii) anhedral grains along plant rootlets (Figure 5c), associated with pyrite framboids and cubes

(iv) rounded grains, embedded in organic matter, associated with pyrite cubes (Figure 9d)

(v) intergrowths with galena and clays

(vi) as very fine-grained linear aggregates of sphalerite, pyrite and galena between plant cell walls (Figure 10a).

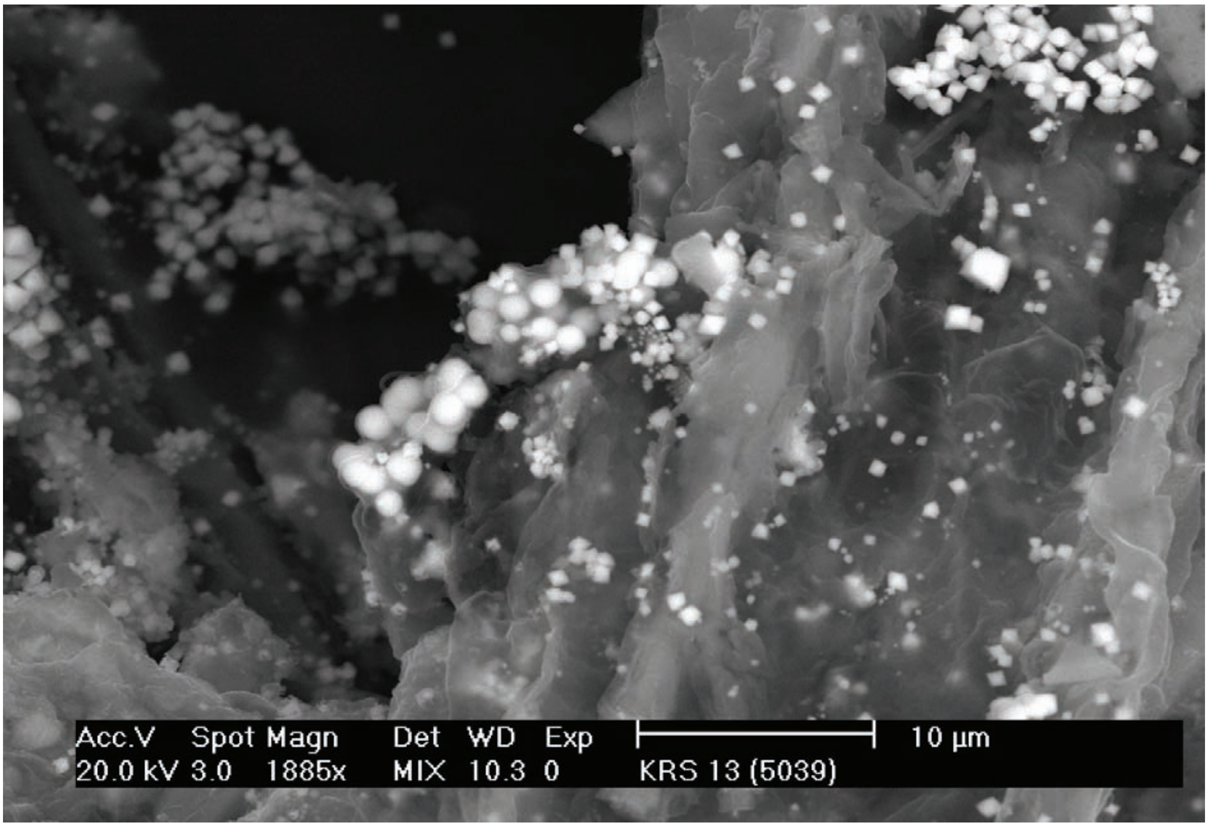

Figure 9a. Aggregates of spherical sphalerite grains (centre) and pyrite cubes (top right) on organic matter. Sample KRS13, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

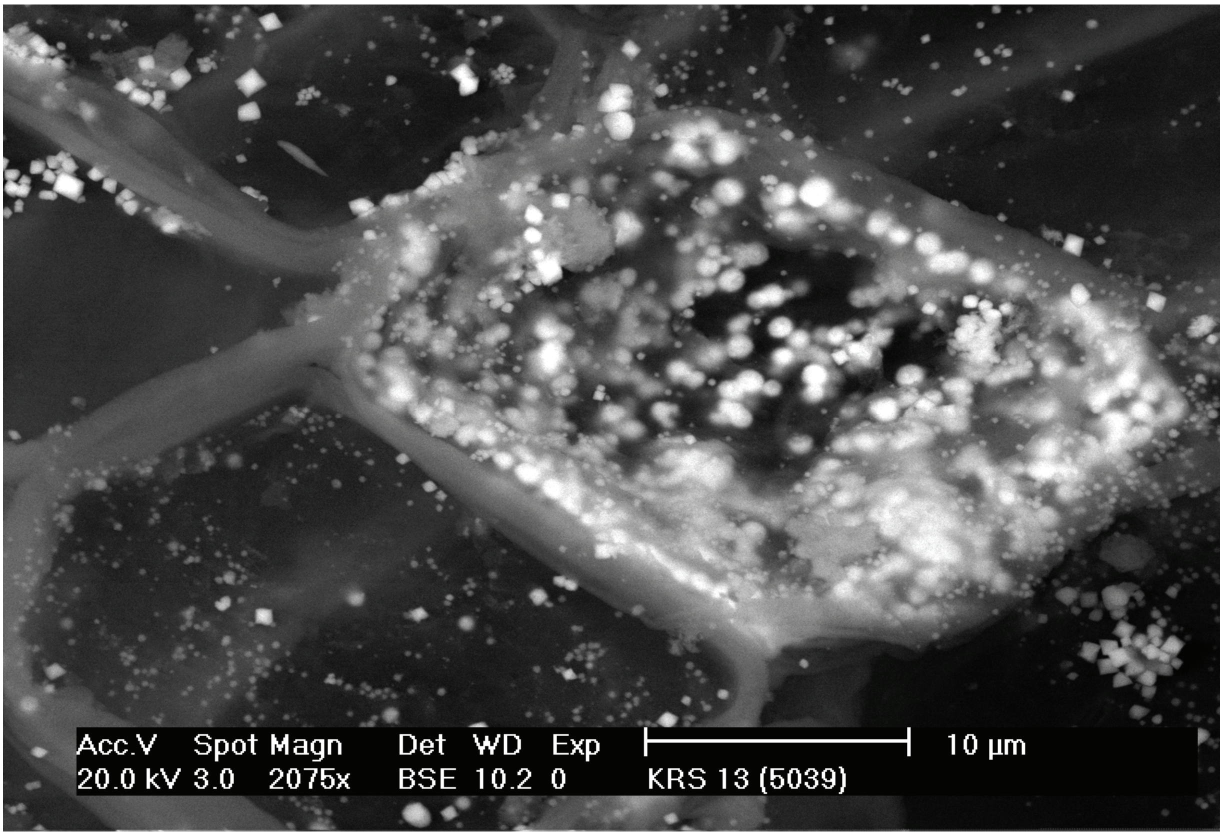

Figure 9b. Spherical sphalerite grains lining plant cell walls. Sample KRS13, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

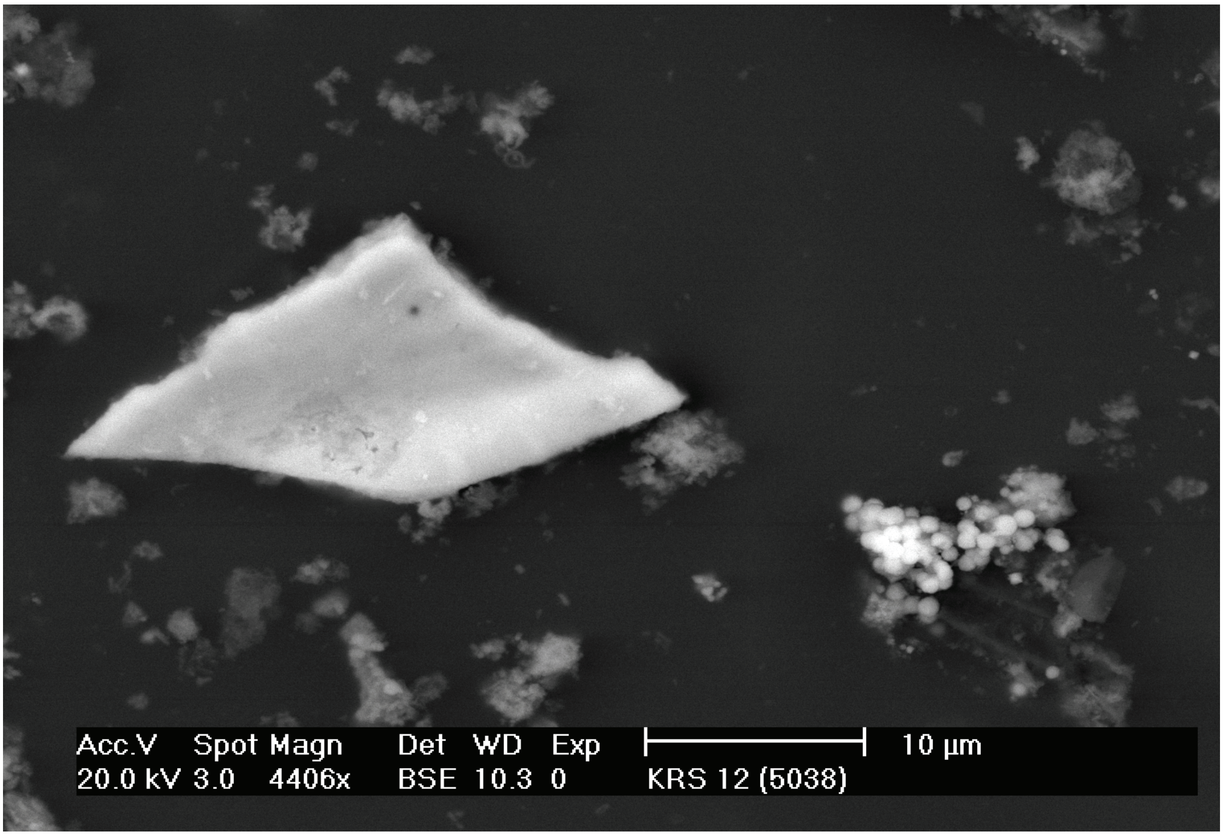

Figure 9c. Sphalerite flake, with dissolution pits, associated with aggregates of spherical sphalerite grains (at right). Sample KRS12, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

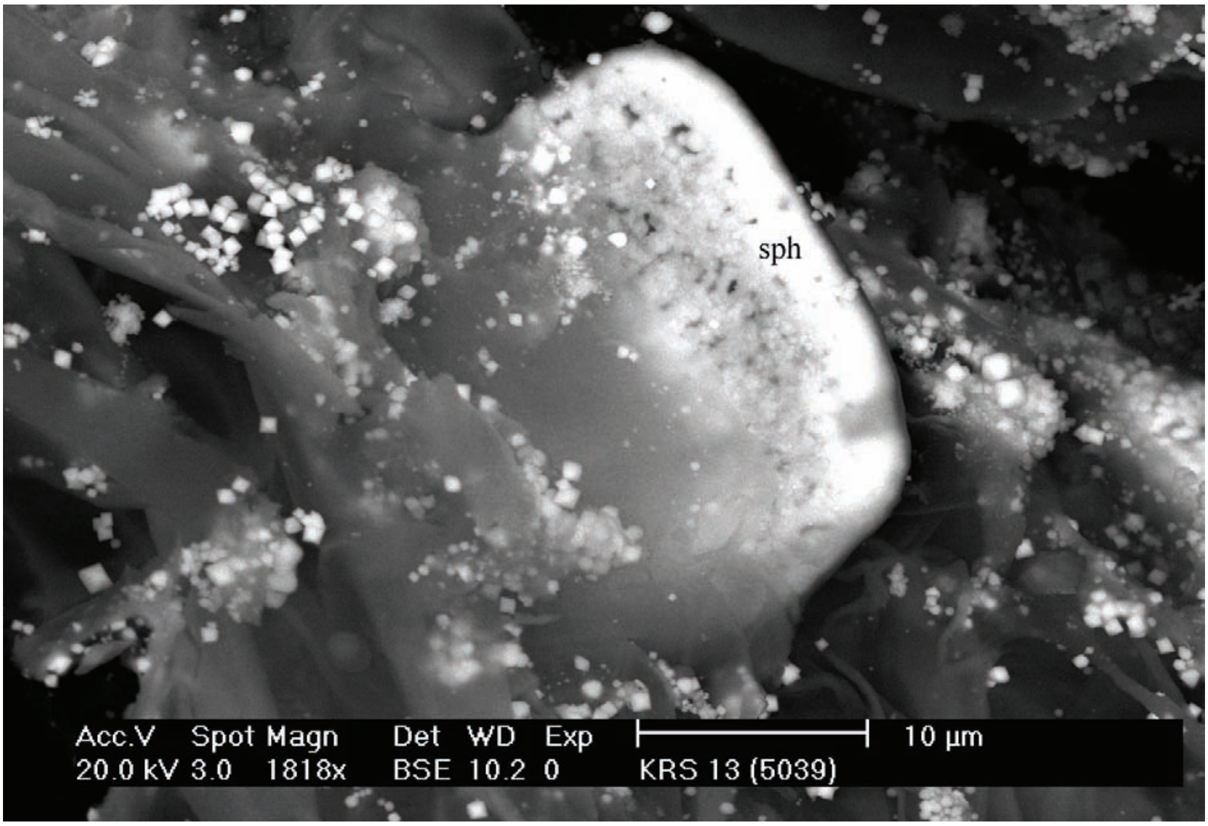

Figure 9d. Rounded sphalerite (sph) grain embedded in organic matter and dusted by fine pyrite cubes. Sample KRS13, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

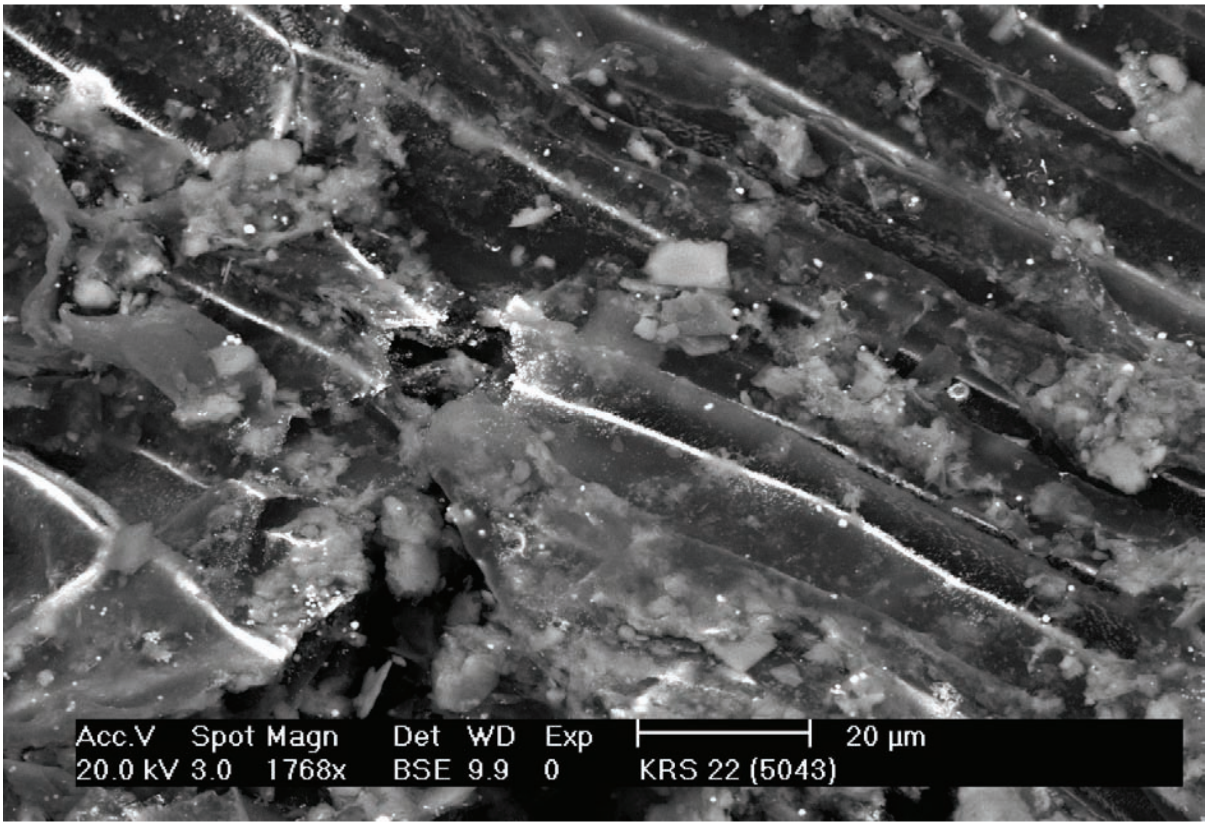

Figure 10a. Very fine-grained linear aggregates of sphalerite, galena and pyrite precipitated between plant cell walls. Sample KRS22. Back-scattered electron image (SEM).

Galena

Galena is less common than sphalerite. It occurs in acid sulfate soils from the mound springs at Wheal Ellen, the wetland along Rodwell Creek to the south of Wheal Ellen, and from a seep to the north, and along strike from, the Mt Torrens prospect. It occurs as:

(i) intergrowths with sphalerite, coated by clays, or with clays and pyrite
(ii) very fine-grained linear aggregates of sphalerite, pyrite and galena between plant cell walls (Figure 10a)
(iii) globular aggregates <1 μm in diameter (Figure 10b).

Chalcopyrite

Chalcopyrite is relatively rare and occurs in the wetland along Rodwell Creek to the south of Wheal Ellen, and in Dawesley Creek, near the old Paringa Cu-Au-Ag-Pb mine, south of Kanmantoo. It occurs as:

(i) fine-grained intergrowths with sphalerite and galena
(ii) disseminated subhedral grains, associated with pyrite (Figure 10c).

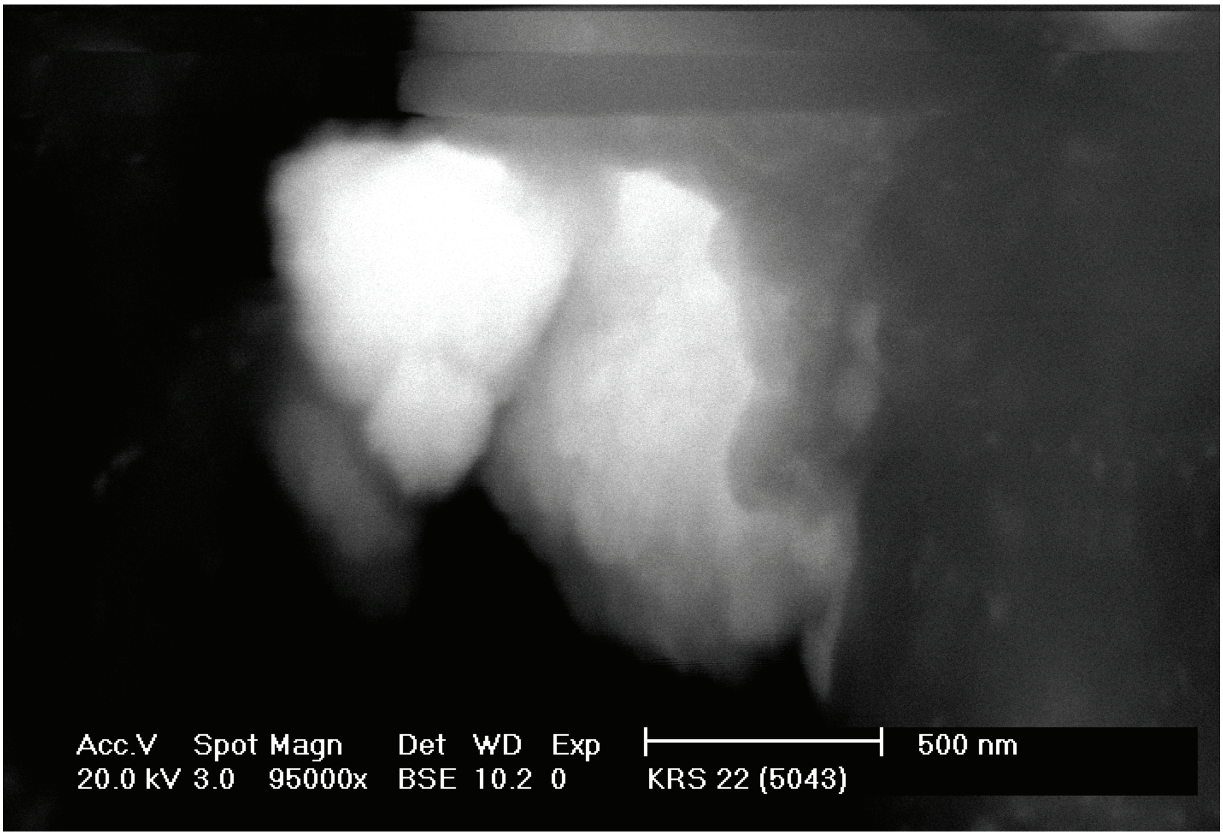

Figure 10b. Aggregate of globular to botryoidal galena grains embedded in mica. Sample KRS22. Back-scattered electron image (SEM).

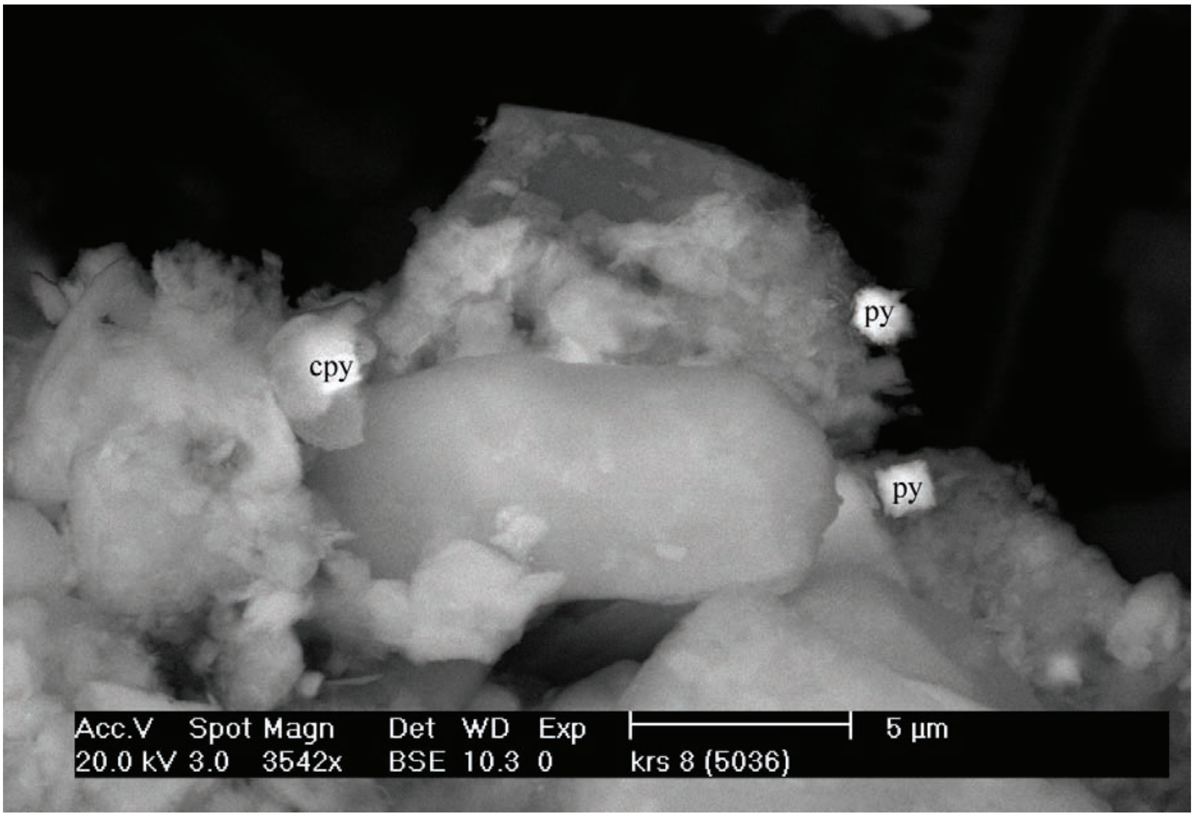

Figure 10c. Disseminated subhedral to euhedral chalcopyrite (cpy) and pyrite (py) grains on quartz and kaolin. Sample KRS8. Back-scattered electron image (SEM).

Mn oxides

Manganese oxides were recorded from the springs at Wheal Ellen and from Dawesley Creek, near the old Paringa mine. Those from Wheal Ellen contain variable minor amounts of Zn, Co and I, whereas those from Dawesley Creek only contain Co. Manganese oxides occur as:

(i) botryoidal aggregates, encrusted by pyrite (Figure 6b)
(ii) anhedral grains associated with organic matter (Figure 10d)
(iii) intergrowths with Fe oxides (Figure 7a).

Native gold

One grain of native gold (containing no detectable Ag) was found embedded in clays (Figure 11a) from Dawesley Creek, near the old Paringa mine.

Barite

Barite was recorded from the springs at Wheal Ellen and from Glenalbyn. It occurs as:

(i) clusters of platy grains (Figure 11b)
(ii) euhedral grains on clays
(iii) anhedral grains with dissolution features (Figure 11c).

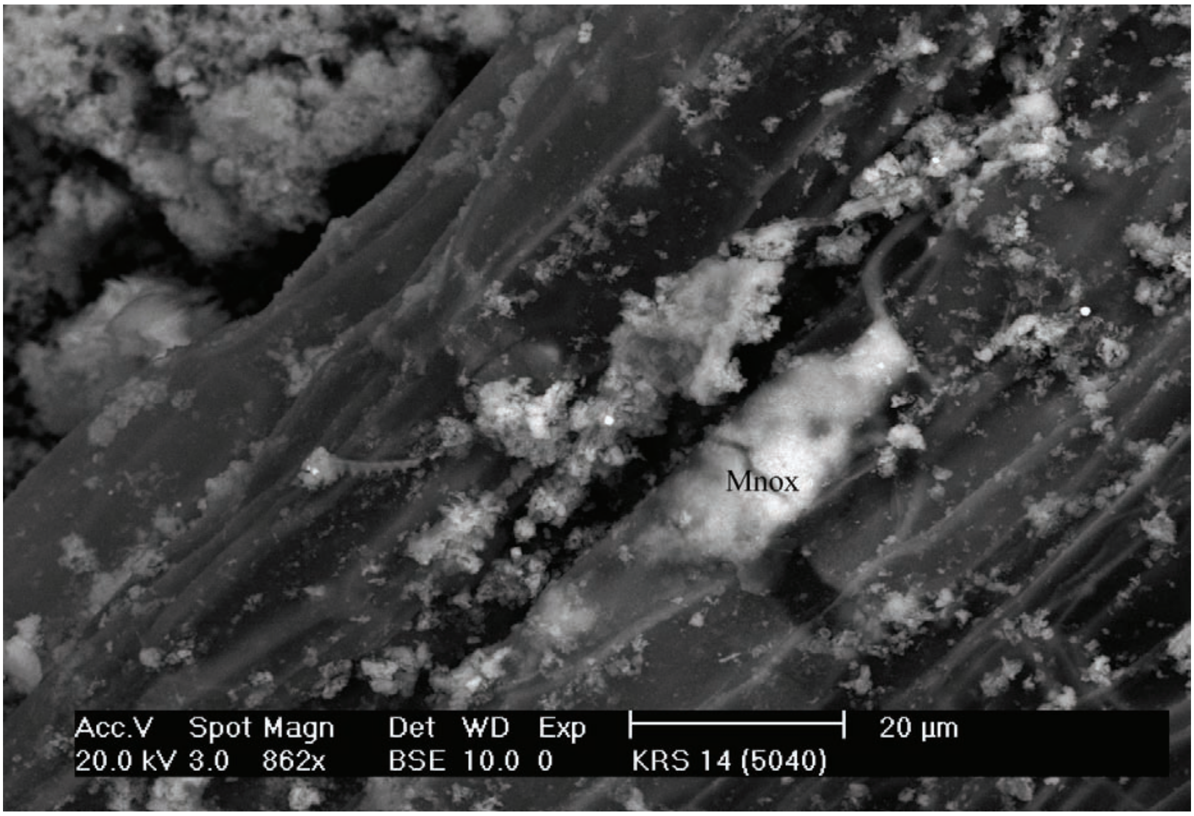

Figure 10d. Iodine-bearing Mn oxide (Mnox) on organic matter and associated with minor disseminated pyrite. Sample KRS14, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

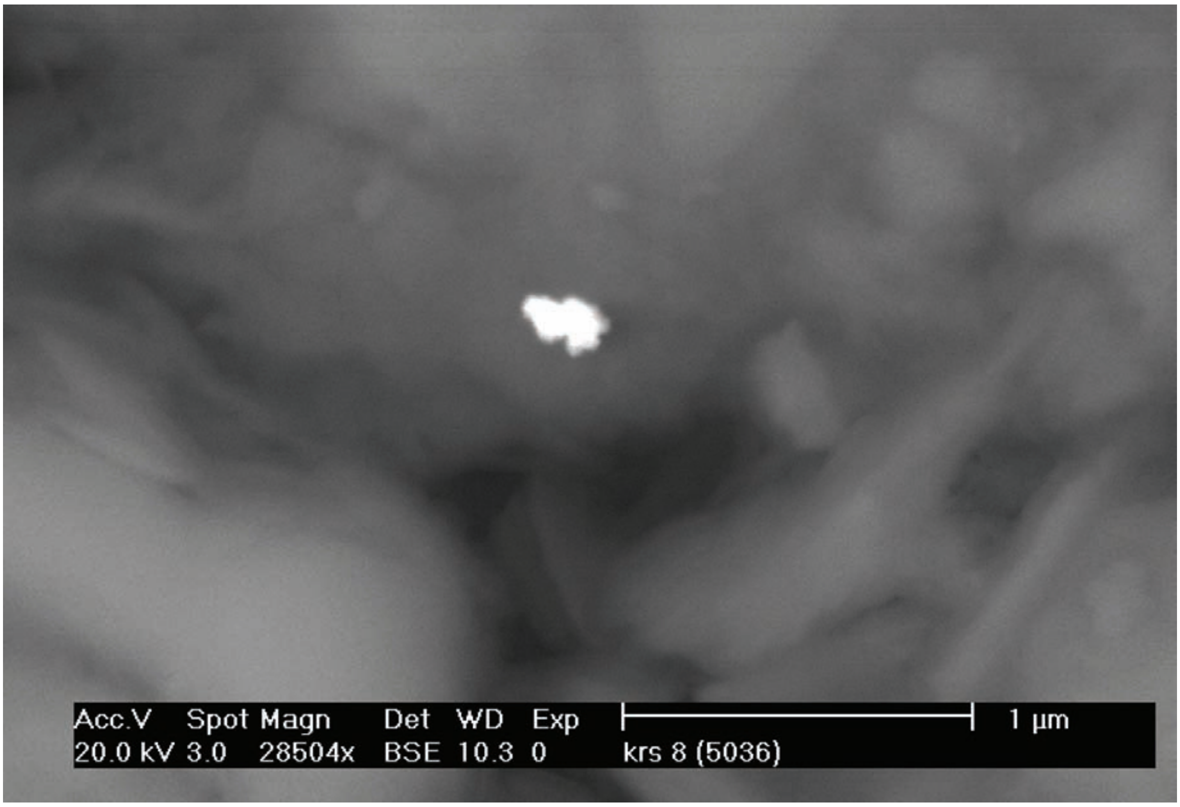

Figure 11a. Anhedral grain of native gold embedded in kaolin. Sample KRS8. Back-scattered electron image (SEM).

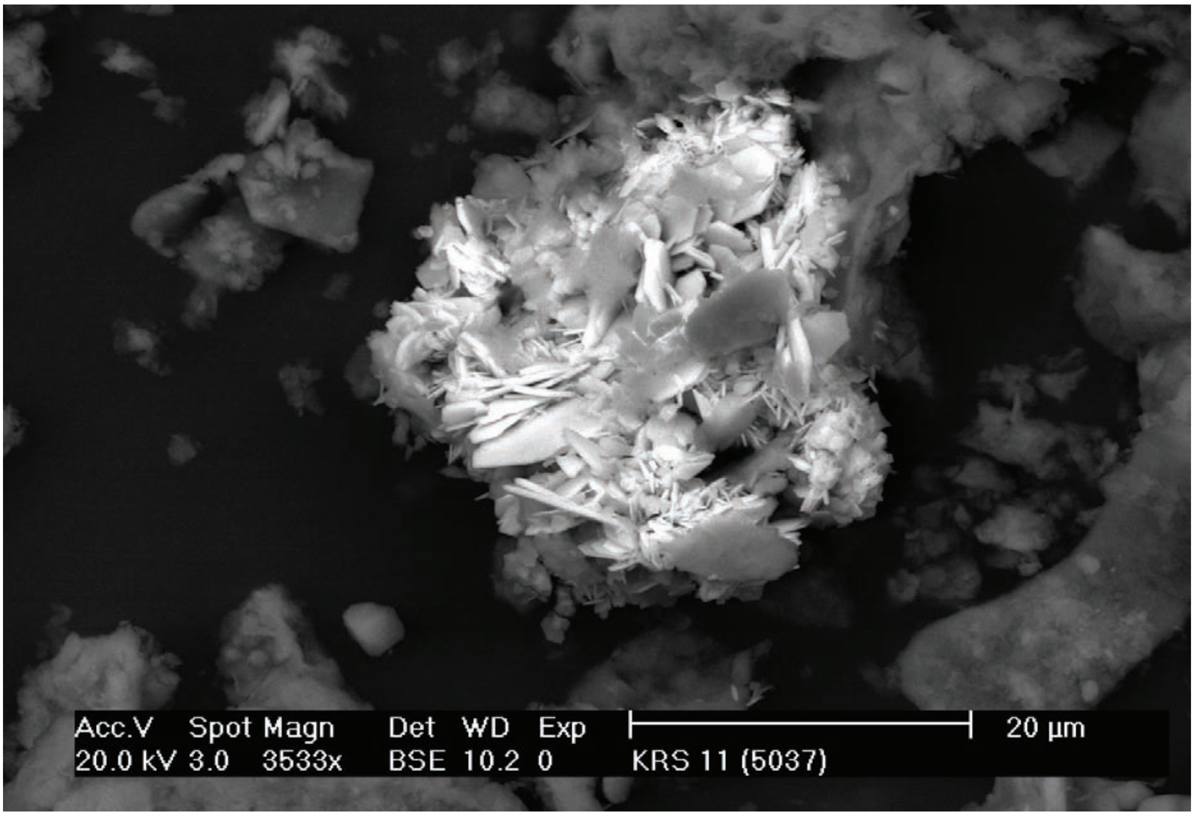

Figure 11b. Aggregate of barite platelets associated with quartz and kaolin. Sample KRS11, Glenalbyn mine. Back-scattered electron image (SEM).

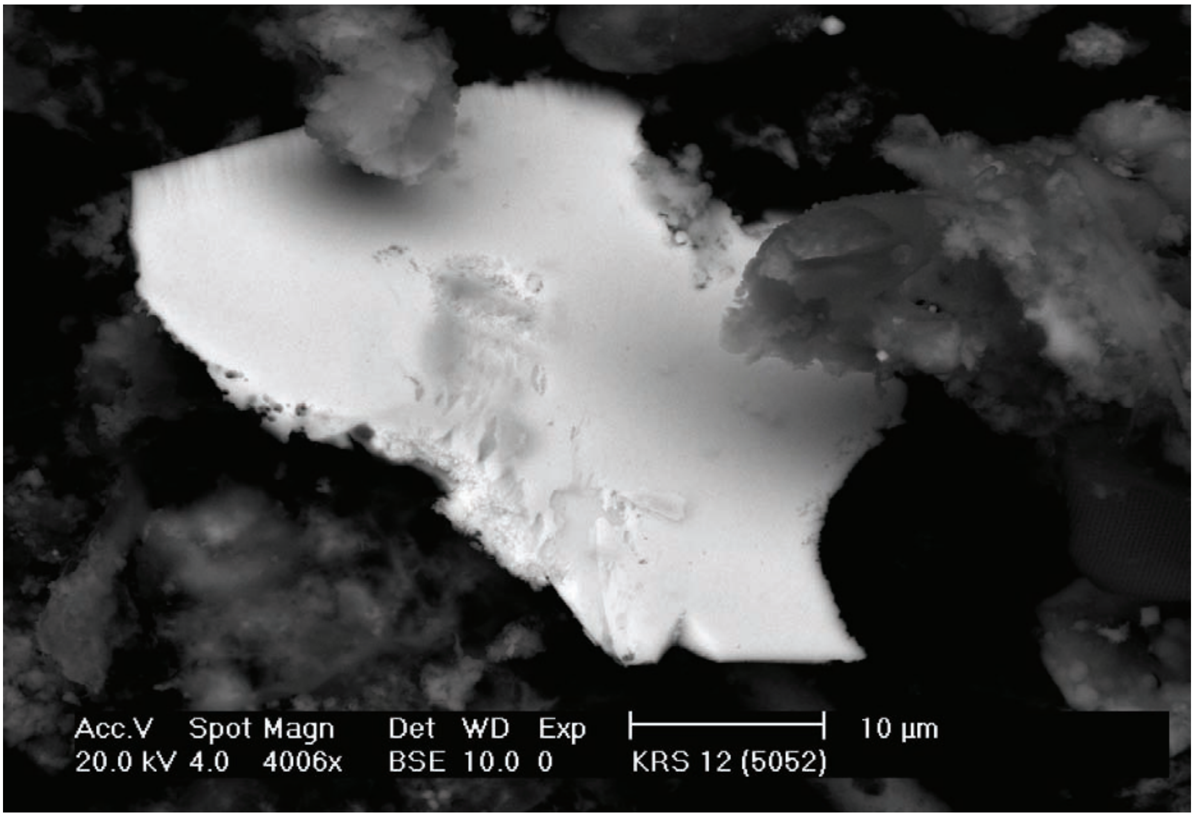

Figure 11c. Anhedral barite platelet, associated with quartz and kaolin, with dissolution pits. Sample KRS12, mound springs at Wheal Ellen. Back-scattered electron image (SEM).

GEOCHEMISTRY

Ore zones in bedrock

Selected samples of fresh or weathered mineralisation from the some of the mines/prospects (Mt Torrens prospect, Bremer mine, Glenalbyn mine, Wheal Ellen, Wheal Margaret and the Monarto Cu prospect) in the district were analysed to obtain indications of the geochemical signatures of the various deposits. The results indicate that there are three broad element associations commensurate with the broad commodity-based mineralisation types listed above (Cu±Au, Pb-Zn-Ag±Au, and Cu-As±Au):

Cu±Au: Cu-Au-Ag-Bi-Cd-Co-In±As±Sb±Te±Zn

Pb-Zn-Ag±Au: Pb-Zn-Ag-Bi-Cd-Co-Hg-In-Mn-Mo-Sb-Tl±As±Au±Cu

Cu-As±Au: Cu-As-Ag-Mo-Sb-Te±Au±Bi±Tl.

REGIONAL GEOCHEMISTRY OF ACID SULFATE SOIL MATERIALS

Ore-associated elements

The regional distribution patterns for Cu, Pb and Zn are shown in Figures 12-14. The following trends were noted in the vicinity of known mines and prospects:

(i) Wheal Ellen: anomalous Ag, Au, Bi, Cd, Co, Cu, Hg, In, Ni, Pb, Sb, Se, Tl and Zn
(ii) Kanmantoo area: anomalous As, Au, Bi, Co, Cu, Ni, Se, Tl and Zn
(iii) Mt Torrens prospect: anomalous Ag, As, Bi, Co, Hg, Mo, Ni, Pb, Tl and Zn
(iv) Monarto Cu prospect: anomalous As, Bi, Cd, Mo, Tl and Zn
(v) Glenalbyn: anomalous Cu, Sb, Tl and Zn.

The following anomalies are not related to known occurrences of mineralisation:

(i) north of Brukunga: Cd, Co, Ni, Tl, Zn
(ii) Guthries: Ag, As, Bi, Pb, Tl, Zn
(iii) north of Wheal Ellen: Ag, As, Bi, Co, Mo, Ni, Pb, Tl, Zn
(iv) south-east Harrogate 1: Ag, Tl, Zn
(v) south-east Harrogate 2: As, Mo, Zn
(vi) Bottroffs Hill: Cu
(vii) Collins Road: Au
(viii) south-east Mount Barker: Pb, Zn.

Trace element concentrations are independent of Fe, Mn or S contents of the samples. Estimated background and threshold limits of selected elements are shown in Table 1.

Lithophile elements

There is a distinct contrast in the geochemical relationship between Na and K on either side of the Bremer Fault (Figures 15-16) and probably reflect geochemical differences in the detrital fraction derived from bedrock. Samples to the east of the fault are characterised by greater concentrations of Na and a negative correlation between Na and K, except for a small subgroup of samples with both relatively low Na and K contents. To the west of the fault, samples exhibit a positive correlation between Na and K. Other elements (Ba, Rb, Sr and Tl) also exhibit geochemical differences similar to K, with positive correlation factors with Na west of the fault, but negative east of it.

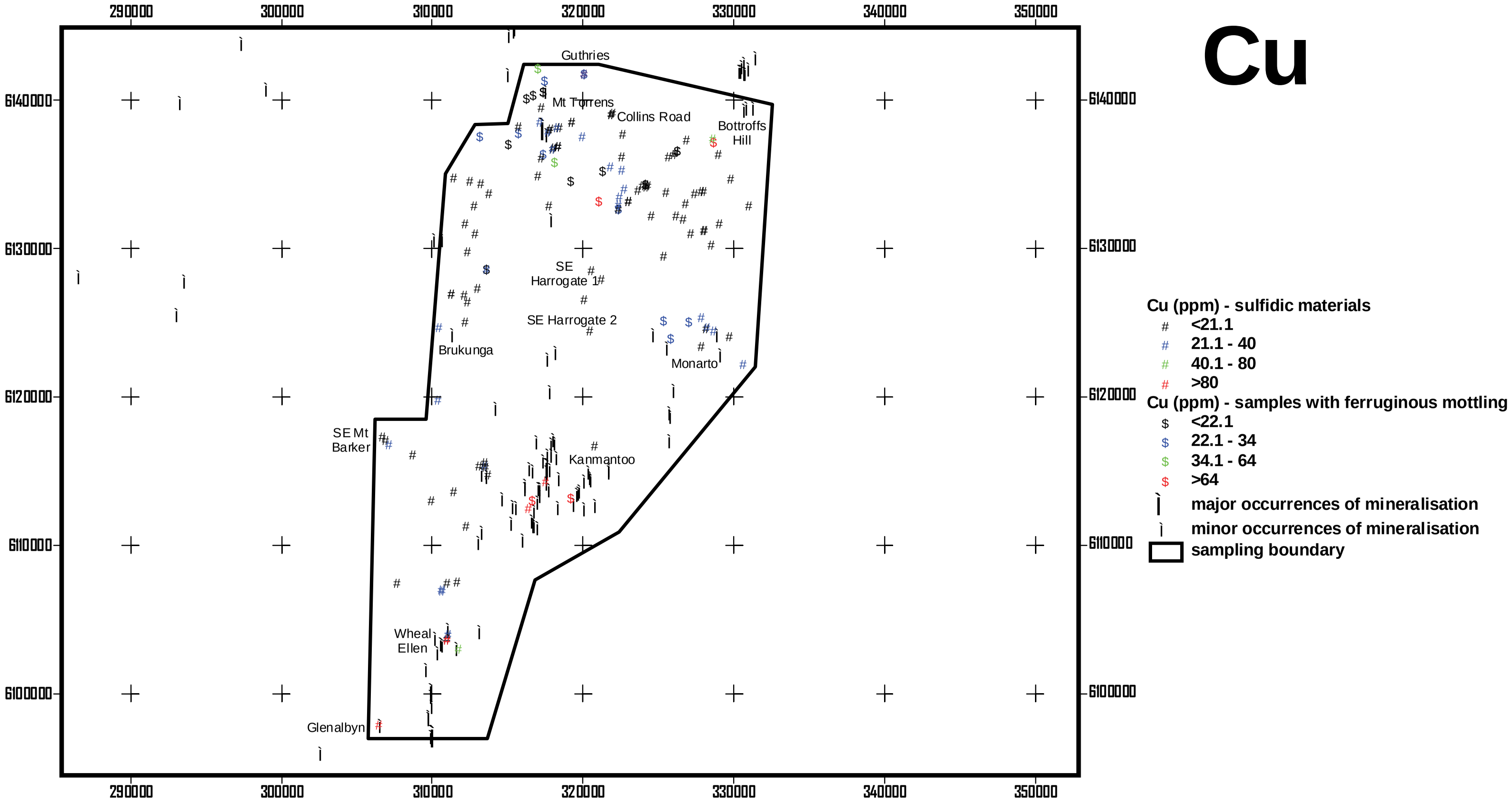

Figure 12. Distribution of Cu (ppm) in acid sulfate soils showing locations of the anomalies.

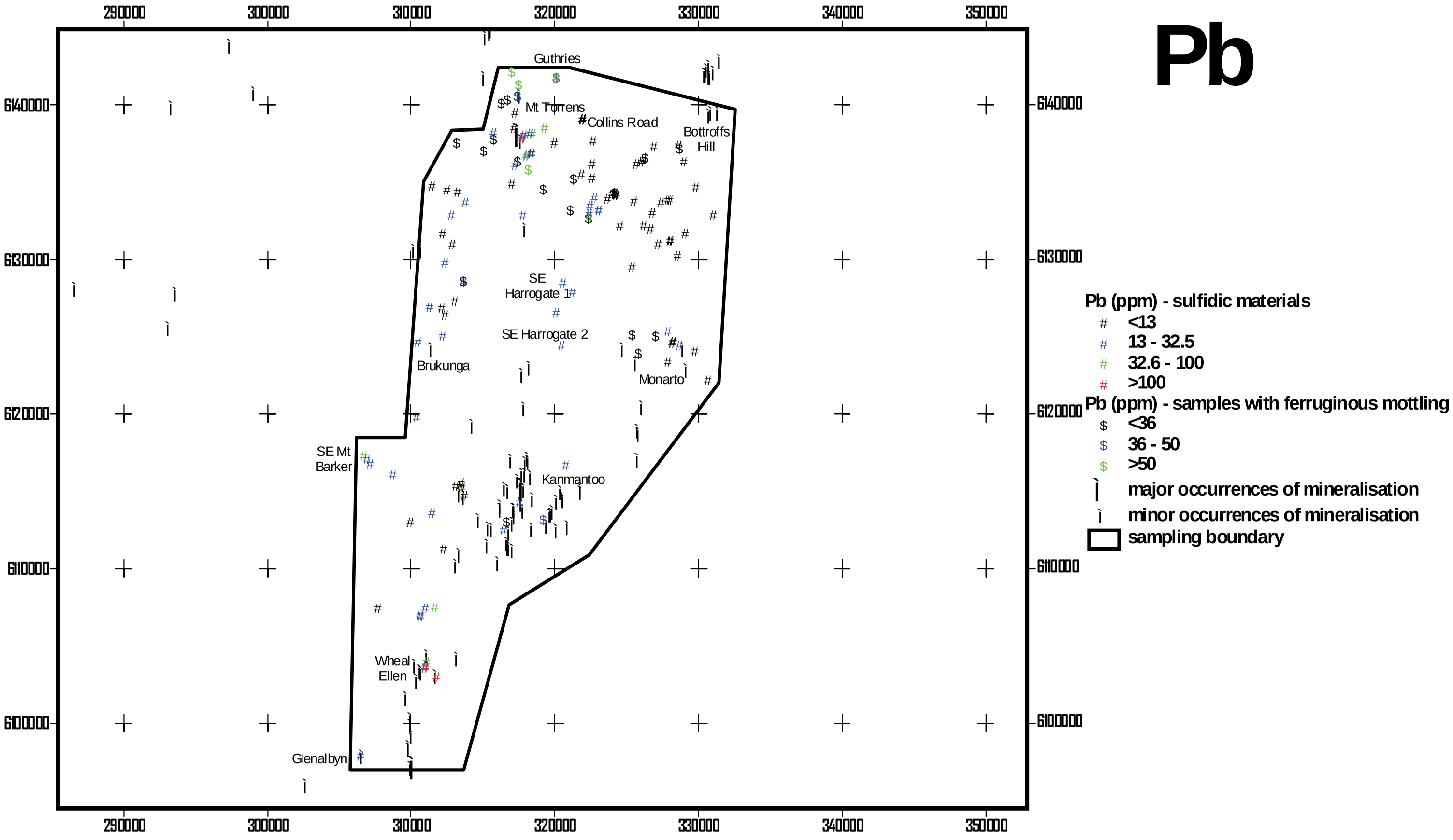

Figure 13. Distribution of Pb (ppm) in acid sulfate soils showing locations of the anomalies.

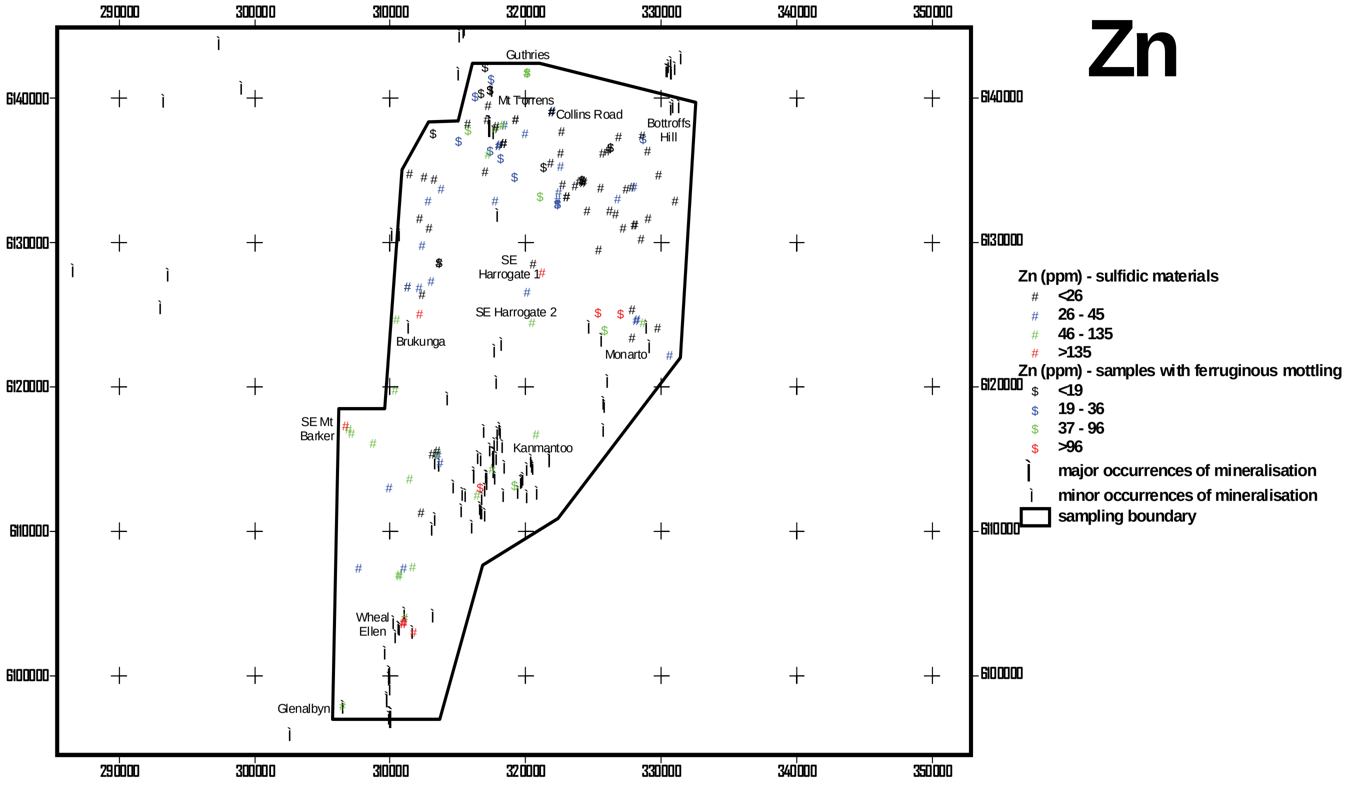

Figure 14. Distribution of Zn (ppm) in acid sulfate soils showing locations of the anomalies.

Table 1. Estimated backgrounds and thresholds (in ppm, except where stated) for selected elements in sulfidic materials.

Element	Background	Threshold
Ag	0.2	0.4
As	10	16
Au (ppb)	3	5.1
Bi	0.3	0.6
Cd	0.3	0.6
Co	8.5	100
Cu	40	80
In	<0.05	0.15
Mo	2	5.5
Ni	16	32
Pb	32.5	100
Sb	<0.5	1.6
Se	<0.5	1.1
Tl	0.4	0.7
Zn	25	135

In contrast, Al has positive correlation factors with Na on both sides of the fault, despite distinct groupings on a Na-Al plot. This could suggest that Na occurs in an Al-bearing phase, such as plagioclase, with more calcic compositions to the west of the fault, and more Na-rich compositions to the east.

These differences may reflect regional addition of Na, or loss of K, east of the fault, rather than addition of K west of it. These differences in alkali chemistry in the Kanmantoo Group have not been previously documented and the reasons for this variation are not clear, but may relate to regional fluid flow related to mineralisation in the west, to differences in regional metamorphism between east and west, or granitoid intrusion and regional metasomatism in the east.

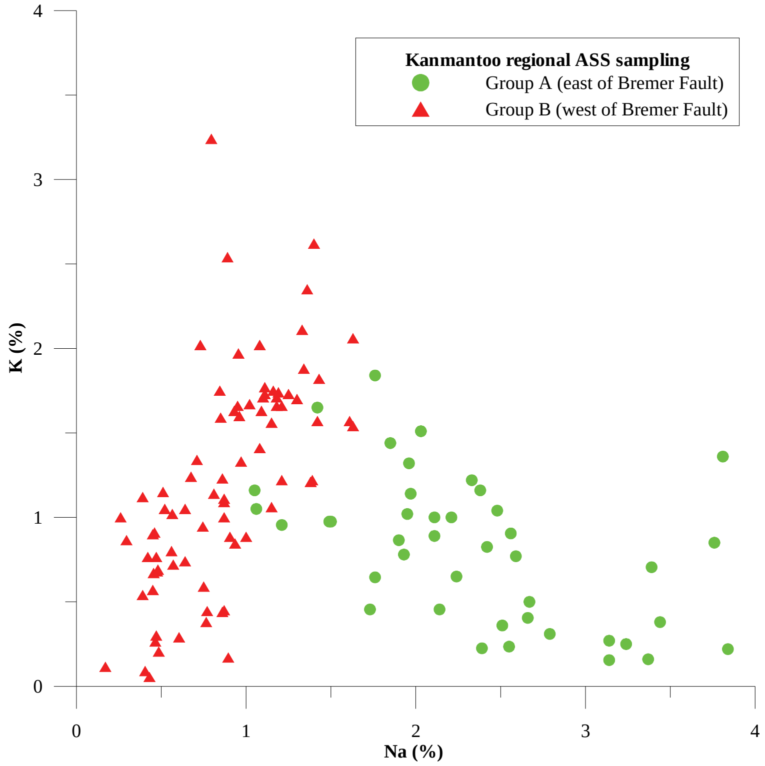

Figure 15. The distribution of Na and K in sulfidic material from acid sulfate-like soils on either side of the Bremer Fault. Group A samples occur on the eastern side of the fault and exhibit a distinct negative correlation between Na and K. Group B samples occur on the west side of the fault and exhibit positive correlation between Na and K. Samples (red triangles) close to the origin of the graph plot to the east of the Bremer Fault in Figure 16.

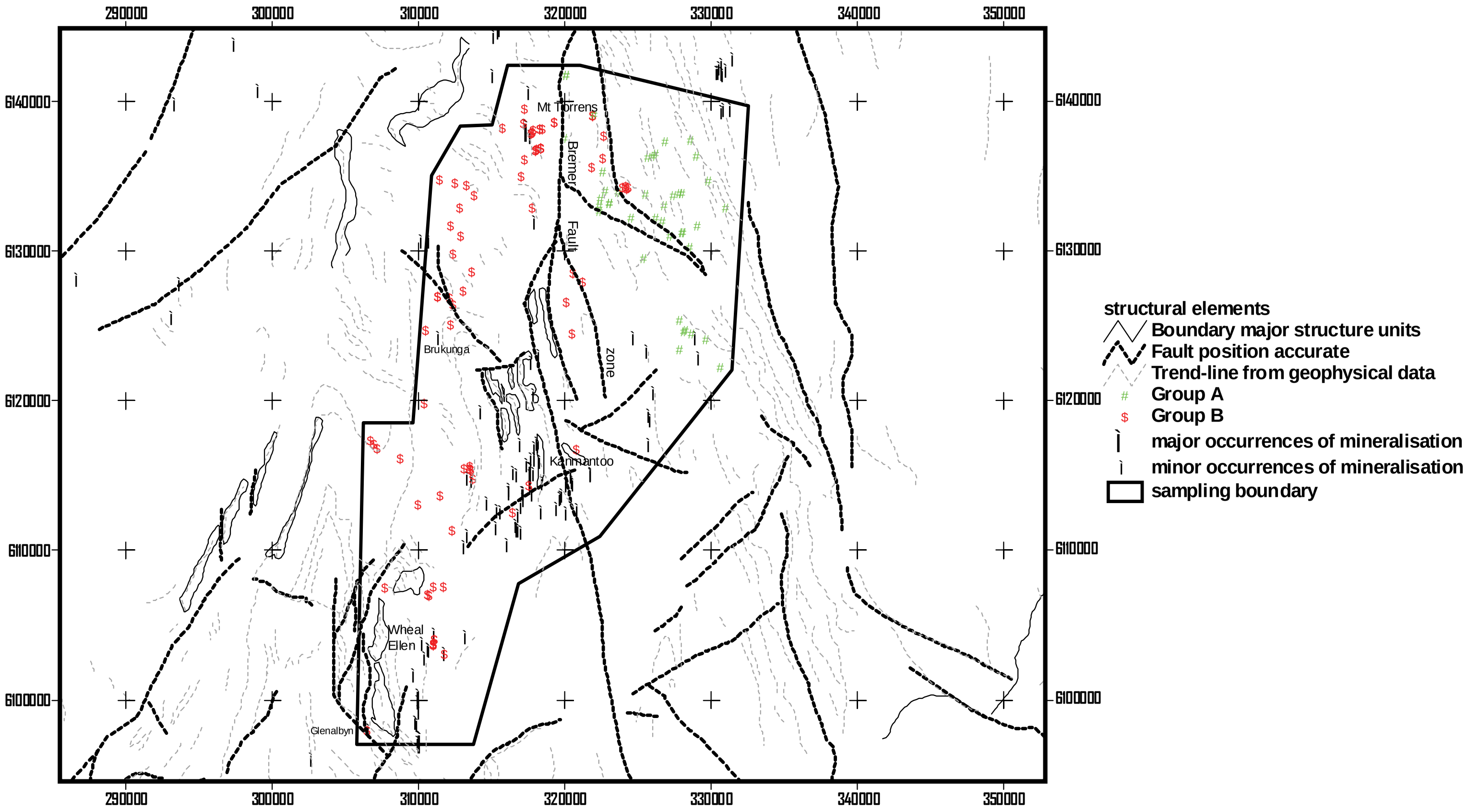

Figure 16. The distribution of the two groups of sulphidic material from acid sulfate-like soils in relation to the Bremer Fault.

CONCLUSIONS

(1) Results indicate that acid sulfate soil materials in seeps, springs, wetlands and creeks are a valid new sampling medium. This investigation has shown that not only are geochemical anomalies related to known mineralisation, but also that new generations of sulfides (pyrite, sphalerite, galena, chalcopyrite) and native gold have precipitated in environments close to these mineralised zones. A soil-landscape model illustrating geochemical dispersion into acid sulfate materials from mineralised zones into seeps, springs and wetlands is shown in Figure 17. Lateral groundwater and through flow transport metals of interest to reduced seepages, where secondary sulfides are precipitated. In some instances, there is clear evidence (from textural data) for biomineralisation being involved in the precipitation of secondary sulfides. These findings corroborate the findings of the orientation survey at the Mt Torrens prospect (Skwarnecki *et al* 2002a).

(2) Geochemical anomalies in acid sulfate soils do not provide drilling targets in themselves. On a regional scale, they are comparable to stream-sediment sampling, but are a more robust sampling medium, in that acid sulfate soils provide a more direct geochemical and mineralogical manifestation of mineralisation. Additionally, geochemical anomalies in acid sulfate soils can detect blind zones of mineralisation, whereas stream-sediment sampling can only detect mineralisation that is, or was, exposed in outcrop and eroded into drainages.

(3) There is a regional contrast in Na and K geochemistry across the Bremer fault zone. This indicates the presence of fundamentally different geochemical provinces.

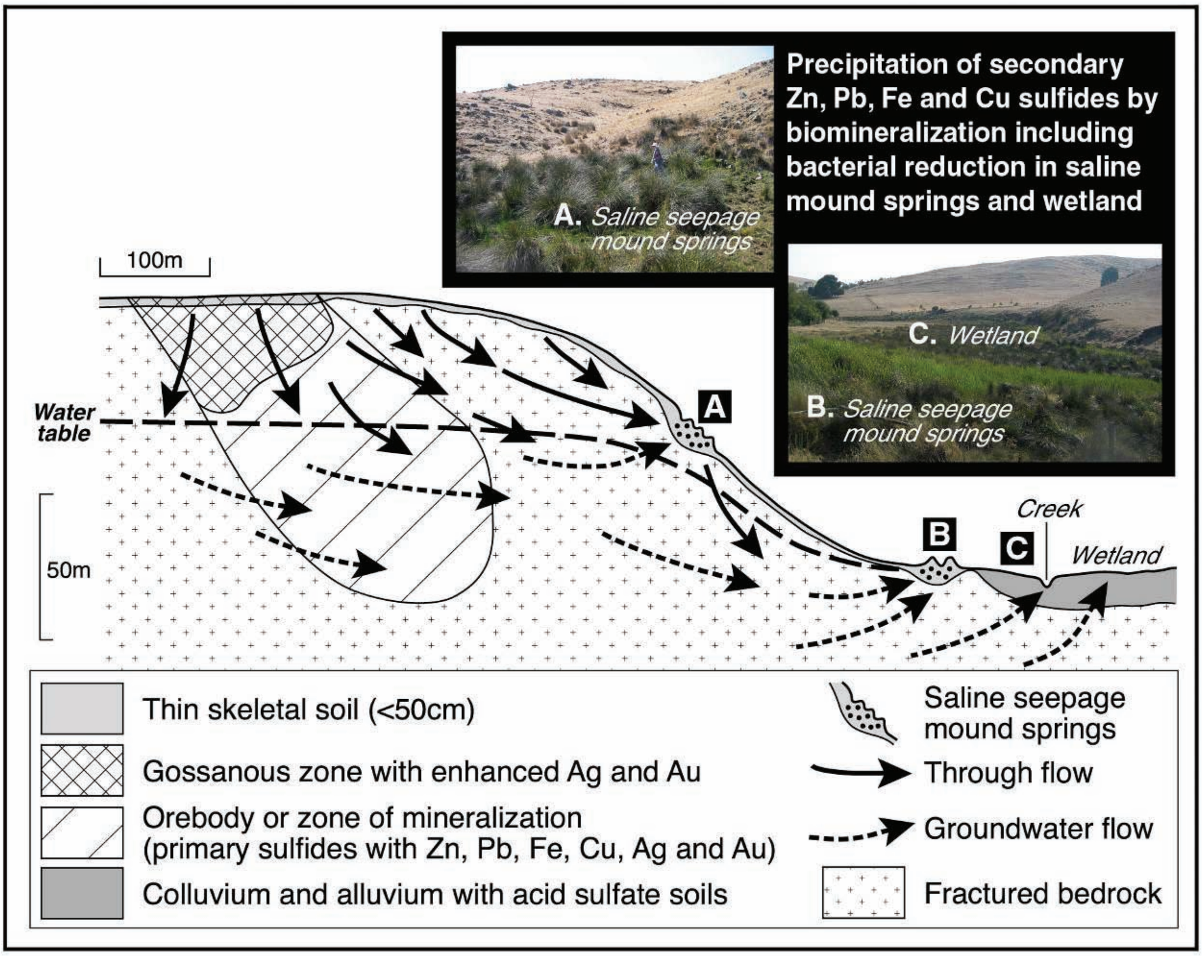

Figure 17. Model for geochemical dispersion from mineralised zones into acid sulfate materials in seeps, springs and wetlands, Mount Lofty Ranges (from Skwarnecki and Fitzpatrick 2003a)

(4) Future investigations should focus on:

(i) mapping the distribution of acid sulfate soils and characterising their mineralogy and composition over a wider region in the Mt Lofty Ranges and other parts of Australia

(ii) regional sampling of seeps, constrained by catchments and areas of known mineralisation, together with background areas with no known mineralisation, to provide further case studies and a more robust evaluation of the technique

(iii) isotopic (Pb, S) and hydrogeochemical studies to better constrain the processes of acid sulfate soil formation and to provide tracers of the mineralisation, to follow-up the preliminary investigations of Giblin *et al*. (1994)

(iv) further characterisation of the highly reactive monosulfide-bearing materials (monosulfide black oozes)

(v) evaluation of coastal acid sulfate soils as a potential sampling medium; detailed geochemical studies on either side of the Bremer fault zone, to determine the reasons for the geochemical disparities on either side of the fault.

ACKNOWLEDGEMENTS

This research could not have been carried out without assistance from the following individuals:

Charles Butt – for his strong support of the project from its inception
Mark Thomas, Richard Merry, Andrew Baker – sampling in the field
Sean Forrester – assistance with sample preparation
Greg Rinder – scanning diagrams and assistance with production of diagrams
Stuart McClure – for assistance with the SEM and electron microprobe
Mark Raven – for XRD patterns
Andy Burtt (PIRSA) – for providing the sample of Wheal Ellen mineralisation
CRC LEME and CSIRO Mineral Exploration & Mining Sector (through the Glass Earth project) - for providing financial assistance

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CHAPTER 5

ANCIENT ACID SULFATE SOILS IN MURRAY BASIN SEDIMENTS: IMPACTS ON BOREHOLE CLOGGING BY AL(OH)$_3$ AND SALT INTERCEPTION SCHEME EFFICIENCY

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INTRODUCTION

The clogging of boreholes by an amorphous white precipitate, identified as amorphous aluminium hydroxide, occurred during pump testing of salt interception scheme (SIS) boreholes in the Loxton Sands at Bookpurnong in the Murray Basin (AWE 2004; Harrington 2004). The clogging, which did not occur during previous testing of boreholes at Loxton, caused a decrease in efficiency of around 80% and led to significant clogging of pumps and impellers (Figure 1).

Figure 1. Clogging of pump and impellers by amorphous Al(OH)3 (from James-Smith *et al* 2005).

Aluminium (Al) is amphoteric i.e. it is soluble under both acidic and alkaline conditions. The solubility of gibbsite is shown on Figure 2, along with the dominant species of Al at different pH. High Al concentrations are well known in association with acid mine drainage (AMD) and disturbed acid sulfate soil (ASS) environments, where associated waters are often very acidic (pH often < 2-3). Other areas include acidic surface waters in poorly buffered hard-rock catchments (Shand *et al* 2005). Although Al is theoretically soluble under high pH conditions, under natural conditions it is often much lower than this simple equilibrium would suggest due to complexation reactions. The groundwaters that were affected by clogging were slightly acidic to neutral in terms of pH, conditions where Al should only be present at a few µg l^{-1}.

Previous studies, based on limited mineralogical data, proposed that the Al was derived from the oxidation and hydrolysis if Fe^{2+}, which was present in the upper Loxton Sands (Harrington 2004):

$$Fe^{2+} + 2H_2O + 0.5\ O_2 + e^- \rightarrow Fe(OH)_3 + H^+$$

The origin of acidity by hydrolysis of Fe^{2+} has also been postulated as the driving mechanism for acid generation in the low pH Lakes of Western Australia (McArthur *et al* 1991). Several criteria were suggested, based on results from the initial study site, for predicting potential occurrences of clogging: 1) high dissolved Fe (> 25 mg l^{-1}); 2) low buffering species; and 3) Al in an available form e.g. sorbed to minerals or organic matter. However, boreholes with low Fe and high buffering capacity were subsequently found to clog (Figure 1) and this study was set up to re-assess the existing model.

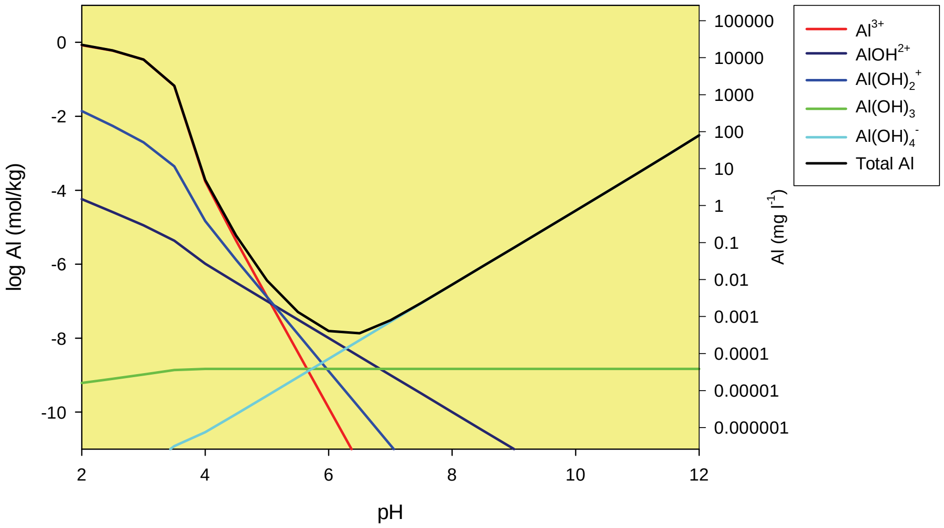

Figure 2. Solubility of gibbsite ($Al(OH)_3$) in relation to pH (calculated using PHREEQC2). Total solubility is high under acidic and alkaline conditions with minimum solubility at circumneutral pH.

The oxidation of pyrite is one of the most acid producing reactions in nature. However, it was not considered as a potential source of acidity since it was not detected in core material. The reaction is complex and proceeds by a variety of steps, but the overall reaction is:

$$2FeS_2 + 15/2O_2 + 5H_2O \rightarrow 2FeOOH + 4SO_4 + 8H^+$$

The aim of this study was to assess potential sources of acidity using existing and new hydrochemical data and to characterise the mineralogy of the Loxton Sands using scanning electron microscopy. Three boreholes were studied in detail: borehole A, where clogging was first observed; borehole B, in which clogging did not occur during initial testing and where the groundwaters had high buffering capacity and low dissolved Fe, and borehole C where clogging was not observed.

GEOLOGICAL BACKGROUND

The Loxton Sands are of Late Miocene to Late Pliocene age and comprise a sequence of lower and upper shoreface, beach, estuarine, dune and back-barrier lagoonal sediments, forming a relatively thin (10-20 m) but extensive sedimentary sequence (Hill *et al* 2004; Munday *et al* 2004). There is an overall coarsening upwards sequence in the Loxton Sands, typically from offshore shelf mud to upper shore facies coarse sands.

Groundwater mounds have formed beneath irrigation districts close to the River Murray leading to higher salt fluxes to the river (Hill *et al* 2004). A number of Salt Interception Schemes have been initiated close to the Murray River to intercept and abstract saline groundwater from the Loxton Sands at Loxton and Bookpurnong. Conceptual models for the geology and aquifer characteristics have been developed with the aid of drill-core lithology characterisation, ground and airborne geophysics and hydrogeological testing (AWE 2004; Munday *et al* 2004).

RESULTS

Hydrochemical data

The groundwaters in the Loxton Sands aquifer at Bookpurnong are saline and of Na-Cl type. A pronounced redox boundary is present in the aquifer at Bookpurnong (James-Smith *et al* 2005), close to the water table and the change from shallow coarser red sands to deeper finer-grained grey silty sands. This boundary has been used to separate the Loxton Sands into upper (ULS) and lower units (LLS). Downhole logging results showed that the aquifer is strongly stratified, with higher electrical conductance (EC) in the upper Loxton Sands (Figure 3), the change occurring close to the redox boundary. The limited hydrochemical data from samples collected during pump tests at boreholes A and B showed that water chemistry changes, becoming less saline with time. The data from borehole A (using data from AWE 2004) are shown on Figure 4. The borehole was screened across the redox boundary at this site and the results show that the source changed from mainly LLS initially to ULS over the duration of pumping. There was also an overall decrease in pH during pumping and an increase in SO_4/Cl ratio at the time of clogging to values above that found in both units prior to pumping. Pump testing at borehole B also showed a decrease in pH and EC, but no overall trend in SO_4/Cl.

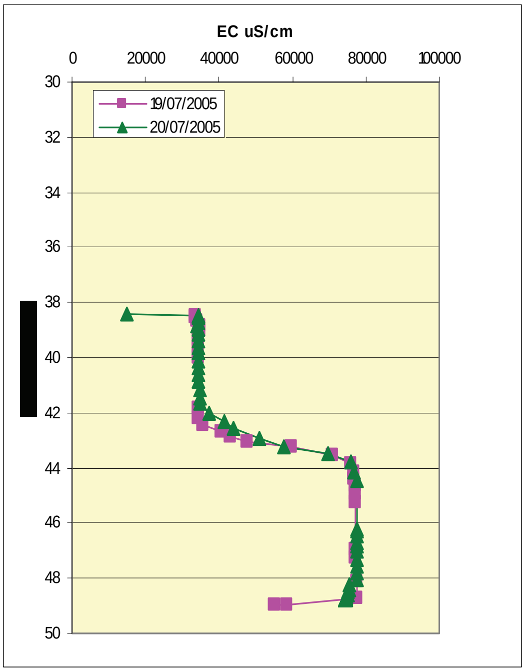

Figure 3. Downhole electrical conductance profiles of groundwater in borehole B (James-Smith & Shand, 2005).

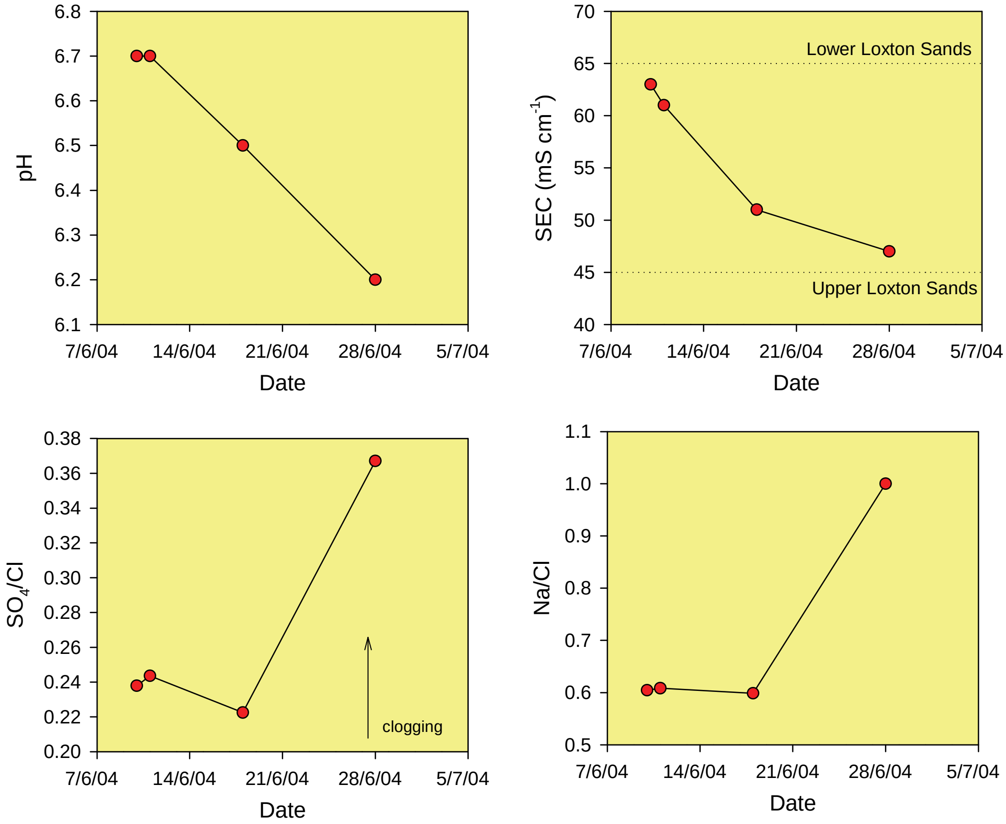

Figure 4. Hydrochemical data collected during a pump test of borehole A. Dotted lines show SEC of upper and lower Loxton Sands groundwater.

Scanning electron microscopy (SEM)

Samples were collected from stored core material at the three sites, mounted onto aluminium mounts and evaporatively coated with carbon. The specimens were placed in a Phillips XL30 FEG-SEM with an attached EDAX DX4 energy dispersive x-ray system, using primary electron beam energy of 10-20 KeV. Imaging was performed using the secondary electron (SE) signal where information about surface topography was required, and the back scattered (BSE) signal where information about chemical composition was required. Energy dispersive X-ray (EDX) analyses were completed to determine the chemical composition of individual points on mineral surfaces. Selected images from each site, at different depths, are shown on Figures 5 to 7.

Samples from above the redox boundary in borehole A were orangey-brown in colour and sand grains were coated with Fe oxyhydroxide minerals (Figure 5). Occasional euhedral crystals of a hydroxy-sulfate mineral with a composition intermediate (Al:Fe 2:1) between alunite ($KAl_3(SO_4)_2(OH)_6$) and jarosite ($KFe_3(SO_4)_2(OH)_6$) were present in association with Fe oxyhydroxide coatings. Pseudomorphs of Fe oxyhydroxides, with the texture of framboids, indicate alteration of original pyrite. Below the redox boundary at ca. 45 m, pyrite was very abundant, forming both framboids and octahedra (Figure 5). Secondary sulfate minerals were also abundant, forming coatings on grains (in close association with pyrite) and as lath shaped crystals forming bridges between sand grains. EDX analysis indicated that these grains were natrojarosite, in contrast to alunite-jarosite at shallower depth. Preliminary X-ray diffraction on this sample has confirmed the presence of natrojarosite as well as jarosite and szomolnokite ($FeSO_4.H_2O$). Pyrite and secondary hydroxysulfate minerals were still abundant at 52 m depth, although the sulfate minerals were intermediate between natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and natroalunite ($NaAl_3(SO_4)_2(OH)_6$). The presence of these hydroxysulfate minerals, which are only stable at very low pH and under very oxidising conditions are the reaction products of pyrite oxidation. The core material sampled had been stored for ca. two years and at least some the oxidation is likely to have occurred during storage. Samples from 60 m depth (not shown on Figure), from the Lower Loxton shells beneath the LLS also contained framboidal pyrite, but no secondary sulfate minerals. Siderite was also relatively abundant throughout the profile beneath the redox boundary.

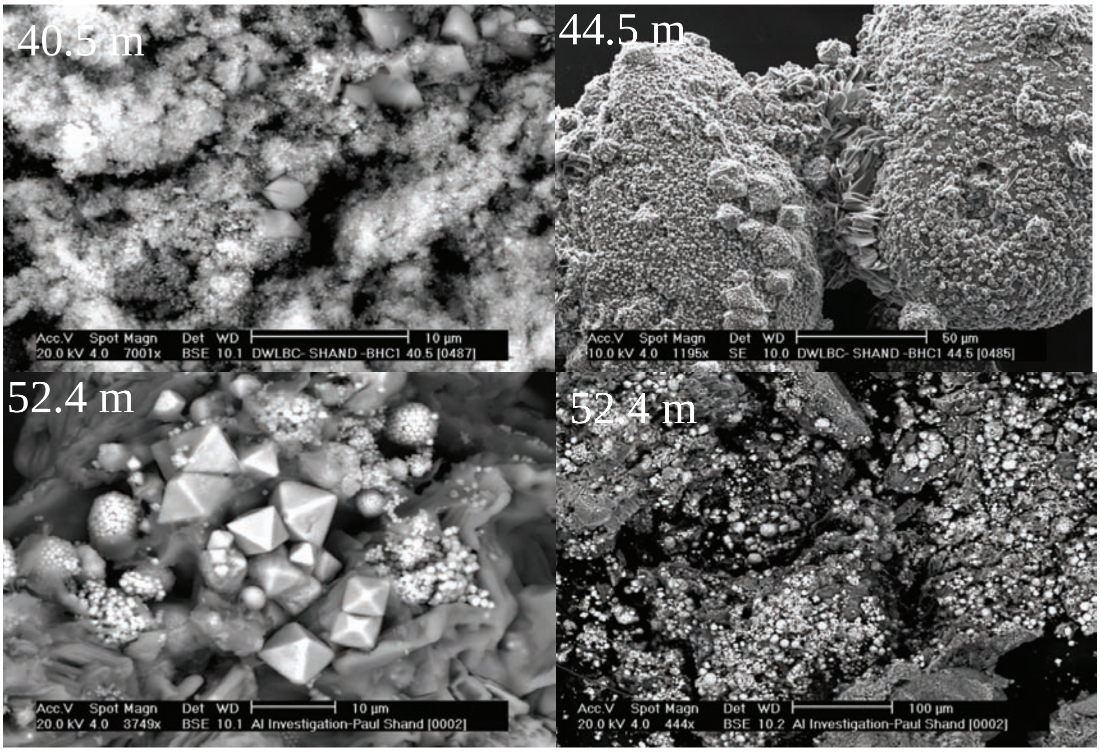

Figure 5. SEM images of samples from borehole A (samples depths shown in metres). 40.5 m: Fe oxyhydroxide coating of sand grain with euhedral to subhedral crystals of alunite-jarosite; 44.5 m: two sand grains coated with abundant euhedral (cuboid and octahedra) pyrite and bridging laths of hydroxysulfate mineral (natrojarosite); 52.4 m (left image) framboidal and octahedral pyrite on a base of natrojarosite-natroalunite; (right image) abundant coatings of framboidal pyrite.

SEM images from borehole B are shown on Figure 6. Pyrite was mainly present as framboids, but not as abundant as borehole A, and no secondary hydroxysulfate minerals were identified. Gypsum was occasionally present as subhedral crystals as well as siderite (Figure 6). Pyrite was difficult to find in samples from borehole C, but was present as occasional framboids (Figure 7). In contrast to samples from boreholes A and B, those in borehole C contained relatively abundant calcite, both as detrital grains and shelly material (probably aragonite).

DISCUSSION AND SUMMARY

The presence of pyrite and secondary hydroxysulfate minerals (which act as stores of acidity) provide a basis for a reassessment of previous models for Al mobilisation and transport in the Loxton Sands at Bookpurnong. Whereas previous models did not account for a full mass balance for hydrogen ions, the presence of pyrite, as well as any secondary hydroxysulfate minerals, provides a primary source of acidity, capable of mobilising Al. Two observations must be taken into account in the formulation of a conceptual model 1) clogging did not occur initially and 2) the pH in the discharge water was not low enough to dissolve significant Al. This implies that pumping induces acidification and/or mobilisation of Al and, in addition, that the transport must be localised and not controlled by the ambient pH conditions as represented by discharge water.

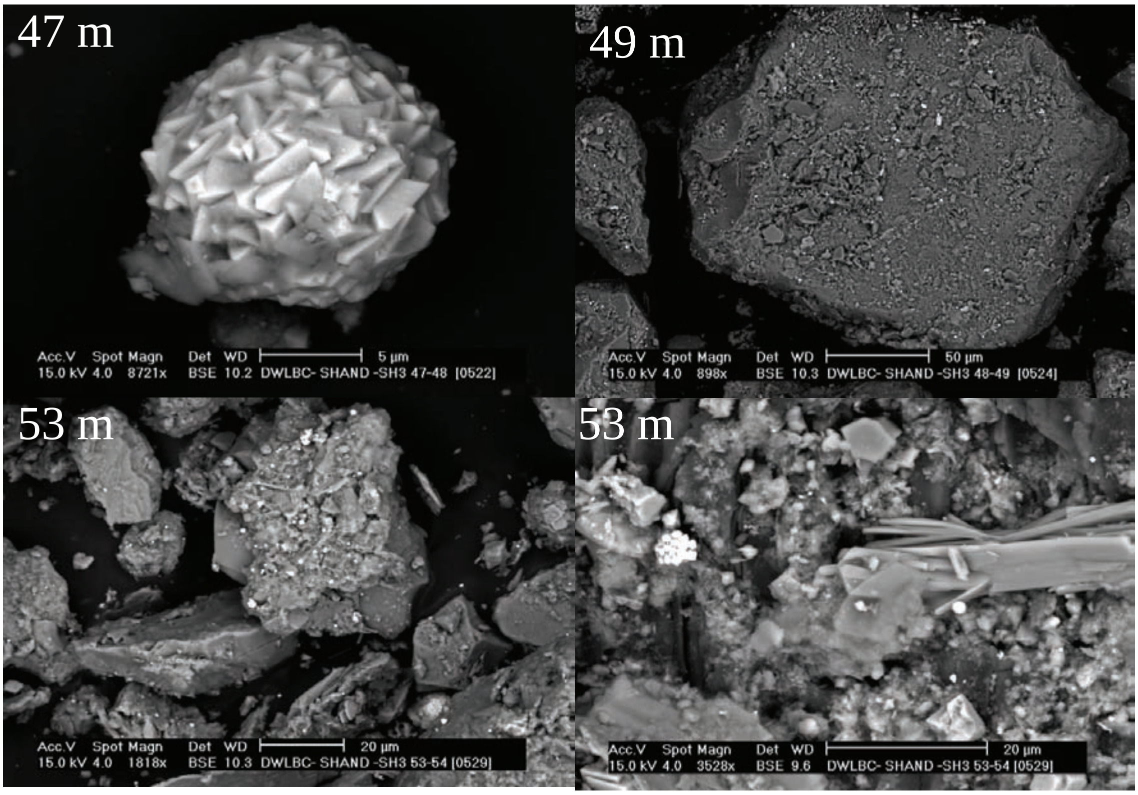

Figure 6. SEM images of samples from borehole B (samples depths shown in metres). 47 m: pyrite framboid; 49 m: two sand grain with pyrite (bright) on surface; 53 m (left image) small grains of pyrite and framboid (lower right); (right image) framboidal pyrite (left), gypsum (right) and siderite (lower right centre).

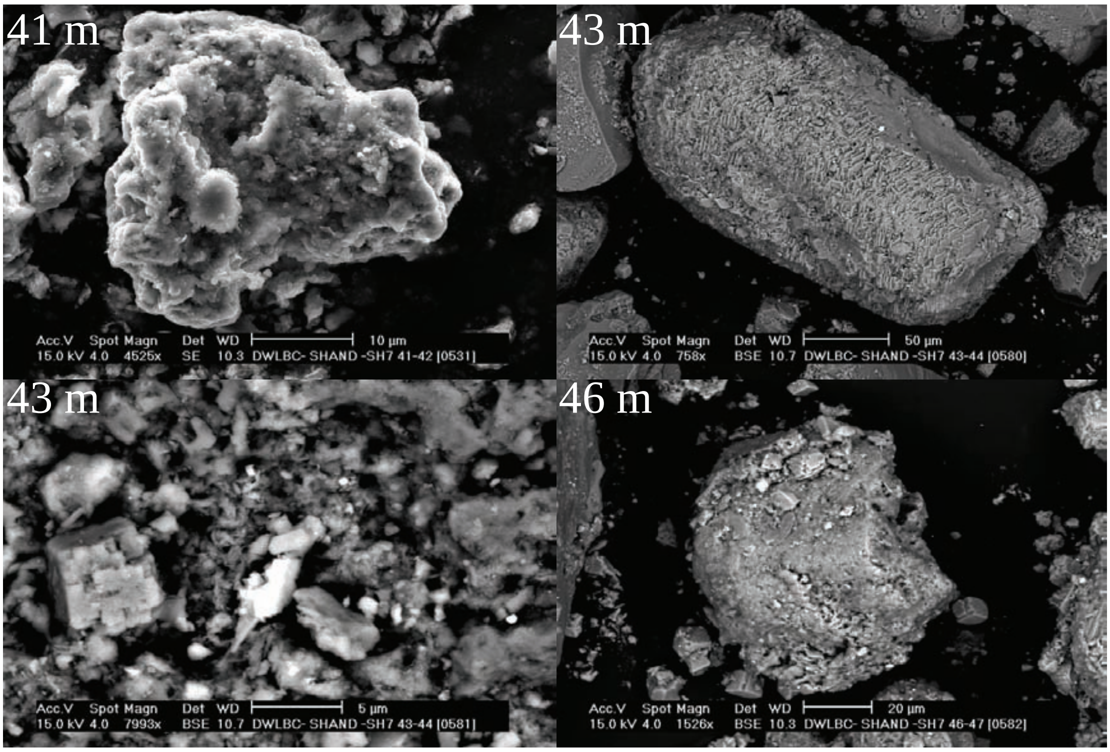

Figure 7. SEM images of samples from borehole C (samples depths shown in metres). 41 m: sand grain coated in Fe oxyhydroxide; 43 m: large calcite grain with minor pyrite (bright); 43 m: siderite (centre left), illmenite (large bright crystal, centre) and minor disseminated pyrite (small bright grains); 46 m: minor pyrite (bright) on sand grain.

A conceptual model has been developed (Figure 8), whereby cavitation and lowering of the water table towards the redox boundary introduces oxygen generating acidity via pyrite oxidation and Al mobilisation at or close to the redox boundary. The mixing of this locally-derived acidic groundwater with circumneutral pH water from above and below the boundary induces rapid precipitation of amorphous $Al(OH)_3$ on borehole screens and pump inlet. This model explains the delay in clogging as well as the conflicting hydrogeochemistry (high Al concentrations at circumneutral pH). The mobilisation of pyrite and/or hydroxysulfate minerals, noted particularly in borehole A, is also indicated by the large increase in SO_4/Cl ratios at this site. The presence of these minerals as a source of both acidity and Al, as well as the presence of pyrite, needs to be taken into account in future predictions of clogging at SIS schemes.

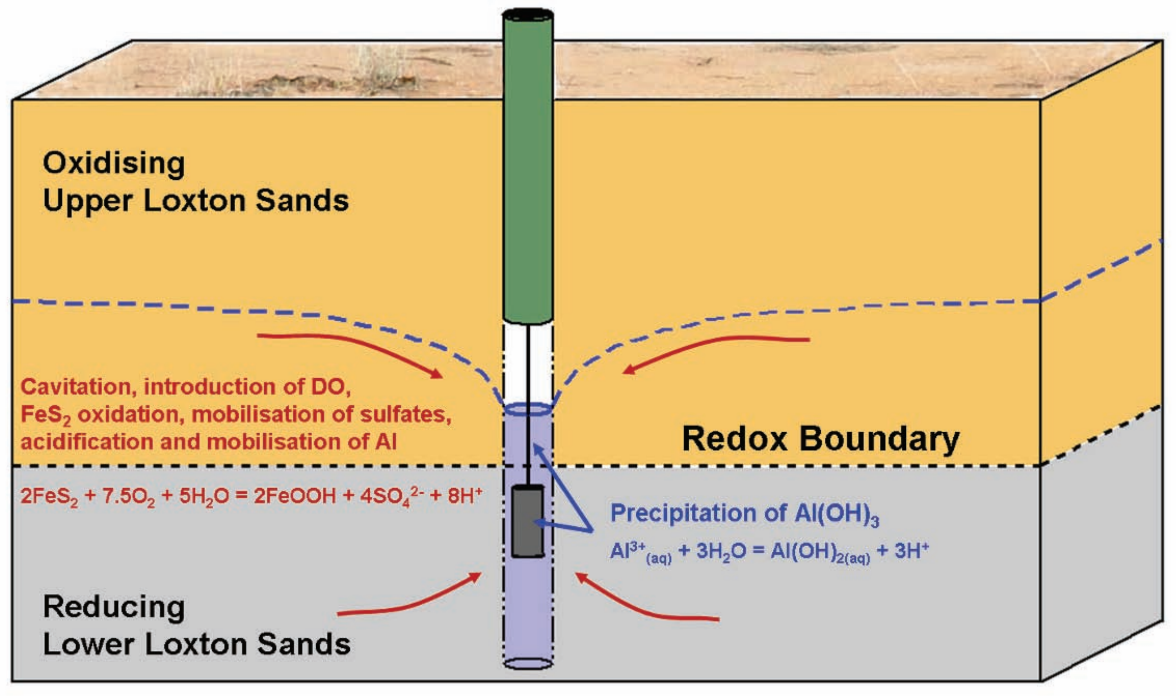

Figure 8. Conceptual diagram showing the development of a cone of depression during extended pumping. Oxygenated water is introduced below the redox boundary allowing pyrite oxidation, the production of acidity and dissolution of Al-rich minerals (e.g. clays). Mixing of this water in the high pH environment of the bore column causes rapid precipitation of Al hydroxide on screens and in the pump.

The variety of pyrite forms and the differences in hydroxysulfate mineralogy are likely to be controlled by a range of environmental factors including redox environment, solution chemistry, different degrees of S saturation, differences in solid phase mineralogy etc. Little is know about the controls on pyrite micromorphology but differences in precursors (e.g. polysulfides or monosulfides) may play an important role. Knowledge of these processes will help provide useful indicators for assessing the changing environmental conditions which give rise to such complex mineral assemblages and allow better predictions of their response to new imposed environmental conditions.

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CHAPTER 6

GREENHOUSE EMISSIONS AND TOXIC GAS EMISSIONS FROM SOIL ORGANIC MATTER AND CARBONATES ASSOCIATED WITH ACID SULFATE SOILS

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GREENHOUSE EMISSIONS

Soil organic matter in wetlands

In their undisturbed state wetland soils are natural accumulators of carbon and sulfur. Jickells and Rae (1997) reported work by Wollast (1991) indicating that shelf sediments appear to be major sinks of organic carbon on a global scale. This review cites further work by Twilley *et al* (1992) in which wetlands are estimated to contain one third of continental shelf carbon with the bulk of this storage in mangrove systems. Chmura *et al* (2003) combined the literature data from tidal saline wetlands at 154 sites to produce a global data set of soil carbon density (i.e. concentration expressed as weight/volume). They found an average carbon concentration for mangrove swamps (5.5±0.04 % w/v) and an average salt marsh carbon concentration (3.9±0.3 % w/v).

The formation and accumulation of pyrite to form an acid sulfate soil first requires the reduction of sulfate by bacteria. This reaction needs organic carbon to proceed and can be represented by the simple equation (Berner 1984):

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^{-}$$

Pyrite formation is thus accompanied by the consumption of metabolisable carbon and the accumulation of residual organic carbon. Berner (1984) described the observed relationship between organic carbon and reduced sulfur in sediments and Morse and Berner (1995) showed that the relationship between this residual carbon and reduced sulfur in sediments could be represented by the equation:

$$R = \frac{2}{f_{CS} f_{SP}} \left(\frac{1}{f_M} - 1 \right)$$

where R is the mole ratio of (residual buried) organic carbon to total reduced sulfur, f_M is the fraction of the total organic carbon deposited in the sediment metabolised, f_{CS} is the fraction of metabolised carbon utilised for sulfate reduction and f_{SP} is the fraction of reduced sulfur buried. In normal (non-euxinic) marine sediments the C:S mole ratio has been found to be 7.5 (±2.1) (Morse and Berner 1995). These ratios are routinely used to distinguish between marine and freshwater paleoenvironments.

This buried residual carbon forms a pool of that has been removed from the active carbon cycle. Disturbance of ASS can return this carbon to the active carbon pool as carbon dioxide either through microbial oxidation or by burning. It may also be remobilised in waterways as dissolved and suspended particulate organic carbon.

Hicks *et al* (1999) conducted a study of coastal wetlands drained for agricultural development in the 1970's and found considerable loss of soil carbon. Two soils were examined, a Typic Sulfihemist and a Typic Sulfaquent. The average carbon concentrations to a depth of 1 m were 5.8% and 2.9% w/v respectively. Drainage of the Sulfihemist resulted in subsidence of more than 1 m and a profile carbon loss of 710 t C ha^{-1} and for the Sulfaquent, 0.29 m subsidence and a profile carbon loss of 220 t C ha^{-1}. These represent a significant loss of soil carbon. The processes leading to loss and remobilisation are likely to be repeated in disturbance of any wetland where carbon has accumulated. Profile data, changes following drainage and processes for the Typic Sulfihemist are summarised in Figure 1.

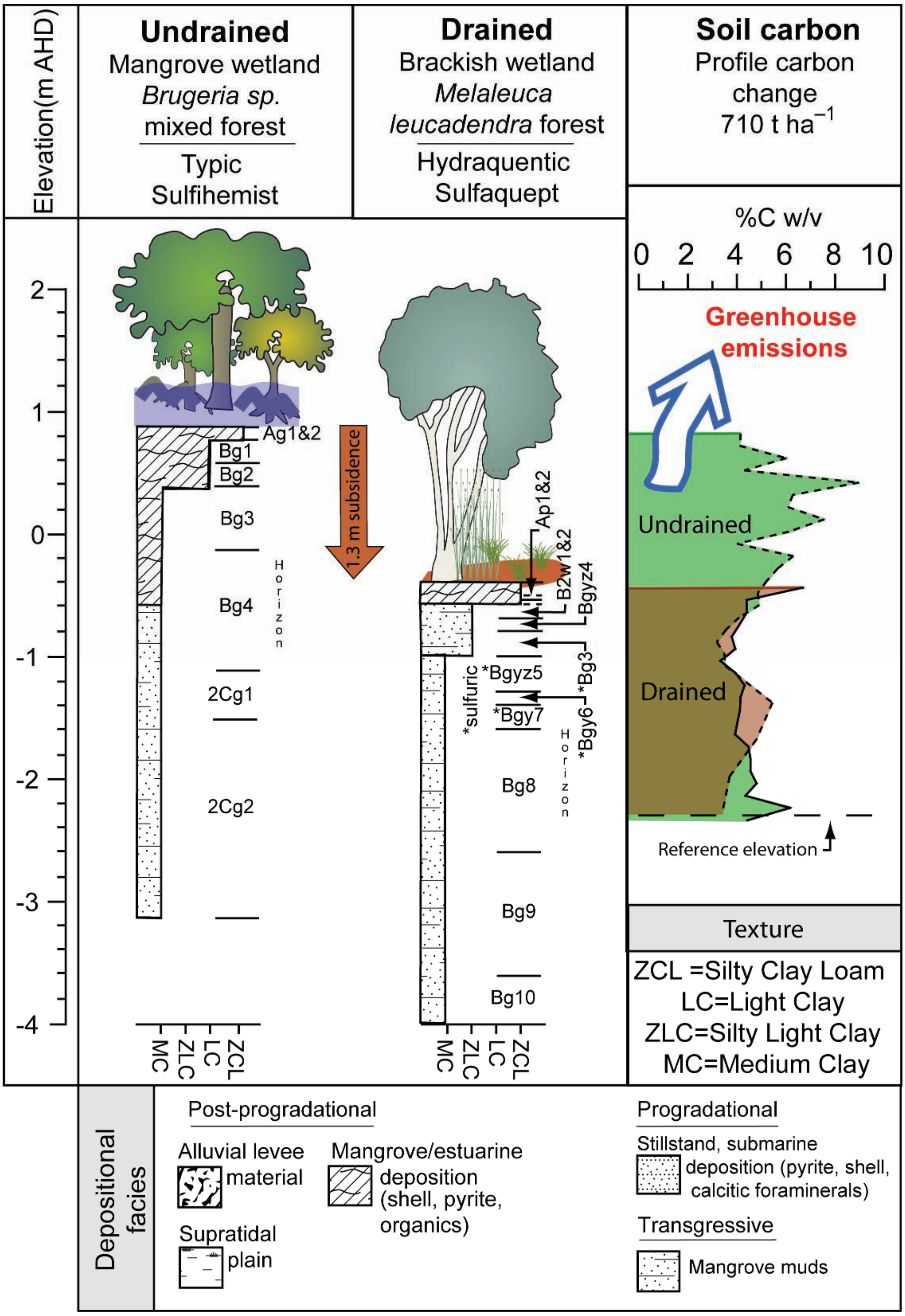


Figure 1. Soil profile data and processes for the disturbance of a Typic Sulfihemist. Profile descriptions according to Soil Survey Staff (1996).

Pedogenic Carbonate

Soils with pedogenic carbonate are estimated to cover about 50% (3.7 million km^2) of the Australian continent and mainly occur across its southern and inland regions where the climate is arid, semi-arid or temperate. Their occurrence, physical and geochemical properties were extensively reviewed by Milnes and Hutton (1983). However limited information exists about the dynamics of this vast pool of soil inorganic carbon in relation to land use and management, and the magnitude of this pool in the wide range of ecosystems in Australia has not been assessed.

Fitzpatrick and Merry (2000) examined the effect of ASS disturbance on pedogenic carbonate in three landscape units in South Australia:

1) Undulating Hills (Natrixeralfs with carbonate layers),
2) Plains (dunes and swales with Petrocalcic Xerochrepts),
3) Coastal (Petrocalcic Xerochrepts).

In summary, they found that calcareous soils are economically important to Australia because they predominate in the dryland cropping zone of southern and eastern Australia and the irrigated grain cropping, horticulture and cotton areas of the Murray-Darling Basin. This made them particularly subject to human alteration. Specifically the environments reported on involved the following controlling factors:

- carbonate formation by rock weathering, which represents a net sink of CO_2 from the atmosphere
- carbonate dissolution, reprecipitation and removal from calcrete layers, which represents a transient gain of CO_2 to the atmosphere as co-released calcium and magnesium ions will eventually remove an equivalent amount of carbon dioxide
- carbonate dissolution in drained mangrove swamps, which leads similarly to a transient gain of CO_2 to the atmosphere.

These processes of carbonate dissolution and formation are accelerated by soil degradation consequent upon human alteration of the ecosystem through the intensification of dryland agriculture and through urban development. Contemporary rising saline ground water tables (containing high levels of Ca and Mg), and acids produced in the nitrogen and carbon cycles of dryland agricultural systems and by oxidation of pyrite in drained sulfidic mangrove soils, for example, may advance the formation, dissolution, reprecipitation and removal of carbonate. Table 1 (from Fitzpatrick and Merry 2000) is a first approximation of the relative importance given to the main processes (parent material source of Ca and Mg, climate and hydrological leaching and acidification) providing weathering products that may control the carbonate pools in weathering environments in South Australia. The net losses and gains of $CaCO_3$ pools are summarised and their relative importance is given. ASS occurred in all but the arid/semi-arid soil weathering environment. In the undulating hills (Natrixeralfs with carbonate layers) disturbance of ASS was likely to result in mobilisation and reprecipitation of carbonates. In the Plains and Coastal soil weathering environments, disturbance of the ASS was likely to result in the loss of pedogenic calcium carbonate; however there would be no net gain of carbon dioxide to the atmosphere as the calcium and magnesium released would eventually sequester an equivalent quantity of carbon dioxide elsewhere.

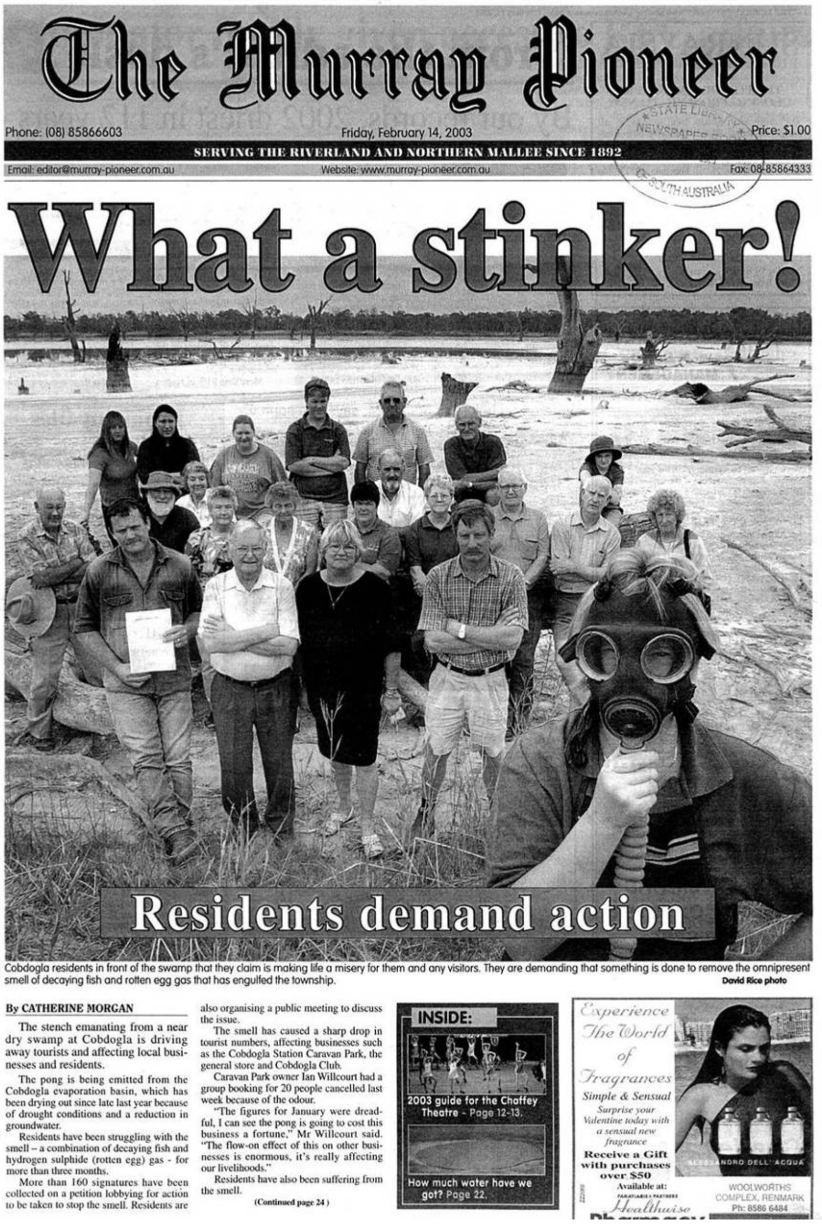
Table 1 Estimates of the various processes, which control carbonate pools in four representative weathering environments in South Australia (from Fitzpatrick and Merry 2000)

Processes providing weathering products	**Soil Weathering Environments (Major calcareous soil type)**			
	Undulating hills	Plains (dunes and swales)	Coastal	Arid/semi-arid
	(Natrixeralfs with carbonate layers; Fig. 2)	(Petrocalcic Xerochrepts; Fig. 3)	(Petrocalcic Xerochrepts; Fig. 4)	(Calcids and Salids)
Climatic and hydrological leaching processes				
Rainfall, Soil temperature regime (downward flow)	550-700 mm Mesic High	300–500 mm Thermic Low	400 mm Thermic Low	< 250 mm Thermic/ Hyperthemic Very Low
Rising saline groundwater (upward flow)	High	High	No	Low
Declining tidal groundwater	No	No	Yes	No
Through flow (lateral flow)	High	No	No	No
Parent material sources of Ca and Mg				
Non-carbonate rocks	Mica schist	None	None	Low
Carbonate-rich deposits	None	Limestones	Limestones	Calcareous
Aeolian deposits	Minor	Moderate	Moderate	Moderate
Acidification processes providing weathering products				
Sulfuric acid from acid sulfate conditions	Moderate	Moderate	High	No
Acid from use of fertilisers & changes in C-N cycle	High	Moderate	No	No
Overall impacts of processes				
Net gain or loss of pedogenic $CaCO_3$	Gain	Static in dunes/ loss in swales	Loss	Static or passive
Areal significance of process	Minor	Major	Minor	Major

TOXIC GAS EMISSIONS

In areas with irrigated agriculture, excess drainage waters are often stored in disposal basins to avoid returning saline waters to rivers. An unexpected environmental concern associated with disposal basins is that some of them emit noxious odours when water levels are lowered or attempts are made to dry them. This phenomenon is commonly observed in saline wetlands and disposal basins of Lower River Murray floodplains, for example in Figure 2. The emission of noxious odours can result in the loss of aesthetic, recreational and tourism values associated with nearby areas and is thought to represent a potential health risk.

The causes and mechanisms of noxious odour generation from disposal basins are not known but are almost certainly associated with the cycle of sulfur (S) in these environments. Sulfur is widespread in the environment and occurs as a very common salt (as sulfates, SO_4^{2-}) in disposal basins and salinised floodplains. However, unlike other common salts such as sodium chloride, SO_4^{2-} salts are biologically reactive and can be transformed into a variety of inorganic compounds (such as pyrite – FeS_2) and organic compounds (S is a key building block of proteins). The raising of water levels in the River Murray and associated floodplain wetlands by the construction of weirs, as well as waterlogging caused by rising water tables has resulted in the widespread occurrence of accumulated reduced sulfur compounds (Lamontagne *et al* 2006; Fitzpatrick *et al* 2008) in the lower River Murray. This has produced a pool of reduced sulfur compounds vulnerable to disturbance through a variety of management interventions such as water level manipulations and salt interception schemes as well as natural phenomena such as drought, all of which are likely to be exacerbated by climate change.



The Murray Pioneer
Phone: (08) 85866603 Friday, February 14, 2003 Price: $1.00
SERVING THE RIVERLAND AND NORTHERN MALLEE SINCE 1892
Email: editor@murray-pioneer.com.au Website: www.murray-pioneer.com.au Fax: 08-85864333

What a stinker!

Residents demand action

Cobdogla residents in front of the swamp that they claim is making life a misery for them and any visitors. They are demanding that something is done to remove the omnipresent smell of decaying fish and rotten egg gas that has engulfed the township. David Rice photo

By CATHERINE MORGAN

The stench emanating from a near dry swamp at Cobdogla is driving away tourists and affecting local businesses and residents.

The pong is being emitted from the Cobdogla evaporation basin, which has been drying out since late last year because of drought conditions and a reduction in groundwater.

Residents have been struggling with the smell – a combination of decaying fish and hydrogen sulphide (rotten egg) gas - for more than three months.

More than 160 signatures have been collected on a petition lobbying for action to be taken to stop the smell. Residents are also organising a public meeting to discuss the issue.

The smell has caused a sharp drop in tourist numbers, affecting businesses such as the Cobdogla Station Caravan Park, the general store and Cobdogla Club.

Caravan Park owner Ian Willcourt had a group booking for 20 people cancelled last week because of the odour.

"The figures for January were dreadful, I can see the pong is going to cost this business a fortune," Mr Willcourt said. "The flow-on effect of this on other businesses is enormous, it's really affecting our livelihoods."

Residents have also been suffering from the smell.

(Continued page 24)

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How much water have we got? Page 22.

Figure 2. Noxious smell events can decrease the aesthetic values associated with wetlands and could also be a community health concern (Barmera, South Australia). Murray Pioneer, 14 February 2003.

What's emitted and how badly can it smell?

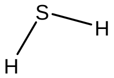
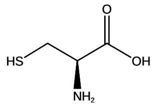
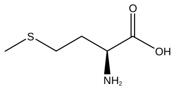
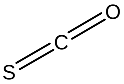
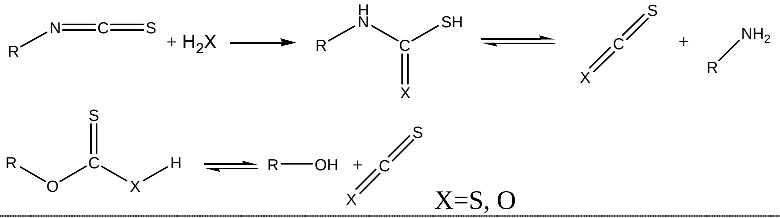
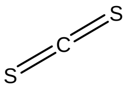
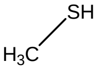
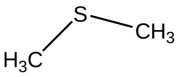
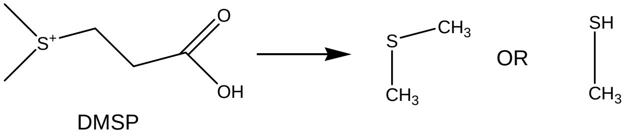
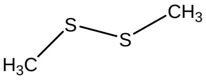
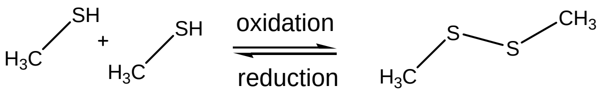
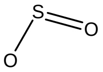
There is evidence from overseas studies that wetlands emit a range of sulfur gases and that they vary according to factors such as salinity, wetting–drying regime, soil type and diurnal cycles (Lomans *et al* 2002). Three main types of S gases can be emitted by wetlands: hydrogen sulfide, volatile organic sulfur compounds (VOSC) and sulfur dioxide (SO_2). These differ in the way they are produced (Table 1). The human nose can detect some of these compounds at very low concentrations.

Hydrogen sulfide: The rotten-egg smell. Under conditions of low oxygen, hydrogen sulfide is produced by microorganisms in the water columns and sediments of wetlands by the process of sulfate reduction (Figure 3). Most wetland sediments will be without oxygen at depth and will have some degree of sulfate reduction occurring. Another mechanism to produce H_2S is also a familiar one – the decomposition of organic matter rich in organic S, like eggs.

VOSCs: A wide variety of volatile organic sulfur gases occur in the environment and many give pleasant tastes and flavours to foods. However, several have very unpleasant odours. Some VOSC even play a role in climate regulation (VOSC emissions from oceans contribute to cloud formation and thus the albedo effect). VOSCs can be produced by a wide variety of mechanisms including: decomposition of organic matter; releases by algae; in marine, estuarine and salt marsh environments, the degradation of dimethylsulfoniopropionate (DMSP) an organic osmolyte (a substance that is part of an organism's salt balance); and as detoxification by-products when organisms are exposed to H_2S. Noxious smells associated with VOSCs are also a problem in waste treatment plants, pulp mills and aqueducts.

Sulfur dioxide: When previously anoxic sediments are exposed to oxygen, sulfur dioxide (SO_2) can be produced during the oxidation of sulfides (e.g., pyrite) by oxygen (Figure 3.). This process can also be catalysed by another group of microorganisms, the "sulfide oxidisers". SO_2 has an acrid smell and can have adverse health effects following chronic exposure. Large quantities of SO_2 are also emitted by volcanoes, and by fossil fuel burning and it is a key ingredient for the formation of smog in cities.

Table 2. Some common sulfur gases.

Compound	**Main origin**
Hydrogen sulfide  H_2S	Reduction of sulfate Decomposition of sulfur-containing compounds in organic matter e.g.  L-Cysteine  L-Methione
Carbonyl sulfide[*] COS 	Reaction of hydrogen sulfide with organic matter e.g.  X=S, O
Carbon disulfide[*]  CS_2	Reaction of hydrogen sulfide/decomposition of organic matter (see above). [*]Interconversion of these two compounds in the soil and atmosphere: $COS + H_2O \rightleftarrows CO_2 + H_2S$ $CS_2 + OH^- \rightleftarrows COS + HS^-$
Methanethiol (MT)  CH_3SH	Reaction of hydrogen sulfide with organic matter. Decomposition of sulfur-containing compounds in organic matter
Dimethyl sulfide (DMS) $(CH_3)_2S$ 	Reaction of hydrogen sulfide with organic matter Decomposition of sulfur-containing compounds in organic matter e.g.: 
Dimethyl disulfide (DMDS) $(CH_3)_2S_2$ 	Oxidation of Methanethiol  Decomposition of sulfur-containing compounds in organic matter
Sulfur dioxide  SO_2	Oxidation of pyrite (FeS_2)

Key biogeochemical processes

It has been observed that disposal basins emit noxious smells mainly when they are drying. In the following, we review in more details the main chemical reactions that occur when saline wetlands are "wet" and the ones that may occur when they are "drying" (Figure 3). As few studies have been conducted on the emission of S gases in Australian wetlands – the mechanisms proposed here are hypotheses that will require confirmation using laboratory and field studies.

Under wet conditions – Inorganic S cycle: There are two key features of the sulfur cycle under wet conditions: 1) the accumulation of sulfides and organic-S in the sediments and 2) the trapping of S gases emitted from the sediments by the water column. In most wetlands, the decomposition of organic matter in the sediments consumes much oxygen, and anoxic conditions prevail within a few millimetres below the sediment-water interface. Under such anoxic conditions, dissimilatory sulfate reduction occurs and H_2S is produced as an end-product (Figure 3). Much of the H_2S produced in the sediments will react with Fe and other metals to form sulfide minerals, but some H_2S can also escape to the water column by diffusion from the sediments. However, most of the H_2S diffusing from sediments to the water column will rapidly react with O_2 (eventually producing sulfate) and thus not reach the atmosphere (Figure 3). A few other factors could influence whether or not H_2S will be emitted from wetlands, including: The diurnal wetland O_2 cycle, density stratification, pH, and ebullition (bubble formation).

Diurnal O_2 cycle: It is common for small Australian wetlands to have large fluctuations in O_2 concentration over a daily cycle. Oxygen is added to the water column of wetlands by diffusion from the atmosphere and by photosynthesis by plants, algae and some bacteria. In return, O_2 is consumed in wetlands by the decomposition of organic matter and aerobic respiration. Because photosynthesis does not occur at night but respiration and decomposition do, there is a tendency for small wetlands to have lower O_2 concentrations at night, especially in summer when warm temperatures increase the rates of decomposition and respiration. It can be hypothesised that H_2S produced in sediments will be more likely to escape to the atmosphere at night when low O_2 concentration in the water column would decrease water column H_2S oxidation rates.

Density stratification: Many wetlands have periods when the water column is stratified into layers with different densities because of differences in temperature and salinity. When stratified, there is a tendency for bottom waters to become anoxic and accumulate H_2S because O_2 consumption rates in sediments can be rapid relative to the rate of diffusion of O_2 from the overlaying water layer. In shallow wetlands, such stratification is seldom long lasting when it occurs because wind can efficiently mix the water column. However, when wetlands destratify rapidly, it is possible that a pulse of H_2S from bottom waters could be rapidly released to the atmosphere.

pH: H_2S is a "weak acid" and a proportion present in the water column will tend to dissociate into either HS^- or S^{2-} at different pH values. In general, at neutral and alkaline pH, the preferred forms in water will be HS^- and S^{2-} (which are not volatile) while at more acid pH values, H_2S becomes favoured. Thus, it should be expected that a higher proportion of the H_2S produced in wetlands will escape to the atmosphere when wetlands are acidic.

Ebullition: Diffusion is not the only process that can transfer H_2S produced in sediments to the water column. When water becomes supersaturated with a given gas (or set of gases), bubbles will tend to form. Bubble formation in sediments is especially common in summer, when decomposition rates (and the production of CO_2, N_2, methane and other gases) are higher. The formation and release of bubbles in sediments could be an effective mechanism to emit sulfur gases produced in sediments to the atmosphere in some wetlands.

Under wet conditions – Organic S cycle: The organic sulfur cycle in wetlands is not as well known as its inorganic counterpart. Sulfur can be integrated in organic matter by the process of assimilatory SO_4^{2-} reduction (Figure 3). This occurs when algae and bacteria consume sulfate and convert it to protein-sulfur within their cells. Organic sulfur accumulates on the bottom wetlands when plants and animals die. Because decomposition rates are slower under anoxic conditions, there is tendency for organic matter (and organic-S) to slowly accumulate in wetland sediments.

VOSCs will be produced in wetland water and sediments when wet, particularly by releases from algae and decomposition in the sediments. Which specific compounds are produced and at what rates is not known for Australian inland wetlands. Some of the VOSCs produced will be consumed by bacteria in the water column. How much of the remaining VOSCs will be released to the atmosphere and the factors controlling the rates of production are not well known. In addition, VOCS emission rates are related to other factors such as temperature, diurnal cycles, degree of sediment wetness and sediment texture. To our knowledge, our recent exploratory sampling of ambient air in the Loveday Basin has been the only study of VOSC emissions from Australian inland wetlands.

Change in S cycling when wetlands are drying: Two key factors could influence the S gas emission rates when wetlands are drying: 1) the exposure of previously anoxic sediments to oxygen, and 2) the loss of the overlying water column as a "trap" for S gases emitted from the sediments. The proposed consequences for the changes in these two environmental factors on the inorganic and organic S cycle are outlined below.

Inorganic S gas emission: When wetland sediments are exposed to the atmosphere, they will gradually oxidise, as oxygen can now penetrate more easily in the sediments. A key inorganic S process under these conditions will be the tendency to oxidise sulfides stored in sediments, producing both sulfuric acid and sulfur dioxide (Figure 3). The rates at which sulfide oxidation will proceed is dependent on the soil texture (lower in clayey, compared to sandy, sediments) and the frequency of desiccation features (which increase the rates of oxygen diffusion in the sediments), residual moisture, and ambient pH. Thus SO_2 as opposed to H_2S is the main S gas emitted by the inorganic S cycle when oxygen is present.

There are potentially two mechanisms by which H_2S could be emitted from drying wetland sediments. Firstly, because the oxidation of sediments occurs gradually from the sediment surface (Figure 3) the anoxic conditions suitable for dissimilatory S reduction (and H_2S generation) could persist for significant lengths of time at depth. Some of the H_2S produced within the anoxic zone could then be released to the atmosphere by diffusion or advection (movement of air through pores induced by winds, temperature contrasts, etc), processes that could be aided by the desiccation features that often develop when wetland sediments dry. Likewise, H_2S produced during organic matter decomposition could more easily escape to the atmosphere in the absence of a water cover. In addition, organic matter decomposition rates could increase once sediments are exposed to the atmosphere.

Regardless of whether H_2S or SO_2 is produced, or the rates of gas production within sediments change, it is likely that gaseous S emissions increase from drying wetland sediments because some of the gases produced are no longer trapped within the wetland by the water column.

VOSCs: VOSCs are produced by various processes in both oxic and anoxic wetland sediments (Figure 3). Here again, there is limited information in the literature to determine whether VOSC emission rates to the atmosphere should increase in drying sediments. It can be speculated that VOSC emission rates will tend to increase in drying wetland sediments because of more rapid decomposition rates of sediment organic matter under oxic conditions and the decreased interception of some VOSCs by the water column. There is also evidence that more VOSCs are produced in sulfide rich environments. This could occur, for example, when microorganisms produce VOSCs as a detoxification mechanism against H_2S or by chemical reactions between H_2S and organic matter.

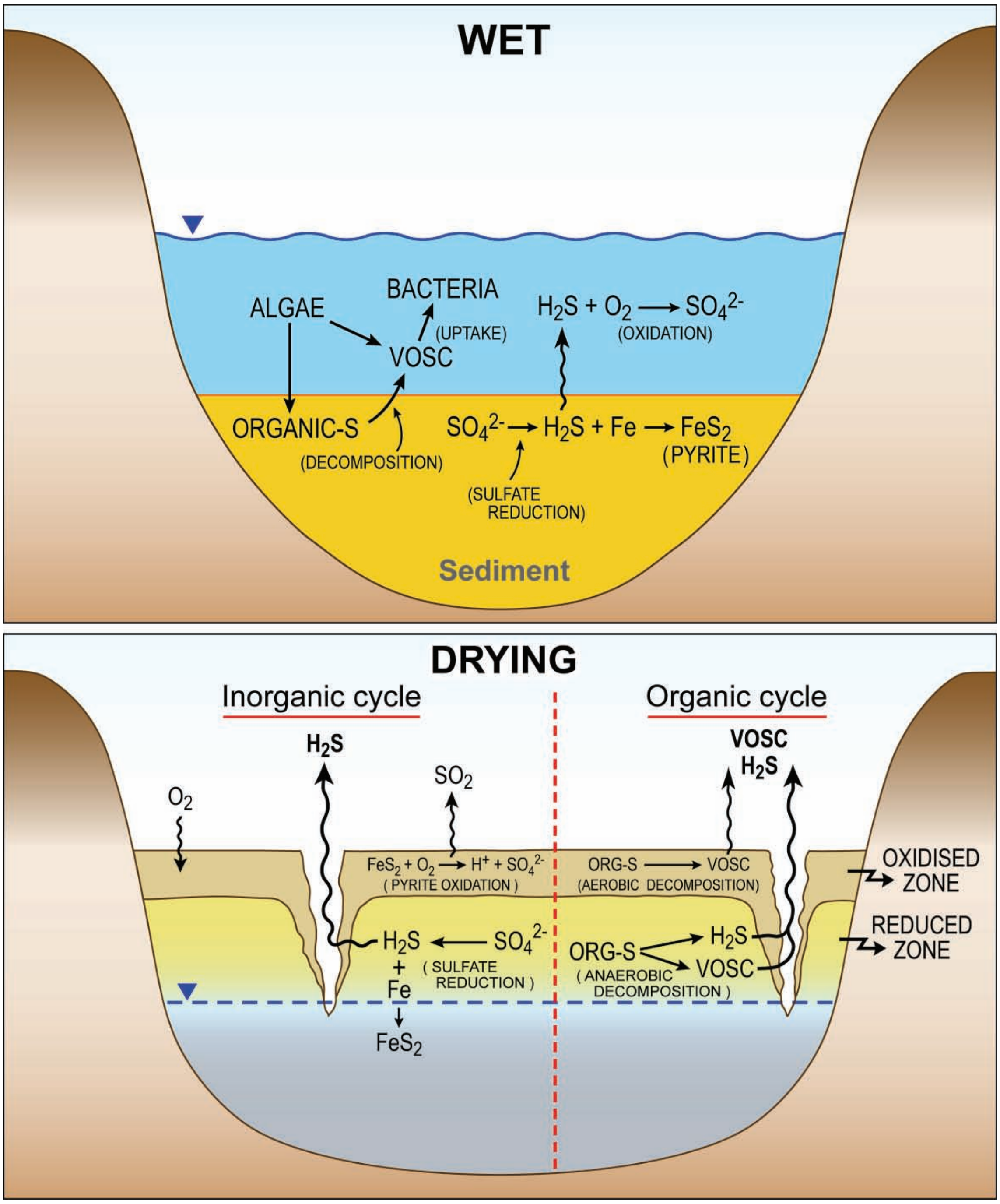


Figure 3. Sulfur cycling in wetlands under wet and drying conditions showing major pathways for sulfur transformations.

Knowledge needs to better manage the noxious odour problem.

Hicks *et al* (unpublished data) undertook exploratory sampling of ambient air at the Loveday Disposal Basin (LDB). As far as we are aware this is the only study to analyse for a comprehensive suite of S-gases. These ambient air measurements revealed the presence of a range of gases in unexpected concentrations. Concentrations were at levels previously thought to be associated only with residues from their use as pesticides and fumigants for soil, grain silos and fruit. The spatial and temporal variation in the occurrence and concentration of these gases warrants further investigation as there is the potential for human health effects. The concentrations of a range of S gases in air samples taken mid-afternoon (~15:00) were at values close to their toxic limit values (Table 3). Early morning samples (~ 06:00) had lower levels of all gases apart from carbonyl sulfide.

Table 3. Ambient air samples where at least one gas was at a concentration above a recommended value. Results are bolded and colour coded to match the relevant exposure value. No value for a particular exposure standard means that it is not explicitly covered by that standard.

	Hydrogen sulfide H_2S	Carbonyl sulfide COS	Carbon disulfide CS_2	Dimethyl sulfide DMS	Dimethyl disulfide DMDS	Dimethyl sulfoxide DMSO
threshold limit value (tlv)/time weighted avg (twa) for occ exp	**10[†]**	**10[†]**	**10[†]; 2[*]**	**2[†]**	**–**	**–**
threshold no effect value[‡]	**10**	**1.25**	**10**	**50**	**0.0035**	**–**
Chronic Ref Exp Level (California)[¶]	**0.008**	**–**	**0.3**	**–**	**–**	**–**
	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v
Loveday Basin, SA 25-Jun-07 14:30 10cm above water						
max	<0.0001	0.02	0.005	0.08	<0.0001	<0.0001
mean	<0.0001	0.008	0.003	0.028	<0.0001	<0.0001
sd		0.008	0.001	0.035		
n	4	4	4	4	4	4
14:45 10cm above soil 1m from waterline						
max	<0.0001	0.04	0.005	0.09	<0.0001	<0.0001
mean	<0.0001	0.020	0.003	0.058	<0.0001	<0.0001
sd		0.014	0.001	0.035		
n		4	4	4	4	4
14:55 10cm above disturbed sediment						
max	**0.06**	**9.4**	**0.800**	**8.6**	**0.800**	0.060
mean	**0.03**	**6.2**	**0.600**	**7.6**	**0.500**	0.043
sd	0.022	2.6	0.216	1.308	0.216	0.015
n	4	4	4	4	4	4
Mussell Lagoon, SA 25-Jun-07 15:35 10cm above soil 3m from waterline						
max	0.007	0.004	0.001	0.002	<0.0001	<0.0001
mean	0.0055	0.0035		0.0015	<0.0001	<0.0001
n	2	2	2	2	2	2

*http://www.oehha.ca.gov/air/acute_rels/allAcRELs.html; http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html
† Chemwatch 2007; ‡ Chemwatch 2006

There have been no studies on the environmental controls on S gas emissions from inland Australian wetlands. Therefore, it is not possible to propose scientifically-defensible management guidelines to minimise noxious odour problems during water level management operations in wetlands and disposal basins. A list of critical knowledge needs to better understand the noxious odour problem includes:

- Determination of which inorganic and organic sulfur gases are emitted from a range of wetlands and disposal basins
- Understanding of the environmental factors controlling the rates of emission for the most common noxious-smelling gases. Based on the literature, these factors would include sediment texture, organic matter content, sulfide content, water content, salinity, pH, time of day, temperature and the presence or absence of a water column
- Determination of the relative significance of dissimilatory sulfate reduction and organic matter decomposition as sources of H_2S emission during wetland drying events.

A number of technical challenges may have to be tackled before some of these questions can be addressed. Instrumentation to measure the concentration of some S gases (H_2S and SO_2) is readily available. However, many noxious odour-generating VOSC cannot be readily measured in the field because they occur at very low concentrations (but can still be detected by the human nose). In addition, measuring the rates of emission ("how much is produced per unit area of sediments per unit time") is logistically more complicated than just measuring the ambient concentration of sulfur gases. In overseas studies, the most widely used method to measure S emission rates from exposed sediments is with incubation chambers. These are either coupled to measuring devices (for gases occurring at higher concentrations) or are used to trap S gases on columns or other media for later analysis in the laboratory. The analytical techniques required to measure S gases at low concentrations are challenging. From our review of the literature, only a handful of laboratories around the world appear to have developed the necessary techniques to measure S gas emissions from wetlands.

CONCLUSION

The S cycle and, in particular, the gaseous components of the S cycle have received limited attention in Australian inland wetlands. Studies overseas should be applied with caution to the Australian context because the environment and management issues associated with S are often different there. As Australian wetland managers must learn to “live with salt”, getting a better understanding of sulfur cycling in inland wetlands should be viewed as a priority.

Ambient air measurements indicate that H_2S may not be the main gas responsible for the foul odours. The observed ambient air concentrations represent the “best case” i.e. the lowest concentrations, as they were made in winter when the maximum amount of the gas is dissolved and microbiological activity is lowest. The highest concentrations occurred 10cm above disturbed sediment, with concentrations above the water and shoreline 1–2 orders of magnitude lower; there was also some diurnal variation with some gas concentrations higher for a mid-afternoon sample and others for a dawn sample. Unexpected concentrations of these gases were also observed at Mussel Lagoon, a control site for LDB studies. It is possible the source is the LDB but observations 150 m distant from the basin on Trussell Terrace found much lower gas levels, with many below the detection limit. This site is elevated with respect to the basin, which may account for this; however it may be that these gases occur more generally as a result of floodplain waterlogging and salinisation.

Sulfur gases also represent a potential threat to the ecology and agricultural industries by affecting the chemical ecology of the environment especially in the riparian zone. They have the potential to affect populations of pollinators and also grape/wine quality. It is also worth noting that the concentrations of hydrogen sulfide observed were relatively low and this gas appears to be a minor component of the gas cocktail. This has implications for monitoring and abatement strategies.

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CHAPTER 7

ACID SULFATE SOIL FORMATION IN TURFGRASS IN A SPORTS STADIUM FROM APPLICATIONS OF EXCESS ELEMENTAL SULFUR AS A SOIL AMENDMENT

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INTRODUCTION

As documented in this monograph, the reactive nature of sulfur as it responds to changes in its redox environment can be troublesome. Here we report on one of the more unusual examples that resulted in considerable damage to a major sports ground's turf grass and a civil lawsuit in excess of 1 million dollars.

Superintendents may often apply elemental sulfur when soil pH exceeds 7.5 simply because they are frequently reminded that the optimum pH for turfgrass performance is between 6 and 7. This may be, in part, because they are concerned that a hidden micronutrient deficiency may occur when soil pH is relatively high. Visible iron deficiencies, exhibited as leaf chlorosis, are common when soil pH approaches 8 (Christians, 1998), although they were not observed in this instance. Attempts to reduce the pH of calcareous sand under turfgrass with elemental sulfur or ammonium sulfate, under conditions similar to those evaluated in this case, would be a waste of time and money. A better approach would be to use fertilizer applications to address potential nutrient deficiencies.

During routine end-of-season ground's maintenance, elemental sulfur was applied to reduce the slightly alkaline pH value. The pre-maintenance inspection report of the soil and turf grass noted "A conglomeration of soil types including sand and loamy sand. These conditions could affect drainage and needs regular surface and sub-surface aeration to reduce its impact". There was also a "dense thatch layer" and "A thin layer of dead plant material and fine material existed on the surface", indicating that the playing field had a range in soil texture, organic matter and permeability. The soil testing laboratory recommended an application of 0.1 t ha^{-1} of granulated sulfur. However the actual application was 2 t ha^{-1}, some 20 times greater. Magnesium sulfate, molasses (50L per hectare) and "Dynamic Lifter" (3 tonnes per hectare) were also applied, adding to the readily available source of organic carbon that already existed in the thatch and providing a labile energy source for soil bacteria. Records of the resulting changes in the soil and turf grass condition indicate that in well drained areas the oxidation of the elemental sulfur caused the pH to drop to around 3.8, however in poorly drained areas waterlogging resulted in reducing conditions and the formation of black material with "strong putrid smell and anaerobic conditions".

DISCUSSION

Sulfur is applied as an amendment to reduce the pH via its oxidation to sulfuric acid by soil bacteria. However Nelson (1982) found that excess sulfur may result in patchy reaction and that unreacted sulfur can accumulate in the soil profile in narrow bands of 2 to 3 cm of affected soil. This appears to have been the case at this sports ground where unreacted sulfur was present and the already variable soil conditions became worse. The excess sulfur application created two problems. In well drained areas excess acid produced a sulfuric horizon (pH<4) (Soil Survey Staff 1999), badly affecting plant growth. In poorly drained areas, the large amount of unreacted sulfur, readily available carbon, applied nutrients and watering regime lead to anaerobic conditions and the formation of sulfides. These waterlogged and anaerobic conditions inhibited and damaged root growth. Belatedly, attempts were made to neutralise the acid by liming, however this action was taken too late to prevent substantial damage and for the ground to be ready for the approaching sports season. Because of the need to bring a major facility back into use, the only solution was to replace the affected soil and returf the ground.

CONCLUSIONS

The two sulfur redox reactions resulted in no-win circumstances for attempts at remediation. Watering to leach acid caused water logging, anaerobic conditions and sulfide formation, and drying led to oxidation and acid formation. Both actions contributed to severe turfgrass damage, creating conditions where improvement to soil and grass condition was impossible. The problem was compounded by failure to recognise that excess sulfur addition was the initial cause.

Hence, to be safe when calcareous sand is present, attempts to adjust pH with sulfur should be avoided. Potential nutrient deficiencies that appear on sand-based calcareous turfgrass areas should be addressed with fertilizer applications.

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CHAPTER 8

A CRIMINAL CASE STUDY INVOLVING TRANSFERENCE OF ACID SULFATE SOIL MATERIAL FROM A CRIME SCENE TO FORENSIC EVIDENCE

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INTRODUCTION

Forensic soil science is the science or study of soil that involves the application of soil science, especially studies that involve soil morphology, soil mapping (assisted by existing soil maps and spatially held soil data), mineralogy, chemistry, geophysics, biology and molecular biology to answer forensic legal questions, problems or hypotheses (Fitzpatrick 2009). Soil science is the term commonly used to study soil as a natural body in the landscape and as a resource to be managed for agricultural production, environmental waste disposal and construction. Forensic soil science is a relatively new activity that is strongly “method-orientated” because it is mostly a technique-driven activity in the multidisciplinary areas of pedology, geochemistry, mineralogy, molecular biology, geophysics, archaeology and forensic science. Consequently, it does not have a large number of past practitioners such as in the older forensic disciplines such as chemistry and physics. These days, “forensic soil science” as a newly developed discipline of soil science has matured to the extent that well-defined questions and successful crime scene investigations can be answered in increasingly refined ways (Fitzpatrick 2008, 2009; Fitzpatrick *et al* 2008).

Forensic soil scientists (or forensic geologists) are more specifically concerned with soils that have been disturbed or moved (usually by human activity), sometimes comparing them to natural soils, or matching them with soil databases, to help locate the scene of crimes. Forensic soil scientists usually obtain soil samples from crime scenes and suspected control sites from which soil may have been transported by shoes, a vehicle or a shovel. Soil properties are diverse and it is this diversity, which may enable forensic soil scientists to use soils with certainty as evidence in criminal and environmental investigations (e.g. see reviews by: Dawson *et al* 2008; Fitzpatrick 2008; 2009; Fitzpatrick *et al* 2008, Murray 2004; Murray and Tedrow 1991, 1975; Pye 2007; Ruffell and McKinley 2004).

In this chapter, consideration of a specific hit-and-run case described by Fitzpatrick *et al* (2007, 2008) highlights the kinds of investigations that have been carried out on highly complex Acid Sulfate Soil materials from shoes and a crime scene by the Centre for Australian Forensic Soil Science (CAFSS). The case example is described in a way that shows parallel approaches to more recent types of case investigations where soil as evidence are being applied with more certainty in criminal and environmental investigations. This hit-and-run case, which involves sulfidic material in an inland Acid Sulfate Soil, will be used as an example in this chapter to illustrate:

- the theory, significance and relevance of established concepts and standard terminologies used in forensic soil science,
- laboratory analytical techniques commonly used forensic soil science,
- systematic ways in which this information (e.g. soil morphology - e.g. colour, consistency, texture and structure, - mineralogy - powder X-ray diffraction, and chemistry (e.g. based upon infrared spectroscopy analyses) are used to distinguish between soils associated with forensic examinations which involves inland Acid Sulfate Soils,
- the ways in which this information can be applied advantageously in forensic casework.

HIT AND RUN CASE STUDY THROUGH A SUBAQUEOUS AND WATERLOGGED ACID SULFATE SOIL ALONG THE RIVER TORRENS

Background to case

This Hit and Run case involved two suspects that left the scene of a fatal car collision. One of the suspects was chased through the Adelaide suburbs at night and was later observed crossing the River Torrens. The suspect ran down the river bank, jumped into the river and onto the extended gravely and stony river bank (Figure 1(ii)) then proceeded up the opposite river bank before disappearing into the adjacent parklands. Figure 1 shows the area through which he is alleged to have run. The suspect was apprehended by police three hours later but denied ever running through this section of the river. As shown in Figure (2a) a small amount of fine yellowish-grey soil was strongly adhered to the side and in the treads of the sole from the suspect's shoes. A sufficient amount of the soil was recovered from the soles and sides of the shoes for forensic soil analyses by gently scraping the fine soil from the shoes using a plastic spatula (Figure 2b).

Figure 1: Map showing the River Torrens in the centre of the image where a Hit and Run offender ran from an adjacent Adelaide suburb, jumped into the River Torrens, crossed and then stepped on the river bank before running into the parklands. The two control samples of gravelly Acid Sulfate Soils (ASS) with sulfidic material from the alleged "crime trail' are located: (i) on the stony and gravelly bank (CAFSS_027.5) where the person is standing in the centre photograph and close-up view of the soil surface near where a shoe impression matching the sole tread of the shoe worn by the offender (Figure 2) was located by police (right hand side photograph) and (ii) in the river channel (subaqueous ASS; CAFSS 027.4). A sufficient amount of fine grained soil material was recovered from the control site samples by sieving the gravely (95% gravel and rock fragments with 5% clay and silt) samples through a 50 µm sieve (i.e. <50 µm fraction). Two additional "alibi samples" were collected from alibi trails or scenes (20 m upstream: CAFSS 027.3 and upper river bank: CAFSS 027) to determine whether or not the suspect had been along the alleged "crime trail'. (from Fitzpatrick *et al* 2008)

A control surface soil sample (0-3 cm) was taken where a shoe impression was located on the lower river bank (Figure 1 CAFSS 027.4) and where the suspect was seen to run (i.e. shoe imprint was similar to the sole tread of the shoe worn by the suspect). A second control soil sample (0-5 cm) was taken beneath 10 cm of water in the river channel one meter from the control sample site on the lower rive bank. These two yellowish-grey to dark brownish-black samples are from Acid Sulfate Soils (ASS) with sulfidic material, which comprise a mixture of 95% coarse gravel and stone fragments and only 5% clay and silt (<50 µm fraction). Although the control ASS comprised 95% alluvial stone and coarse gravel with only 5% clay and silt, a sufficient amount of fine soil (<50 µm) was recovered by sieving. As shown in Figure 2 (e), this fine soil material closely resembles (colour and texture) the fine soil material that was tightly trapped in grooves and treads in the rubber sole of the suspect's shoe (Figure 2 b). Analyses of these two soil materials using soil morphological descriptors (e.g. Schoeneberger *et al* 2002; Munsell Soil Color Charts, 2000; Fitzpatrick *et al* 1999), microscopical, XRD and DRIFT methods indicated that the soil from the river bank and soil on the suspect's shoes were similar (see below).

Two alibi samples were collected on the surface (0-3 cm) of: (i) a gravelly hydromorphic soil on the lower river bank, 20 m upstream (CAFSS 027.3; one meter from the river edge) from the two control sites and (ii) a non-gravelly alluvial soil on the upper river bank (CAFSS 027.6; five meters from the river edge, to determine whether or not the suspect had run along the alleged crime trail shown in Figure 1 (soil analyses are not reported in this paper).

Figure 2. Contact traces of yellowish-grey soil on the side and in the treads of the sole of the suspect's shoes [(a) left hand side and middle] and sample scraped from the shoe [(b) right hand side). Control soil specimens from the river channel [(c) left hand side] and bank of river shown in Figure 1 [(d) middle], which both comprise mixtures of 95% coarse gravel and rock fragments and only 5% clay and silt (<50 µm fraction). Photograph of the <50 µm fraction separated from the stony river bank soil sample (d) by sieving through a 50 µm sieve [(e) right hand side]. (from Fitzpatrick *et al* 2008)

SOIL AS A POWERFUL CONTACT TRACE

This section is essentially a summary of several recent reviews (Fitzpatrick 2008, 2009) and case study examples (Fitzpatrick *et al* 2008).

Theory of transfer of materials from one surface to another as a result of contact

The transfer of trace evidence is governed by what has become known as the "The Locard Exchange Principle" (Chisum and Turvey 2000), which states: "Whenever two objects come into physical contact - an exchange of materials takes place." When two things come in contact, physical components will be exchanged. For example, the exchange can take the form of soil material from a location transferring to shoes of a person who walked through a particular area. These types of transfers are referred to as primary transfers. Once a "trace material" has transferred, any subsequent movements of that material, in this case from shoes are referred to as secondary transfers. These secondary transfer materials can also be significant in evaluating the nature and source(s) of contact. Hence, the surface of soils can provide information linking persons to crime scenes.

Aardahl (2003) lists the properties of the ideal trace evidence: "(1) nearly invisible, (2) is highly individualistic, (3) has a high probability of transfer and retention, (4) can quickly be collected, separated and concentrated, (5) the merest traces are easily characterised, and (6) is able to have computerized database capacity." In this context, Blackledge and Jones (2007), consider that glitter (i.e. entirely manmade tiny pieces of Al foil or plastic with vapour-deposited Al layer) may be the ideal contact trace. Soil materials may be considered as approaching the ideal "contact trace', and the following brief discussion considers how closely they fulfil the criteria of Aardahl.

Soil is highly individualistic

The major question posed is how can soils be used to make accurate forensic comparisons when we know that soils are highly complex and that there are thousands of different soil types in existence? For example, according to the United States Department of Agriculture (USDA), which collects soil data at many different scales, there are over 50,000 different varieties of soil in the United States alone! Parent material, climate, organisms, and the amount of time it takes for these properties to interact will vary worldwide.

The following key issues are especially important in forensic soil examination because the diversity of soil strongly depends on topography and climate, together with anthropogenic contaminants:
Forensic soil examination can be complex because of the diversity and in-homogeneity of soil samples. However, such diversity and complexity enables forensic examiners to distinguish between soil samples, which may appear similar to the untrained observer.

Soil has a high probability of transfer and retention

In general, soil usually has a strong capacity to transfer and stick, especially the fine fractions in soils (clay and silt size fractions) and organic matter. The larger quartz particles (e.g. > 2mm size fractions) have poor retention on clothes and shoes and carpets. Fine soil material (e.g. their <50-100 µm fractions) may often only occur in small quantities, as illustrated in a Hit and Run case illustrated in this chapter (Figures 1 and 2; Fitzpatrick *et al.* 2007), where a remarkably small amount of fine soil was transferred from a gravelly and stony soil on a river bank (control site) to running shoes (forensic evidence items).

Soil can quickly be collected, separated and concentrated

Although a suspect may be unaware that soil material – especially the fine fraction - has been transferred directly to the person (e.g. shoes) or surroundings, soil materials are easily located and collected when inspecting crime scenes or examining items of physical evidence (e.g. Figures 1 and 2). Traces of soil particles can easily and quickly be located directly using hand lenses or light microscopes.

Soil samples must be carefully collected and handled at the crime scene or control sites using the established approaches and then compared by a soil scientist with forensic science experience to ensure that the soil samples can be useful during an investigation. The size and type of samples to be taken are strongly dependent on the nature of the environment being investigated, especially the type of soil and nature of activity that may have taken place at the scene (e.g. if suspect footwear is heavily coated with mud on the uppers and the ground is wet and soft then the control sample should be collected to a depth of around 0 to 10 cm; e.g. Figures 1 and 2). Subaqueous soils from the bottom of river channels, streams, ponds, lakes or dams can be obtained by pressing a plastic tube or container into the bed and removing it with a scooping action. In deeper water, samples can be taken using specialized sampling devices such as the Russian D-auger. If the soil is very hard and dry; and only the shoe tread was in contact with the soil, then collect the 0 to 0.5 cm – or thinner.

Several standard methods are available for quick separation and concentration of soil materials or particles such as for example sieving (e.g. described and used in Figure 2), magnetic extraction and heavy mineral separation (e.g. Figure 3).

Soil is nearly invisible

As described in the hit-run case study in Figures 1 and 2, under typical viewing conditions by the naked eye we do not really see the yellow-brown colour of the fine 5% clay and silt (<50 µm fraction) fractions hidden in the gravelly soil [Figure 2 (d)] until the sample is sieved and the fine fraction concentrated [Figure 2 (d) and (e)]. This is for example, often unlike the more obvious bright transfer colours of blood, lipstick smears and paint. Hence, not being obviously aware of the presence of fine soil materials, especially when they impregnate vehicle carpeting, shoes or clothing, a suspect will often make little effort to remove soil materials.

Computerised Soil Databases: Capacity

Soil profiles and their horizons usually change across landscapes, and also change with depth in a soil at one location. In fact, soil samples taken at the surface may have entirely different characteristics and appearances from soil dug deeper in the soil profile. One common reason why soil horizons are different at depth is because there is mixing of organic material, in the upper horizons, and weathering and leaching, in the lower horizons.

Easy to characterise soil materials: Large and trace amounts

Soil morphological descriptions follow strict conventions whereby a standard array of data is described in a sequence, and each term is defined according to both the USDA Field book for describing and sampling soils, Version 2.0 (Schoeneberger *et al* 2002) and National standard systems (e.g. Australian Soil and Land Survey Field Handbook by McDonald *et al* 1990). Soil morphological descriptors such as colour, consistency, structure, texture, segregations/coarse fragments (charcoal, ironstone or carbonates) and abundance of roots/pores are the most useful properties to aid the identification of soil materials (e.g. Fitzpatrick *et al* 2003) and to assess practical soil conditions (e.g. Fitzpatrick *et al* 1999).

Examples of several standard methods and results from various analytical methods used in forensic soil examination will be discussed below – e.g. see also several reviews covering mainly “forensic geology” by several workers (Murray 2004; Pye 2007; Dawson *et al* 2008; Ruffell and McKinley 2004).

COMMON AND STANDARDIZED TECHNIQUES USED BY FORENSIC SOIL SCIENTISTS

Evaluation of degree of similarity between questioned samples and control soil samples

It is important to first define the word “compare” because no two physical objects can ever, in a theoretical sense, be the same (Murray and Tedrow 1991). Similarly, a sample of soil or any other earth material cannot be said, in the absolute sense, to have come from the same single place. However, according to Murray and Tedrow (1991) it is possible to establish “with a high degree of probability that a sample was or was not derived from a given place”. For example, a portion of the soil (or other earth material) could have been removed to another location during human activity. Pye (2007) summarises different schemes commonly used by various members of the Forensic Science Service to convey weight of evidence relating to forms of comparisons such as trace or DNA evidence. For example, he has developed a “verbal categories” ranging from 0 (no scientific evidence) to 10 (conclusive) – with no statistical significance of the ranks implied. He also states that there is a long history of the use of numerical scales in the context of evidential and legal matters.

APPROACHES AND METHODS FOR MAKING COMPARISONS BETWEEN SOIL SAMPLES

Forensic soil scientists must first determine if uncommon and unusual particles, or unusual combinations of particles, occur in the soil samples and must then compare them with similar soil in a known location. To do this properly, the soil must be systematically described and characterised using standard soil testing methods to deduce whether a soil sample can be used as evidence (Figure 3). This systematic approach for forensic soil examination is outlined in several recent papers (Fitzpatrick 2009; Fitzpatrick *et al* 2008), which combines soil morphology (e.g. colour, consistency, texture and structure), mineralogy (powder X-ray diffraction), chemistry (e.g. based upon infrared spectroscopy analyses), biology and spatial field mapping information.

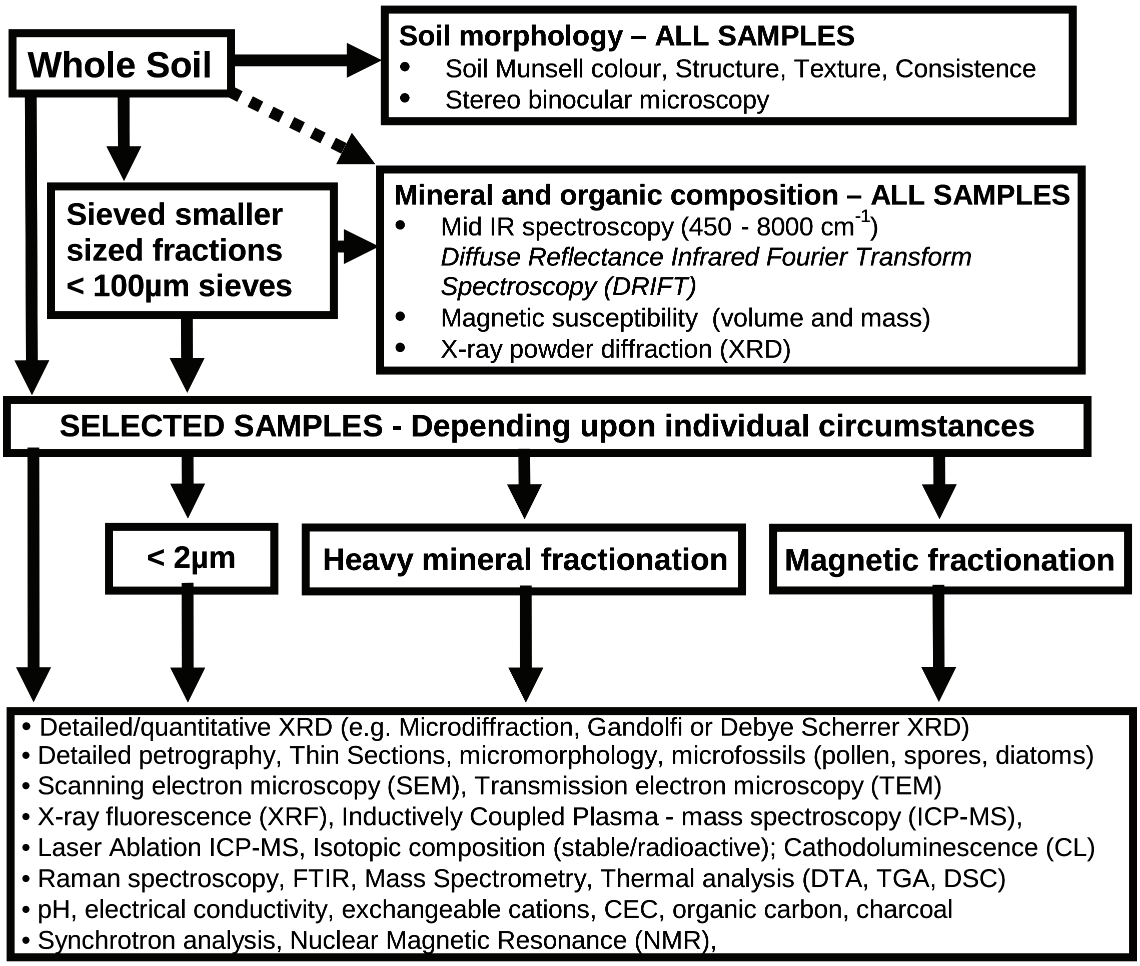

Figure 3. A systematic approach to discriminate soils for forensic soil examinations where, , FTIR is Fourier Transform Infrared spectroscopy, DTA is Differential Thermal Analysis, TGA is Thermogravimetric Analysis, DSC is Differential Scanning Calorimetry and CEC is Cation Exchange Capacity (modified from Fitzpatrick *et al* 2006; Fitzpatrick *et al* 2008).

These methods are applied in three stages:

- Rapid characterisation of composite soil particles in whole soil samples for the quick screening of samples (Stage 1)
- Detailed characterisation and quantification of composite and individual soil particles following sample selection, size fractionation and detailed mineralogical and organic matter analyses using advanced analytical methods (Stage 2)
- Integration and extrapolation of soil information from one scale to next, to build a coherent model of soil information from microscopic observations to the landscape scale (Stage 3).

This combined information is used for geographic sourcing to identify the origin of a crime scene soil sample by placing constraints on the environment from which the sample originated.

FORENSIC APPLICATIONS

The following soil analyses methods were required in this hit-run case, which was briefly outlined above. The first step was to visually compare the questioned soil samples from the suspect's shoes (i.e. adhered soil scraped from the soles and sides of the running shoes shown in Figure 2) and control samples (i.e. soils shown in Figures 1 and 2). The control samples were obtained from sulfidic material (Soil Survey Staff 1999) in the subaqueous Acid Sulfate Soils located both in the river and on the river bank where the suspect was seen to run and left a shoe impression, which was similar to the sole tread of the shoe worn by the suspect.

The visual comparison of the questioned samples from the shoe and control samples after sieving to obtain fine fractions (<50 µm) was conducted by eye and by low power stereo-binocular light microscopy. From these visual observations, it appeared that the fine fractions (<50 µm) from sulfidic material in the Acid Sulfate Soils in both the river bank and in the channel samples had a similar yellow colour to the soil adhered to the shoe (Munsell Soil Color Charts 2000). Consequently, because the river bank sample contained over 95% coarse gravel and stones, a sub-sample was sieved using a 50µm sieve to obtain a finer fraction (<50 µm). The fine soil fraction from the river bank and soil on the shoe had a remarkably similar colour (Munsell Soil Color) and mass magnetic susceptibility. Hence, in accordance with the systematic approach outlined in Figure 3, the third step was to check their mineralogical and chemical composition by using XRD and DRIFT analyses.

The XRD patterns - that can be likened to finger print comparisons- of the shoe (suspect) and ASS river bank (control) soil samples closely relate to each other (Figure 4). However, what is the significance of this close similarity in XRD patterns to the degree of similarity in terms of mineralogical composition? If the two soil samples, for example, contain only one crystalline component such as quartz (i.e. silicon dioxide), which is very common in soils, the significance of the similarity and its evidential value in terms of comparison criteria will be low. If, however, the two soils contain four or five crystalline mineral components, some of them unusual, then the degree of similarity will be considered to be high. In both cases, it was possible to evaluate the mineralogical data and formulate an opinion regarding the significance of the results obtained. The mineralogical compositions of the two samples are summarised in Table 1 and have a high degree of similarity because they both contain quartz, mica, albite, orthoclase, dolomite, chlorite, calcite, amphibole and kaolin. Relative proportions of the minerals are slightly different, likely due to the different distributions of particle sizes of the samples.

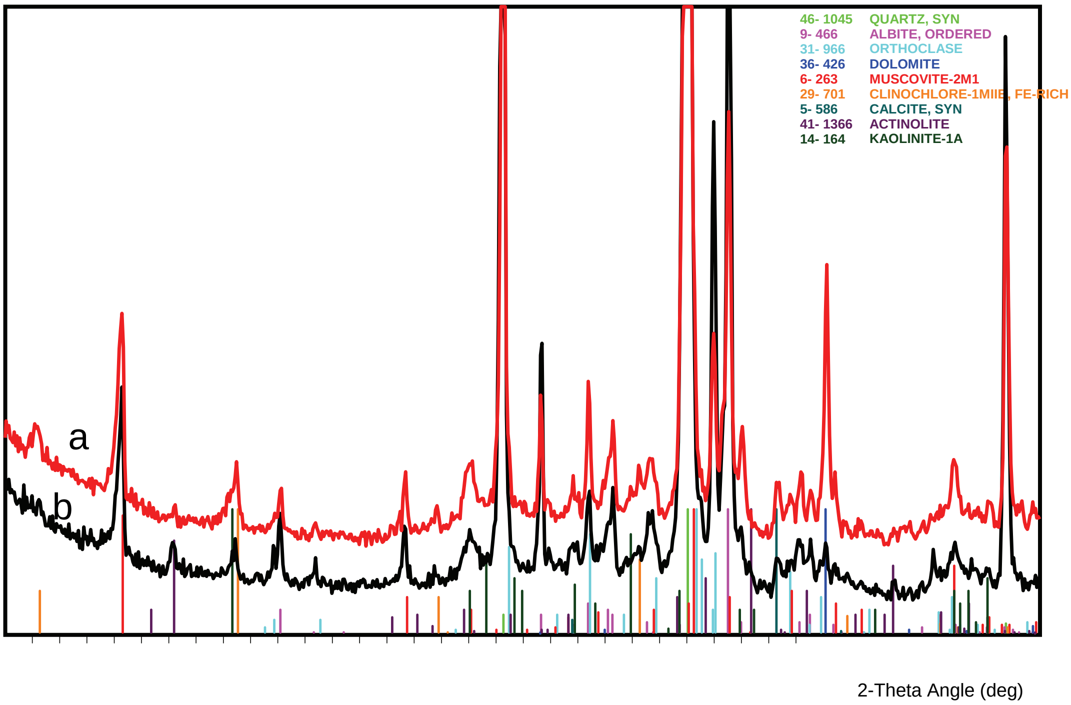

Figure 4. Comparisons between X-ray diffraction (XRD) patterns of soil samples from the shoe (b) and river bank (<50µm fraction) (a) shown in Figures 1 and 2. The <50 µm fraction was separated from the stony river bank soil by sieving through a 50 µm sieve. Shoe and river bank samples were both ground using an agate mortar and pestle before being lightly pressed into aluminium sample holders for XRD analysis. XRD patterns were recorded with a Philips PW1800 microprocessor-controlled diffractometer using Co K radiation, variable divergence slit, and graphite monochromator (from Fitzpatrick *et al* 2007).

Table 1. Summary of mineralogical composition from XRD analysis (from Fitzpatrick *et al* 2007; 2008).

Soil samples	Quartz	Mica	Albite	Orthoclase	Dolomite	Chlorite	Calcite	Amphibole	Kaolin
[1]River Bank	D	SD	M	M	M	T	T	T	T
[2]Shoe	D	M	M	M	T	T	T	T	T

Where:
[1]River bank sample (LRJ-1/ CAFSS 027.5) was sieved (<50µm fraction).
[2]Shoe sample (CAFSS 027.0) was not sieved (i.e. approximately <50µm).
D-Dominant (>60%), SD–Sub-Dominant (20-60%), M-Minor (5-20%), T-Trace (<5%).

DRIFT analysis was conducted on the same samples after XRD analyses (Fitzpatrick *et al* 2007). Electromagnetic energy in the mid-infrared range (4000-500 cm^{-1}) is focused on the surface of the air-dried, finely ground soil samples (using an agate mortar). Some of the beam penetrates a small distance into the sample and is reflected back into the spectrometer where the spectrum is collected, the spectra are expressed in absorbance (A) units (where A = Log 1/Reflectance). Whilst the two samples are spectrally similar (Figure 5) they do differ slightly in the amount of aliphatic organic matter (Table 2), which is reflected in peaks centered on 2850 and 2930 cm^{-1} (i.e. because the shoe sample has a slightly higher organic carbon content). They are very similar with regards to clay mineralogy (kaolinite clay 3690-3620 cm^{-1}) and the amount of quartz (2000-1650cm^{-1}) in the samples. A peak around 2520cm^{-1} also indicates the presence of a small amount of carbonate in both samples, with marginally more in the bank sample. These comparisons indicate that the two samples have a high degree similarity and most likely to have been derived from the same general location. In contrast, there is a lower degree of similarity with the two alibi soils samples (data not shown in Figure 1) and briefly described above.

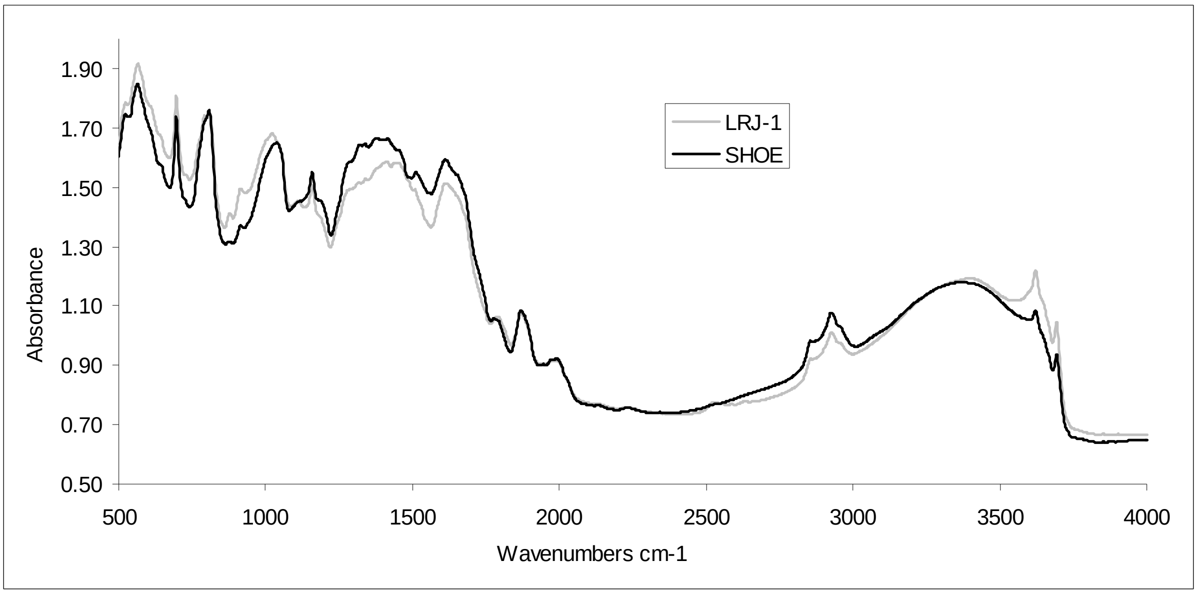

Figure 5. Comparison of Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra between the yellow-brown soil on the shoe (black tone) and the <50µm fraction in the stony soil from the river bank (grey tone). Shoe and river bank samples were both ground using an agate mortar and pestle (from Fitzpatrick *et al.* 2007).

Table 2. Predictions of charcoal (char), total organic carbon (TOC), pH (CaCl2), calcium carbonate (CaCO3), cation exchange capacity (CEC), clay, silt and sand contents from MIR-PLS analysis (Janik *et al* 1998).

Sample CAFSS	Char	TOC	pH $CaCl_2$	$CaCO_3$ %	CEC	Clay	Silt	Sand
	%	%		%	meq/100g	%	%	%
[1]Shoe 027.0	0.2	6.1	4.9	1.5	17	6	27	68
[2]River Bank 027.5 Lrj-1	0.2	3.4	5.5	4.6	15	12	35	53

Where:
[1]Shoe sample not sieved because it was already fine (i.e. approximately <50µm).
[2]The River bank was sieved <50µm fraction (Lrj-1/ CAFSS027.5).

To conclude, sufficient soil morphological, mineralogical (XRD) and physicochemical (DRIFT and MIR-PLS) data was acquired on the two samples to be able to determine if they “compare” or “do not compare”. The soil from the shoe has a high degree of morphological, chemical and mineralogical similarity to the fine fraction (<50µm) contained in the stony / gravelly soil on the river bank and in the river. Hence, the soil from the shoe is most likely sourced from the stony/gravelly soil on the river bank and in the river. Partly as a result of these analyses, the suspect was subsequently found guilty of ‘Hit and Run’ in the supreme court of South Australia.

SUMMARY AND CONCLUSIONS

The crime scene example described in this chapter uses combined pedological (including field investigations), mineralogical and spectroscopic methods in the forensic comparison of small amounts of soil adhering to a suspect’s shoe with control soil specimens from an inland subaqueous and waterlogged Acid Sulfate Soil (ASS) in the Torrens River and on its banks where a Hit-Run offender ran through. This case example illustrates that forensic soil examination can be very complex because of the diversity and heterogeneity of the soil samples involved. Although the ASS comprised 95% alluvial stone and coarse gravel with only 5% clay and silt, a sufficient amount of fine material (<50 µm) was recovered by sieving. This fine soil material closely resembled the fine soil material that was tightly trapped in grooves and treads in the rubber sole of the suspect’s shoe. Analyses of the two soil materials using visual, microscopical, XRD and DRIFT methods indicated that the soil from the river bank and soil on the suspect's shoes were similar. Such diversity and complexity of soil materials enables forensic soil examiners to distinguish between soils. The interpretation of soil forensic tests and methods is not equally applicable to all soils and should also be made in the context of the forensic soil examination (e.g. the sieving of large amounts of stone and gravel from ASS samples to obtain a more representative sample to make comparisons).

Soil materials are routinely encountered as evidence by police (physical evidence branch) for crime scene investigators and forensic staff. However, most forensic and physical evidence laboratories either do not accept or are unable to adequately characterise soil materials. The main reason for this is that morphological, mineralogical and spectroscopic analytical knowledge required to examine and interpret such soil evidence needs a large amount of training and expertise.

There is a general lack of expertise in this relatively new area among soil scientists. For research and practical application in this area to grow appreciably, it will need to be considered and taught as an integral part of both soil science and forensic science courses. Finally, according to Fitzpatrick *et al* (2008) an attempt should be made to develop and refine methodologies and approaches to develop a practical “Soil forensic manual with soil kit for sampling, describing and interpreting soils”.

ACKNOWLEDGEMENTS

Mr Adrian Beech for chemical analyses and Mr Stuart McClure for SEM analyses from several previous forensic soil investigations. Dr Jock Churchman, Mr Richard Merry and Dr Phil Slade for constructive editorial comments.

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CHAPTER 9

A NEW WEB-BASED APPROACH FOR THE ACQUISITION, COLLATION AND COMMUNICATION OF COMPLEX INLAND ACID SULFATE SOILS DATA

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INTRODUCTION

Soil-landscape systems are inherently complex and the product of a unique integrative history of ancient and modern hydro-pedological processes, making it difficult for scientists and resource managers to quantify the sustainability of environmental systems (i.e. to make balanced and integrated judgements on natural resource and environmental conditions in specific regions). To assess soil-landscapes involves selecting key attributes and methods to describe, quantify and integrate pedological, hydrological, geological, biogeochemical, isotope and mineralogical information in order to seek answers to important environmental questions across a variety of temporal and spatial scales (i.e. from the molecular scale up to the macroscopic environmental systems scale in paddocks, catchments or regions). To incorporate these factors, Fitzpatrick et al. (2003) developed a systematic approach, which incorporated a sequence of steps to construct easy-to-follow pictorial manuals for identifying critical soil indicators, land use options and best management practices. These manuals contain sketches of typical landscape cross-sections (i.e. idealised descriptive, explanatory or predictive mechanistic toposequence models) with colour photographs of soils to enable farmers to readily compare these features with their own soil-landscape. This approach has been successfully applied and adopted in three regions (Mt Lofty Ranges in SA, Glenelg catchment management authority in Victoria and Iraq marshlands). However, apart from these areas the approach has not been adapted to other regions around the world, probably because: (i) there is no interactive, systematic framework to help integrate the large quantities of variable data often used to construct soil-regolith models and (ii) it is expensive to print colour documents and manuals, which may need to be altered as subsequent research causes the conceptual models to evolve.

Scientific researchers are often faced with the task of summarizing, condensing and effectively communicating large amounts of complex data (Benda, Poff et al 2002). Poor planning and a lack effective communication can produce vast quantities of complex and confusing information that is difficult to digest. Universities and research organisations produce countless remarkable discoveries, insights and advances. However, their ability to share this knowledge with the community, government and industry rarely matches their research capability (Cribb and Hartomo 2002). Consequently, in earth science, a structured approach is needed to ensure suitable soil-regolith indicators are selected and used efficiently.

The new approach described in this paper was originally inspired by: (i) the difficult task of collating large amounts of geological, soil, hydrological, geochemical and mineralogical data to construct mechanistic toposequence models and (ii) effectively communicating this information as part of a PhD thesis. To achieve these goals, a high level of data organisation was achieved through a web-based data site, which allowed large quantities of information to be rapidly reviewed and discussed in a logical manner. Subsequently, it was deemed advantageous to adopt and expand on this approach to develop a framework to cope with vast quantities of data generated by: (i) a large multidisciplinary, acid drainage project in the wheat belt of Western Australia (Baker and Fitzpatrick 2005; Fitzpatrick, Baker et al. 2005; Rogers and George 2005) and (ii) an environmental consultancy, which examined inland acid sulfate soils in the River Land of South Australia (Fitzpatrick, Hicks et al. 2006).

Hence, the objective of this paper is to describe a systematic web-based approach for improved acquisition, collation and communication of diverse soil-regolith data. A significant problem with large multi-disciplinary and multi-organisational research and consulting efforts is uniformity in data acquisition, collation and communication (ACC). This can be overcome, independent of project size, by implementing a series of minimum, basic requirements that must be adhered to during ACC. This systematic approach incorporates any or all of the highly effective techniques for soil-regolith field description protocols, such as the USDA Field book for describing and sampling soils, (terminology from: Schoeneberger et al. 2002) Australian Soil and Land Survey Field Handbook, (McDonald et al. 1990) as well as the commonly used project management tools (e.g. Gantt Charts etc.) to create a flexible and dynamic template for ACC. The steps outlined in this paper will assist in:

- Planning environmental and mineral exploration soil-regolith projects of any size
- Maintaining uniformity of field protocols and hence quality of data acquisition
- Rapid and effective communication within a multidisciplinary project team
- Dynamic progress reporting to clients and other interested parties
- Production of final report
- Providing a cost effective alternative to colour filled pamphlets and booklets
- Reporting findings to the general public via the internet

METHODOLOGY

The methodology described here outlines ways of structuring large data sets to provide a tool for rigorously planning data acquisition, coupled with rapid and effective communication. Web display and delivery was chosen due to its almost universal availability. While Microsoft FrontPage 2003 was used to construct the web-based data site, any web authoring software is appropriate. The builder (author) of the data web site requires a basic to advanced knowledge of the web authoring program (depending on the desired sophistication of the data site) and a good scientific grasp of the content, relevance and impact of the data being displayed. The sequential steps outlined in Box 1 and Figure 1 summarise the procedures necessary for developing a generic soil-regolith, web-based data site.

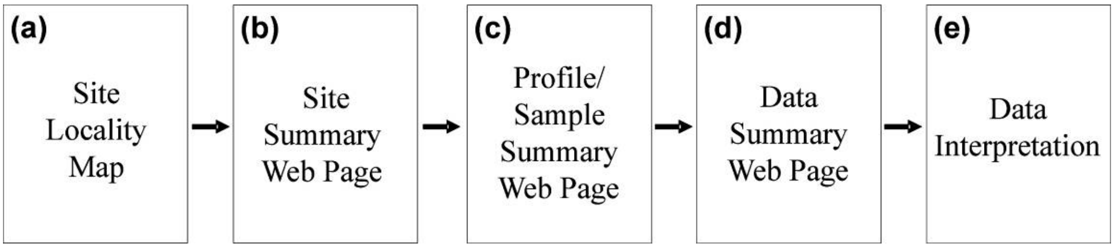


Figure 1. Flow diagram outlining the main components of a web-based data site.

BOX 1. Steps for constructing a web-based data site

Stage 1. *Prior to field work*

a. Define the project objectives.

b. Identify the spatial coverage of the area to be studied.

c. Break the area down into sites where observations and samples will be taken (new sites can be added at any time during field work).

d. Identify methodologies and laboratory techniques required, available and budgeted for to achieve project objectives.

e. Ensure field equipment required for sample collection is appropriately matched to chosen methodologies and laboratory techniques.

Stage 2. *In the field (at each site)*

a. Reconfirm site location with GPS.

b. Photograph site from a number of perspectives including any defining features (e.g. large trees) in fields of view.

c. Sample and describe soil, rocks, vegetation according to established conventions (e.g. McDonald et al 1990; Schoeneberger et al 2002) and appropriate to the techniques that will be applied in the laboratory.

d. Collect representative sub-samples to be stored in chip trays.

e. Photograph each sample, with scale, from a minimum of two perspectives and zoom settings.

f. Draw a brief schematic diagram highlighting important landscape features, photograph locations and sample locations.

Stage 3. *Data collation and communication*

a. Construct a site locality map using appropriate software (e.g. Arc GIS) to begin to highlight any spatial relationships between sites (Figure 1a).

b. Import map into web authoring program.

c. Use site photos, schematic diagram and field notes to construct a summary web page of each site, providing some general information and links to more detailed data (Figure 1b).

d. Use HyperText Markup Language (HTML) to link each site locality on the map (Figure 1a) to the corresponding site summary web page (Figure 1b).

e. Use sample photos and field notes to construct a summary page for each sample, group of samples or profile as appropriate (Figure 1c) and use HTML to link back to site summary web pages (Figure 1b).

f. Create data summary pages for each sample, group of samples or profile that contains or has links to all detailed field observations and laboratory results (Figure 1d).

g. As more data is returned from the laboratory it can easily be added to the data site via the data summary pages (Figure 1d).

h. Once all the data has been uploaded to the web site HTML links can be incorporated to highlight relationships between samples from different locations that share physical and chemical characteristics.

i. Further data interpretation facilitates the addition of graphs, statistical analysis, diagrams and conceptual models to the web site. This provides a convenient storage location that keeps the interpretation within the bounds of the project.

j. Each product of interpretation (e.g. graphs, conceptual models etc.) is HTML linked to the sample, sample site and data that produced it (Figure 1e).

DISCUSSION

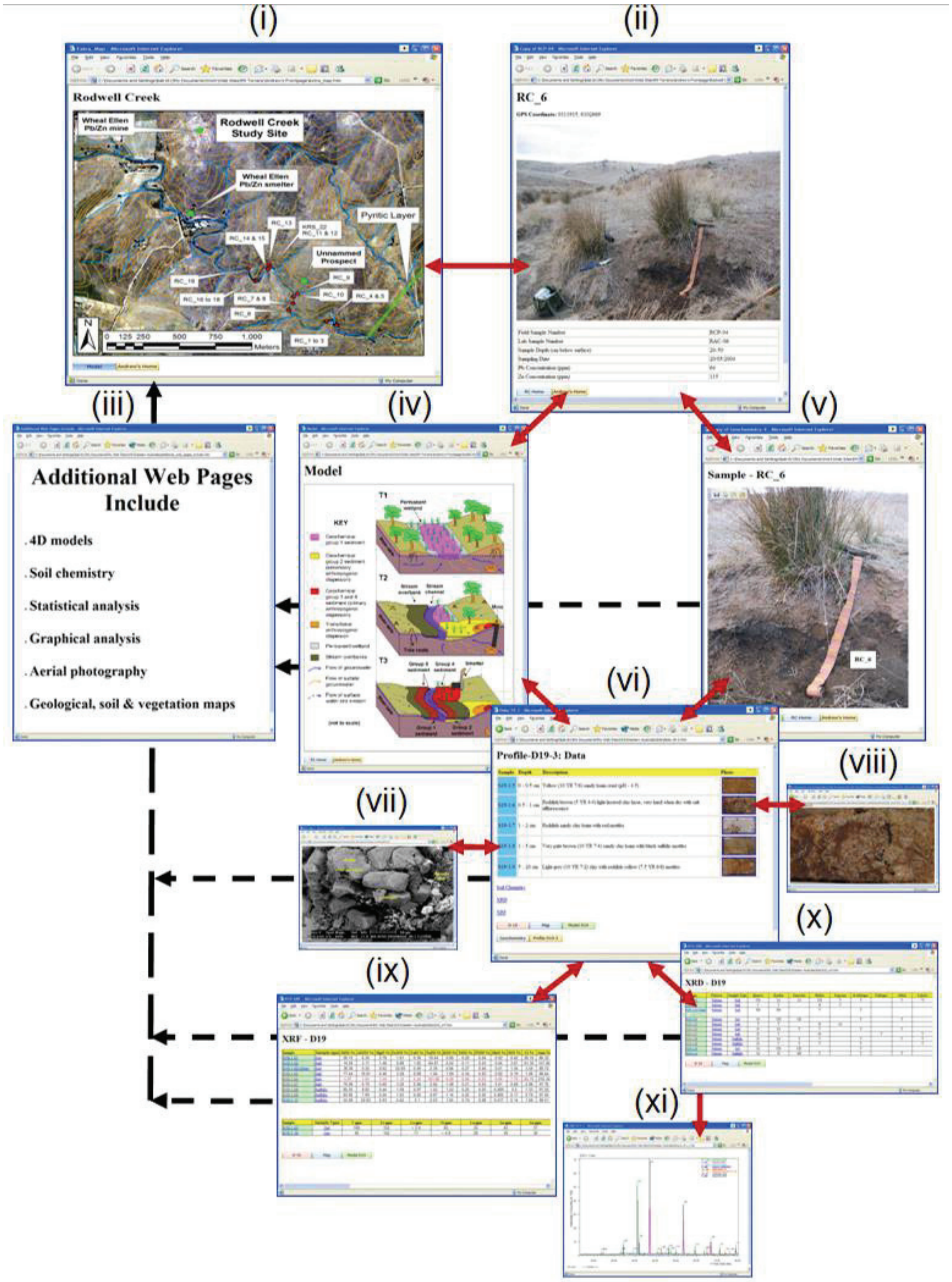
The steps listed in stages 1.a-e (Box 1) seem obvious but are vitally important for the efficient and cost effective implementation of a field based soil-regolith project. Careful planning can shorten time spent in the field and decrease the likelihood of unnecessary follow up data collection. Identifying all possible methodologies and laboratory techniques that may be used during the project will mean that any specialised equipment required for data collection will be on hand.

Stage 2.a-2.f (box 1) outlines the steps that should be taken to maintain the value of data collected in the field. Irrespective of the money spent on laboratory techniques and sample analysis, data becomes useless if it is not known where the sample comes from or its context in the regolith environment. A "mud map" or schematic diagram recording sample and photo locations aids in accurately documenting data collection. Chip trays provide a simple yet vital method of communicating regolith characteristics to: (i) members of a project team, (ii) the client and (iii) the scientists conducting subsequent laboratory investigations. Chip trays are photographed and digitally incorporated into the web-based data site to facilitate rapid communication. Digital photos are an effective method of documenting site and sample characteristics. They are an aid to memory and provide relative locations at sample sites. Photographs are an excellent method of communication and hence a vital component of a web-based data site.

The points raised in stage 2 (Box 1) do not replace good quality, thorough field observations. These steps simply ensure that field work maintains its value whilst providing the means to construct a tool for highly effective and rapid communication.

Stage 3.a-j (box 1) concerns the collation and subsequent communication of soil-regolith data collected in the field. The aim of the web-based data site is to provide HTML links in every location where a user requires further information. This can only be achieved if the person constructing the data site has a firm grasp of the science being displayed and the requirements of the end user. The first stage is to group data according to where it was collected. This is most easily achieved by constructing a map of the study area delineating site locations (Figure 2 - (i)). The locality map, when linked to the site summary pages allows rapid and simple navigation between sites and provides links to more detailed information. The location of each sample or group of samples taken at each site is displayed on photos in the site summary pages (Figure 2 - (ii)). This provides an accurate record of each sample's locality relative to that of others and their spatial distribution in the regolith environment. For this reason it is vital to obtain good quality site photographs in the field. Each sample, group of samples or profile can then be investigated in more detail via a HTML link to a sample summary page (Figure 2 - (v)). These pages give more detailed information on each sample and their relative location within a profile or group of samples. Good quality photographs, with a scale, of each sample can be invaluable in later data interpretation. Data summary pages (Figure 2 - (vi)) contain or have direct HTML links to all the observations and data recorded in the field (e.g. pH, Eh etc.), subsequent laboratory observations and results from laboratory techniques (XRD, XRF, ICP-MS etc.). Once the basic structure of the data site (described above) has been constructed any additional data can be added quickly and easily. Data, such as SEM photos, can be made available as soon as they have been acquired (Figure 2 - (vii)). Photographs of soil materials in the chip trays can be added to the data site to save the need to retrieve samples from storage (Figure 2 - (viii)). Often multi-organisational and multi-disciplinary research efforts involve team members spread over vast distances making it impractical for all to have access to samples. Spreadsheets containing geochemical data (e.g. XRD (Figure 2 - (ix)) and XRF (Figure 2 - (x)) can be made available for download, via the data site, without risking the original data. There is no practical limit to the amount and type of data that can be stored and displayed in this fashion (Figure 2 - (iii)).

Interpretation can commence contemporaneous with or following data upload to the web-based data site. Data can be grouped via HTML links according to shared physical and chemical characteristics. Interpretive models (Figure 2 - (iv)), graphs, statistical analysis and other forms of interpretation can be included in the site. The advantage of this is that interpretation does not exist independent of the data that created it, which is instantly accessible via HTML link.



Additional Web Pages Include

- 4D models
- Soil chemistry
- Statistical analysis
- Graphical analysis
- Aerial photography
- Geological, soil & vegetation maps

Figure 2. Flow diagram constructed of web views from one project's web-based data site. Views represent; (i) Site locality map, (ii) site summary web page, (iii) additional web pages that were included in the data site, (iv) 4-dimensional, interpretive model, (v) profile/sample summary page, (vi) data summary page, (vii) SEM photograph, (viii) chip tray photograph, (ix) XRF data, (x) XRD data, (xi) XRD spectra.

The web-based data site provides a dynamic framework to manage large, complex projects (Figure 3). A project team often includes numerous scientists from many different fields (Figure 3a). A huge range of complex information is often gathered during the life of a multidisciplinary project (e.g. geochemical data, soil data, water chemistry and spatial information). This data is passed on to the data web site manager (Figure 3b) who collates it (described above) to produce a web-based data site (Figure 3c). The data site can then be used by the different members of the project team to communicate internally. Information is easier to interpret (Figure 3e) because it can be viewed within the context of the whole project rather than in discipline defined subsections. Throughout the project the client has access to the collated data and the subsequent interpretation via the web-based data site (Figure 3d). This improves communication between the client and project team thus increasing the likelihood of a satisfactory outcome for all parties.

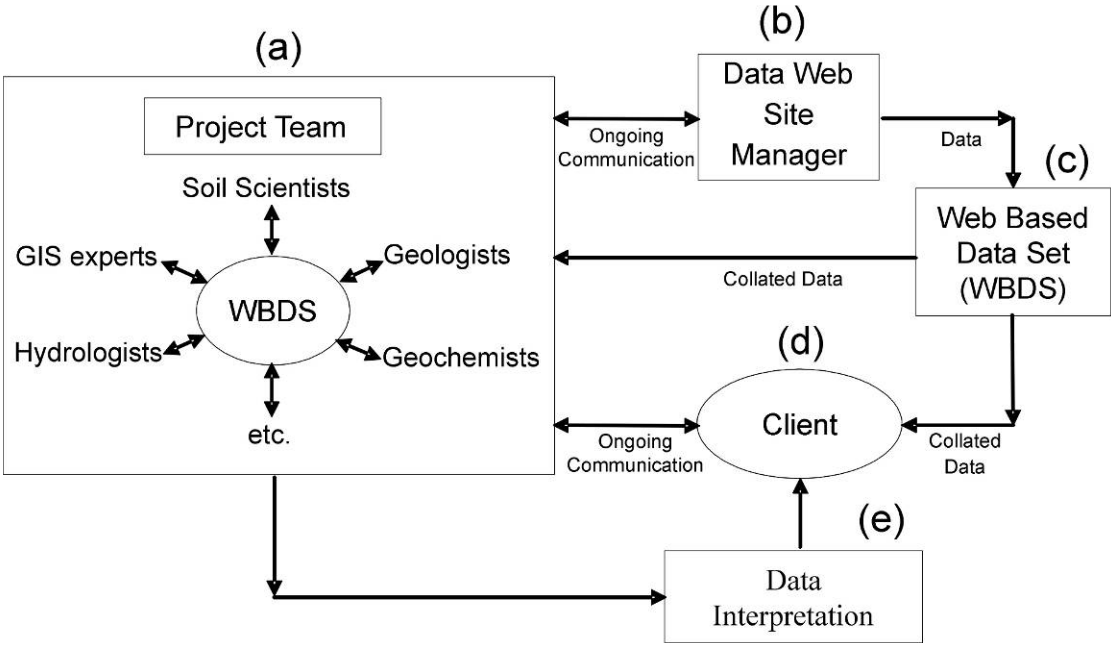


Figure 3. How a web-based data site should be used as part of a dynamic framework to manage large, complex projects.

An extension of the web-based data site is to use a SharePoint web site. This allows any member of a project team to add and alter information on the site. Any additions or updates to a SharePoint web site occur immediately. The site is always live and reflects changes as they are made. This can however create confusion as team members use the SharePoint site as a dumping ground for data. The site can rapidly lose cohesion unless all team members have excellent communication skills and a firm grasp of the authoring program and the data being entered. Hence it is recommended that SharePoint sites be avoided for the authoring of this type of data site.

An available alternative in most web authoring software is for team members to create data site sections that can be screened and uploaded by the data site author. In this circumstance a SharePoint web site is very useful for exchanging data between team members and conveying data and/or data site sections to the data site author.

This approach has been adopted to develop a framework to cope with vast quantities of data generated by: (i) a large multidisciplinary, acid drainage project in the wheat belt of Western Australia (Baker and Fitzpatrick 2005; Fitzpatrick et al. 2005; Rogers and George 2005) and (ii) an environmental consultancy, which examined inland acid sulfate soils in the River Land of South Australia (Fitzpatrick, Hicks et al. 2006).

Future projects that will utilise aspects this approach include:

- A major consulting project in Brunei
- National coastal acid sulfate soil atlas.
- National inland acid sulfate atlas.
- Acid drainage project in the wheat belt of Western Australia.

CONCLUSIONS

An interactive, web-based data site was devised to store and interrogate the large quantities of complex and varied data collected as part large multi-disciplinary and multi-organisational research and consulting efforts – involving inland ASS projects. Web display and delivery was chosen due to its almost universal availability. This approach can be used to plan environmental and mineral exploration soil-regolith projects of any size. It allows rapid and effective communication between members of multidisciplinary project teams and clients.

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CHAPTER 10

AVON BASIN, WA WHEATBELT: AN OVERVIEW OF GEOCHEMICAL RISKS OF SALINE ACIDIC DISCHARGE FROM DEEP DRAINS USED TO MANAGE DRYLAND SALINITY IN WESTERN AUSTRALIA

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INTRODUCTION

Salinisation due to rising watertables is a significant management issue in many parts of the Western Australian (WA) Wheatbelt and is expected to continue increasing in extent (Hatton *et al* 2003). The primary cause in many parts of Western Australia is an increase in groundwater recharge following native vegetation clearance for annual crops and pastures (Clark *et al* 2002).

There is increasing interest by landholders in using deep (2-3m) open drains to lower or prevent watertables from rising within several metres of soil surfaces (Dogramaci and Degens 2003; Kingwell and Cook 2007). More than 10,000 kilometres of salinity earthworks have already been constructed in parts of the WA Wheatbelt (ABS 2003) and it is likely that at least 5,000 kilometres of these are deep open drains that intercept shallow groundwater. Few deep drains have regional linkages (Ali *et al* 2004) and most are less than 20km in length.

There is increasing interest in linking drains to form catchment scale networks, principally to improve the management the waters from drains (Ruprecht *et al* 2004). Discharge for some existing smaller drains generally occurs only during the initial dewatering of regolith profiles (1-2 year), however, others continue discharging for many years at rates of up to 20L/s depending on the length of the drainage network (Dogramaci and Degens 2003). The quality of water discharging from existing drains is largely unclear, though is expected to be saline, since shallow groundwater is commonly saline in Wheatbelt valley floors (Salama *et al* 1994). One larger drainage network (>150km of channels) is known to discharge acidic waters (Ali *et al* 2004). The geochemical risks of discharge waters from drains in the WA Wheatbelt are not known and this information is required for effective planning and managing the risks of regional drainage.

We report on the results of a recent catchment-scale hydrogeochemical survey of deep drains and shallow groundwater in the WA Wheatbelt, including an evaluation of the current condition of lakes and surface waters in rivers and creeks. This survey was linked with targeted hydropedological investigations to identify key inland ASS-related processes influencing risks within drains and receiving environments (see Fitzpatrick *et al* 2008).

Materials and methods

Samples were collected from more than 200 bores, 80 groundwater drains, 55 creeks/rivers (surface waters) and 90 lakes (drainage-receiving, and non-receiving) in the eastern WA Wheatbelt across an area spanning 90 000 km^2 comprising the inland reaches of the Avon catchment (east of the Meckering Line) and the southern part of the Yarra Yarra catchment. Multiple sampling events were carried out over three years (2004–06) to characterise a range of surface waterways (drains and creeklines) and lakes in different stages of drying (though most were in the final stages). Groundwater samples were mostly obtained by low-flow pumping the bores, though some were obtained by hand-bailing, and all others were grab samples of surface waters. Measurements of pH, electrical conductivity (EC), temperature and oxidation-reduction potential (using Ag/AgCl probe; converted to Eh) were taken on-site at most sampling points. Drain/creek flows were also estimated whenever possible.

All samples were filtered in the field through 0.45 µm membrane filters in the field and preserved by either addition of ultrapure nitric acid (to a final concentration of 0.1%) or retained unacidified and stored at 5 degrees C. The concentrations of Cu, Zn, Co, Ni, Cr, Mn, P, V, Fe, Al, Ca, Mg, Ti, Na, K, and S were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The elements Ag, Ba, Cd, Mo, Pb, Sb, Sn, Y, Hf, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U and Se were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Arsenic was also determined using the hydride generation coupled to ICP. Selected anion analyses (SO_4, NO_3, NH_4, PO_4) were completed using ion chromatography. Only selected results from these analyses are discussed here.

Results and discussion

More than 56% of the deep drains in the eastern Wheatbelt of Western Australia were found to have waters with $pH < 5.5$, with many discharging at between 0.5 and 4 L/s (Figure 1). The acidic waters contained high concentrations of iron and aluminium — exceeding 500 mg/L in some cases (Figure 2). Manganese was also present, though typically in concentrations generally less than 6 mg/L. This water quality is similar to that typical of acid mine drainage (Gurung 2001; Cravotta 2008) or drainage from oxidising acid sulfate soils (Cook *et al* 2000; Johnston *et al* 2004), although significantly more saline.

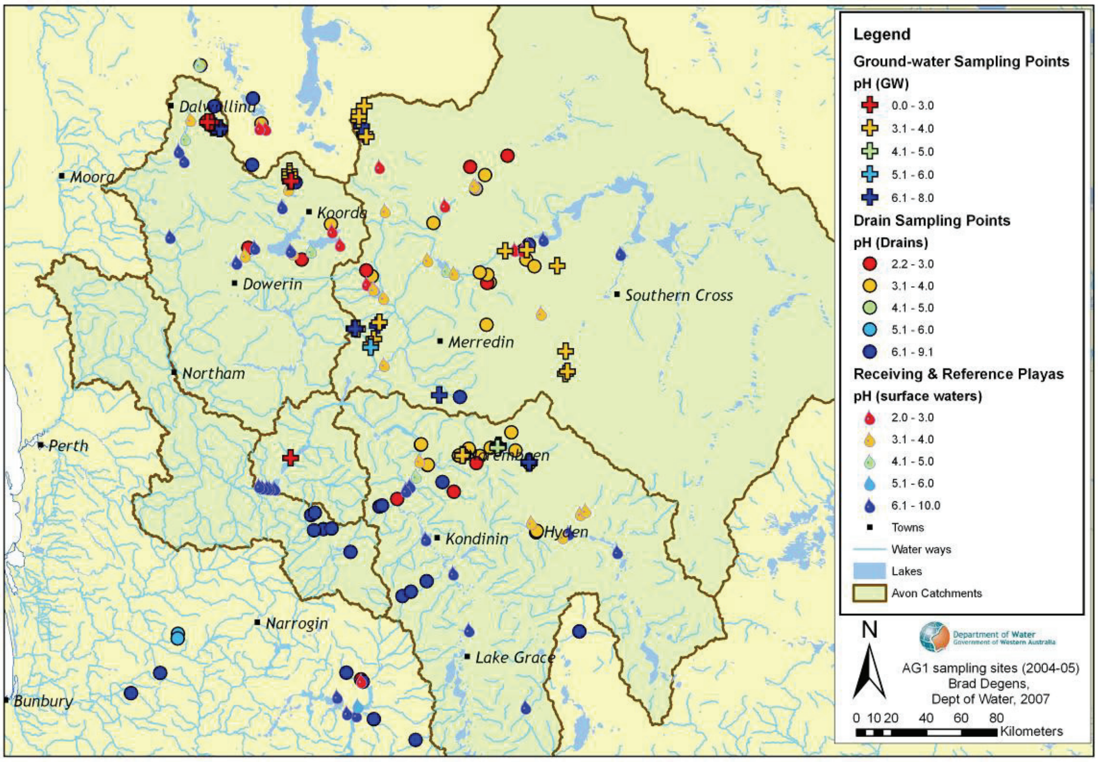

Figure 1. Locations of drain, lake and groundwater sampling sites (classified by sample pH) in the central WA Wheabelt.

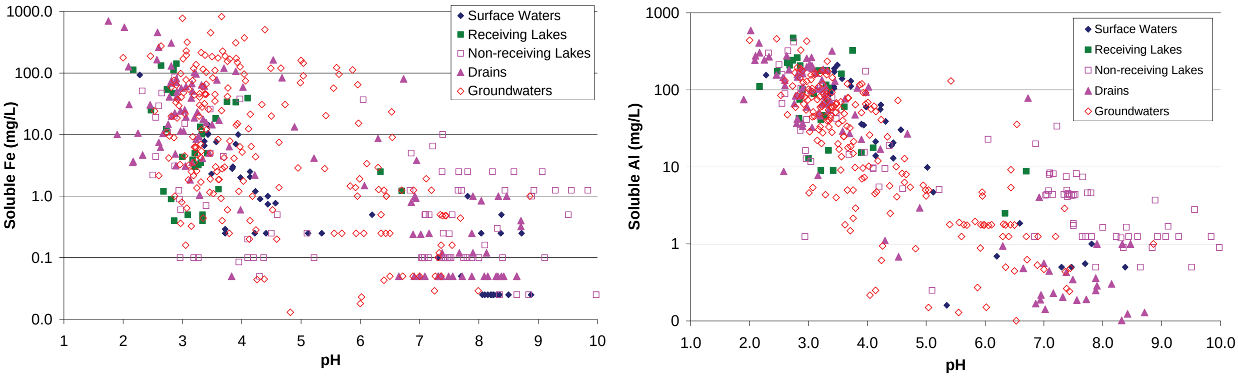

Figure 2. Soluble iron and aluminium concentrations distinguished by pH in creeks/river (surface waters), lakes, drains or groundwaters in the eastern WA Wheatbelt.

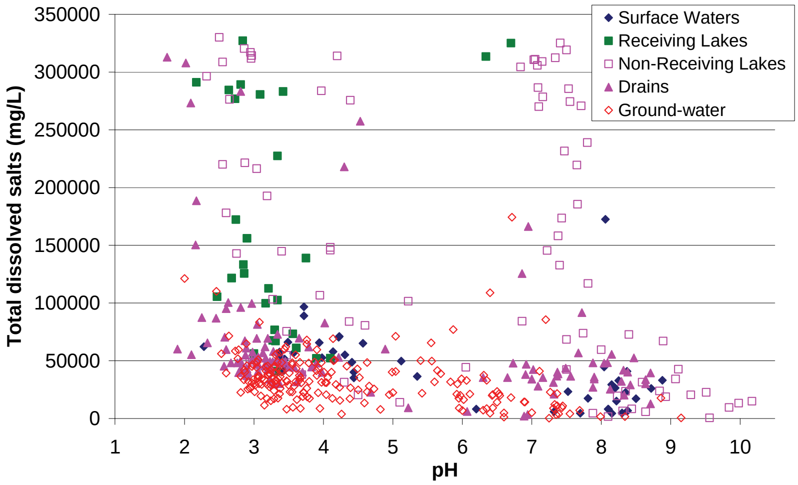

Figure 3. Total dissolved salt concentrations in relation to pH of waters in the WA Wheatbelt.

The salinity of flowing drain waters ranged from 9200 mg total dissolved salts (TDS)/L to over 90 000 mg TDS/L for both alkaline and acidic drains (Figure 3). Higher TDS concentrations were often due to increased evapoconcentration of salts in drain waters during summer. Regional groundwaters in the area surveyed were generally less saline, generally ranging between 8000 and 65 000 mg /L TDS, with a tendency for alkaline groundwaters (>pH 6.5) to be less saline (Figure 3). By contrast, the lakes contained waters up to 330 000 mg/L irrespective of pH. The ionic composition of all waters was dominated by Na and Cl (followed by Mg, Ca and SO_4^{2-}) and broadly similar to that of evaporated seawater.

Groundwater pH across the eastern Wheatbelt ranged from highly acidic (pH < 3.5) to alkaline (> 7.5). Many groundwater samples were obtained from areas where deep open drains are absent, indicating that drains have not caused groundwater acidity to develop, even though they may change the expression and mobility of the acidity. Acidic groundwaters (pH < 5.5) frequently contained high concentrations of iron (45% exceeding 25 mg/L; Figure1) and/or aluminium (66% exceeding 25 mg/L; Figure 2). The range in concentrations of these metals is similar to that in acidic drainage waters and was evidence that the chemistry of groundwater discharge significantly influences the acidity of waters in deep drains. The groundwater chemistry is also similar to that encountered in broad valleys further east in the Goldfields (Gray, 2001).

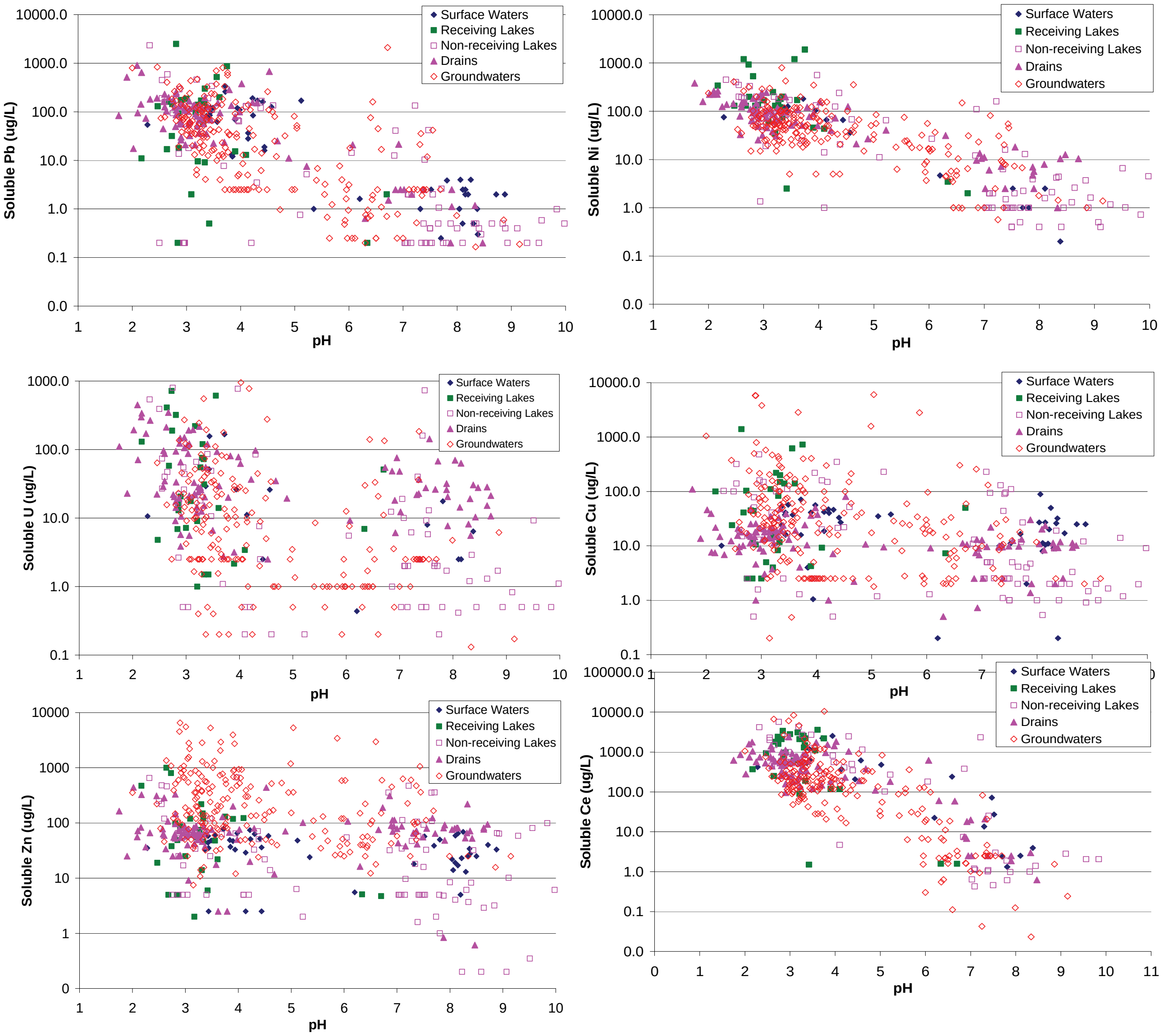

Figure 4: Selected soluble trace metal concentrations distinguished by pH in flowing surface waters, lakes, drains or groundwaters in the eastern WA Wheatbelt.

The concentrations of trace metals such as Cu, Cd, Zn, Ni, Pb and U in acidic drains broadly reflected those of the groundwaters, though there was a tendency for drainage waters to contain less Zn and Cu (Figure 4). This highlights that, as ground-waters discharge and flow along drains, there may be geochemical processes such as adsorption or precipitation retaining these elements. Despite this, trace metals such as Ni, Cu, Zn, U and Pb occurred in high concentrations in drainage waters, some exceeding 250 µg/L (particularly Zn, U and Pb). Other elements of environmental concern, such as Cd and As, were generally below detection limits within acidic drainage waters, though one sample contained up to 5.1 µg Cd/L and another unrelated drain contained 40 µg As/L. Detailed analyses of the acidic drains, lakes and groundwaters also found that they contained up to 10 mg/L of Ce (Figure 4) and 3.8 mg/L of La, with generally lesser concentrations (generally < 0.1 mg/L) occurring in alkaline waters. Most trace metals in alkaline drainage waters were below 20 µg/L, except for Zn and U (Figure 4), which could occur in concentrations of up 300 ug/L. It is also noteworthy that there were some alkaline drains and groundwaters that had concentrations of some trace metals (eg Pb and U) similar to those in acid drains and groundwaters.

A number of surface waters and lakes (both receiving and non-receiving) could contain concentrations of trace metals similar to those in drains (Figure 4). High concentrations of trace metals such as Cu, Ni, Pb, U and Zn occurred in some lakes, often corresponding with high TDS concentrations (Figure 2 and 4). Many lakes were in the advanced stages of drying at the time of sampling, thus evapoconcentration most likely played a dominant role in influencing trace metal concentrations in the absence of any precipitation and/or adsorption mechanisms. Acidity was also present in some river and creek waters, though these were generally low discharges (mostly < 2 L/s) occurring as baseflows in creeks and some major floodways. Larger flows (more than 5000 L/s) in the main channels of rivers were all alkaline. This is consistent with a similar broader survey of water quality in waterways of the Avon catchment where acidic waters were generally only evident in low flows (Degens and Muirden, 2006).

Acidity and trace metals contained within drainage waters pose a threat to environments into which this water is discharged. Acidity threats include the capacity for the waters to acidify lakes, creeks and floodplains which will result in decreased aquatic life in saline systems (Halse, 2004) and is likely to be similar to the impacts associated with drainage from coastal and inland acid sulfate soils. In this context, impacts of drainage on aquatic ecosystems are likely to be accentuated during catchment runoff events when acidic waters (from drains or in stored in lakes) partially mix with alkaline surface waters. High iron concentrations in drainage waters carry the risk that significant concentrations of iron precipitates might form during mixing of waters and smother the benthic organisms in waterways and lakes. Similar iron concentrations in acid drainage from coastal acid sulfate soils and acid mine drainage environments are widely reported to result in impacts on waterways (Sammut *et al* 1996). Partial neutralisation of waters with high aluminium concentrations may result in significant concentrations of Al species (e.g. $Al(OH)^{+}$, $Al(OH)^{2+}$) forming that are known to be toxic to some aquatic organisms (Sammut *et al* 1996).

Trace elements such as lead, cadmium, uranium, arsenic and selenium carry longer-term risks of accumulation in lakes and waterways, direct toxic effects on aquatic life and possible longer-term bioaccumulation through aquatic food-chains. These risks largely depend on the extent to which the acidic ground-waters reach surface environments. Furthermore, the risks are likely to be significantly modified by the complex inland ASS-type geochemical processes occurring within acidic saline drains and receiving environments that concentrate and modify the mobility of acidity and trace metals (Fitzpatrick *et al* 2008).

CONCLUSIONS AND MANAGEMENT IMPLICATIONS

Deep drains used to manage shallow watertables in the eastern Wheatbelt can intercept and convey acidic saline waters, thereby creating conditions for the development of inland ASS processes in drains and acidified receiving environments. The hydrochemistry of the waters from deep open drains appears to reflect that of regional groundwaters, which in many areas are acidic in the absence of drainage. Although at somewhat greater depths from the surface, similar acidic saline waters also occur east of the Wheatbelt in the Goldfields (Gray 2001).

These investigations highlight the need to manage not only the impacts of rising saline groundwaters in the broad palaeodrainage systems of inland south-western WA but also the impacts of geochemical processes coupled with this discharge. In particular, both interventionist and non-interventionist management strategies need to consider the discharge of acidity and associated trace metals. Engineering options, such as deep drainage and groundwater pumping, increases the expression and transport of acidity and trace metals in inland south-western WA. These will require management that may involve treatment (Degens *et al* 2008). Similarly, management approaches that involve no interventions to manage salinity (i.e., adapting to salinity) will need to consider managing acidity and trace metals due to regional ground-water discharge in lakes and floodways of the eastern Wheatbelt. Given that groundwater rise continues to occur across the eastern Wheatbelt (Hatton *et al* 2003), discharge of acidic groundwaters to surface soils and environments is also likely to increase.

Management implications

- Consideration must be given to the occurrence of acidic waters being generated by any deep drainage activities in the paleodrainage systems of the eastern WA Wheatbelt
- Soils, groundwater geochemistry and pilot excavations should be assessed by sampling of fresh ground-water inflow before drain construction to determine the risk of acid groundwater and trace element issues
- Acid waters discharging from drains will need to be managed to contain potential risks of discharging these to lakes and waterways. This management may involve treatment of waters or drain design to minimise export of acidic waters while maximising hydrological effectiveness (eg shallower, more frequently spaced drains)

ACKNOWLEDGEMENTS

We thank Adrian Beech, Claire Wright and Jason Kirby for sample analyses and Peter Geste, Geoff Sadgrove, Claudia Hadlow, Riasat Ali and John Byrne for assisting with sample collection.

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CHAPTER 11

AVON BASIN, WA WHEATBELT: ACIDIFICATION AND FORMATION OF INLAND ASS MATERIALS IN SALT LAKES BY ACID DRAINAGE AND REGIONAL GROUNDWATER DISCHARGE

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INTRODUCTION

Shallow, acidic (pH<4) saline groundwaters are widespread in lowlying landscapes of the eastern WA Wheatbelt (Shand and Degens 2008). In many parts of the WA Wheatbelt, watertables are continuing to rise (George *et al* 2008) and increase the discharge of these groundwaters, with associated salinity and acidity, to broad valley floors. Deep open drains are increasingly being used by landholders to manage the rising water-tables and recover or protect land from salinisation in these areas (Dogramaci and Degens 2003; Kingwell and Cook 2007). Such drains are frequently acidic as a result of intercepting shallow acidic saline groundwater. Furthermore, drains commonly discharge to sacrificial lakes or floodways, where flows eventually collect in lakes further down-stream (Dogramaci and Degens 2003; see also several chapters in Shand and Degens 2008).

The geochemical impacts of acidic saline groundwater in the WA Wheatbelt are poorly understood, though likely to be similar to that of inland Acid Sulfate Soils (ASS). Although the impacts of secondary salinisation are well documented (Hatton *et al* 2003), the prospect of regional discharge of acidic groundwaters to surface environments or discharge from deep open drains poses an additional threat to surface waterways and lakes.

Acidic groundwater has long been recognised to occur in the eastern Wheatbelt, particularly in deeper strata (Bettenay *et al* 1964; Mann 1983). Surface expressions of this acidity are noted in some large salt lakes on the Yilgarn River within the WA Wheabelt (Mann 1983; Cale *et al* 2004) and the southern Goldfields (McArthur *et al* 1991; Clark 1994). Surface water monitoring in the eastern Avon basin also identified acidic baseflow in waterways across the inland Avon basin, indicating that the impacts of shallow acid groundwaters may be more widespread that originally thought (Degens and Muirden 2006). The significance of increasing discharge of acidic waters for trace metal mobilisation, and the risk that this poses to aquatic ecosystems, should increasing drainage occur, has not been investigated and is the main focus of this report.

A regional survey of surface waters in salt lakes of the eastern WA Wheatbelt was carried out with a nested survey of soil and sediment hydropedological properties to investigate the impacts discharge from salt-land drainage on salt lake geochemistry. A range of reference sites, not impacted by drainage, were sampled as comparisons to nearby drainage impacted lakes.

Methods

Grab samples of surface water were taken at sixty six lakes and one constructed evaporation basin between October 2005 and August 2006 (Figure 1). Thirteen of these sites were identified as receiving drainage waters by the Department of Water from a GIS evaluation of surface flow paths from drain sites sampled in October 2004 (Fitzpatrick *et al* 2008) using aerial photography and spatial data on watercourses and flow paths. Verification that drain flows discharged into lakes or that lakes were in the immediate flow-path downstream of drain discharge points was conducted as part of on-ground investigations. A similar process was used to identify reference lakes, which were control sites not receiving drainage or off-line from main water courses and containing water at the time of sampling.

All samples were filtered in the field through 0.45 µm membrane filters in the field and preserved by either addition of ultrapure nitric acid (to a final concentration of 0.1%) or retained unacidified and stored at 5 degrees C. Measurements of pH, electrical conductivity (EC), temperature and oxidation-reduction potential (using Ag/AgCl probe; converted to Eh) were taken on-site at most sampling points. The concentrations of Cu, Zn, Co, Ni, Cr, Mn, P, V, Fe, Al, Ca, Mg, Ti, Na, K, and S were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The elements Ag, Ba, Cd, Mo, Pb, Sb, Sn, Y, Hf, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U and Se were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Arsenic was also determined using the hydride generation coupled to ICP. Selected anion analyses (SO_4, NO_3, NH_4, PO_4) were completed using ion chromatography. Only selected results from these analyses are discussed here.

Most sites were only sampled once. However, as a result of summer flooding in the Lockhart Catchment and the permanency of some water-bodies, it was possible to sample a number of these several times. Sampling of sediments for evaporite minerals and clastic sediments (Fitzpatrick *et al* 2008) was undertaken at fourteen sites during February 2006 to provide an indication of the dominant hydrogeochemical processes occurring within the lake environments including the fate of trace metals and acidity.

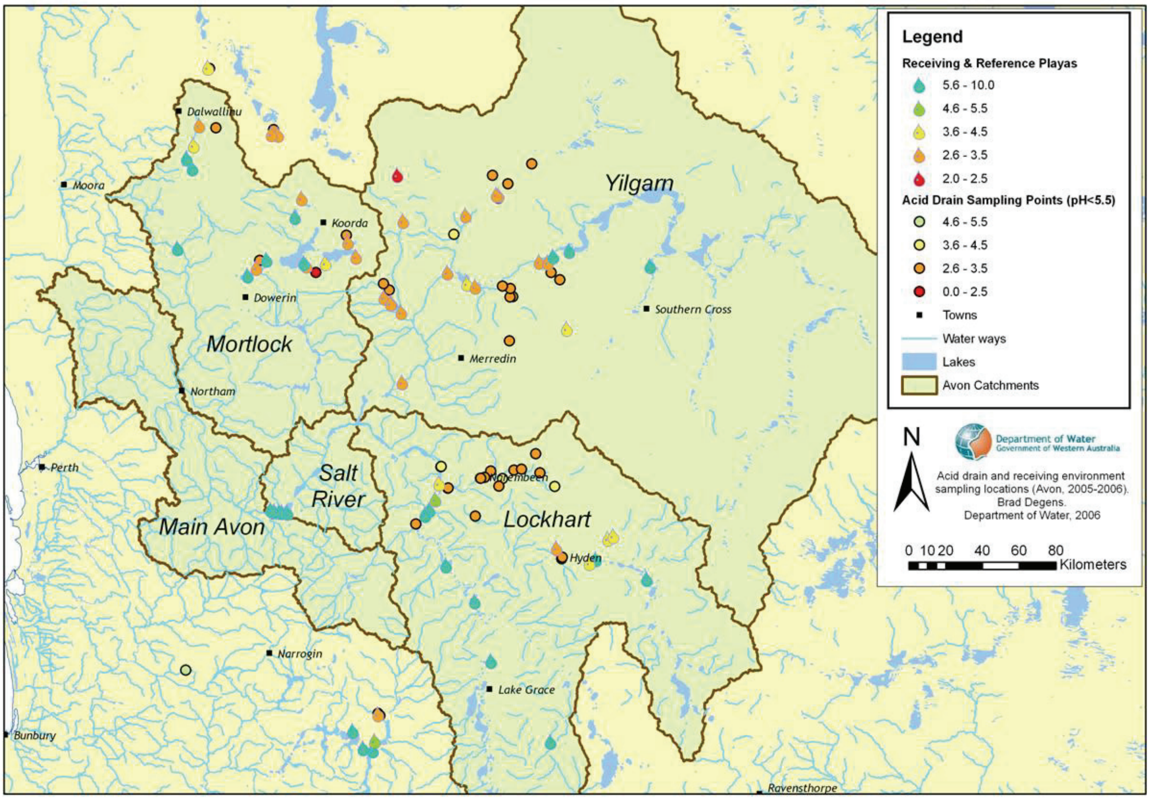

Figure 1. Outline map of reference and receiving lake sampling sites, drains discharging to the receiving lakes and the pH of these in the Avon catchment (WA).

Along with water samples, observations of water depth, recent maximum filling depth, sediment characteristics, hydrological connectivity (open or closed to low flows upstream or from the localised catchment) and evidence of aquatic/faunal life were made, where possible.

Sediment samples were collected and analysed, as described in (Fitzpatrick *et al* 2008), from 14 lakes (7 receiving lakes/sites and 7 reference lakes) in summer-autumn, corresponding with maximum formation of evaporate minerals. Briefly, sediment samples were collected at a number of zones within each lake, selected to provide information on geochemical processes above the high-water mark (beach), in the evaporation zone and within the bed sediments. Localised variations in morphology, determined by colour, texture, mineral precipitates and depth below surface, guided sampling within each zone.

Sediments were analysed for basic soil properties ($pH_{1:5}$, $EC_{1:5}$, organic C and carbonate C), major and minor elements by XRF and ASS properties. The latter analyses included potential acidity determined by analysis of sulphide-S using the chromium reducible S method (Ahern *et al* 2004) and existing acidity (total actual acidity) determined by titration to pH 6.5 with NaOH in a 1M KCl suspension (standard acid sulfate soil analysis method 23F; Ahern *et al* 2004). These analyses allowed better understanding of the extent to which sediments had acidified that was not apparent from pH alone.

RESULTS AND DISCUSSION

Surface Water Acidity and Salinity

Surface waters within reference lakes ranged from acidic (pH<5.5) to alkaline (pH>7). Over 45% of reference lakes were alkaline (pH>6.5; Figure 1 and 2), particularly in upper Lockhart River and mid-North Mortlock catchments. However, there were numerous lakes with acidic water (the majority less than pH 4) in the upper North Mortlock and central Yilgarn catchments (Figure 1), despite there being no known deep drainage discharge in the catchments of these lakes. Few lakes were found to contain alkaline water because many of these may only fill to any extent after significant rainfall events (eg >50mm). In contrast, many acidic lakes were likely dominated by groundwater discharge and/or down-stream of floodways with near surface groundwater which provided runoff conditions for these lakes to be filled to a depth of least 100mm after small rainfall events (eg <20mm).

This survey indicates that acidic lakes may occur across a much larger area of the eastern WA Wheatbelt than previously recognised. Waters in lakes in the eastern Wheatbelt around Narembeen and Bruce Rock are considered to be naturally acidic (Halse *et al* 1993) and there are reports of acidic ground-waters discharging to lakes (Mann 1983; McArthur *et al* 1991), though some of these contained alkaline surface waters (Mann 1983). Prior to clearing it was likely that there were localised discharges of acidic ground-waters on the margins of some lakes and from sand seeps (Bettenay *et al* 1964; McArthur *et al* 1991), however it is unlikely that significant acidity in surface waters was present to the large spatial extent found in this survey.

Discharge of regional acidic groundwaters may have contributed to the acidification of lakes that were acidic in the absence of drainage discharge and this may be increasing with on-going ground-water discharge. Many acidic reference lakes were not open to annual surface-water inflows (ruling out any possible unidentified drainage impacts) and were effectively closed basins primarily under the influence of rising regional ground-waters (Figure 3). Acidic groundwater is widely distributed in the WA Wheatbelt (Shand and Degens 2008) and it is possible that discharge of this to lakes, floodways and creeklines with poor neutralising capacity would result in acidification of some of these water-features. The similar chemistry of acidic reference lakes and acidic drain receiving lakes (Figures 2 and 4) also indicates a similar acid origin. The titratable acidity of surface waters in many acidic drainage receiving lakes was similar to that of acidic reference lakes (Figure 4) and is dominated by dissolved aluminium (Figure 4).

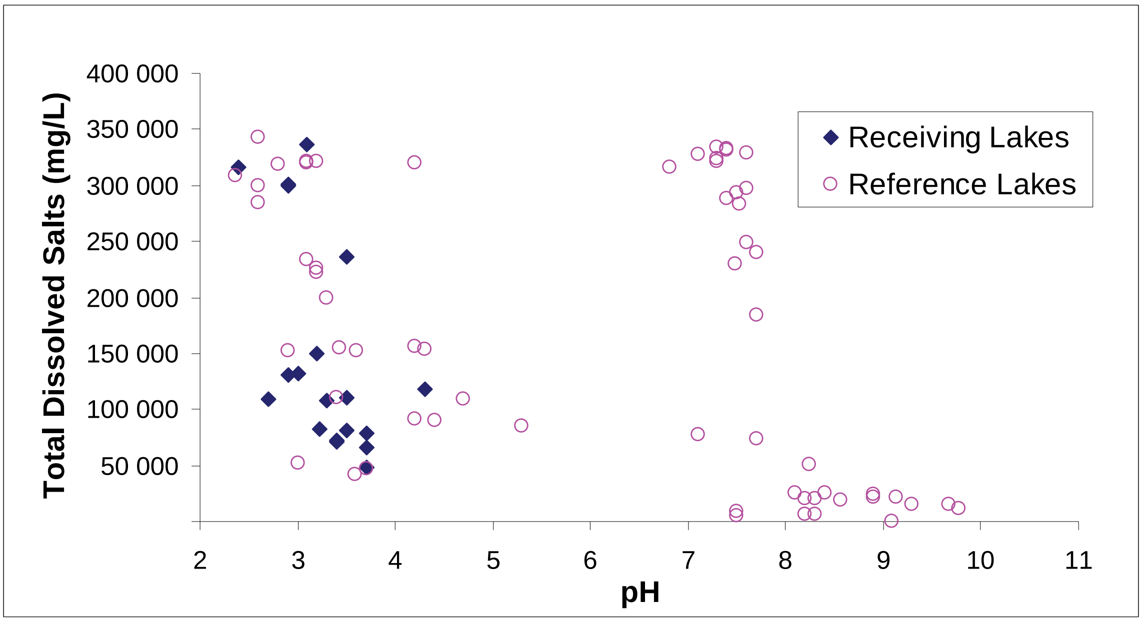

Figure 2. Lake water pH and salinity (total dissolved salts; TDS) in reference and receiving lakes in the Avon catchment, WA (at various stages of drying).

Lakes into which acidic drainage water directly discharge (receiving lakes) or those immediately down-stream of floodways receiving acidic drainage water all contained acidic waters (with pH<3.8; Figure 1). Over 75% of these lakes also contained waters with >50 000 mg l^{-1} TDS at the time of sampling (Figures 1 and 2). Lakes may have acidified as a result of discharge or were acidic prior to discharge (this was not readily distinguishable in all cases). If lakes were alkaline prior to discharge, it was clear that there is limited capacity of any lakes to neutralise acidic drainage waters – at least in the short-term (<5 years).

Figure 3. An example of an acidic reference lake acidified by regional groundwater discharge (Askews Lake, Beacon)

A wide range of salinity levels were found across all the sites, with many sites containing waters exceeding 150 000 mg l-1 TDS (Figure 2), which in many cases indicated that many lakes were in advanced stages of drying, reflecting limited rainfall in the months prior to sampling. Where lakes contained waters with less than 50 000 mg l-1 TDS, this was commonly due to recent filling by surface water inflows, either by high winter rainfall during 2005 or remnant-cyclone rainfall occurring during the summer of 2006.

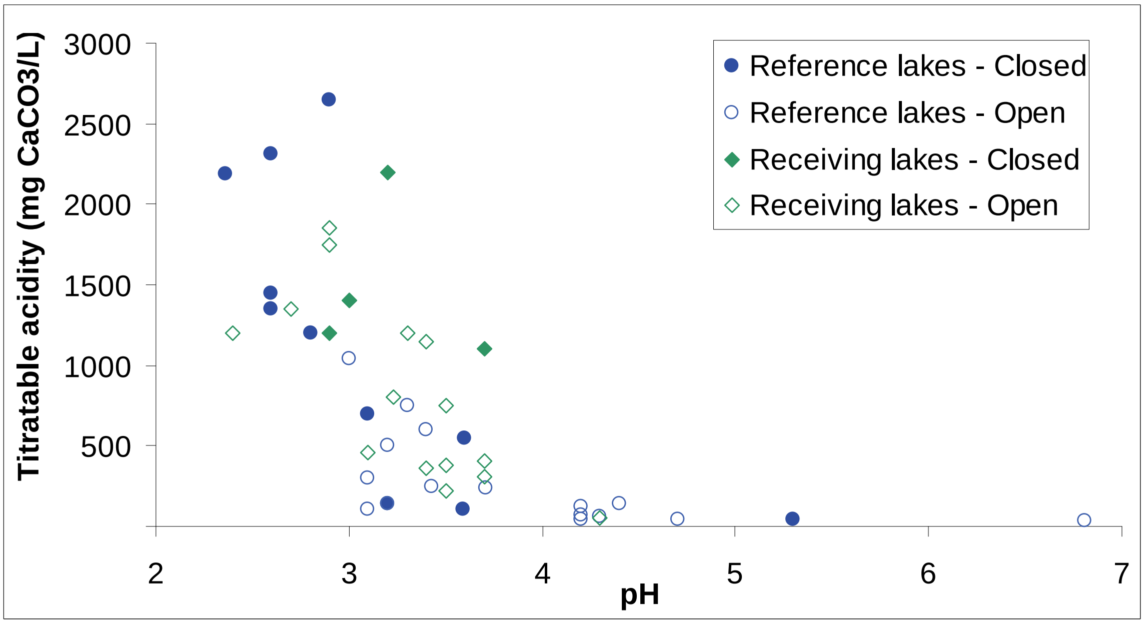

Figure 4. pH of lake waters in relation to titratable acidity for reference and receiving lakes (where pH<7) in the Avon catchment, WA (distinguished by whether the lakes were deemed open or closed to regional surface water flows).

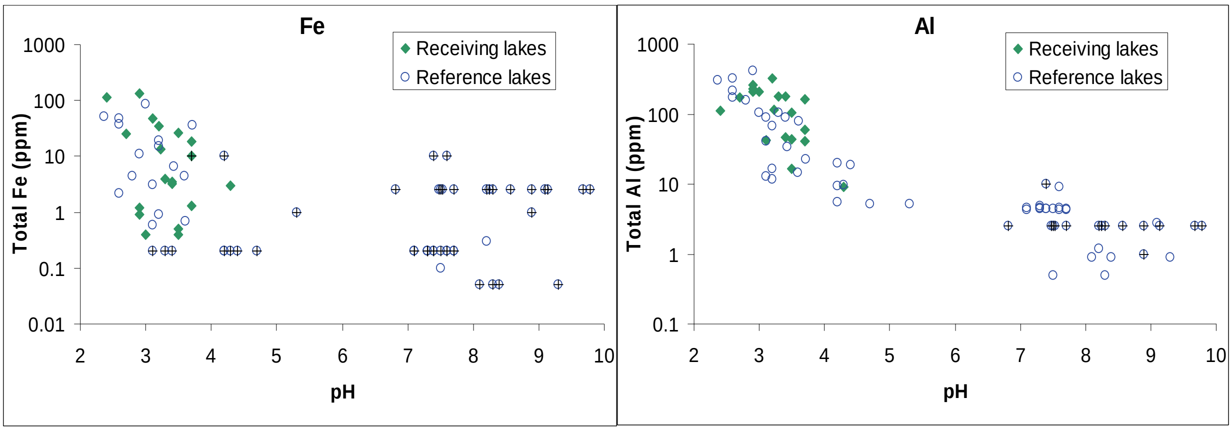

Figure 5. Distribution of soluble iron and aluminium concentrations in relation to pH for reference and receiving lakes. NB: Values below detection are plotted at the detection limit (marked with +) and concentrations are shown on a logarithmic scale.

Trace elements in surface waters

The acidic lake waters contained high solute concentrations of some trace elements (including Al, Fe, Co, Ni, Pb, and the rare earth elements) at generally more than 10 times the concentrations occurring in non-receiving lakes with alkaline waters (Figure 5 and 6). Other trace elements such as As, Cu, Su, U and Zn were not dissimilar between acidic and alkaline reference lakes (Figure 5).

The greatest concentrations of trace elements such as Cu, Co, Ni, Pb, U and Zn occurred in waters in lakes receiving acidic drainage and were generally at least 1.2 times greater than the maximum concentrations in acidic reference lakes (Figure 5). However, the ranges of most trace element concentrations in lakes receiving acidic drainage were similar to those in acidic reference lakes. For example, waters of a receiving lake north of Bodallin contained 2500 µg Pb l^{-1}, but a non-receiving lake at Beacon (100 km north-west) contained 2300 µg Pb l^{-1}. Similarities between the waters in receiving and non-receiving lakes may reflect the similar geochemical processes at the sites determining metal solubility (e.g. precipitation and adsorption driven by evapo-concentration and mineral precipitation processes). These may have diminished any original differences that might be due to different rates of metal loading (from drains or direct regional ground-water discharge).

The risk posed by metals in lakes receiving acidic drainage and acidic reference lakes is unclear. Algae and aquatic crustaceans (eg Paratemia spp) were observed at a number of acidic reference lakes (e.g. King Rocks Rd, East Hyden; McKay Rd, Pithara and Doodlakine-Kununoppin Rd lake, Trayning). The presence of these organisms presents the possibility that there may well be pathways by which bioaccumulation of some metals (e.g. Pb, U, Cd) could occur, thereby posing some risk to bird-life evident at many lakes and reported to occur elsewhere (Goodsell 1990). There has been very little investigation of ecotoxicological effects of metals in hyper-saline waters (Wang 1987) and even less is known about the ecological impacts in temporary or ephemeral lake systems (Smith *et al* 2004). The high concentrations of Cl in seawater may reduce uptake of some metals by aquatic organisms (i.e. reduce bioavailability), although, in contrast there are some metals (e.g. Cd) where high Cl concentrations can increase uptake by aquatic organisms (Wang 1987 and Campbell 1995). Greatest risks may also occur in the period after filling by floodwaters, when the pH of lake waters can increase, salinity decreases and aquatic food-chains can be most active (Davis *et al* 2003).

Inland acid sulfate soil materials in lake and shoreline sediments

Discharge of acidic drain waters and regional groundwater seepage has promoted the formation of inland actual ASS materials in the sediments of lakes. Lakes (and the one new evaporation basin) receiving acidic saline waters (<pH 5.5; as sampled in spring, 2005) also contained acidic bed sediments (pH<5.5 in 1:5 deionised water). Likewise, reference sites with acidic waters also contained acidic bed sediments. Conversely, lakes with alkaline waters contained alkaline sediments.

Acidic drainage waters have the capacity to acidify some lake bed sediments. Seepage of acidic drainage waters into alkaline sediments (pH>7 in 1:5 deionised water) was still evident at one receiving site (Gambles Rd, Cowcowing) where a thin layer of acidic surface sediments (pH<4, 0-1cm) overlay more alkaline bed sediments (pH>6.3, 1-30 cm). There were no free carbonates in the deeper sediments of this lake, though these may have been present at some time in the past, since the bed sediments of an adjoining reference lake (Ski Lake, Cowcowing) contained up to 9% by mass $CaCO_3$ within the surface 15 cm.

The majority of acidity in acidic receiving and reference lakes is contained in the shallow sediments (<40cm) rather than overlying waters (Table 1). Some sites contained up to several thousand times more existing acidity in sediments than in waters at the time of sampling in spring 2005 (Table 1). These results indicate that neutralisation of acidic waters in acidic drain receiving lakes must take into account the acidity store within the sediments since these will tend to buffer the pH of the system. Significant amounts of reactive soluble and exchangeable acidity can be present in shallow lake sediments requiring up to 9.7 tonnes per hectare of pure limestone (as $CaCO_3$) to neutralise, even in acidic reference lakes. Notably, these estimates only indicate the more readily neutralisable acidity, generally present as exchangeable cations and soluble Al and Fe minerals, and do not include less reactive forms of acidity (McElnea *et al* 2002) that were present as iron (e.g. jarosite and natrojarosite) and aluminium hydroxysulfate (e.g. alunite) minerals at some sites.

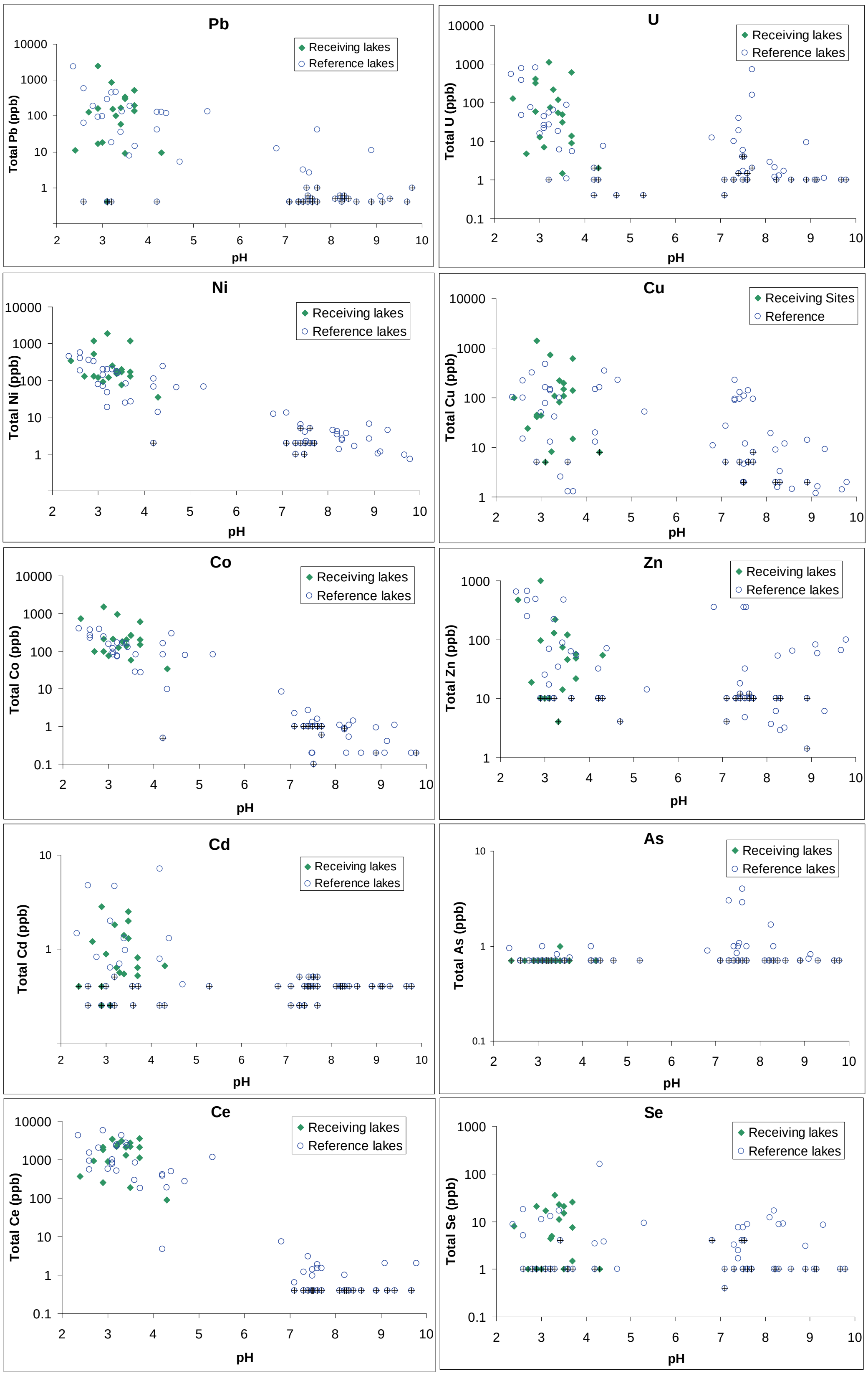

Figure 6. Concentrations of selected trace elements in reference and receiving lake waters of varying pH. NB: Values below detection are plotted at the detection limit (marked with +) and concentrations are shown on a logarithmic scale.

The soils fringing many acidic lakes (in the beach zone) contained greater amounts of existing acidity than those in the mid-part of lakes (Table 1). The accumulation of acidity and formation of inland actual ASS soils in these zones at most acidic reference lakes was probably due to concentration of acidity by evaporation of local ground-water discharge on the margins of the lakes. This process has also been reported in larger, less hydrologically disturbed salt lake systems in the goldfields (McArthur *et al* 1991) and is likely to be increasing with rising water tables in many lakes in the eastern WA Wheatbelt. Lateral leakage of acidic waters from the main lake (with evapo-concentration in surface soils) may also have contributed to the accumulation of acidity in the beach zone at some sites receiving acidic drainage discharge, though the effect is constrained to within 10's of metres of the lake edges. The beach zone at many sites included an area inundated by water during winter 2005 (a year when generally average rainfall fell across the Wheatbelt) and at all sites would certainly be inundated during flooding events (except for the Bodallin evaporation basin which is protected from the hydrological impacts of flooding). Acidity accumulated in Al- and Fe-bearing surface salt efflorescences (e.g. rozenite) would be rapidly washed into the main water body during most winters and after flood filling.

Potential acidity was also present as sulfides in the bed sediments and occasionally beaches of eight receiving and reference environments (Table 1), as well as at three alkaline lake sites (not listed in the table). It was notable that the majority of acidic reference and receiving lakes did not contain sulfides. In the acidic lakes, the potential acidity in the sediment was generally more than an order of magnitude greater than that that present as titratable acidity in the profiles (Table 1). The acidity stored in the sulfidic materials does not pose a threat to the environment providing that the lake beds remain anoxic (waterlogged) and/or saturated and are not disturbed by excavation.

Sulfide minerals were generally concentrated in the shallowest 10 cm of bed sediments (up to 0.6% S) and often occurred with significant accumulations of organic matter (up to 2.4% organic C in some horizons). It is likely that sulfides accumulating in bed sediments of the smaller lakes (in particular) have formed due to microbial sulfate reduction fuelled by organic inputs to the lakes and maintenance of water-logged conditions in the early stages of secondary salinisation. Organic C inputs may have occurred as a result of algal and macrophyte blooms during past lake filling events (evident at some sites as dried macrophytic material deposited on shorelines during most recent lake filling events) and/or as deposition of sediments and organic residues washed from the topsoil of adjacent agricultural areas during flood events. Waterlogged conditions in bed sediments between these events were probably maintained by rising ground-water levels due to land-clearing. Sulfide minerals present in lakes with acidic waters and sediments (receiving and reference) were most likely formed prior to acidification, since sulfate reduction and sulfide formation is generally favoured in alkaline environments (Langmuir 1997, Ward *et al* 2004). Occurrence of sulfides in acidic reference lakes may be evidence that the lakes were alkaline in the past and have undergone acidification in recent times, most likely because of increased discharge of acidic ground-waters occurring after land-clearing.

Data from this broad survey indicated that the concentrations of most trace metals in the bed sediments of most lakes receiving acidic drainage were not obviously elevated compared with the acidic reference lakes and two alkaline reference sites. Limited sampling within each receiving or reference environment (<4 sites) might have failed to detect differences in metal accumulations due to large spatial variation in metal accumulation. Spatial variation in deposition of precipitates (and associated trace metals) in the lakes receiving acidic drainage may be uneven, particularly where prevailing winds result in re-suspension and deposition of precipitates on the leeward side of lakes. It is also possible that some receiving lakes were acidic prior to drain discharge and the magnitude of discharge impacts (i.e. accumulation of trace metals) was indistinguishable compared with trace metal accumulation from previous regional acidic ground-water discharge.

Table 1. Estimated acidity (as equivalent kg CaCO3 per ha) in different zones within lakes (ponded waters, sediments and beach zones) for acidic reference lakes and lakes receiving acidic drainage (see footnotes for explanation of acidity pools).

Site[1]	Acidity in ponded waters (as equivalent kg CaCO3/ha)[2,3]	Existing acidity[3] in lake bed sediments (as equivalent kg CaCO3/ha)	Existing acidity[3] in beach soils (as equivalent kg CaCO3/ha)	Potential acidity[4] as sulfides in lake-bed sediments (as equivalent kg CaCO3/ha)
McKay Rd lake, Pithara (Ref)	0.4	9	267	439
Carter Rd lake, Jibberding (RE)	0.9	833	1 454	11 776
Gambles Rd lake, Cowcowing (RE)	1.8	288	209	16 519
Doodlakine-Kununoppin Rd, Trayning (RE)	3.0	4 018	Not sampled	393
Doodlakine-Kununoppin Rd, Trayning (Ref)	1.2	5 165	3 039	0
Yilgarn lake, Boodarockin (RE)	0.9	7 879	26	0
Yilgarn lake, Boodarockin (Ref)	0.4	416	2 304	0
Bodallin Evaporation Basin (RE)	11.0	2 596	2 919	0
Lake Ardath (RE)	4.1	2 564	664	0
King Rocks Rd, East Hyden (Ref)	0.6	9 745	Not sampled	0
Lake Gounter, Hyden (RE)[5]	1.4	773	3 843	8 691

[1] Ref = reference site, RE = receiving site. Site location details in Shand and Degens, 2008.
[2] Estimated from depth of water in lake at time of sampling in early October 2005 and titratable acidity.
[3] Existing acidity expressed as equivalent kg of H2SO4 estimated by summation of total actual acidity for all horizons in a profile (<40cm depth) calculated on a per hectare basis assuming a uniform bulk density of 1.5g/cm3 for all materials (Note: this is a conservative estimate since bulk density of hydrated materials may be less, which would increase acidity storage/ha). Total actual acidity is determined by titration to pH 6.5 of a 1M KCl-soil suspension (Ahern *et al* 2004). Acidity is expressed as equivalent weight of H2SO4 (in kg) per hectare that would need to be neutralised to raise the pH of the soils to 6.5.
[4] Potential acidity = acidity within sulfides determined by chromium reducible S analysis (assuming no contribution of acidity from monosulfides). These were calculated as equivalent kg of H_2SO_4 and summed for all horizons in a profile and calculated on a per hectare basis assuming a uniform bulk density of 1.5g/cm3 for all materials.
[5] Calculations for Lake Gounter focus on smaller permanently inundated NW corner of lake and not the larger eastern and SE flood fill zone (which was only occasionally inundated).

Drain discharge may increase surface concentrations of some trace elements in lakes, though this was not consistent for all receiving lakes. Elevated concentrations of some elements (e.g. Pb and U) were evident in surface horizons at several sites receiving acidic drainage (Doodlakine-Kununoppin Rd receiving lake, Trayning and Gambles Rd receiving lake, Cowcowing). Such an assessment was based on evidence of increasing concentrations of the metals in surface horizons relative to deeper horizons and comparison of concentrations of the trace metals with respect to horizons of a nearby reference lake. However, sediment concentrations of some elements may be similar in all environments. For example, Pb and U concentrations were generally similar (5-52 mg l^{-1}) in lake bed and beach sediments in an acidic reference lake, a lake receiving acidic drainage and an alkaline reference lake near Boodarockin. Notably, this survey identified concentrations of Pb that were frequently an order of magnitude greater than acid digestible metal concentrations in an earlier survey of sediments in WA lakes (Lyons *et al* 1990), although Cu, Zn and Cd concentrations were generally within similar ranges.

The formation of inland ASS materials in sediments in lake systems, by whatever the cause, poses a significant risk to aquatic habitat and the long-term integrity of aquatic ecosystems. These impacts are in addition to those caused by changes in hydroperiod and increasing salinity (Halse 2004). Loss of habitat through acidification of sediments may impact greatest on sites where resting stages of aquatic organisms can survive between lake filling events. Furthermore, while acidity in surface waters might be periodically neutralised by floodwaters or during lake filling events, this is less likely to occur for the acidity within bed and shoreline sediments. Neutralisation of acidic sediments during lake filling events is likely to be slow and limited because of restricted seepage and slow diffusion of alkaline waters. In a worse case scenario, the acidic sediments could result in progressive consumption of alkalinity of lake waters after flood filling resulting in acidic conditions prevailing from the early part of the drying phase. This is a period during lake hydrological cycles that is commonly the most critical for aquatic ecosystems; when the lake is fullest, freshest and significant growth and reproduction of aquatic organisms occurs (Smith *et al* 2004; Davis *et al* 2003).

Mobilisation of trace metals from acidic sediments to water columns may also be increased under certain conditions, for example formation of anoxic bottom waters after lake filling resulting in reductive iron dissolution and release of trace metals. A similar situation can occur if bottom waters become acidic due to acidity emanating from bottom sediments.

CONCLUSIONS AND MANAGEMENT IMPLICATIONS

Acidic drainage discharge to lakes can result in acidification of waters, soils and sediments and formation of inland ASS materials. However, in some cases lake waters and sediments may have been acidic prior to discharge in which case the impacts would dependent on the magnitude of drain discharge compared with regional ground-water discharge. Concentrations of Al, Fe and trace metals including Pb, Ni, Co and U appear to be increased in the surface waters of sites receiving acidic drainage, particularly when compared with alkaline lakes. This acidification and associated increased trace metal solubility may result in impacts on aquatic ecosystems, including loss of habitat and reduced ecosystem functioning during lake filling events.

Lakes can be acidic in the absence of discharge from deep drains, most likely due to the discharge of regionally acidic ground-waters. Numerous acidic lakes occurring in the upper reaches of the Lockhart, Mortlock and Yilgarn catchments were found to be acidic with no evidence of deep drainage discharge. These lakes may have always been acidic since before land-clearing began, however, there is sedimentary evidence that some lakes may have become acidic in recent times. Notably, the acidic reference lakes exhibited geochemical conditions similar to those in lakes receiving acidic drainage.

Some existing alkaline lakes may be under on-going acidification pressure if discharge of regionally acidic ground-waters continues to occur. For current acidic lakes, this will result in increasing acidification and accumulation of trace elements (determined by rates of ground-water discharge). For current alkaline lakes this could result in acidification.

Preliminary results indicate that acidic drain discharge does not necessarily result in readily distinguishable elevated accumulations of trace metals compared with lakes not receiving acidic drainage. Some concentration of trace elements may occur in the shallowest sediments of receiving lakes. However, the sampling density was too sparse for this to be certain. Further, more detailed investigations will be required to predict which drains are likely to result in increased accumulation of trace metals in receiving environments compared with acidic reference lakes. These investigations should involve comparisons of paired lakes (acidic reference and acidic drain receiving lakes) as well as before-after investigations of trace metal accumulation in environments receiving acidic saline drainage.

Initial overflows from acidic lakes (both receiving lakes and non-receiving lakes) following a rainfall events are likely to be laden with high concentrations of dissolved aluminium and iron and potentially high concentrations of trace metals. These may form significant concentrations of Al hydroxide species (e.g. $Al(OH)^{2+}$, $Al(OH)_2^+$) that can be toxic to aquatic to some aquatic biota and iron floc (smothering benthic communities) on mixing with neutral/alkaline floodwaters. The greatest risk of this is likely to occur during the first flush part of flood-flows and for small rainfall events that result in localised lake filling, and therefore concentration of discharge, in the Avon. These will require greatest management emphasis.

Management Implications

- Acidic lakes due regional ground-water discharge (ie not drainage) may require management of geochemical risks including acidity and soluble trace metals to protect alkaline down-stream environments
- Acidic ground-water discharge is best managed by containment and/or treatment in sites with minimal risk of down-stream transport which may be difficult to achieve which discharge to lakes in the central floodway
- Where drains discharge acidic waters to sites with poor containment, management of geochemical risks to down-stream environments will need to focus on acidic and metal mobilisation occurring during the first flush
- Containment of acidic saline discharge may require treatment with neutralising agents (e.g. limestone or coastal lime-sand) at regular intervals, depending on the risk to down-stream environments. This periodic treatment of accumulated acidity may be more cost effective than continuous treatment of drain discharges, which can be difficult in remote sites
- Soils with carbonates surrounding receiving environments could be mixed into the bed or used to line lakes to provide some capacity to neutralise acidic waters and sediments
- Use of alkaline flood flows to neutralise acidic sediments in acidic lakes may only be likely with significant volumes of water and flooding time.

ACKNOWLEDGEMENTS

We thank Adrian Beech, Claire Wright and Jason Kirby for sample analyses and Margaret Smith for assisting with sample collection.

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CHAPTER 12

AVON BASIN, WA WHEATBELT: ACID SULFATE SOILS AND SALT EFFLORESCENCES IN OPEN DRAINS AND RECEIVING ENVIRONMENTS

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INTRODUCTION

Salinisation due to rising watertables is a significant management issue in many parts of the Western Australian (WA) Wheatbelt and is expected to continue increasing in extent (Hatton *et al* 2003). The primary cause in many parts of Australia is related to an increase in groundwater recharge following native vegetation clearance for annual crops and pastures. In valley floors of the Wheatbelt, there is increasing use of engineering methods such as deep (2–3 m) drains and groundwater pumping to manage rising groundwater and to protect low-lying land from salinisation or to rehabilitate marginally saline lands.

More than 3000 km of deep drains have already been constructed: most are less than 20 km long and discharge into saline lakes, creeklines and floodways. Although some drains discharge only during the initial dewatering of regolith profiles, others continue discharging for many years at rates of up to 10L/s. The interest in further expansion of drainage from individual properties to regional integrated drain systems has been met with concerns regarding the prospects of safe disposal of waters created by these schemes, particularly since some saline drain discharges are acidic (Ali *et al* 2004). The occurrence of acidic groundwaters in the eastern Wheatbelt regions of WA (and Goldfields) has been known since the 1980s (Mann 1983). These waters were known to locally contain elevated concentrations of trace metals. The geochemical risks associated with deep drainage include the potential to release metals and other elements and colloids harmful to flora and fauna that inhabit receiving areas. Assessment of these risks requires considering the biogeochemical and mineralogical processes in the soils and sediments of these complex systems. Consequently, the objectives of this case study, involving the Avon Basin (Figure 1), is to illustrate the:

- Development of a robust field sampling program and experimental approach to characterise the following wide range of materials in drains and receiving playas:
    - Acid Sulfate Soil materials (sulfidic materials/sediments, sulfuric materials/sediments and monosulfidic black ooze) and associated features (salt efflorescences, salt crusts, gels, iron-rich crusts, mobile colloids and waters), and
    - Soil materials (drain batters; and naturally occurring saline-sodic soils on the edge and adjacent of the drains).
- Development of conceptual models that encapsulate various soil-water processes to:
    - Assess impacts of deep open drains on the production, export and fate of leachate and minerals on receiving environments, and

- o Recommend generalised principles that lead to implementation of "best management practices" for ameliorating identified categories of degraded drain sediments and acid sulfate soils.

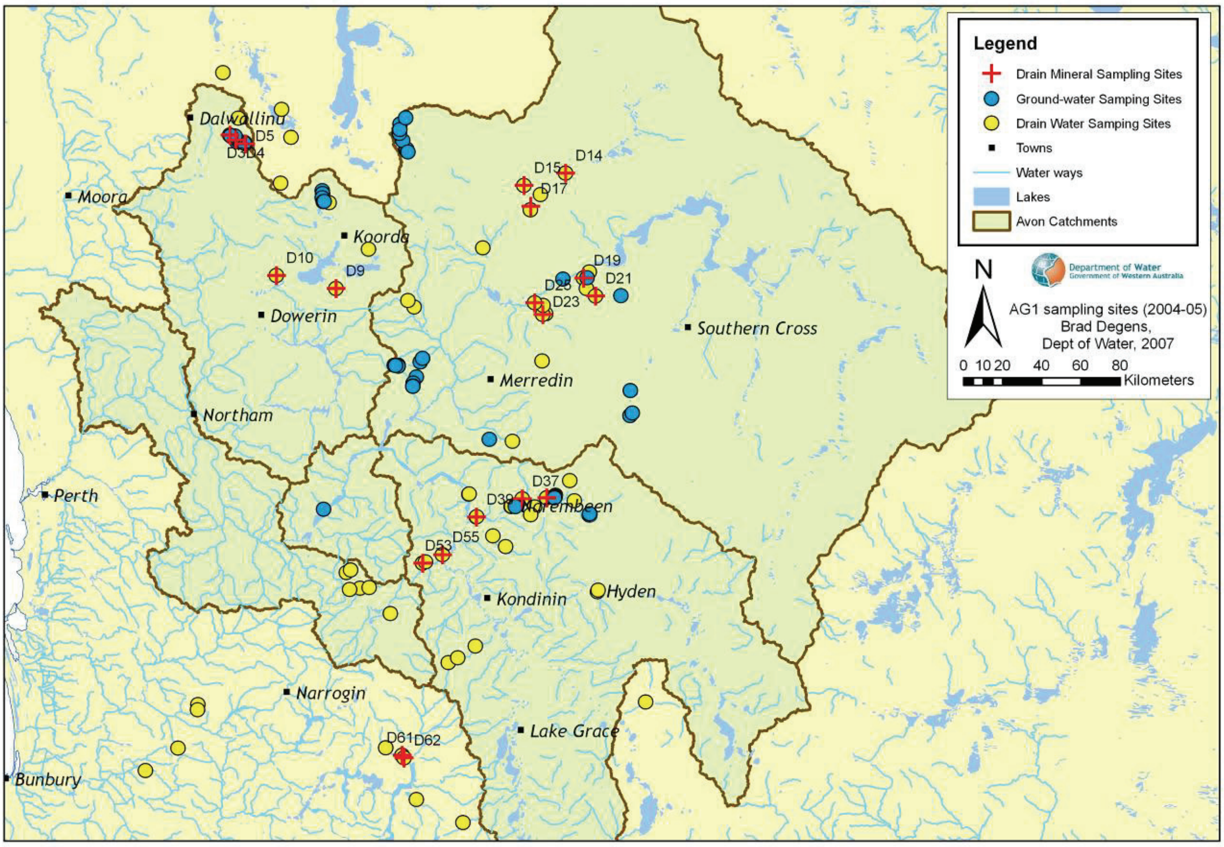

Figure 1. Locations of drain sampling sites (water and mineral sampling) in relation to existing acid drain sites in the Avon catchment (WA).

METHODS

Sediments and soil materials were surveyed at 19 representative acid drain sites (January 2005), 8 receiving lake sites and 6 reference lake sites (February 2006) in the Avon catchment (Figure 1; Shand and Degens 2008). At each site the following materials (over 300 samples) were described and sampled: sulfidic materials/sediments, sulfuric materials/sediments, gels, salt efflorescences, salt crusts, iron-rich crusts, soils (drain batters; and naturally occurring saline-sodic soils on the edge and adjacent of the drains). Samples were variously treated and fractionated (sub-samples) according to procedures outlined in the flow diagram (Figure 2).

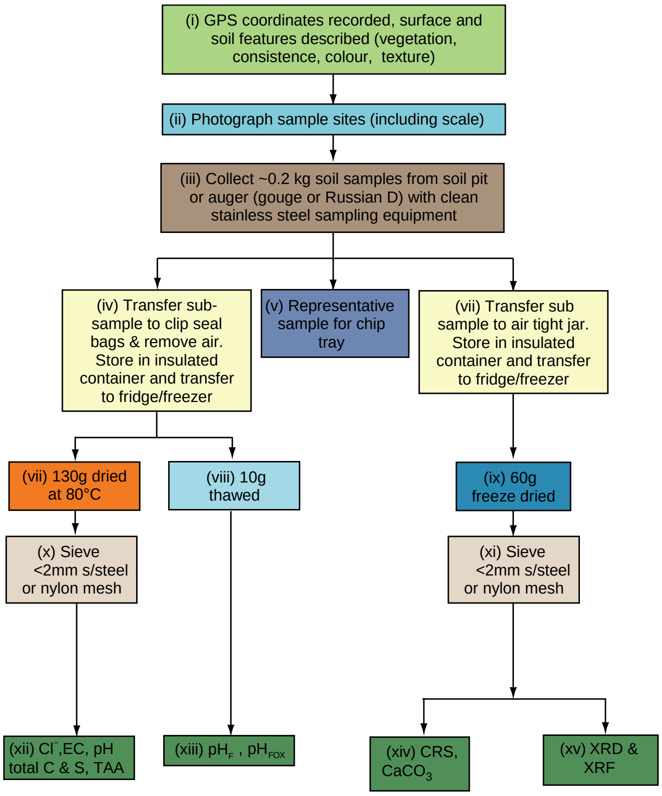

Figure 2. Flowchart for sample collection, preparation and analysis.

Specialised laboratory analyses (Figures 2 and 3) were conducted on selected sub-samples from each site using geochemical (XRF and ICP), mineralogical (XRD and scanning electron microscopy) and chemical methods to determine what biogeochemical and mineralogical processes were taking place in the drains and receiving environments. In addition, drain waters were sampled for flow, salinity, pH, major metals, trace elements, rare earth elements and other elements such as uranium.

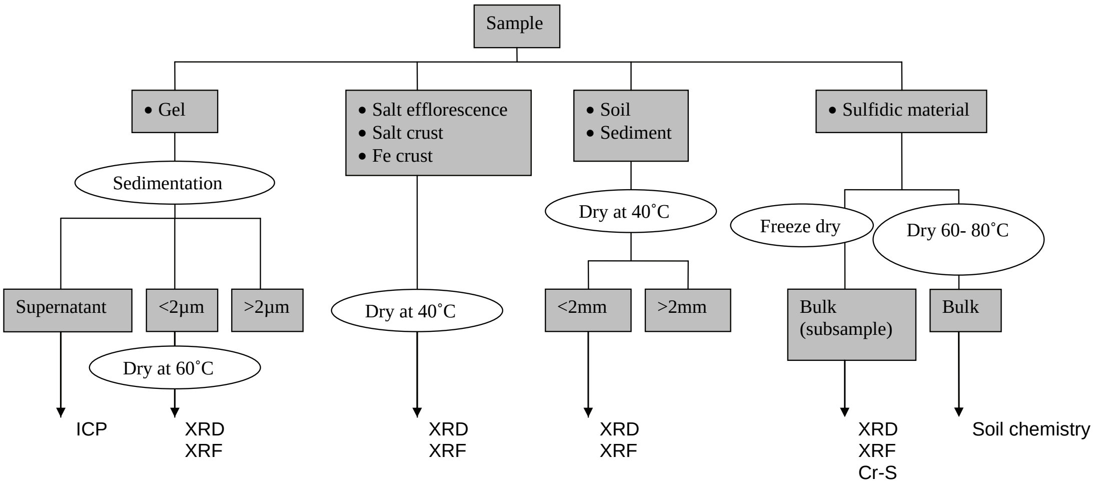

Figure 3. Flowchart summarising preparation and fractionation of various sub-samples and analytical methods used to characterise mineralogy, geochemistry and chemistry of sub-samples. Where: XRD = X-ray diffraction, XRF = X-ray florescence, ICP = Inductively Coupled Plasma analyses, Soil chemistry = pH, EC (Electrical Conductivity), organic carbon, carbonate content, exchangeable cations and SAR (Sodium Adsorption Ratio).

RESULTS AND DISCUSSION

Systematic web-based approach for acquisition, collation and communication of soil-regolith data

All the descriptive field information and laboratory data was stored in a web-based data-base, which was specifically designed as a framework for the acquisition, collation and communication of all information (Baker and Fitzpatrick 2005; Fitzpatrick *et al* 1996). The online database was constructed using Microsoft FrontPage 2003 to ensure that large data sets were structured and could be managed in a methodical way to allow the rapid and effective communication of results. The visual information (e.g. landscape, soil profile and chip tray colour photographs) and data (field and laboratory including XRD data and XRD spectra) stored in the web-based data-base is shown in the flowchart in Figure 4. This new approach permitted the easy collation of geological, soil, hydrological, geochemical and mineralogical data to help construct cross-section diagrams and mechanistic models of soil-regolith and water processes for each case study site. For example, the locality map (Figure 4 (i)) is linked to all site summary pages, which permits rapid and simple navigation between sites and provides links to more detailed information. The location of each sample or group of samples, taken at each site is displayed on photos in the site summary pages (Figure 4 (ii)). This provides an accurate record of sample localities relative to each other and their spatial distribution in the drain and receiving environments. Each sample, group of samples or profile can then be investigated in more detail via a HTML link to a sample summary page (Figure 4 (v)). These pages provide more detailed information on each sample and their location within a profile or group of samples, with quality colour photographs, with a scale, of each sample (e.g. Chip tray photos in Figure 4 (viii)). Interpretive toposequence models (Figure 4 (iv)) are included for each site. Data summary pages (Figure 4 (vi)) have direct HTML links to all the observations and data recorded in the field (colour, texture, pH, Eh etc.) and results from laboratory techniques (XRD, XRF, ICP-MS etc). Spreadsheets containing geochemical data (e.g. XRD (Figure 4 (ix)) and XRF (Figure 4(x)) is made available for download, via the data site, without putting the original data at risk. Data, such as SEM photos, are also made available (Figure 4 (vii)).

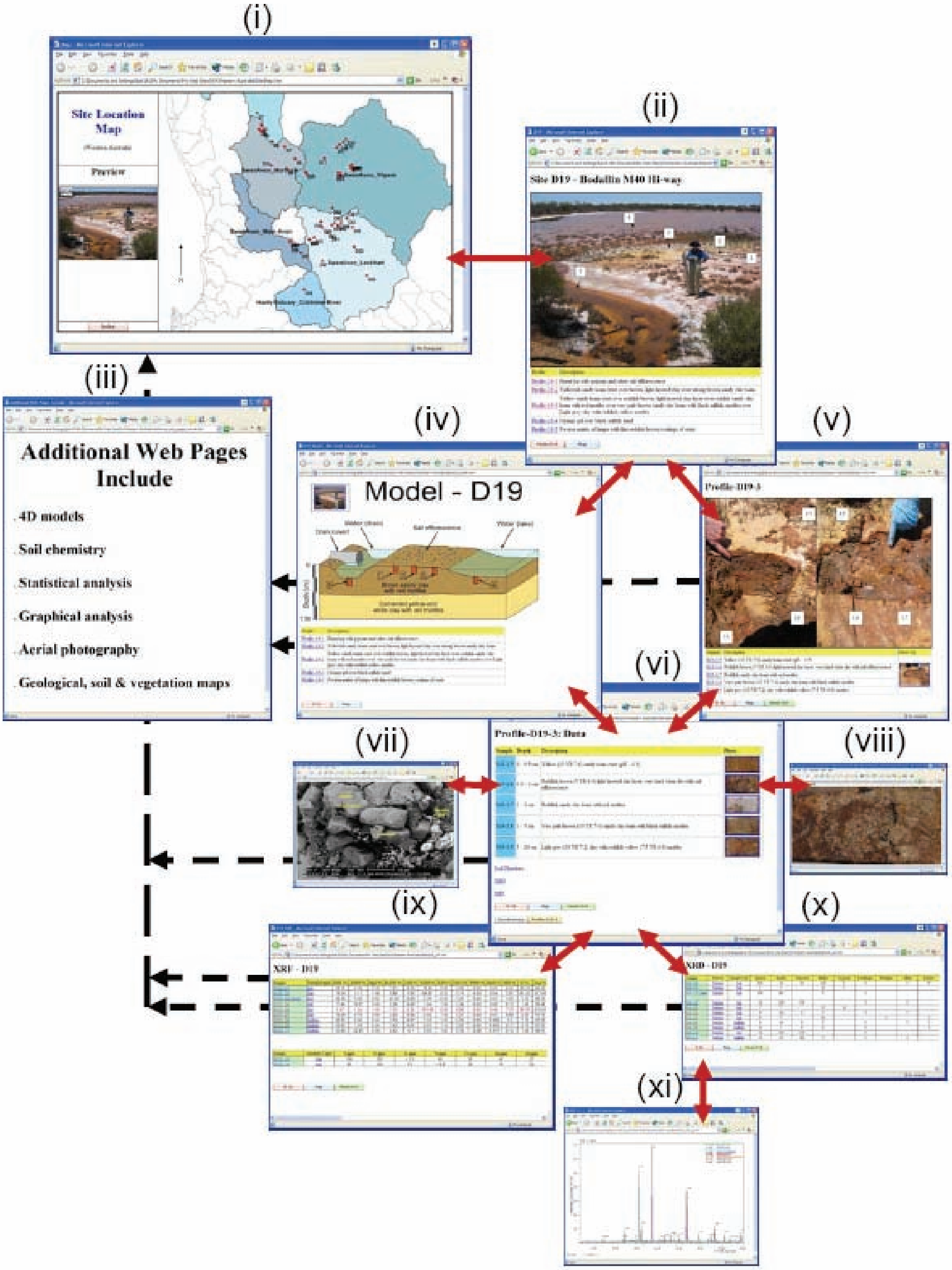

Figure 4. Flowchart constructed of web views from a typical acid drain entering an acid receiving lake site (D19: Boodarockin, Koorda-Bullfinch Rd see Figure 5.6) containing acidic water and Acid Sulfate Soil web based data set. Views represent: (i) Site locality map of Avon basin, (ii) site summary web page, (iii) additional web pages that were included in the data set, (iv) 3-dimensional, interpretive model, (v) profile/sample summary page, (vi) data summary page, (vii) SEM photograph, (viii) chip tray photograph, (ix) XRF data, (x) XRD data, (xi) XRD spectra.

Drain water salinity and acidity

Most drains were typically very saline at the time of sampling (January) with specific electrical conductance (SEC) in the range 60-100 dS/m (approximating TDS of 38 to 64 ppt). Low pH is widespread, with more than half of the drains sampled in October 2004 being less than pH 3. Drain pH decreases during summer, probably due to oxidation of ferrous iron in groundwaters, iron minerals in sediments and/or evaporation. Results indicated two broad groups of drain pH and salinity. The pH was lowest east of a line from Dalwallinu to Dumbleyung (pH less than 3.5) and highest (pH greater than 6) in the western and central part of the Basin, though there were few drains flowing in this area. Only a few sporadic high pH (alkaline) samples were taken from drains in the eastern areas. Data show that in most eastern drains with a low pH (less than 4.5), iron, aluminium, cobalt, copper, zinc, lead, uranium and a range of other trace elements and rare earth elements all elevated.

Drain mineral environments

Several materials were generally evident within the drains and were used to indicate different geochemical process zones. These materials broadly consisted of (from the original excavated base of the drain): unconsolidated saturated sediments including sulfidic materials, monosulfidic black oozes, sulfuricic materials, saturated gels and precipitates, salt crusts overlying saturated sediments and salt crusts in the capillary zone above the drain waters. Not all materials were present within all drains. For example, in recent constructed drains (<3 years age) or drains with little sedimentation, there was little sedimentation and therefore minimal sediment profile development, gels and precipitates. The main materials and key processes that these indicate are discussed in the following sections.

Sulfidic materials

Sulfidic material occurred in almost all the drain sediments (Figures 4 b & c; and 11) as a thin horizon/layer (5 to 10 cm thick) representing a pool of stored acidity, that could contribute to drain water acidity seasonally or in aged drains. The sulfidic material mostly consists of accumulations of iron sulfide minerals, one of the end products of the process of sulfate reduction (i.e. the use of SO_4^{2-} instead of O_2 during microbial respiration). Sulfate reduction is a natural process that occurs in virtually all the drains. However, the quantities or thickness of sulfidic material that accumulate in the drains is a function of many factors. The key requirements for high rates of sulfate reduction and sulfide accumulation are: (i) a high concentration of sulfate in surface or groundwater, (ii) saturated iron rich soils and sediments for periods long enough to favour anaerobic conditions, and (iii) the availability of labile carbon to fuel microbial activity. Saline groundwaters in the wheatbelt generally contain quite large concentrations of sulfate and ferrous iron. Thus, drains that intercept saline groundwater should be expected to accumulate some sulfides in their sediments over time, especially if they are permanently flowing or waterlogged. Two forms of iron sulfide minerals are of importance from an environmental point of view: monosulfides (FeS) and pyrite (FeS_2). Soils and sediments rich in monosulfides (or “black ooze”) tend to be very dark and soft. Monosulfides can react rapidly (minutes to hours) when they are disturbed and exposed to oxygen (Sullivan et al 2002). Pyrite will tend to occur as more discrete crystals in the sediment matrix and will react more slowly when disturbed (over days to years). Layers of sulfidic material also occur in receiving lakes (e.g. Figures 5 - in this case the sulfidic material has recently oxidised / transformed to sulfuric material). If flushed out of the drain as floodwaters scour drain channels, they will oxidise and may become acidic. However, in some drains the ubiquitous presence of carbonates of calcium, magnesium and sodium in drain sediments and banks may neutralise drainage acidity. The extent to which this occurs, however, it dependent on whether the carbonates remain in contact with the acidic waters and are not armoured with precipitates or buried.

Monosulfidic black ooze

Monosulfidic Black Ooze (MBO) is readily observed in the surface sediments of most drains (Figures 4b & 4c) and in receiving lakes (e.g. Figure 5). The high nutrient environment, especially at the edges of drains and the activity of algae and micro-organisms cause reducing conditions to develop and the formation of black, smelly iron monosulfides and other sulfides. Erosion of organic rich topsoils and influx of saline ground-water, with low redox potentials (reducing), into the drains are also likely to contribute to MBO formation. MBO is very reactive if exposed to oxygen, but provided that the materials remain anoxic and undisturbed they are relatively non-reactive.

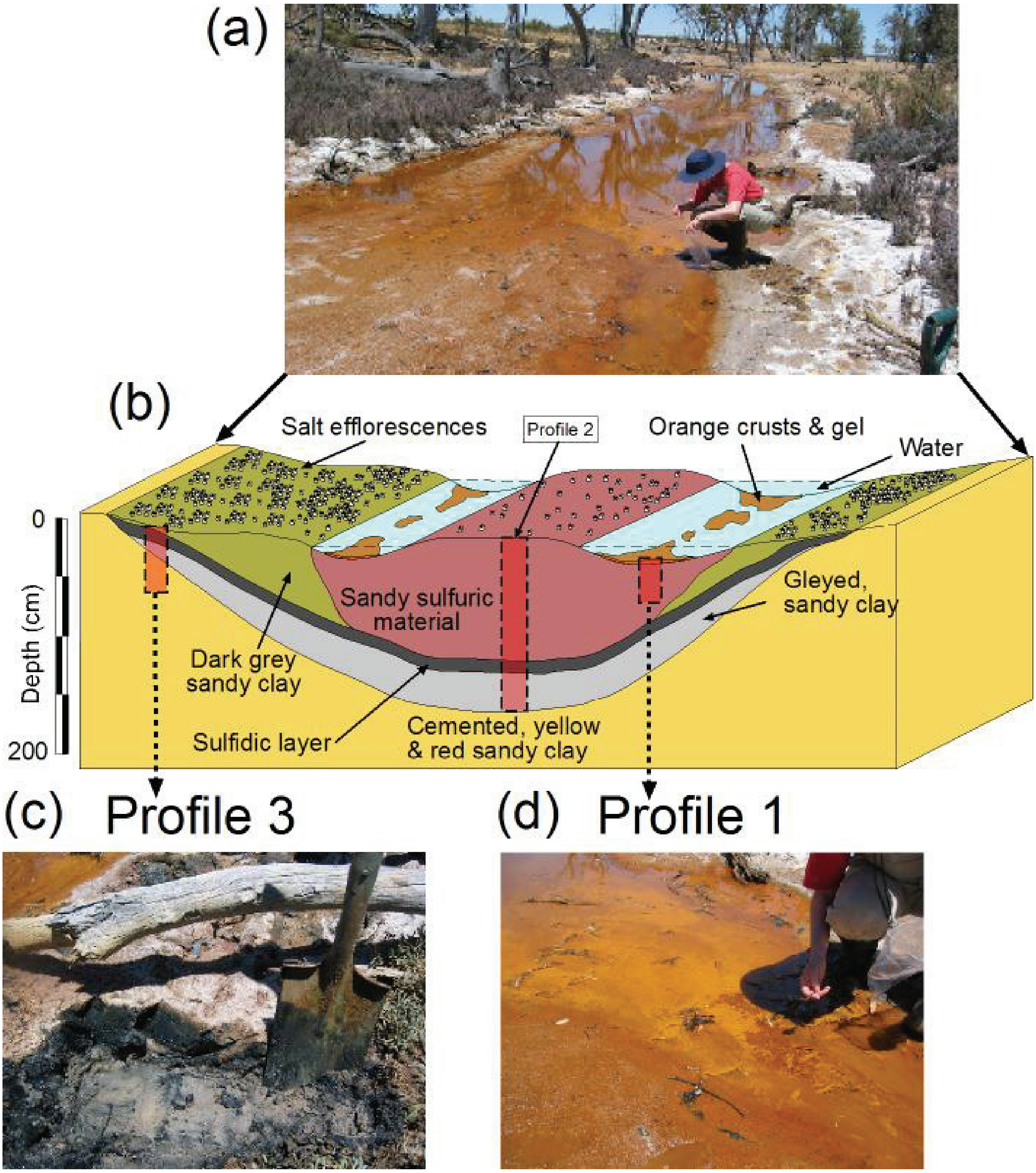

Figure 4. Schematic cross-section or hydro-toposequence (b) through a drain showing acid sulfate soils with orange crusts and gels (a and d) comprising mostly of Fe-oxyhydroxides (akaganéite: βFeOOH; see Figure 4) and Fe-oxyhydroxysulfates (schwertmannite: $Fe_8O_8(OH)_6SO_4$) in surface waters overlying soil horizons consisting of: (i) reddish sulfuric material (pH <3.5), soft and sandy in Profiles 1 and 2, (ii) black sulfidic material (pH >4) friable and sandy clay in profiles 1, 2 and 3, (iii) greyish gleyed sandy clay and (iv) yellow matrix with red mottles, hard, sandy clay. White salt efflorescences occur on the sides of the drain in profile 3 overlying a mixture of uniform black, sulfidic material and monosulfidic black ooze, which in turn overlies mottles of black, sulfidic material in a yellowish-greenish-grey to olive mottled clay.

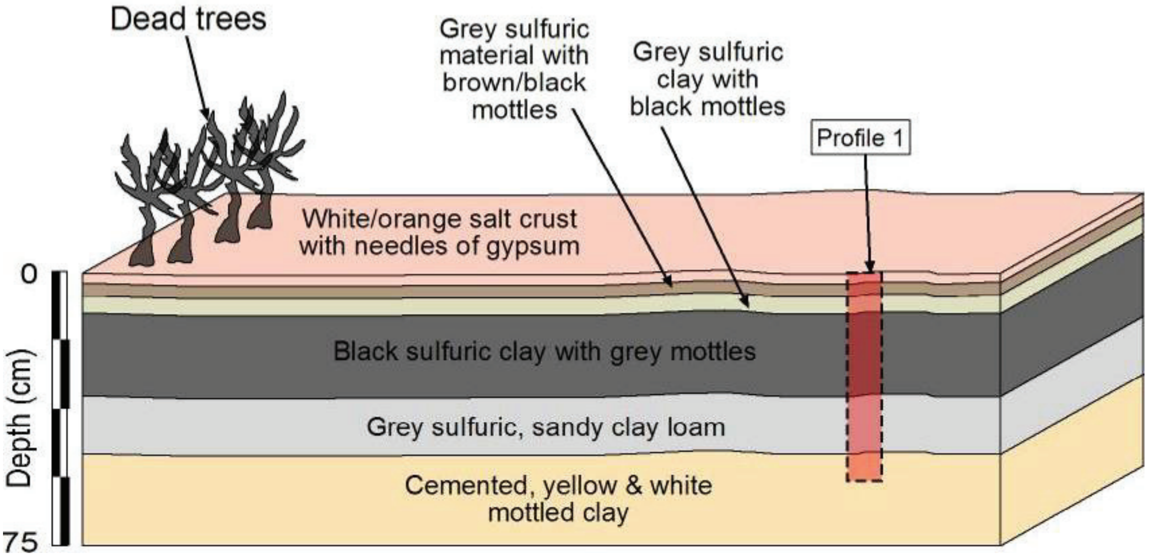

Figure 5. Schematic cross-section or hydro-toposequence through receiving lake D17 (Cunderdin Rd, Elachbutting) showing various white salt efflorescence crust with needles of gypsum overlying layers of black and grey sulfuric material (profile 1).

Sulfuric materials – including gels and precipitates

Subaqueous soil horizons and sediments in some drains and receiving environments are highly acidic (pH <3.5) and by definition classify as “sulfuric materials’ according to Isbell (2002). Acidity can form through several mechanisms:

(i) primarily by iron hydrolysis reactions (e.g. (Mann 1983) or ferrolysis (Brinkman 1979) when anoxic ground water containing dissolved ferrous ions is exposed to air and ferrous ions are oxidised to the ferric ions, which reacts with water to form orange -brown precipitates, gels or crusts of ferric oxyhydroxides, releasing free hydrogen ions in the process

(ii) When sulfidic materials are drained and exposed to air, they oxidise and produce sulfuric acid (e.g. Dent & Pons 1995). If the amount of acidity produced exceeds the buffering capacity of water and sediments, acidification occurs. Prior to draining, materials that can cause acidification by sulfide oxidation are called sulfidic materials (i.e. potential acid sulfate soil materials or PASS). Once sulfidic materials are drained, they may transform to sulfuric materials (i.e. actual acid sulfate soil materials or AASS).

In the WA wheatbelt drains, the dominant source of acidity appears to be the acidic, oxidised, iron rich shallow ground-water discharging to the drains (where the water is acidic prior to drainage), though formation of secondary minerals in the drain sediments provides additional pathways of acid storage and release.

Mineral precipitates and gels present in the drains were indicative of specific geochemical conditions occurring (or having occurred). The occurrence of bright yellow natrojarosite mottles in some of the clay-rich sulfuric horizons are indicative of acid conditions in the pH range 3.5-4. Similarly, the occurrence of orange coloured mottles, gels and crusts (Figures 4a & d) are indicative of schwertmannite and akaganéite, which forms from the oxidation of ferrous iron in acid conditions in the range pH 4-5. Many of these minerals occurred in drains above the ground-water level, indicating that there is a store of acidity in soil profiles that could contribute to future, if not current drainage acidity. The minerals also present a reactive surface that can alter the solubility of trace metals in the drainage waters (see below). Saline and subaqueous soils with sulfuric material may occur in receiving lakes (e.g. Figures 5 and 6).

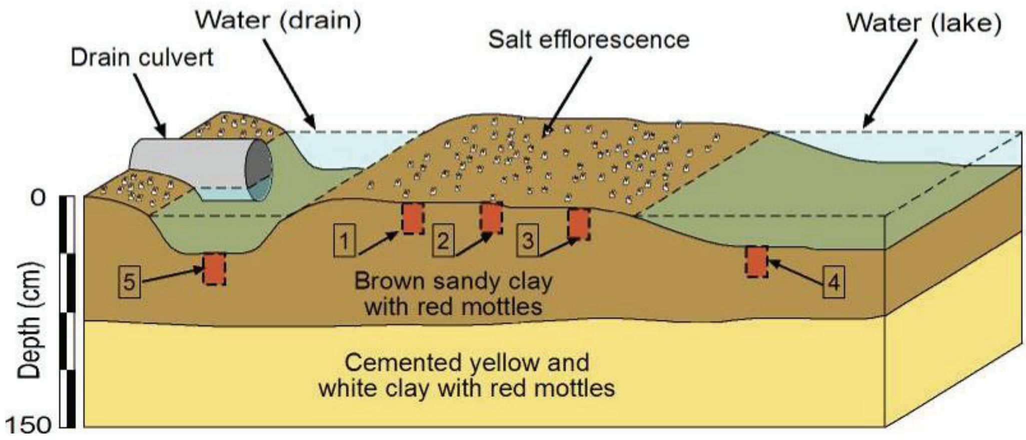

Figure 6. Schematic cross-section or hydro-toposequence through receiving lake D19 (Boodarockin, Koorda-Bullfinch Rd) showing: (i) acid water overlying subaqueous soils with sulfuric material (profiles 4 and 5) and (ii) white salt efflorescences overlying sulfuric material (profiles 1, 2 and 3)

Salt crusts - Sulfate-containing salt efflorescences and oxyhydroxysulfate minerals

Soluble sulfate/chloride-containing minerals in efflorescences are produced by evaporation of ground and capillary waters. These evaporite minerals reflect the geochemical reactions resulting from the combination of groundwater, drainage water and drained soils in regions. For example, zones under:

- alkaline conditions (e.g. surface soil horizons in the drain batters) where Na/Ca ratio >4, eugsterite, gypsum and thenardite (i.e. Na-Ca-sulfate salts) form
- acid conditions (e.g. interface of groundwater and drain batter in the base of drains) where Na/Ca ratio <4; bloedite and pentahydrite (i.e. Na-Mg-sulfate salts) form.

A predominance of sulfate-containing evaporite minerals occur in the drains because of the specific chemical composition and pH of inflowing drainage waters containing Na, Ca, Mg, Cl, Ba and SO_4. This composition probably arises from saline groundwaters enriched in sulfate (with other elements sourced from mineralised zones) seeping through soils. Declines in pH of the waters (due to oxidation of ferrous iron) on exposure to air or mixing with oxygenated waters can cause additional mineral dissolution and contribute to precipitation of a range of sulfate-containing minerals, each reflecting different geochemical conditions in the drains. These minerals include:

- pentahydrite, starkeyite, bischofite, bassanite, carnallite, rozenite, barite, halite and gypsum in sandy sulfuric horizons with pH <3.0
- natrojarosite and jarosite in clay-rich sulfuric horizons with pH 3.5-4
- eugsterite, bloedite, thenardite, glauberite, gypsum, thenardite, mirabilite, schwertmannite, lepidocrocite, akaganéite and colloidal poorly crystalline, pseudoboehmite-like (white) precipitates in sulfidic materials with pH >5.

Movement and accumulation of soluble salts is typical in many drains but, the salt crusts in the Avon catchment contain an assemblage of previously unrecorded types of sulfate-containing evaporite minerals as detected by X-ray diffraction and SEM (Figures 7- 9).

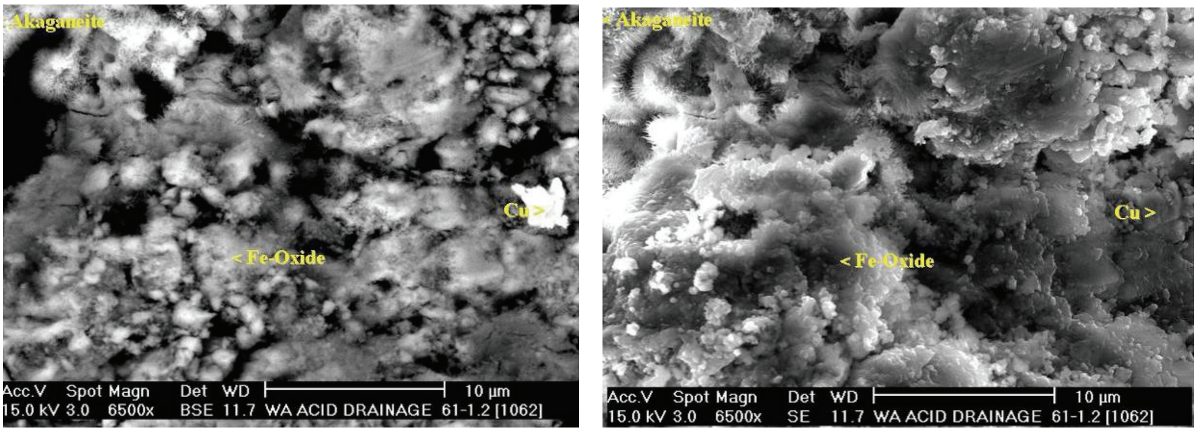

Figure 7. SEM images of orange coloured iron oxide crusts and gels in the soil profile 1 (d) near the centre of the drain shown in Figure 4. The crust and gel comprises mostly of akaganéite with some minor schwertmannite, which scavenges metals (e.g. Cu).

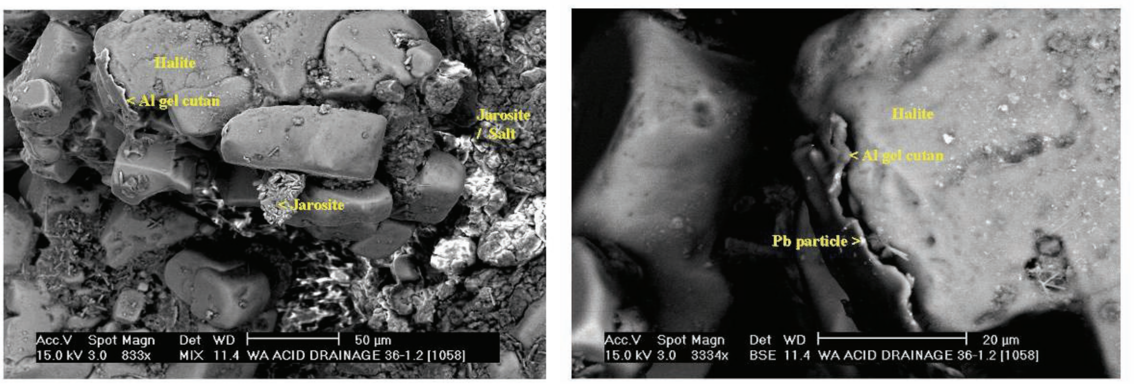

Figure 8. SEM images of salt efflorescence (halite and natrojarosite). The halite crystal has a coating (cutan) of Al-gel that contains small particles of lead (Pb).

The occurrence of these minerals is caused by the unique geochemistry of the drainage environment. The components of the evaporite minerals are generally derived by leaching of products from the oxidation of iron sulfides and then precipitated as specific minerals at various stages during the drying/evaporation of the drained soils and sediments. Sulfate-containing salt minerals accumulate steadily in the lower parts of drains immediately below/under the carbonate-rich or calcrete layers and above the sulfidic layers (Figure 4d) because of limited lateral movement of water to carry the soluble salts away in the drains. It is likely that annual cycling of these salts occurs, with evapo-concentration and metal accumulation during summer followed by dissolution of the salts and transport in drainage waters during winter rainfall. A change in mineral composition will indicate a change in the nature of the salts entering the system from drain or ground waters.

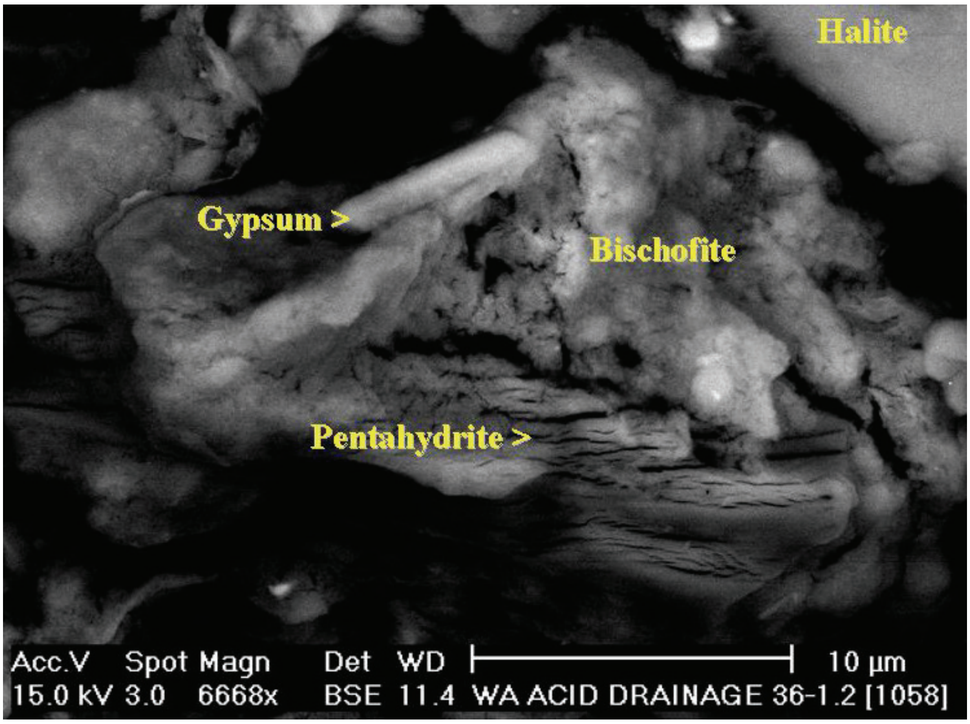

Figure 9. SEM image of a salt efflorescence in an acidic receiving lake (D19 - Boodarockin, Koorda-Bullfinch Rd) containing mixtures of halite (NaCl), gypsum (CaSO4 2H2O), pentahydrite (MgSO4.5H2O) and bischofite (MgCl2.6H2O) in close proximity to each other

These minerals range in morphology from thin, powdery, and very transient efflorescences to thicker, more persistent, soil-cementing crusts (e.g. Figures 9 and 11). Formation of these complex sulfate salts of Fe, Al, Na, Pb, Ca, As, Zn, Mg, jarosites, oxyhydroxysulfates and oxyhydroxides are indicative of rapidly changing local environments and variations in Eh, pH and rates of availability of S and other elements. As such, these evaporite minerals are indicators of soil-water processes operating in specific landscapes. A detailed understanding of these minerals and biogeochemistry in acid sulfate soils and sediments reveal important dual applications for environmental land management and mineral exploration.

Concentrations of Major and Trace elements in Drain Materials

Gels: The gels were mainly composed of kaolin and smectite (probably derived from drain walls), locally with significant amounts of quartz and halite, and less commonly, gypsum and akaganéite. Trace to minor amounts of feldspars, carbonates, jarosite or anatase may occur as phases within the gels.

Compared with other sample types, the gels contain significantly higher concentrations of Ti, Al, Fe, Cr, I, Nb, Sn, Th and V (see selected box plots in Figure 5.10). Gels could also contain relatively anomalous concentrations of Mg, P, As, Cd, Cu, Mo, Pb, Rb and Y. Rare earth elements tend to correlate with each other and with Y, whereas SiO_2 is negatively correlated with most elements. Niobium and Ti correlate with each other, presumably reflecting their occurrence in anatase. Strontium, Ca and Mg tend to correlate with each other, indicating that they occur in carbonates; Sr also correlates with Na, Br and Cl, suggesting some association with halides. Rubidium correlates with K, Ba, Cr, Ni and Zn, suggesting that these elements may be present in smectites.

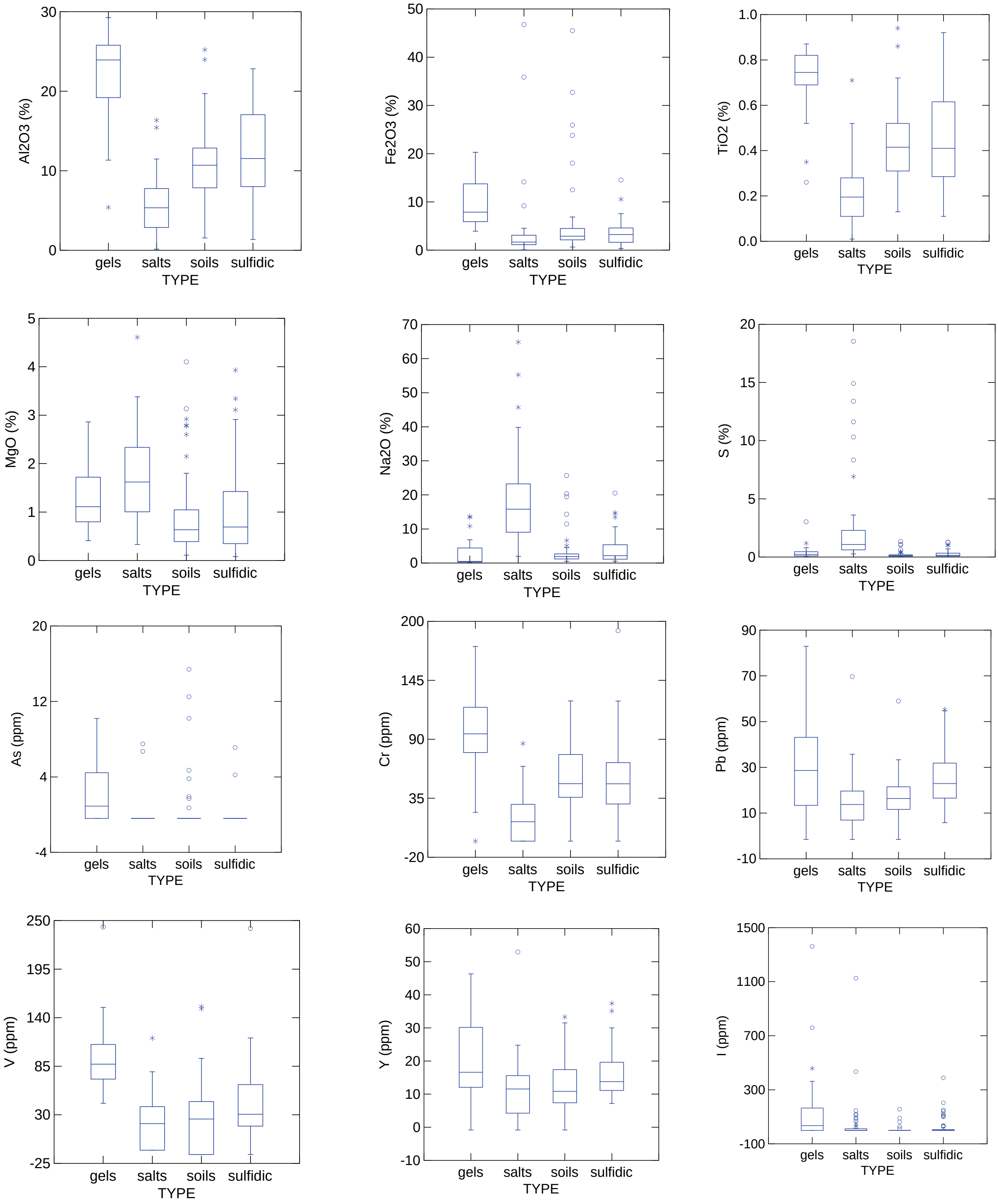

Figure 10. Concentrations of selected major and trace elements in gels, salts, soils and sulfidic materials in drains (box plots)

Salts: Halite and gypsum were the dominant salts, but may be associated with significant amounts of quartz. Minor to trace amounts carbonates, clay minerals and sulfates or chlorides of Mg, Ca, K and Fe were also present.

The salts contain the most significant concentrations of Ca, Na, Cl, S and Sr, and may contain anomalous concentrations of Mg, Cd, Cu, I and Mo (see selected box plots in Figure 5.10). They contain the lowest concentrations of Ti, K, Co, Cr, Ga, Nb and Ni (Figure 5.10), suggesting that these elements are immobile in this environment. Sulfur correlates with Na, Ca, Sr and Cl (reflecting their occurrence in gypsum and halite), but are negatively correlated with elements found most commonly in silicates (especially Si, Ti, Al, Fe, K, Ba, Cr, Ga, Nb and Rb. Rare earth elements correlate with each other and with Th and Y.

Soils: The soils were mainly composed of quartz, kaolin and smectite, with minor to trace amounts of feldspar, carbonate, Fe oxides and mica. Variable amounts of halite and gypsum could also be present.

Silicon exhibits negative correlation with most other elements, and as a consequence, elements found in silicate minerals (Ti, Al, Fe, Mn, Mg, K, Ba, Cr, Ga, Nb, Ni, Pb, Rb, Th, Tl, V, Y and Zn) tend to correlate with each other. Sulfur correlates with Mg, Na, Ca, Cl, Br and Sr, indicating their occurrence in halite, gypsum and carbonates; these elements are also negatively correlated with Si.

Sulfidic materials: The sulfidic materials are mineralogically similar to soils, except that Fe sulfides and oxides are more common. Sulfidic horizons contain anomalous concentrations of P, Ba and Pb (Figure 5.10), but are generally similar to soils in composition. Element associations are similar to those for soils, with most elements being negatively correlated with Si.

Evaluation of potential risks

Sulfate-containing evaporite minerals found in salt efflorescences in drains and receiving lakes are an integrated indicator of the complex geochemical conditions in these environments and play a critical role in drain erosion processes by salt fretting. These minerals are a transient storage of components (Na, Ca, Mg, Cl, Sr and SO_4), which will dissolve during rainfall and contribute to the formation of the saline monosulfidic black ooze in the drains. The metals concentrated within these salts (e.g. Al, Fe, Cd, Cu and Mo) also indicate a significant potential environmental risk since many are in a position to be flushed (potentially in concentrated pulses) into receiving environments by rainfall events.

Gels and iron rich precipitates that form in and on the gels pose efficient scavengers of trace metals (eg Cr, Sn, Th, V and occasionally As, Cd, Cu, Mo), but the fine colloidal nature of these materials places these at risk of being suspended and flushed from the drains by low flow velocities. The chemical association of the metals with the precipitates and gels is not known and it is conceivable that the materials could act as transport vectors for metals from the drains if not managed.

The accumulation of significant sulfidic materials increases the risk of additional acidification of drainage waters. Discharge of acidic, ferrous iron rich groundwater (Figure 5.4a & b) and the subsequent oxidation of this appears to be the main processes causing low pH, however the contribution of this source compared with sediment sources over the life of the drain is not clear. Acidification could conceivable be dominated by the release of stored acidity from sulfidic materials after cessation of ground-water discharge (and drying occurs) or if the materials are excavated or flushed from the drains. This acidification risk is greatest where carbonate minerals are absent or spatially separated from the sulfidic drain sediments.

Accumulations of metals within the sulfidic materials further compounds the geochemical risks posed by drains to receiving environments. In addition to lowering pH, disturbance and oxidation of sulfidic materials during flow events could lead to significant, short-term pulses in dissolved metal concentrations in surface waters, including aluminium, iron and other metals released from the sulfidic materials (e.g. Pb, *Cu or Cr, see Figures 7 & 10). Drains sampled in eastern areas were typically acid and contained large amounts of Fe, Al, salt, metals (Pb, Cr, Mn, As) and the rare earth elements, lanthanum, cerium (see Section 4). The increase in solubility of metals combined with hydrological variability of the drains under acidic conditions may be more harmful to biota than the low pH itself.

Accumulations of iron precipitates on vegetation blown into the drains poses a risk to hydrological function, particularly if burnt. The effect of burning of vegetation residues at D14 (Elachbutting) is a dramatic example of where an intense fire resulted in the formation of an irreversibly fused, iron plug, which blocked a drain pipe (Figure 11).

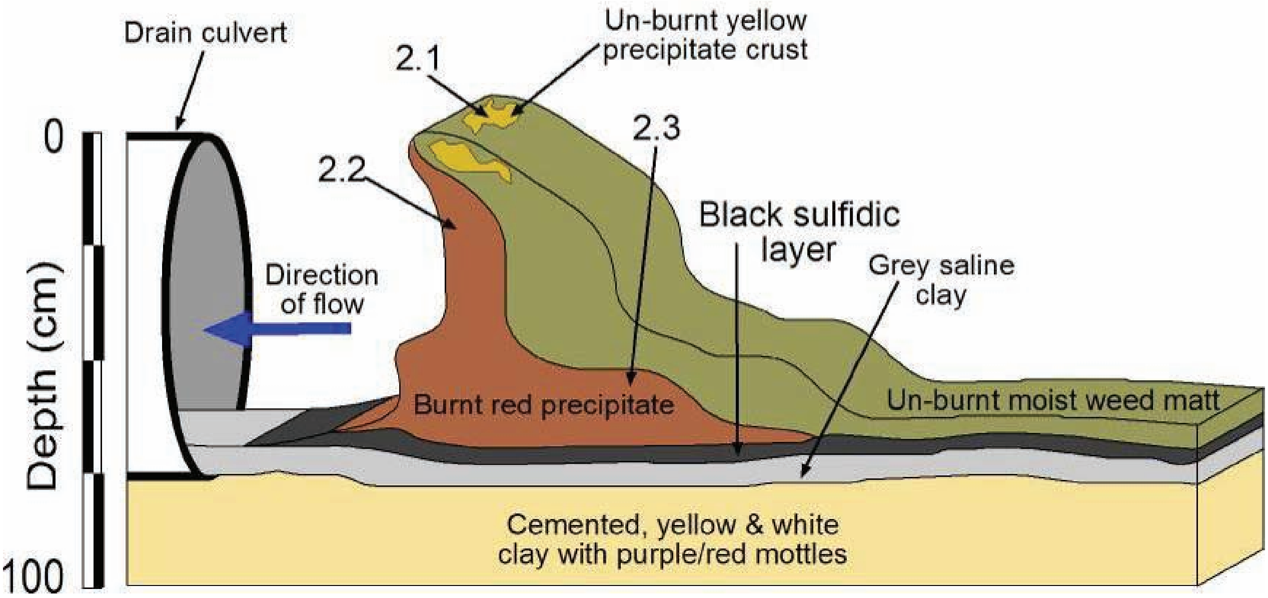

Figure 11: Schematic cross-section or hydro-toposequence through drain D14b (Elachbutting) showing: (i) black sulfidic layer in the base of the drain underlying a hard cemented (ceramic-like) burnt zone, which has permanently clogged the outflow pipe at the entrance of the drain culvert and (ii) un-burnt zone.

CONCLUSIONS AND MANAGEMENT RECOMMENDATIONS

As a result of the data analysis from this work the following approaches, methods, assessment and management guidelines are suggested:

Summary of approaches developed:

- Developed experimental procedures for field sampling in the WA Wheatbelt to determine changes in soil and water characteristics in drains and receiving environments
- Established key laboratory analyses methods for gels, salts, soils and sulfidic materials in drains and receiving environments
- Devised and applied a systematic web-based data system for acquisition, collation and communication of detailed data sets (e.g. soil morphology, chemistry and mineralogy) dealing with gels, salts, soils and sulfidic materials in drains and receiving environments
- Identified and quantified formation processes of the hypersaline soils (drain batters) and sodic soils (edge of drain) in a range of drains and receiving environments
- Identified and quantified formation processes of the “reddish-brown and orange-yellow precipitates or gels” of ferric-oxyhydroxides and ferric-oxyhydroxysulfates, which release free hydrogen ions in the process of formation (develops when the ferrous iron rich waters in the drains and receiving lakes containing dissolved ferrous ions are exposed to air and ferrous ions are oxidised to the ferric ion minerals - iron hydrolysis)
- Identified various types of hydrated oxyhydroxides (ferrihydrite), iron oxyhydroxysulfates (schwertmannite and akaganéite), oxyhydroxides (goethite) and oxides (hematite) in various localities in the drains and receiving environments. Established that these minerals are indicative of rapidly changing local environments and variations in Eh, pH, rates of availability of S / other elements and temperature (e.g. burning). As such, these minerals are indicators of soil-water processes operating in these environments
- Identified and quantified occurrences of sulfidic and sulfuric materials (acid sulfate soil materials) in drains and receiving environments. Established that excavation or disturbance of the sulfidic materials in drain sediments risks oxidation of pyrite and release sulfuric acid to form sulfuric materials
- Deduced that the specific types of salt efflorescences are an integrated indicator of complex biogeochemical conditions and transformations occurring in the drains and play a critical role in drain

erosion processes by salt fretting. Salt efflorescences, especially the sulfate containing minerals, can cause detachment of soil during crystal growth and degrade drain walls

- Concluded that the soluble sulfate/chloride-containing minerals in efflorescences play important roles in the transient storage of components (Na, Ca, Mg, Ba, Sr, Cl, Br, I and SO_4). They can detach soil during crystal growth and degrade drain walls. They will also dissolve during rainfall and contribute to formation of saline monosulfidic black ooze in drains and receiving environments
- Data showed that the gels and sulfuric horizons contain elevated trace element and metal concentrations (Al, Cu, Pb, Cr, Pb, Zn, Mg and rare earth elements)
- Developed list of key management strategies: some specific to drains: e.g. anthropogenic burning results in the formation of irreversibly fused, particulate and discrete iron-rich artifacts, which can block drain pipes
- Several new assemblages of sulfate-containing evaporite minerals, oxyhydroxysulfate minerals and sulfides have been identified in the wide range of ASS environments that have formed in drains in the Avon catchment
- New occurrences and formation of "types of salt efflorescences" are an integrated indicator of the complex biogeochemical conditions and transformations occurring in ASS and play a critical role in water quality and erosion processes.

Suggested management recommendations:

- Drains need to be designed and managed to minimise turbulent flow velocities to minimise flushing of precipitates and gels (frequently containing trace metals) and disturbance of sulfidic sediments (being a store of acidity and trace metals). In particular, entry of surface waters from catchments to the drains should be avoided without measures to contain flow velocities
- Drain design to maximise hydrological residence times and formation of precipitates will contribute to maximising retention of trace metals within the systems
- Management of trace metal mobility and acid release will need to be considered when maintenance cleaning of sediments from drains is carried out. This might include mixing of sediments with alkaline drain spoils, placement within depressions on drain spoils (allowing drying and containment but contact with alkaline spoils) or collection and containment in a site without risk of off-site impacts (i.e. outside of a surface flow path)
- Accumulated vegetation in drains (e.g. roly poly residues) is best removed using an excavator particularly where large compact accumulations of materials occur in conjunction with iron precipitates. Burning of residues can result in the formation of a cemented iron plug that can significantly impede flows.

GENERAL MANAGEMENT RECOMMENDATIONS

It is vital for all landholders, community groups, drainage contractors and local governments in the Avon catchment to be aware of the many impacts that result from: occurrence of sulfuric materials and disturbance of sulfidic materials as these have important consequences for environmental, engineering, economic, and quality of life perspectives. Disturbance and oxidation of sulfidic material can to destroy wetlands, acidify and deoxygenate waterways and increase the incidence of fish kills and disease, contaminate valuable groundwater resources and public park space, facilitate the mobility and accumulation of heavy metals, corrode, attack and destabilise roads, concrete and steel infrastructure, stimulate blooms of marine blue-green algae, decrease the agricultural productivity of land, increase odour problems and increase mosquito and arbovirus incidence.

ACKNOWLEDGEMENTS

We are grateful to Clare Wright, Jason Kirby, Adrian Beech and other staff at the CSIRO laboratories in Adelaide for water analysis.

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CHAPTER 13

FARM-BASED TREATMENT OF ACID DRAINAGE WATERS COUPLED WITH INLAND ACID SULFATE SOIL MATERIALS IN WESTERN AUSTRALIA

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INTRODUCTION

Shallow saline groundwaters are extensive in the Western Australian (WA) Wheatbelt, particularly in broad valley floors, and the area affected by these is expected to keep increasing for 50 years or more (Hatton *et al* 2003). This threat has led to increasing use of engineering methods, such as deep (2–3m) open drains and groundwater pumping, to manage rising groundwaters in broad valley floors and protect or recover low-lying land from salinisation (Dogramaci and Degens 2003). More than 5000 km of deep open drains have already been constructed, mostly at farm scales, and there is interest in expanding this to catchment scale drainage networks. This interest has arisen because of the poor success rate of many alternative, mostly vegetation based approaches for managing water-table in broad valley floors. Recent work has identified that many shallow groundwaters in the inland WA Wheatbelt are acidic (pH< 4.5) and may have significant concentrations of trace metals in addition to high concentrations of dissolved salts (Shand & Degens 2008). Deep open drains can intercept these waters and potentially accelerate the transport of acidity and trace metals from catchments.

The ongoing use of deep drains will require safe, practical, and cost-effective options for managing the disposal of such saline, often acidic, waters. Geochemical processes within drains are influenced by the formation of inland acid sulfate soil materials (Fitzpatrick *et al* 2008) and compound the risks that the drains pose to receiving environments. Treatment of drainage waters may be necessary to halt or control the onset of these inland ASS processes and the impacts of drainage waters on off-site environments.

The acidic waters in WA wheabelt drains are similar to those generated by acid mine drainage and oxidising acid sulfate soils, only more saline (Degens *et al* 2008). A wide range of technologies has been developed and successfully adapted and applied to treat acidic drainage waters (PIRAMID Consortium 2003; Younger *et al* 2002; Waite *et al* 2002). Treatment may be either active or passive. Active treatments use neutralising agents or modified reactive materials in mixing, pumping and settling systems to treat acidity and remove trace metals and are often intended for short-treatment periods or large acidity loads. By contrast, passive treatments involve low maintenance; are frequently gravity–driven (i.e. no pumping), and are intended for long-term operation. Passive treatments can involve the use of neutralising agents such as calcium carbonate or microbial-based neutralisation and metal treatment. The latter approach involves microbial reduction of sulfate to generate alkalinity and promote formation of sulfide minerals that can remove trace metals from waters.

We report on the results of adapting and evaluating selected treatment technologies for acid mine drainage and acid sulfate soils to treat acidic saline waters generated by deep open drains in the WA Wheabelt. Such treatments would be applicable to the treatment of drainage water from any inland ASS. Field-scale evaluations consisted of lime-based and compost-based (sulphate-reducing) treatment systems within and at the discharge point of drains. Results of two field trials are presented, with an outline evaluation of a range of other treatment options based on WA-based treatment trials.

Materials and methods

Six acidic water treatment evaluations were established in or at the end of drains at Doodlakine and Beacon, in the eastern WA Wheatbelt. The treatment trials were designed for specific acidity loads and treatment durations. These trials consisted of treatments at source within drains and at the end of drains prior to discharge:

- In-drain lime-sand application: application of lime-sand to form riffle beds within a drain (45 tonnes of lime-sand to treat water for > 2 years)
- Composting drain: creation of an anerobic wetland in ponded sections of a drain (200m section) using wheat straw mixed with sheep manure (5% by volume)
- Lime-sand pond: passive treatment using lime-sand lining a shallow 20m x 25m holding basin for drainage waters (90 tonnes of lime-sand to treat water for >1 year). Water was pumped in and treated in batches of approximately 500kL after which water was pumped out
- Lime-sand tank reactors: pumping of drainage waters through (a) 1.5 tonnes of lime-sand suspended on 4 tables in a 9000L tank or (b) through 400-500kg of lime-sand fluidised in pulsed flow within a 779L column (2.85 m length, 0.6m diameter)
- Hydrated lime dosing: pumping of drainage waters with pH controlled dosing (using a proprietary dosing unit) with 40% $Ca(OH)_2$ suspension prior to discharge to a creek line
- Anaerobic composting wetland: creation of a 300m^2 (100m length x 3m width) shallow (0.5m depth) anerobic composting wetland using wheat straw mixed with sheep manure (5% by volume) for treatment of waters at the end of a drain prior to discharge.

The lime-sand used for the trials consisted of 92% $CaCO_3$ with 99% by weight <0.5 mm sand. A mixture of locally available organic materials (straw and sheep manure) was used in the composting systems based on previous reports (PIRAMID Consortium 2003). Only the results of the lime-sand riffle bed and compost wetland are presented in detail here.

The effectiveness of treatment was evaluated by monitoring the volume and quality of water entering and leaving the treatment systems within the drains (lime-bed, in-drain compost system) and at the ends of drains (lime-sand tank reactor, compost wetland and hydrated lime dosing site). Volumes were continuously monitored using flow meters or water level recorders with V-notch weirs.

Grab samples were taken for water quality and were filtered through 0.45 µm membrane filters in the field then preserved by either addition of ultrapure nitric acid (to a final concentration of 0.1%) or else retained unacidified and stored at 5 degrees C. The concentrations of Cu, Zn, Co, Ni, Cr, Mn, P, V, Fe, Al, Ca, Mg, Ti, Na, K, and S were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The elements Ag, Ba, Cd, Mo, Pb, Sb, Sn, Y, Hf, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U and Se were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Arsenic was also determined using the hydride generation coupled to ICP. Selected anion analyses (SO_4, NO_3, NH_4, PO_4) were completed using ion chromatography. Titratable acidity and alkalinity was measured by titration to a pH end-point of 8.3 with NaOH and titration to a pH end-point of 4.5 with H_2SO_4, respectively. Titratable acidity for these trials was similar to acidity calculated from major metal ions (mostly because acidity was dominated by soluble aluminium) and was used to calculate net acidity (acidity – alkalinity). Water sampling also included measurements of in-situ pH, EC, temperature and Eh. Only selected results from these analyses are discussed here.

RESULTS AND DISCUSSION

Drainage water quality

The saline drainage waters used for the field evaluations ranged between pH 2.8 (in summer) to pH 4.2 (in winter), containing 20–250 mg Fe/L, 5–150 mg Al/L and 5–10 mg Mn/L contributing to total titratable acidity ranging from 150 to 900 mg $CaCO_3$/L. Concentrations of total dissolved salts in the waters ranged from 31 000 to 110 000 mg/L and were dominated by Na and Cl. The ranges of trace element concentrations in the acidic waters were 0–8 µg As/L, 0–4 µg Cd/L, 1–20 µg Cu/L, 30–150 µg Ni/L 12–260 µg Pb/L, 10–340 µg U/L and 5–120 µg Zn/L.

Treatment evaluations

The effectiveness of lime-sand in passive treatment situations was limited by high concentrations of dissolved iron in the waters, resulting in rapid coating of the lime-sand with iron oxides (armouring), and decreased neutralisation rates. This is a common problem encountered when neutralising iron–rich acidic waters in passive treatment situations using slow dissolving materials such as $CaCO_3$ (PIRAMID Consortium 2003). Application of lime-sand to an acidic drain as a riffle bed (designed to slow armouring) was effective in increasing water pH from 3.3 to 4.4 and reducing acidity by up to 32% for up to 10 days before significant armouring occurred (Figure 1). Some removal of trace metals such as Pb (from 26–39 µg/L to 16–19 µg/L) was achieved, though there was no significant effect on the concentrations of most. The onset of armouring resulted in neutralisation rates decreasing to a level where less than 20% of the acidity in water flowing through the lime-sand riffles was neutralised (Figure 1). Despite this, consistent neutralisation of approximately 5% of the acidity load was maintained for at least five months after the onset of armouring.

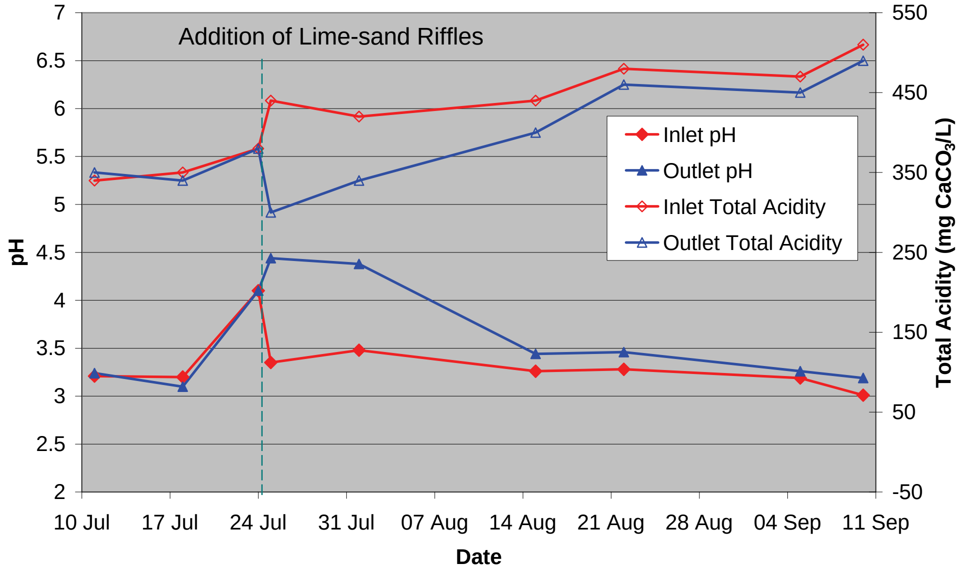

Figure 1: pH and total titratable acidity of inflow and outflow waters for a 200m section of drainage channel treated with lime-sand riffles (drainage flows of 130–216 kL/day).

Similar problems with armouring of lime-sand occurred in the 9000L tank reactor within 2 hours when acidic water (pH 3.1) was percolated through lime-sand suspended on 4 tables. These problems did not occur when lime-sand was fluidised in a pulsed flow (on 1 minute cycles) within a column tank reactor. In a single pass through the system, the water pH was increased from 2.9 to more than 5.6 and net acidity was reduced to less than zero (ie outflow waters contained residual alkalinity), despite the waters containing more than 20 mg Fe/L. This effectiveness was sustained for more than 48 hours of treating waters at a rate of 45L per minute (equivalent to 64.8 kL per day). Over several weeks of continuous treatment, acidity treatment fell to a consistent 50-55% of inflow acidity (which ranged from 580 to 620 mg $CaCO_3$/L). Notably, passage of waters through the reactor does not remove any trace metals and these would be expected to be removed from the water by adsorption to alkaline precipitates and sediments in oxidation and settling ponds.

Use of lime-sand as a lining for an evaporation basin was initially effective (for the first two batches) for treating acidic waters, though neutralisation times ranged from 30–50 days. Treatment effectiveness diminished in subsequent batches mainly because of the formation of a clay gel interlayered with a gypsum–rich crust over the lime–sand bed, rather than distinctive armouring by iron oxides. Removal of this crust rejuvenated the effectiveness of this low-cost treatment.

Compost treatment systems harnessing microbial sulfate reduction were effective in neutralising highly acidic waters and removing a wide range of trace metals from these waters for at least six months. Both composting treatment systems achieved high rates of treatment (>95% acidity load), however this was not maintained in the in-drain anaerobic compost treatment system. Inflow pH to the compost wetland decreased from 3.5 to 2.9 over 160 days; although the system consistently maintained an outflow pH of greater than 5.5 (Figure 2). Minimal maintenance was needed over this period, solely consisting of occasionally checking the inflow and clearing amorphous mineral precipitates forming in the outflow pipes. Both the in-drain anaerobic compost treatment and anaerobic compost wetland could remove a wide range of trace elements such as Al, Cu, Cd, Ni, Cu, Zn and Pb to less than 10% of inflow concentrations, though had little effect on Mn, Cr and As. Declining performance in the in-drain compost system was linked with acidity loads being greater than expected which contributed to gradual acidification of the system. Under-performance can be overcome by charging the organic mix with a greater proportion of decomposable organic matter (initially added as sheep manure) to fuel rates of microbial reduction of sulfate at a rate sufficient to cope with the acidity load to the drain section.

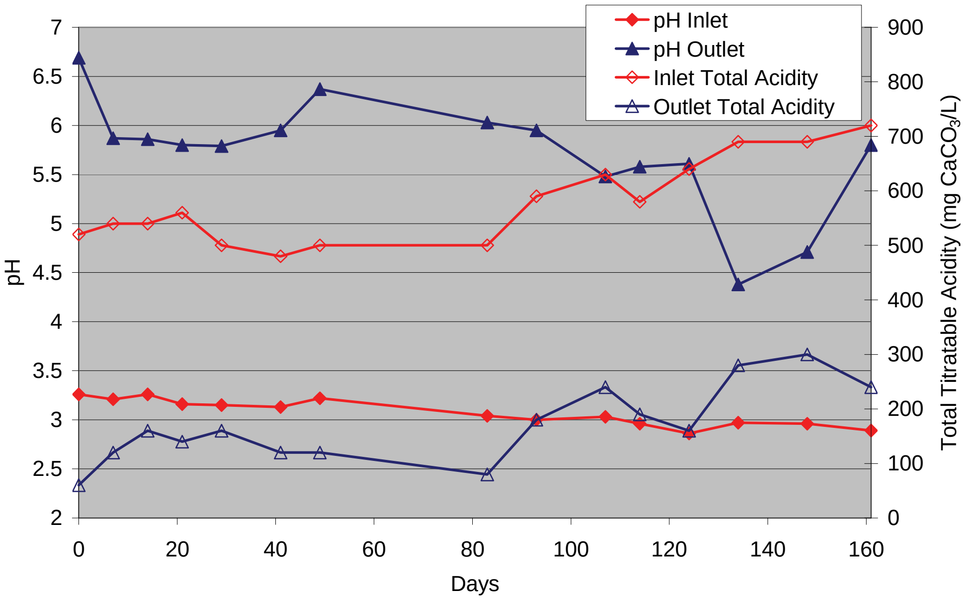

Figure 2: pH and total titratable acidity of inflow and outflow waters for the compost wetland (treating an average of 3.2 kL/day).

Treatment comparison

In a comparative evaluation of the treatment options it was clear that anaerobic compost treatment systems show most promise in achieving low–cost passive treatment of these waters over long time periods (Table 1). In comparison, lime-sand would have limited applications in treating acidic drainage waters containing high iron concentrations without use of fluidised flow systems with regular monitoring and maintenance (Table 1). Reasonable and consistent performance of lime-sand as a neutralising agent appears achievable with a pulsed flow lime-sand reactor offering a low-technology, potentially cheap option (based on the low cost of lime-sand) for waters with high acidity and few trace elements. However, full treatment using a lime-sand reactor would require multiple holding ponds and at least 2 treatment units. In contrast, treatment using the more reactive hydrated lime represents a very attractive option for the short term, though is not ideally suited to long-term treatment (over more than 12 months) due to ongoing pumping costs, reagent supply and reagent storage requirements (Table 1). An important consideration for all neutralising approaches is the need to trap and store iron and aluminium precipitates (which can adsorb and concentrate trace metals) prior to down stream discharge or re-use of waters (e.g. for desalination, saline aquaculture, solar ponds or salt harvesting). Within composting systems, these are mostly retained within the system design (ie not requiring removal).

Land availability may limit where compost wetlands can be used. The 300 m^2 pilot compost wetland treated acidic waters at a conservative, sustainable average of 1.1 kg $CaCO_3$ per day, which suggests that up to 1.2 ha of land would be required to treat average baseflow acidity loads from a drain discharging at

1 L/s (assuming a titratable acidity of 500 mg $CaCO_3$/L). Long-term effectiveness of this treatment depends on attention to design in order to handle expected acidity loads and use of organic materials that will support sustained rates of sulfate reduction. The trials demonstrate that even with a minimal mix of cheap and locally available organic materials (5-6% sheep manure in straw) it is possible to achieve extended treatment of highly acidic waters.

Table 1: Summary of effectiveness (acidity and trace metals) and operational maintenance requirements of a range of passive and active saline acidic drainage treatment options trialled in the WA Wheatbelt.

Treatment Option	Effectiveness (acidity)	Effectiveness (trace elements)	Operational maintenance requirements
Passive lime-sand riffles (in-drain)	Very limited with Fe-rich waters (>5 mg/L), greater with Al dominated acidity	Very limited adsorption of metals (poor Fe floc development)	• Retention of Al precipitates within drainage channels and regular cleaning (no Fe floc formation occurred) • Annual reapplication of lime to drains • Regular, monthly removal of iron crust will be required to achieve >20% acidity treatment efficiency
Passive lime-sand lined storage/ evaporation basin	Initially high effectiveness (>80% acidity) decreasing with time (beyond 1 month). Limited with Fe rich waters	Effective removal of some elements including Al, Fe, Pb and to a lesser extent U, Ce, La, but not Mn, Ni or Se.	• Annual removal and disposal of Al and Fe precipitates (with trace metals) and fine clays washed into basin may be required • Regular reapplications (broadcasting) of lime or removal of iron/gypsum crusts may be required to maintain high acidity treatment effectiveness
Active lime-sand tank reactor (vertical flow, fluidised reactor)	Can be >100% during first 48 hours, sustained at 50-60% over longer term.	No removal in reactor. Dependent on elements treated & Fe floc formation (removal by adsorption to Fe precipitates/ sediments).	• Retention of Al and Fe precipitates (with trace metals) within settling tanks/ponds • Cleaning and disposal of Al and Fe precipitates (also likely to contain trace metals) • Ongoing addition of lime-sand and regular, monthly removal of non-reactive/armoured lime-sand • Pump maintenance and continuous power supply
Active hydrated lime dosing (dosing unit with pumping, dosing and mixing)	Highly effective for a range of acidity loads to target end-point pH. Aeration can be included to facilitate treatment of Fe-rich waters	Can be highly effective for most elements, except Mn and Ni (in trials).	• Retention of Al and Fe precipitates (with trace metals) within settling tanks/ponds • Cleaning and disposal of Al and Fe precipitates (also likely to contain trace metals) • Ongoing reloading of hydrated lime slurry (requiring specialist transport and on-site storage) • Pump, dosing and mixing unit maintenance • Continuous supply of power/fuel for pump
Passive anaerobic compost wetland	Can achieve >100% treatment of acidity (pH>6) for more than 6 months when design and organic mix is optimal.	Highly effective for a range of trace elements (e.g. Al, Cu, Cd, Fe, Ni, Pb, U, Zn) but not Mn.	• Periodic additions of new organic matter may be required (every 2–5 years?) • Occasional cleaning of outflow pipes and flow checks
Passive in-drain anaerobic compost system	Can achieve >100% treatment of acidity (pH>6) for more than 6 months when design and organic mix is optimal.	Highly effective for a range of trace elements (e.g. Al, Cu, Cd, Fe, Ni, Pb, U, Zn) but not Mn.	• Periodic additions of organic matter may be required (possibly every 2–5 years) • Sediments will require on-site containment and/or treatment on cleaning of drains (every 5–10 years)

The uncertainties regarding performance of individual passive treatment options over months to years can potentially be offset using a combination of sequential treatment options distributed throughout a drainage network (often called a treatment train). This can potentially provide some level of redundancy and capacity to handle changes in acidity loads over future years. Use of multiple options distributed throughout a drainage system also mitigates risks due to under-sizing treatment options. The success of many passive treatment options is dependent on sizing to handle expected acidity loads, which may be difficult to obtain for WA Wheatbelt drains prior to construction.

Management Implications

- Marginal gains in acidity treatment and metal removal can be made with cheap, low-technology passive treatments using a range of locally available materials
- Anaerobic compost-based treatment systems can effectively treat acidic drainage waters removing a wide range of trace elements, but construction will require land area and consistent performance depends on correct sizing and use of suitable mixtures of organic materials during construction
- Passive treatment options are likely to be most applicable in many Wheatbelt drains over the long term since landholders are not likely to have the time to maintain and service active treatment systems. Passive treatment options concentrate effort in the design and construction stages
- It may be possible to integrate passive treatment options of acidic drainage waters within drainage systems to achieve progressive neutralisation of acidity and removal/retention of trace metals at source and during transit down drains. This may also need to be followed by final polishing treatment at the discharge point of drains
- Active treatment can be highly effective in treating acidic drainage waters, but will involve greater on-going maintenance and costs than passive treatment systems.

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CHAPTER 14

PRELIMINARY ASSESSMENT OF THE OCCURRENCE OF SULFIDIC MATERIALS IN SEMI-ARID WETLANDS WITH CONTRASTING WATER AND SALINITY REGIMES

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INTRODUCTION

Landscape salinisation is a widespread phenomenon resulting from irrigation agriculture and river regulation in arid and semi-arid climates (Jolly *et al* 2008). In the Lower River Murray floodplains of Southern Australia, it is currently estimated that 25% of the floodplains area is impacted by salinity, with this proportion potentially increasing to 50% by 2050 (River Murray Water Catchment Management Board 2003). Salinity is threatening the health of many ecosystems in these floodplains, including several wetlands of high conservation value and large tracts of River Red Gum (Eucalyptus camaldulensis) forests. There are several causes for the salinisation of the floodplains, including a decreased flooding frequency and an increased input of saline groundwater induced by vegetation clearing and irrigation returns (Jolly 1996). Salinisation is also caused by increased soil waterlogging in the floodplains, including from raised pool levels behind weirs and barrages and the conversion of wetlands into disposal basins for excess irrigation water (Walker 1992, Jolly 1996).

We hypothesised that the changes in the hydrological regime and the increase in the salinisation of Lower River Murray floodplains during the last century should have fostered the accumulation of sulfidic materials in floodplain wetlands. "Sulfidic materials" here are defined as any soil material or sediment with sufficient concentrations of reduced inorganic sulfur, such as pyrite (FeS_2) and monosulfides (FeS), to be considered an environmental hazard. Environmental risks associated with sulfidic materials include acid sulfate soils (Dent and Pons 1995), deoxygenation of water column following sediment resuspension (Sullivan *et al* 2002a), H_2S toxicity (Luther *et al* 2004) and aesthetic concerns such as the production of foul odours when wetlands are dried (Lamontagne *et al* 2004; Hicks and Lamontagne 2006). In Lower River Murray wetlands, sulfidic materials would have recently formed because 1) the increase in SO_4^{2-} concentration co-incident with the increase in salinity would have favoured greater rates of sulfate reduction and 2) the loss of the drying phase in formerly ephemeral wetlands would have favoured the storage of sulfides over their loss by oxidation. In the Murray-Darling Basin, SO_4^{2-} concentrations vary from as low as 1 μmol L^{-1} in some freshwater environments (Mackay *et al* 1988) to >10 mmol L^{-1} in saline groundwater (Herczeg *et al* 2001). Holmer and Storkholm (2001) quote a threshold sulfate concentration ranging between 8 to 40 μmol L^{-1} to induce sulfate reduction and Berner (1984) gives a value of 5 mmol L^{-1} for when sulfate reduction rates become independent of sulfate concentration. Thus, even moderate salinisation of freshwater wetlands could substantially increase their rates of sulfate reduction.

The hypothesis that sulfidic materials have recently developed in River Murray floodplains was tested by sampling nine wetlands representing a gradient in water regime and salinity in the Lower River Murray region. The wetlands were small (15 – 380 ha), shallow (<2 m), and varied in salinity and water regime from freshwater ephemeral wetlands to permanently flooded hypersaline disposal basins. We predicted that the concentration of sulfides in sediments would increase from the freshwater to the more saline end-member of the salinity gradient. Because many of the currently proposed remediation strategies for wetland salinity in the Murray-Darling Basin will involve exposing sediments to the atmosphere, in a second objective, the acidification risk of the wetlands was assessed using a series of pedological and mineralogical analyses.

Materials and Methods

Detailed site description and sampling methods can be found in Lamontagne *et al* (2004; 2006) and will only be briefly summarised here. A range of wetland types were sampled including an ephemeral wetland which had been dried since 1996 (Clover), fresh to brackish permanent wetlands (Merreti, Woolpolool, Bottle Bend, Ross), and saline to hypersaline floodplain disposal basins (Hart, Ramco, Berri and Loveday). Disposal basins are former ephemeral wetlands which have been isolated from the river by control structures and are used to store and evaporate excess drainage from nearby irrigated areas. All wetlands were sampled in August 2003, when low water levels brought by a drought in the Murray-Darling Basin had exposed the sediment surface in many of the wetlands.

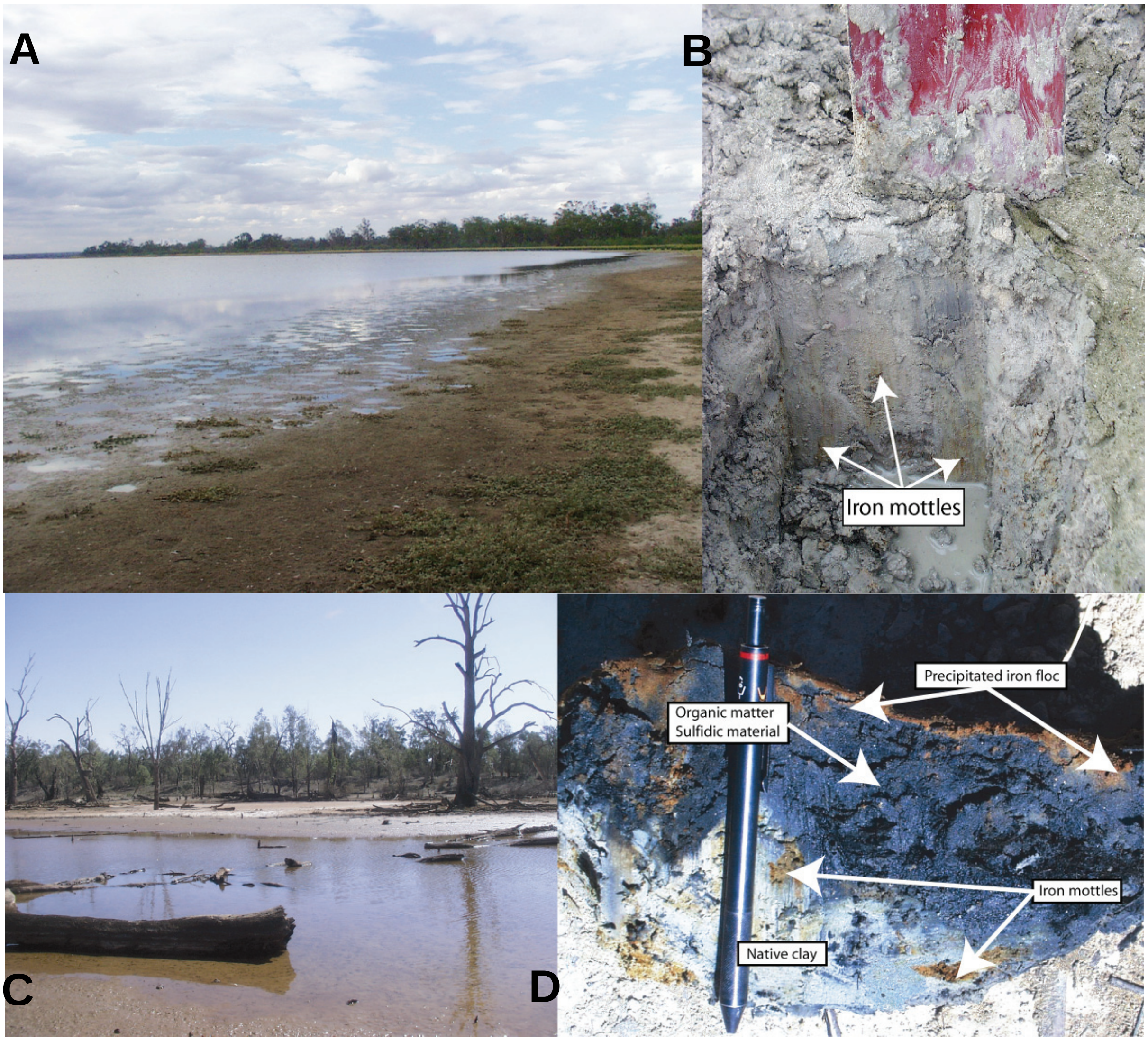

Figure 1. Comparison of sediment features at Merreti (freshwater and alkaline) and Bottle Bend (brackish and acidic). A) Shoreline at Merreti; B) Pit profile at Merreti shoreline; C) Shoreline at Bottle Bend, showing iron staining; D) Sediment profile at Bottle Bend Site 1.

One or two sites were sampled for each wetland and one or two pits or sediment cores were investigated at each site (Lamontagne *et al* 2004). At least one site was located in an area where a potential sulfidic material was detected by preliminary sampling (presence of a dark sediment horizon, H_2S smell, or black ooze; Figure 1). The preferred method of sampling was by collecting sediment cores at 30 cm water or greater depths using a Dormer undisturbed wet sampler (Dormer Engineering). However, because of dry beds, low water levels, or very soft sediments, sampling could only be done by digging pits at the water's edge in many wetlands. At Loveday and Bottle Bend, an additional site was also sampled where sediments had been exposed to the atmosphere for a month or more following recent declines in water level. Full details of sample collection equipment and methodology are given in Lamontagne *et al* (2004).

Grab samples of surface water and/or pore water were collected at each site, with the exception of Clover (which was dry and had a water table deeper than 1 m). Pore water was sampled by excavating to below the depth of free water and allowing the pit to fill. Water samples were split into unfiltered sub-samples for field measurement and alkalinity determination and filtered sub-samples (0.45 µm) for laboratory analysis. A second sub-sample was collected for chloride analysis. The remaining filtered sub-sample was acidified to pH < 2 with analytical grade hydrochloric acid for laboratory analysis of major ions. The sum of major ions was used to calculate salinity (as total dissolved solids; TDS) at the time of sampling in the wetlands.

Sample descriptions

Soil pits were dug to a depth varying between 5 to 75 cm, generally near the interface with the water table. A representative profile face in the pits was selected and the master horizons demarcated and photographed. Cores were extruded in trays and described in a similar fashion. Soils were described according to the USDA Field book for describing and sampling soils, Version 2.0 (Schoeneberger *et al* 2002) and Australian Soil and Land Survey Field Handbook (McDonald *et al* 1990). Further details are given in Lamontagne *et al* (2004).

Laboratory analyses

Total carbon was measured by thermal combustion and carbonate carbon using a manometric technique (Sherrod *et al* 2002), with organic carbon calculated by difference. The estimates for organic carbon content will also include charcoal; however, its inclusion will not affect this study's conclusions. The detection limit of the manometric method used for carbonate determination was 0.012 % as C (or 0.1 % as $CaCO_3$). This value is low enough to estimate both organic carbon and carbonate neutralising capacity. To estimate the organic C content, a value of 0.006 %C was used for the carbonate concentration for samples below the detection limit. The sulfur content of sediments was assessed by measuring total S (S_{tot}) and chromium reducible S (S_{Cr}; Sullivan *et al* 2000). S_{Cr} is a combined measurement for all reduced inorganic S species (including pyrite, monosulfides and elemental S). The difference between S_{tot} and S_{Cr} provides an estimate of the combined oxidised S and organic S fractions (S_{ox+org}). Sediment samples for laboratory measurements were freeze-dried, homogenised and analysed at CSIRO's Adelaide Analytical Laboratory, with the exception of S_{Cr} analyses, which were made at the Environmental Analysis Laboratory (Southern Cross University, Lismore NSW).

Assessment of acidification risk

The acidification risk of a wetland will be the relative balance between the potential to produce acidity and the potential to neutralise it. The net acid generation potential (NAGP) is a measure used to assess the potential for acidification in acid mine drainage and in coastal acid sulfate soil (NSW ASSMAC, 1998). NAGP is the gross acid generation potential (AGP) minus the acid neutralising capacity (ANC) of a rock, soil or sediment.

$$\text{NAGP} = \text{AGP} - \text{ANC} \qquad (1).$$

As is the practice for Australian coastal acid sulfate soils, we used the carbonate concentration as a measure of ANC and the reduced sulfur concentration to calculate the gross acid generating potential (NSW ASSMAC 1998). AGP is estimated by assuming that each mole of reduced sulfur in sediments can generate two moles of acidity (H^+) (Nordstrom 1982; Burton *et al* 2006).

RESULTS AND DISCUSSION

Wetlands with a wide range in salinity were sampled, with TDS ranging from 0.57 to 100 g L^{-1} (Table 1). The wetlands also had elevated sulfate concentrations (0.52 – 115 mmol L^{-1}) and were neutral to alkaline (pH = 7.5 – 9.4), with the exception of Bottle Bend Lagoon which was mildly acidic (pH = 5.5). Organic matter was the main form of carbon in the wetlands, with concentrations ranging from 0.10% to 6.8%C and the highest concentrations found in the disposal basins (Lamontagne *et al* 2006). Sediment carbonate concentrations ranged from <0.012 to 3.9%C and were also highest in disposal basins. Both organic and carbonate C concentrations tended to be highest at the sediment surface and to decline with depth. S_{Cr} and S_{ox+org} concentrations were also highest in disposal basins. S_{Cr} concentrations ranged from <0.01%S to 0.97%S and were highest in Berri and Loveday (Fig. 2). To put these reduced S concentrations in perspective, they exceed the recommended guidelines to trigger management action (0.06% and 0.1% for medium and fine-textured material, respectively; Ahern *et al* 1998) for coastal acid sulfate soil in all disposal basins and in several of the other wetlands. S_{ox+org} concentrations ranged from <0.01 to 2.7% and was the main form of S in less saline wetlands. As gypsum was found in most disposal basin sediments (Lamontagne *et al* 2006), the S_{ox+org} fraction is likely to contain both organic-S and sulfate salts in the more saline wetlands.

Table 1. Water quality characteristics for the wetlands investigated during the study. Clover wetland was completely dry at the time of the study.

Location	**EC** (dS m^{-1})	**pH**	**ANC** (mg HCO_3^- L^{-1})	**SO_4^{2-}** (mmol L^{-1})	**TDS** (g L^{-1})
Berri*	120	7.5	270	115	100
Loveday	50	9.0	122	58	45.3
Ramco	62	8.5	230	22	41.2
Hart*	21	7.4	520	15	19.8
Bottle Bend	13	5.5	2	2.9	6.9
Woolpolool	5	9.4	46	7.6	2.9
Ross	5.2	9.0	160	2.0	2.7
Merreti	1.3	9.0	200	0.52	0.57
Seawater	53	~8	150	11.5	34.5

*from pit samples

Acid generation potential

There were significant differences in AGP and ANC between wetlands (Fig. 3) and vertically within many sediment profiles (Lamontagne *et al* 2004; 2006). AGP and ANC were higher in disposal basins relative to the other wetlands. While less saline wetlands (Ross, Merreti and Clover) had greater ANC than AGP at all depths, the vertical patterns in AGP and ANC were more complex in more saline wetlands and disposal basins (Lamontagne *et al* 2006). On an areal basis, only the Bottle Bend Lagoon sites and Loveday Site 2 Pit 2 had a positive NAGP (Fig. 3), also corresponding to the sites where potential acid sulfate soils were detected with a peroxide oxidation test (Lamontagne *et al* 2006). Some of the variability in the magnitude of AGP and ANC between sites and wetlands may have been caused, in part, by differences in the depth of the pits and cores sampled. In particular, AGP and ANC may have been underestimated at Hart and Berri because only shallow pits were sampled at these sites, whereas peak sulfide concentrations were deeper in similar disposal basins (Ramco and Loveday). These trends in AGP and ANC indicate that high sediment sulfide concentrations by themselves are not a reliable indicator of the acidification risk because of the large variability in sediment ANC between wetlands. For example, despite moderate sulfide concentrations, Bottle Bend is most at risk of acidification because it has little sedimentary carbonates. In contrast, despite elevated sulfide concentrations, disposal basins appear at a lesser risk of acidification because they also have high sedimentary carbonate contents.

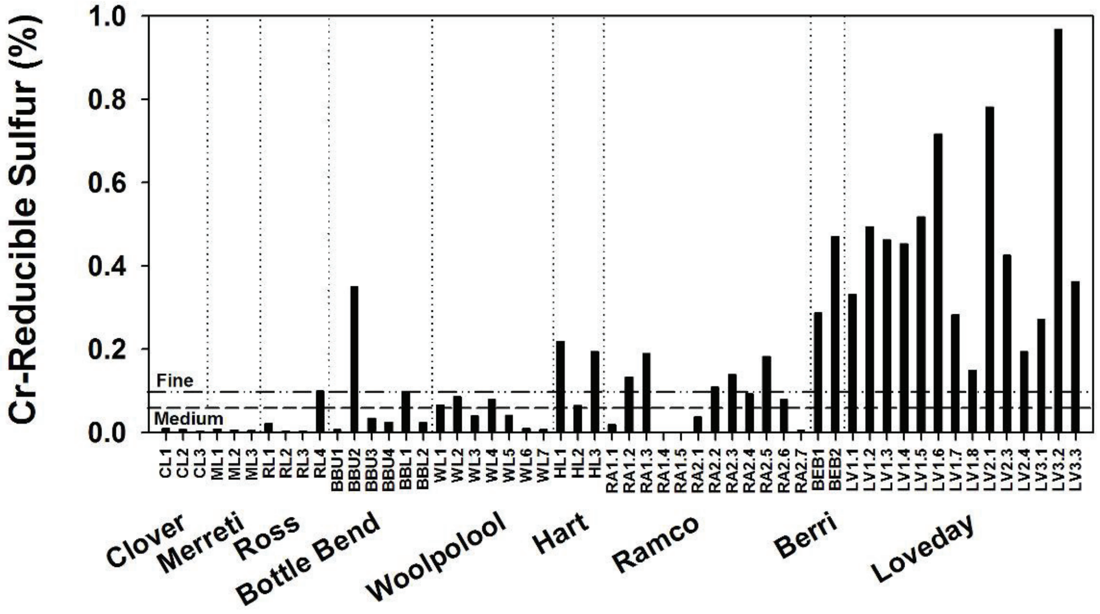

Figure. 2. Reduced sulfur in Lower River Murray floodplain wetland soil and sediment samples. For comparative purposes, the horizontal dashed line represents the trigger value for further investigation in Australian coastal ASS environments for medium (0.06%) and fine textured (0.1%) sediments (the trigger value is 0.03% for coarse textured sediments).

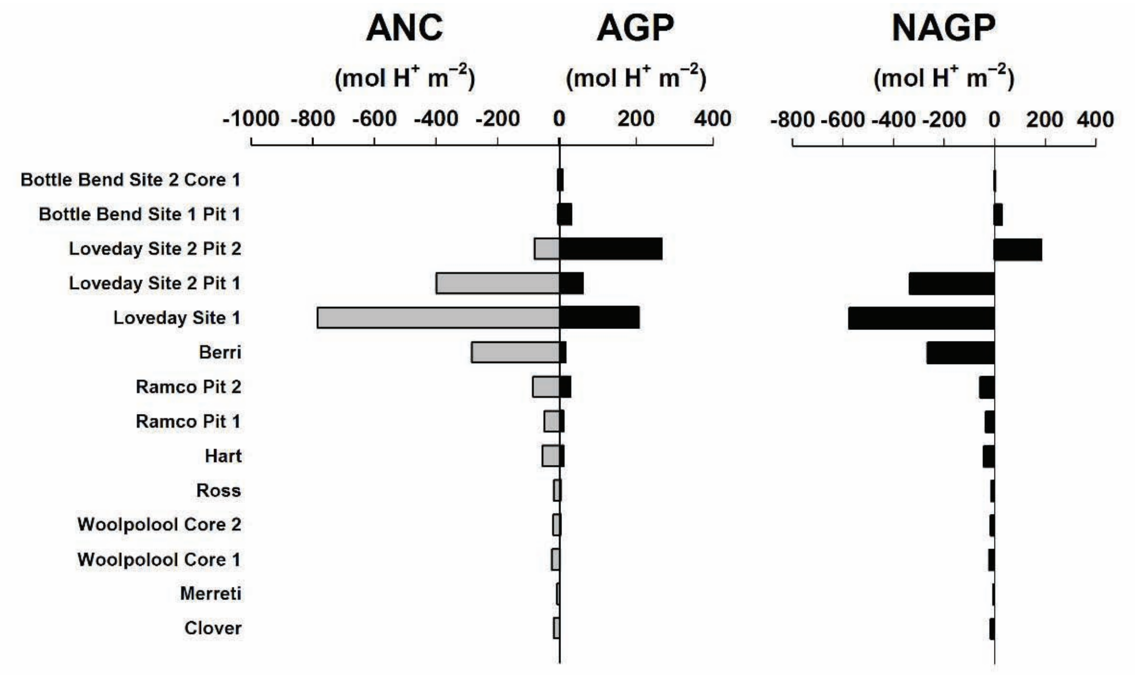

Figure. 3. Areal estimates of acid generation potential (AGP), acid neutralisation capacity (ANC) and net acid generation potential (NAGP) in disposal basins and wetlands. AGP and ANC calculated assuming a bulk density of 1.5 g cm^{-3} for soil and sediments (Slavich *et al* 1999) and 0.8 g cm^{-3} for oozes.

CONCLUSION

This preliminary survey of sulfide distribution in Lower Murray wetland soils and sediments demonstrated that environmentally significant concentrations of reduced sulfur are widespread in this environment, consistent with other similar recent studies in the Murray-Darling Basin (Sullivan *et al* 2002b; Sullivan *et al* 2004; Hall *et al* 2006; Wallace *et al* 2006). However, whether or not these sulfide deposits are also acid sulfate soils is dependent on the acid neutralising capacity stored in the soils or sediments. In particular, many of the disposal basins with high S_{Cr} concentrations also had elevated ANC and do not appear to be at risk of acidification at the scale of the whole wetland. This is consistent with the endorheic surface water hydrology of disposal basins, where the alkalinity produced during sulfate reduction over time should have remained largely stored within the system (Lamontagne *et al* 2006). This role of wetland hydrology on the fate of alkalinity generated within the system must be considered when designing management strategies to improve wetland salinity. In other words, “opening” the water balance of disposal basins to mitigate salinity could also result in the formation of acid sulfate soil conditions in the longer-term if a net export of ANC occurs.

Despite limited sampling, this study demonstrated that sulfide and ANC concentrations vary widely within Lower Murray wetlands. Thus, a precise assessment of the acidification risk in this environment will require more detailed investigations than the ones used here. This will include a characterisation of the AGP and ANC across the wetland surface and vertically within soil or sediment profiles. In particular, the balance of AGP and ANC was variable at depth (at the decimetre scale) in disposal basin, with a positive NAGP frequently observed in the middle of the sediment profiles (Lamontagne *et al* 2006). The mechanisms responsible for this vertical variability in AGP and ANC within soil and sediment profiles are not known at present.

This study also provided circumstantial evidence that the changes to the water regime of Lower River Murray wetlands since European settlement have increased sulfide concentrations in their soils and sediments. The ongoing salinisation of these wetlands has increased sulfate concentrations in the environment, one of the limiting factors for the rates of sulfate reduction in sediments. Moreover, the current water regime of Lower Murray floodplains has resulted in many formerly ephemeral wetlands to be permanently waterlogged. Permanent waterlogging of wetland soils and sediments should have promoted the accumulation of sulfides by fostering the anoxic conditions necessary for sulfate reduction. Current management initiatives for Lower Murray wetlands frequently aim to return flooding and drying cycles to permanently flooded wetlands. Future studies in Lower Murray wetlands should explore in more detail the cycle of sulfide formation and oxidation when wetlands are flooded and dried.

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CHAPTER 15

SPATIAL VARIABILITY IN THE STORAGE OF SULFUR, CARBON AND ACID GENERATION POTENTIAL IN AN INLAND SALINE SULFIDIC WETLAND, LOWER MURRAY RIVER FLOODPLAINS, SOUTH AUSTRALIA

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INTRODUCTION

While acid sulfate soils (ASS) have long been recognised in marine environments (Dent 1986; Dent and Pons 1995; Lin and Melville 1994; Pons *et al* 1982; Van Breemen 1982), they have more recently been identified in inland settings, particularly in landscapes affected by salinisation (Fitzpatrick *et al* 1996). ASS are all soils in which sulfuric acid may be produced, is being produced, or has been produced in amounts that have a lasting effect on main soil characteristics (Pons 1973). In coastal environments these soils are typically composed of a lower horizon with sulfidic materal (potential ASS or PASS) overlain by an upper acidic (pH <3) horizon comprising sulfuric material characterised by the formation of jarosite (actual ASS; AASS) resulting from sulfide oxidation (Van Breemen 1982). Due to high carbonate concentrations inland sulfidic sediments are generally less acidic (pH 4-5) upon oxidation (Fitzpatrick *et al* 1996).

Sulfides form in reduced saline environments rich in sulfate and organic carbon, proceeding through a complex series of microbially mediated reactions (Andreae and Jaeschke 1992; Berner 1984; Canfield *et al* 1998; Howarth 1979; Morse *et al* 1987). In ASS, where pyrite is the dominant sulfide, the overall reaction of sulfide formation can be simplified to (Dent 1986):

$$Fe_2O_{3(s)} + 4SO_4^{2-} + 8CH_2O + \frac{1}{2}O_2 \rightarrow 2FeS_{2(s)} + 8HCO_3^- + 4H_2O \qquad (1)$$

The formation of sulfides is not sufficient by itself to produce potential acidity because an equal amount of acid neutralising capacity (here as HCO_3^-) is generated. A key step in the formation of potential acidity is the removal of the acid neutralising capacity from soil maerials, leaving a net store of potential acidity in the remaining sulfides. In coastal environments carbonate is removed from sediments by tidal flushing (Dent 1986) whereas carbonate remains with sulfides in inland sulfidic materials (Fitzpatrick *et al* 1996; Hall *et al* 2006; Lamontagne *et al* 2006a).

Under reduced conditions sulfidic material remains relatively benign and poses little threat to the surrounding environment (Dent 1986). However, when sulfidic material is exposed to oxidising conditions, pyrite can be oxidised by molecular oxygen and ferric iron (Luther and George 1987; McKibben and Barnes 1986; Moses *et al* 1987; Nordstrom and Southam 1997; Singer and Stumm 1970), producing sulfuric acid and forming sulfuric material. The overall reaction for the complete oxidation of pyrite and hydrolysis of iron produces 4 moles of H^+ for every mole of FeS_2 and can be written as (Dent 1986):

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \qquad (2)$$

The draining of sulfidic material in many coastal environments has resulted in sulfide oxidation and the development of sulfuric material (Kinsela and Melville 2004; Lin *et al* 2004; MacDonald *et al* 2004; Oborn 1989; Osterholm and Astrom 2002; Smith *et al* 2003; Van Breemen 1982; Ward *et al* 2004). The low pH (<3) of sulfuric material can cause significant environmental damage to surrounding environments and infrastructure directly (e.g. Sammut and Lines-Kelly 1996; White *et al* 1997), and also indirectly by mobilising iron, aluminium and heavy metals (e.g. Astrom and Astrom 1997; Sammut and Lines-Kelly 1996; Sammut *et al* 1996).

Salinity impacts an estimated 25 % of the Lower Murray floodplains area and the area affected is expected to double over the next 50 years (Allison *et al* 1990; Evans and Kellett 1989; Lovering *et al* 1998; Simpson and Herczeg 1994). Sulfate constitutes ~20% of salts in the saline waters of the Murray-Darling Basin (Herczeg *et al* 2001; Jones *et al* 1994; Stephenson and Brown 1989). Recent surveys of wetlands in the Murray-Darling Basin have demonstrated that sulfides are widespread, especially in more saline wetlands (Fitzpatrick *et al.* 1996; Hall *et al* 2006; Lamontagne *et al* 2006a; Sullivan *et al* 2004). Wetlands converted into evaporative saline disposal basins, including the Loveday Basin, have become hyper-saline (Evans 1989; Trewhella 1989). Lamontagne *et al* (2006a) identified the Loveday Basin, which had been partially dried, as having high but variable concentrations of sulfide and carbonate. Currently, the extent of sulfidic material within the Loveday Basin, the effect of water manipulations on the distribution of sulfides and carbonate, and the potential for sediments to become acidic, are unknown.

In this study we have examined the sediments / soils of the Loveday Basin in detail to establish the distribution of sulfur and carbon stores under different water regimes and the potential for sediment / soil acidification upon oxidation. It is hypothesised that (1) sulfur and sulfides will be concentrated in the upper sediments of the basin, (2) water regimes within the basin will control the spatial distribution of sulfur and carbon stores, and (3) the basin has sufficient amounts of carbonate to neutralise the potential acidity stored in the sulfidic material.

Site description

The Loveday Disposal Basin is a 3.3 km^2 hyper-saline wetland located in the lower Murray River floodplains, South Australia (34º15′S, 140º24′E; Figure 1). The climate is semi-arid, having cool winters and hot dry summers with variable rainfall (100-500 mm y^{-1}) and a high potential evapo-transpiration (~2000 mm y^{-1}) (Hostetler and Radke 1994). Originally a stranded meander lake of the Murray River, the basin sits within the Coonabidgal Clays, a silty clay aquitard, which overlies the Monoman Sand aquifer and abuts the Parilla-Loxton Sand aquifer within the Murray floodplains (Hostetler and Radke 1994). The basin was disconnected from the Murray River via floodgates and converted into an evaporation basin in 1972 to dispose of saline irrigation water for nearby irrigation districts (Evans 1989). Additionally, the basin is inundated during flood events of the Murray River (river height >10AHD; (Hostetler and Radke 1994)) and, sitting below the Cobdogla Irrigation Area groundwater mound to the east and the River Murray to the west (Figure 1), may also receive saline groundwater discharge (Hostetler and Radke 1994). Over three decades the basin has been essentially a terminal site for salts, including sulfate, with the principal loss of water through evaporation (Hostetler and Radke 1994). In addition to sulfate the basin also contains significant accumulations of sulfides (Lamontagne *et al* 2006a). Basin sediments were partially dried in 2000 due to a reduction in irrigation discharge and lack of floods. The basin sediments have since remained partially dry with intermittent wetting and drying due to variable inputs of water from rain events and irrigation and groundwater discharge.

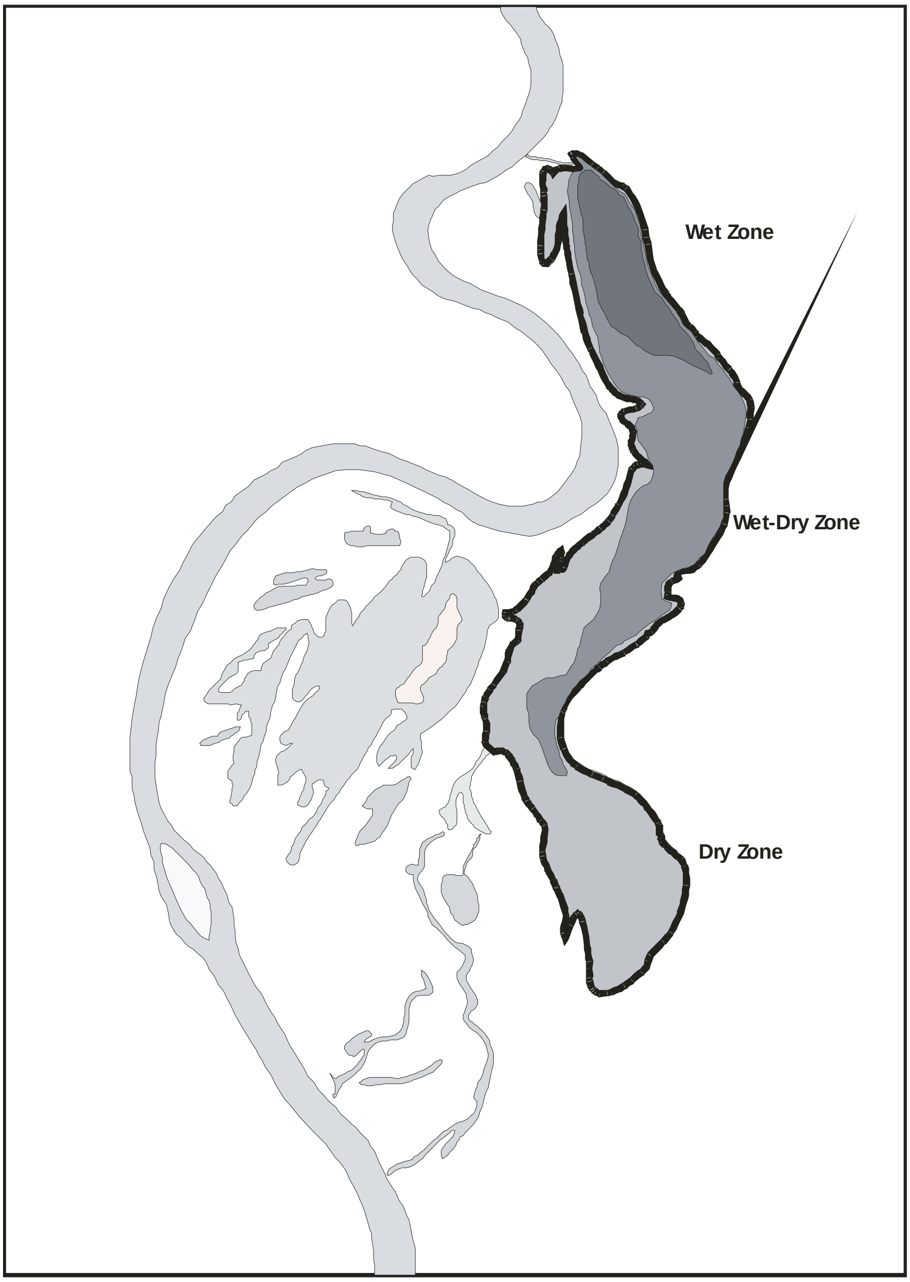


Figure 1 Map of Loveday basin.

METHODS

Sampling and analysis

Sediments were sampled with a shovel and/or PVC sediment corers from 0-50 cm and with a soil auger from 50-250 cm. Samples from 12 depth profiles were taken at 5 cm increments from 0-50 cm and for each major unit, from 50-250 cm. Samples of surface sediments were taken at another 70 sites from 0-5 cm and 20-25 cm. Samples from 0-50 cm were collected in screw-top polyethylene containers and samples from 50-250 cm collected in zip-lock sample bags, with all samples frozen on dry-ice in the field and transported to a -20ºC freezer. Frozen samples were subsequently freeze-dried and hand- or machine-milled for analysis.

Hand milled samples were analysed for the mineralogy of bulk sediments and density separated clay fractions by Cu Kα X-ray diffraction (XRD) on a Siemens D500/D501 series XRD (Moore and Reynolds 1989). Bulk samples were dried at 40ºC, hand ground to between 1-10 µm, spiked with zinc oxide and scanned from 2-70º 2θ at 2º per minute in 0.02º steps. Oriented magnesium saturated clay fractions were scanned from 2-42º 2θ, re-scanned from 2-35º 2θ after glycolation, and scanned again from 2-28º 2θ after heating at 350ºC for 1h. Output files of intensity against 2θ were analysed with EVA^{TM} mineral identification and SIROQUANT mineral quantification softwares.

The concentrations of reduced inorganic sulfur minerals (FeS and FeS_2) were analysed by the acid volatile sulfur (AVS; FeS) method (Fyfe *et al* 2004) and chromium reducible sulfur (CRS; FeS + FeS_2) method (Sullivan *et al* 1999; Sullivan *et al* 2000). AVS was conducted in the field on wet sediments as well as in the laboratory, along with CRS on freeze-dried machine milled samples. These methods liberate the reduced inorganic sulfur fractions as H_2S, which is trapped in a zinc acetate solution as zinc sulfide and quantified from iodometric titration. The AVS fraction has commonly been assumed to represent the monosulfides (amorphous FeS, FeS_{1-x} and Fe_3S_4), but recent studies demonstrate that other sulfur fractions might be included in the extraction and that not all the monosulfides are removed (Rickard and Morse 2005). The authors acknowledge the limitations of this method while referring to this fraction from here on as the “monosulfides” for comparison with other studies that have used this method. As the CRS method measures the total inorganic reduced sulfur (FeS + FeS_2), pyrite (FeS_2) is calculated from the CRS fraction minus the AVS fraction, likewise, for comparison with other studies that have used these methods.

Organic sulfur content was measured by analysing total sulfur in CRS residues, where inorganic reduced sulfur is removed as H_2S and any remaining oxidised sulfur removed by rinsing with Milli-Q. (Nriagu and Soon 1985). Total sulfur was analysed on all samples by X-ray fluorescence (XRF) and total sulfur and total carbon analysed on a suite of 50 samples by LECO-CNS induction furnace analysis (conducted at CSIRO). Carbonate carbon was quantified by a manometric technique (conducted by CSIRO) on all samples, after removal of large shell fragments, with the difference between total carbon and carbonate assumed to be organic carbon. The sulfate fraction was calculated by subtraction of the CRS and organic sulfur from the total sulfur. The presence and amounts of gypsum, pyrite and jarosite were confirmed with a Cambridge 360 scanning electron microscope (SEM) with energy dispersive spectroscope (EDS) analyser (Riemer 1998).

Sediment pH and EC were measured on wet sediments in a 1:5 sediment-Milli Q water mix with duplicate samples oxidised with 30 % H_2O_2 (Ward *et al* 2002).

Amounts of sulfur, carbon and acidity

The amounts of sulfur and carbon fractions have been calculated from their average concentrations in each sedimentary unit multiplied by the bulk density of sediments and the volume of each unit.

$X_A = X_C \text{ x } BD \text{ x } V_U$

Where X_A is the amount (weight) of the sulfur or carbon fraction in each unit, X_C is the average concentration (weight/weight) of sulfur or carbon in each unit, BD is the bulk density of sediments (g cm^{-1}) and V_U is the volume of each unit. The bulk density of sediments is assumed to be 1.3 g cm^{-1} for sediments below 10 cm and 0.9 g cm^{-1} for sediments above 10 cm (Beavis *et al* 2006).

The acid generation potential (AGP) of each unit has been calculated assuming 2 moles of H^+ are produced for every mole of CRS and the acid neutralising capacity (ANC) has been calculated assuming 2 moles of H^+ are consumed for every mole of carbonate. The net acid generation potential (NAGP) of sediments is assumed to be equal to the AGP minus the ANC.

NAGP = AGP – ANC

Positive NAGP values indicate a net store of acidity whilst a negative NAGP corresponds to an excess of alkalinity in sediments.

RESULTS AND DISCUSSION

Basin sediment characterisation

The mineralogy and grain size distributions of the Loveday Basin's sediments (3.3 km^2) are summarised in Tables 1 and 2. The basin sediments are principally homogenous grey (5Y6/1) clays (Coonambidgal Clays; unit C) to a depth of 150 cm composed of kaolinite, illite, muscovite and feldspar overlying quartz-rich light grey (5Y7/2) silts (150-200 cm depth, unit D) and light yellowy grey (5Y8/2) sands (200-250 cm depth; unit E) of the Monoman Sands (Tables 1 and 2). Since the partial drying of the basin in 2000, intermittent wetting and drying of sediments has produced three distinct zones within the surface 30-40 cm of sediments. These zones have been mapped from aerial photographs, LANDSAT image mosaics and field observations and have been termed in this study the Wet Zone, Wet-Dry Zone and Dry Zone, each following topographic contours of the basin (Map Figure 1).

Table 1 **Grain size distribution of basin sediments**

Grain Size Weight %	A (Wet)	A (Wet-Dry)	A (Dry)	B (Wet)	B (Wet-Dry)	B (Dry)	C	D	E
Silt and Clay (<63um)	98.42	98.61	85.12	94.80	94.40	86.07	87.93	90.11	40.91
Very Fine Sand (63-125um)	0.65	0.84	8.20	1.38	2.24	7.71	5.37	3.71	10.55
Fine Sand (125-250um)	0.50	0.32	5.92	2.10	2.16	5.62	5.16	3.59	39.48
Medium Sand (250-500um)	0.38	0.17	0.47	1.61	0.43	0.44	0.79	0.71	1.13
Coarse Sand (0.5-1mm)	0.04	0.04	0.01	0.03	0.34	0.01	0.35	0.76	0.87
Very Coarse Sand (1-2mm)	-	0.02	-	0.08	0.43	0.14	0.21	0.64	0.75
Gravel (>2mm)	-	-	0.29	-	-	-	0.20	0.49	6.31

Table 2 **Bulk mineralogy of basin sediments**

Mineral Weight %	A (Wet)	A (Wet-Dry)	A (Dry)	B (Wet)	B (Wet-Dry)	B (Dry)	C	D	E
Quartz	24.0	22.3	43.1	30.3	30.3	39.0	47.1	46.4	56.2
Orthoclase	3.1	3.1	5.6	5.2	4.0	4.4	4.0	3.8	5.1
Albite	2.8	1.8	6.9	7.6	3.4	5.1	5.1	3.1	3.2
Muscovite	0.9	0.8	1.4	0.9	1.2	12.2	5.3	1.0	0.9
Kaolinite	1.9	1.8	1.8	4.8	3.9	5.5	3.7	2.7	2.0
Illite	4.1	12.0	2.5	7.0	7.0	8.0	13.2	5.9	6.2
Montmorillonite	16.0	7.0	10.4	23.3	24.2	7.8	6.4	17.3	15.2
Calcite	3.9	4.6	3.0	0.3	2.9	1.0	3.7	2.7	2.0
Sodium Chloride	7.0	8.8	7.3	3.9	6.3	2.9	1.0	1.5	1.2
Gypsum	8.3	17.3	0.1	0.4	0.5	2.4	0.5	0.3	0.9
Pyrite	2.1	1.4	1.9	4.8	3.3	0.7	-	-	-
Jarosite	-	-	-	-	0.3	-	-	-	-
Amorp. Content	25.8	19.1	15.7	11.4	12.9	11.1	13.5	17.1	8.5

The three zones have been further subdivided into a saline clay unit (0-10 cm depth; unit A) and a mottled clay unit (10-40 cm depth; unit B). The Wet Zone sediments (0.6 km^2; pH 7-8) have a permanent water cover with unit B characterised by dark grey clays (5Y4/1) with black (5Y2/1) sulfidic mottles, covered by sulfidic black (5Y2/1) ooze of unit A. The Wet-Dry Zone sediments (1.1 km^2; pH 3-7) are currently exposed to the atmosphere in dry periods but intermittently saturated during wet periods, resulting in cyclic wetting and drying. Shrinkage of the clays during drying has produced desiccation cracks (20 cm deep) that have propagated to form polygonal desiccation features (Lamontagne *et al* 2006a). In the Wet-Dry Zone unit B is dark grey (5Y4/1) to dark reddish brown (5YR4/2) and contains prominent red (2.5YR4/8) iron-rich mottles intermingled with black (5Y2/1) sulfidic mottles and isolated pale yellow (5Y8/4) mottles of jarosite associated with pH <4. Unit A of the Wet-Dry Zone is covered in salt efflorescence during dry periods and in sulfidic black (5Y2/1) ooze during wet periods. The Dry Zone sediments (1.7 km^2; pH 6-7) are predominantly dry, only forming a water cover during large flood events. In the Dry Zone the grey (5Y6/1) sandy clays of unit B contain reddish brown (2.5YR4/8) iron-rich mottles, with unit A being predominantly light grey (5Y7/2) dry flocculated sandy clays. The distinct textural characteristics of the basin's three surface zones indicate these areas have ether formed under different sedimentary conditions or evolved from the same parent material due to subsequent environmental changes.

The clays of the Wet and Wet-Dry Zones are almost identical in mineralogy and grain size distribution (Tables 1 and 2). Both the Wet and Wet-Dry Zones have a large silt-clay grain size fraction of >94% with low quartz (22-30%) and muscovite (0.8-1.4%) contents (the sand size fraction increases in the Wet and Wet-Dry Zone along the basin's eastern side due to input from the adjacent Loxton-Parilla Sands. Additionally, in both the Wet and Wet-Dry Zones, unit A has high gypsum (8-17%) and unit B has high smectite (23-24%) concentrations (Table 2). The Wet and Wet-Dry Zones are distinctly different in grain size and mineralogy from the Dry Zone (Tables 1 and 2). The Dry Zone has a lower silt-clay grain size fraction (85-86%), with greater amounts of sand (5-8%) and higher quartz concentrations (39-43%). Unit B of the Dry Zone also has higher muscovite (12%) and lower smectite (7.8%) concentrations than unit B of the Wet and Wet-Dry Zones (Table 2). The grain size distribution and clay mineralogy indicate that the sediments of the Wet and Wet-Dry Zones have formed from the same parent material, which is distinctly different to the parent materials which have formed the Dry Zone sediments.

The Dry Zone sediments are similar in mineralogy and grain size distribution to the underlying unit C (Table 2). Both sediments have high quartz and muscovite concentrations and lower amounts of smectite. The principal difference between the two units is the higher salt content of the Dry Zone (halite 2.9-7.3%; gypsum 0.1-2.4%). This suggests the Dry Zone sediments are principally the exposed surface of unit C which has accumulated salts due to evaporation of saline waters. However, the different mineralogy and grain size distribution of the Wet and Wet-Dry Zones indicate these sediments are not formed from unit C. The deposition of smectite-rich clays over the coarser quartz- and muscovite-rich unit C is a common sedimentary sequence within flooded wetlands of the lower Murray floodplains often referred to as 'wetland clays'. Although water flow has been restricted between the Loveday Basin and the River Murray for the last 30 years, the basin is still inundated during flood events (river level above 10m AHD; (Hostetler and Radke 1994)), which will deposit the majority of the wetland clays. Gell *et al* (2007) measured the sedimentation rates of the Loveday Basin (Wet Zone) to be >1.0 cm/y above 60 cm depth (post-1958 to 2006) using ^{137}Cs isotopes, pollen and optically stimulated luminescence (OSL) techniques. This demonstrates that the majority of the basin's wetland clays (~30-50 cm depth) have been deposited since the basin's conversion into a disposal basin in the 1970's. The regulation of basin waters appears to have promoted the settling of the fine clays, forming the smectite-rich wetland clays that overly unit C in the Wet and Wet-Dry Zones.

The textural features and clay mineralogy of the Loveday Basins sediments reflect the basin's dominant water regimes. The Dry Zone has not accumulated any detectable smectite-rich wetland clays, demonstrating that this area of the basin has not had prolonged water cover since basin water regulation and is probably only inundated under high flood events. The Wet and Wet-Dry Zones are comprised of 30-50cm of smectite-rich wetland clays which indicate, from sedimentation rates (Gell *et al* 2007), that these areas have mostly maintained a permanent water cover since Loveday's conversion into a saline disposal basin in the 1970's. Subsequent intermittent drying of these smectite-rich wetland clays since 2000 has resulted in the formation of the prominent desiccation features and iron-rich mottles of the Wet-Dry Zone. The Wet Zone has maintained a water cover during these dry periods and sediments have remained largely undisturbed with no evidence of oxidation or the formation of desiccation features. The three dominant water regimes of the Loveday Basin have produced these three distinct sedimentary units.

Distribution of sulfur and carbon stores

Sulfur

The Loveday Basin sediments have a wide range of sulfur concentrations and amounts with depth (Figures 2 and 3). The principal forms of sulfur are sulfate (based on XRD analysis showing predominantly gypsum with minor amounts of jarosite), pyrite (CrS-AVS), monosulfides (AVS) and organic sulfur (OS). Total sulfur concentrations are relatively low between 40 cm and 250 cm depths (units C, D and E) ranging from 0.04 to 0.15%S but increase significantly in sediments above 40 cm depth where concentrations in unit B range from 0.04 to 1.51%S and in unit A from 0.08 to 5.74%S. The basin's sulfur is dominated by sulfate (0.04-5.67%S) which is present in all sediment units. The reduced forms of sulfur, pyrite (<0.002-1.31%S), monosulfides (<0.002-0.42%S) and organic sulfur (0.04-0.08%S), are largely restricted to the sulfur-rich upper 40 cm of basin sediments (Figure 2).

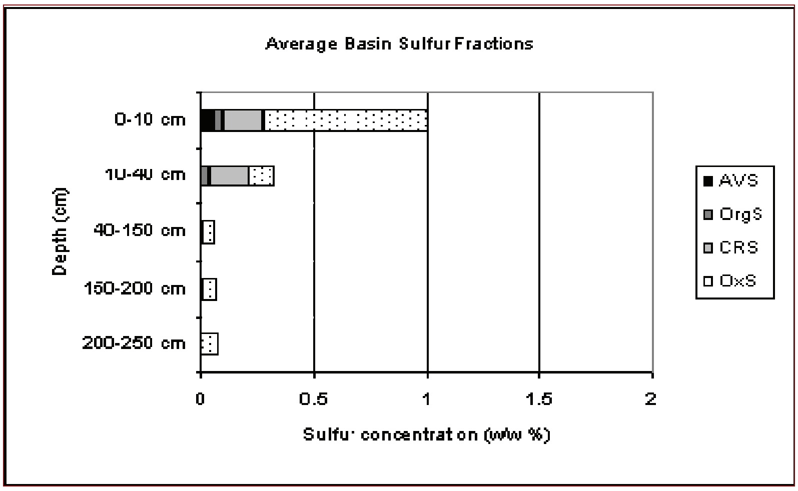


Figure 2 Total basin sulfur concentrations

This sulfur-rich upper 40 cm of sediments, although making up only 5% of the basin's total volume, contains 64% (12.72 kt S) of the basin's sulfur with 52% (7.41 kt S) of sulfate, 90% (3.89 kt S) of pyrite and <95% (0.39 kt S) of monosulfides (Figure 3). The high near-surface sulfate concentrations demonstrate that for most of the basins history sulfate concentrations have been low and sulfate accumulation from the recent evaporative disposal of saline waters has been restricted to the upper 40 cm of sediments, with limited movement into the underlying unit C. Additionally, the restriction of reduced sulfur to the upper 40 cm demonstrate that it is only since the regulation of the basin waters that conditions have been favourable for the formation and preservation of significant amounts of sulfides.

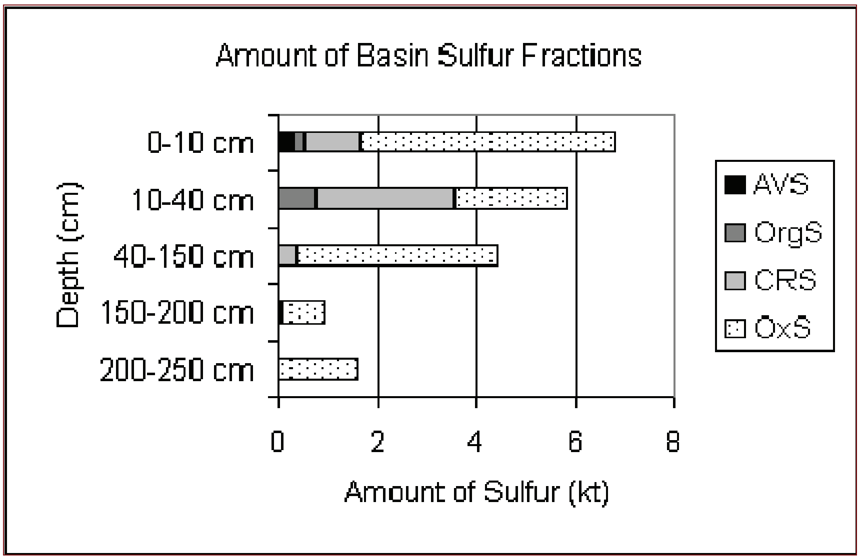


Figure 3 Total basin sulfur amounts

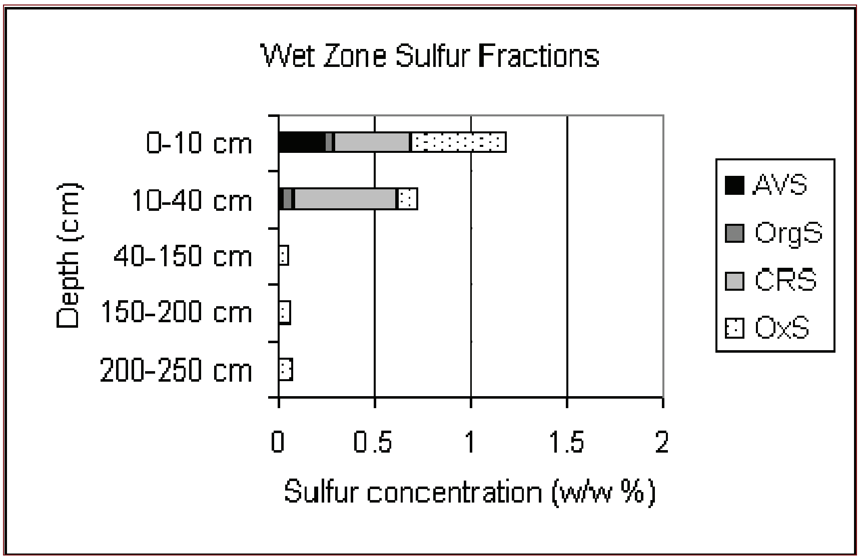


Figure 4. Wet Zone sulfur concentrations

Variations in the form and concentration of sulfur in the sulfur-rich surface 40 cm are distinct between the Wet Zone, Wet-Dry Zone and Dry Zone (Figures 4, 5 and 6). Sulfides are the dominant form of sulfur in the Wet Zone (averaging 0.6%S), present predominantly as pyrite with monosulfides concentrated in unit A (Figure 4). The Wet-Dry Zone also contains significant concentrations of sulfides (averaging 0.2%S) but sulfate, in the form of gypsum and isolated mottles of jarosite, is most prevalent, averaging 1.5%S in unit A (Figure 5). The Dry Zone contains relatively low concentrations of sulfur as sulfate (averaging 0.3%S) and only minor amount of sulfide (averaging 0.04%S), largely in the unit A (Figure 6). These differences between the three zones indicate the three water regimes that have produced the distinct textures and clay mineralogies have also produced distinct distributions of sulfur minerals.

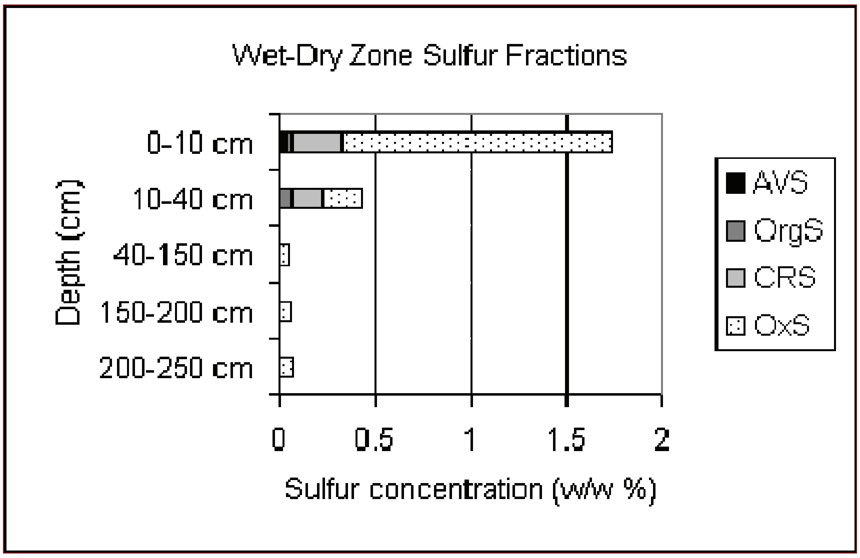


Figure 5. Wet-Dry Zone sulfur concentrations

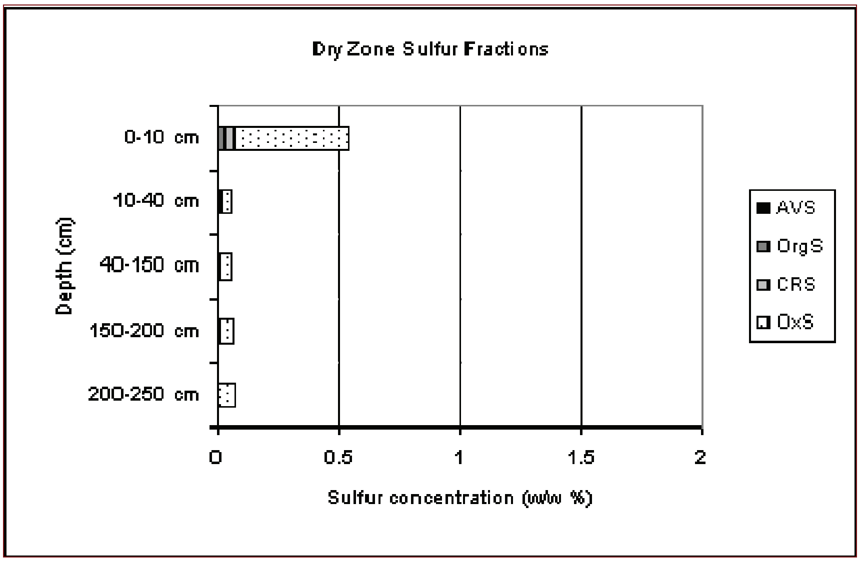


Figure 6. Dry Zone sulfur concentrations

Whilst the spatial range in sulfate and sulfide concentrations is relatively low within the Wet and Dry Zones, concentrations within the Wet-Dry Zone are highly variable (Figures 7 and 8). Low sulfate (<1%) and sulfide (<0.2%) concentrations are consistent throughout the Dry Zone at both 0-10cm and 10-40cm depths. Sulfate accumulation may be restricted in the Dry Zone as the flooding of the basin to the elevation of the Dry Zone sediments is infrequent (Hostetler and Radke 1994) and significantly reduces the basin salinity (Lamontagne *et al* 2006b), lowering sulfate concentrations. Additionally, the infrequent flooding of this zone and exposure to the atmosphere would limit the formation and preservation of sulfides (Dent 1986). This indicates that the predominantly dry conditions of the Dry Zone have produced the consistently low sulfate and sulfide concentrations observed. Within the Wet Zone, sulfate concentrations are consistently below 1% at both 0-10cm and 10-40cm and sulfides are consistently greater than 0.2%S at 0-10cm, increasing at 10-40cm depth. This indicates that sulfate reduction and the preservation of sulfides are consistently high across the entire Wet Zone, where a permanent water cover has been present. In contrast to the Wet and Dry Zones, sulfate and sulfide concentrations across the Wet-Dry Zone range over two orders of magnitude (<0.01-5.67%S and <0.01-1.1%S respectively), suggesting the heterogeneity is due to the wetting and drying of sediments.

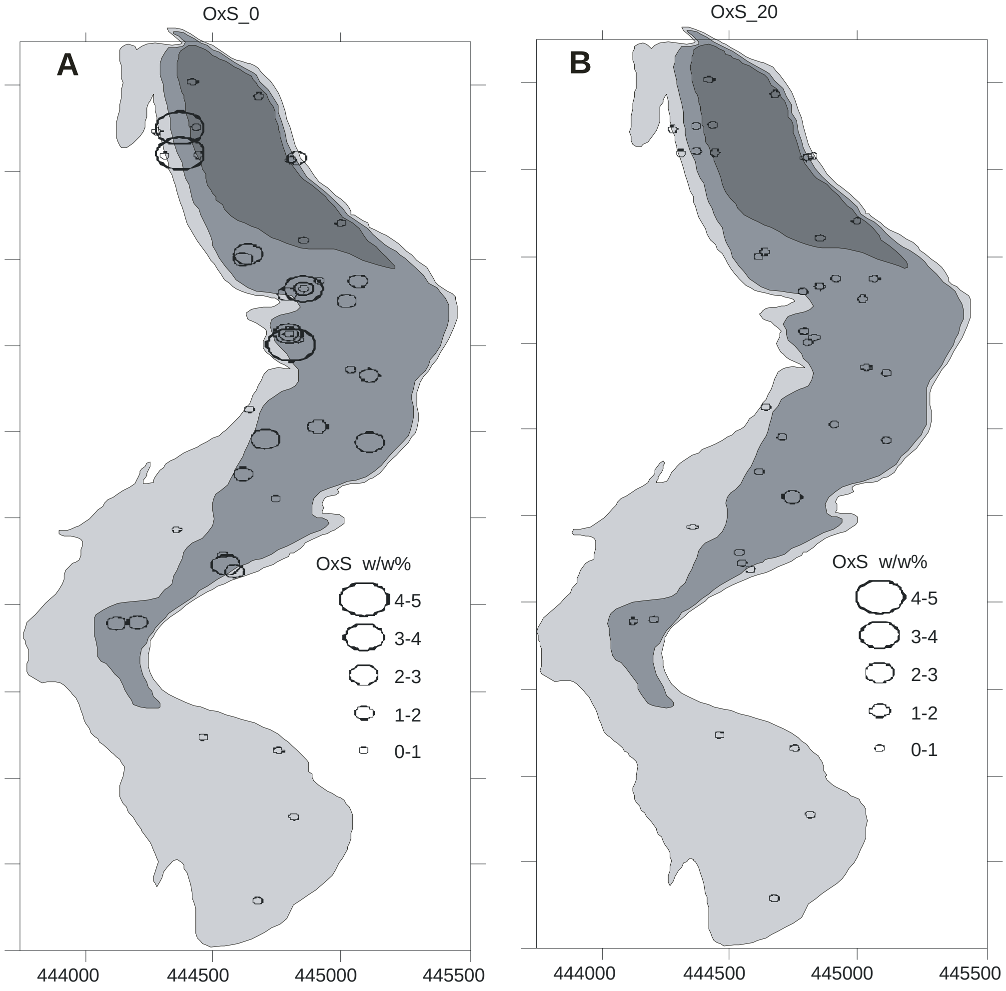


Figure 7 Sulfate concentrations of unit A (0-10 cm) and unit B (10-40 cm) through the Wet, Wet-Dry and Dry Zones.

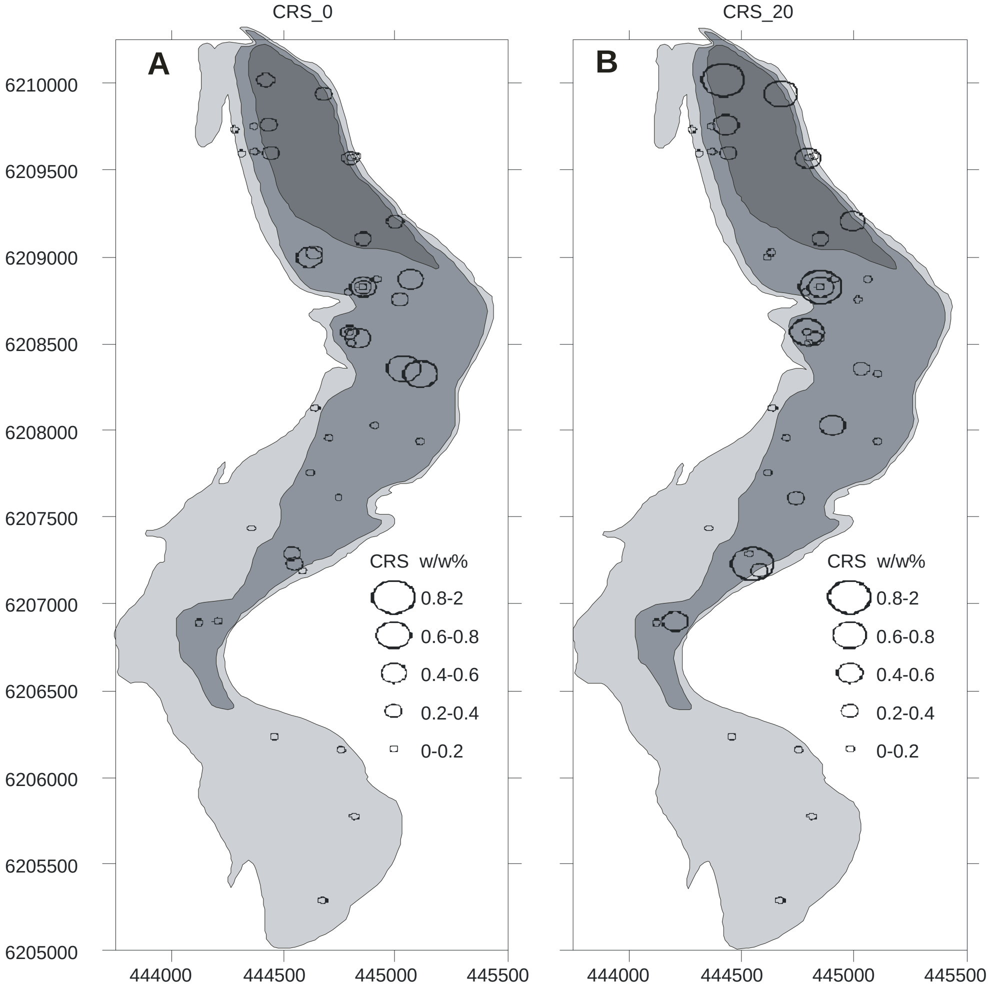


Figure 8 Sulfide concentrations of unit A (0-10 cm) and unit B (10-40 cm) through the Wet, Wet-Dry and Dry Zones.

The Wet-Dry Zone was formed under similar conditions to the Wet Zone prior to sediment drying since 2000 and has accumulated wetland clays and high concentrations of sulfide (up to 1%S). Like the Wet Zone, with a largely permanent water cover for 30 years, the Wet-Dry Zone most likely had sediments with relatively homogenous low sulfate and high sulfide concentrations. This would indicate that the localised higher sulfate concentrations at the surface of the Wet-Dry Zone relative to the Wet Zone represent an increase in sulfate (Figures 7 and 8) and the localised lower sulfide concentrations of the Wet-Dry Zone relative to the Wet Zone represent a decrease in sulfides (Figures 7 and 8). An increase in sulfate and decrease in sulfide concentrations during the wetting and drying of the saline sulfidic sediments can be explained by the oxidation of sulfide upon exposure to the atmosphere and the evaporative concentration of sulfate in surface salt efflorescence since sediment drying in 2000. The variable distribution of sulfate and sulfides in the Wet-Dry Zone indicates that the accumulation of sulfate salts and the oxidation of sulfides during wetting and drying phases do not proceed evenly throughout the sediments. These observations show that, whilst predominantly dry and predominantly wet sediments have consistent distributions of sulfate and sulfide, the wetting and drying of sulfidic sediments produce highly variable distributions of sulfate and sulfide.

Carbon

The sediments also have a broad range of organic carbon and carbonate concentrations which range from <0.002 to 3.89%C and from <0.005 to 1.69%C respectively. Organic carbon concentrations are relatively low below 40 cm depth (units C, D and E), ranging from <0.002 to 0.32%C, but it increases in concentration in the upper 40 cm from 0.11 to 3.89%C (Figure 9). Carbonate is generally in high concentrations (averaging 0.6%C) in units D and E whilst the majority of unit C has low carbonate concentrations (averaging 0.05%C; Figure 9). The basin's carbonate concentrations increase in the upper 40 cm of sediments, averaging 0.14%C in unit B and 0.38%C in unit A (Figure 9). The amounts of carbonate and organic carbon are given in Figures 10. Like sulfur, carbon concentrations in the upper 40 cm of the basin show distinct differences between the three water regimes. The average organic carbon and carbonate concentrations follow similar trends to sulfide concentrations through these zones with generally high concentrations in the Wet Zone (2.3%C and 0.5%C respectively; Figure 11) which decrease in the Wet-Dry Zone (1.75%C and 0.2%C respectively; Figure 12) and are much lower in the Dry Zone (0.8%C and <0.1%C respectively; Figure 13). The consistently organic-rich wetland clays of the Wet and Wet-Dry Zones demonstrate that the high water levels that trapped the fine clays have also trapped organic carbon. These distinct trends indicate that the amount and distribution of organic carbon and carbonate, like those of sulfate and sulfide, are controlled by the prevailing water regime.

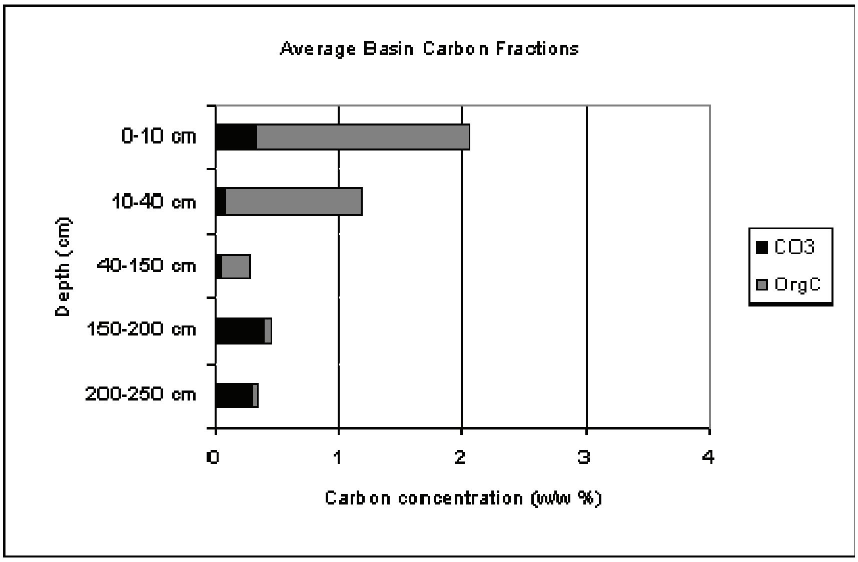


Figure 9. Total basin carbon concentrations

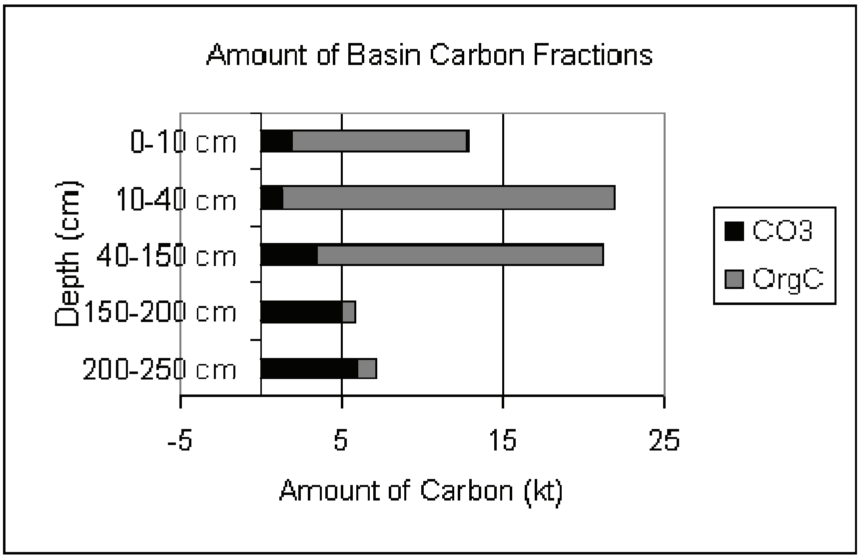


Figure 10. Total basin carbon amounts

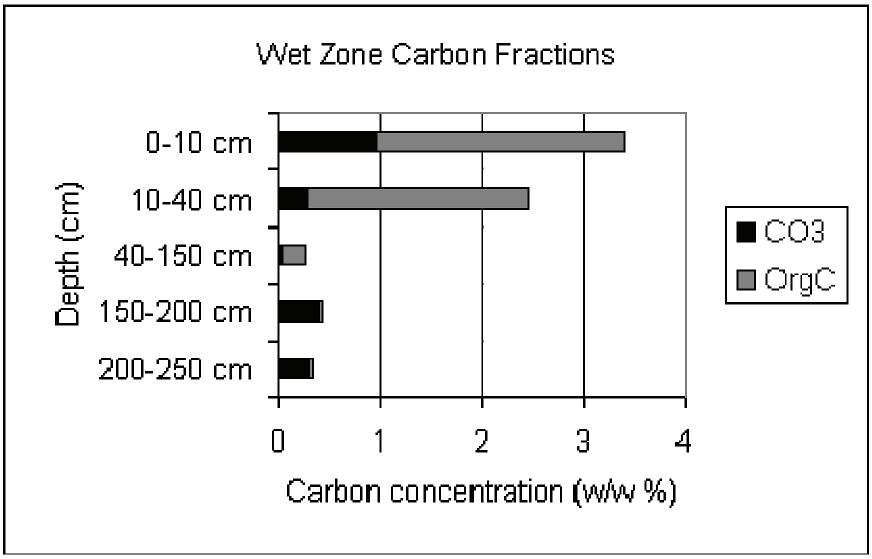


Figure 11. Wet Zone carbon concentrations

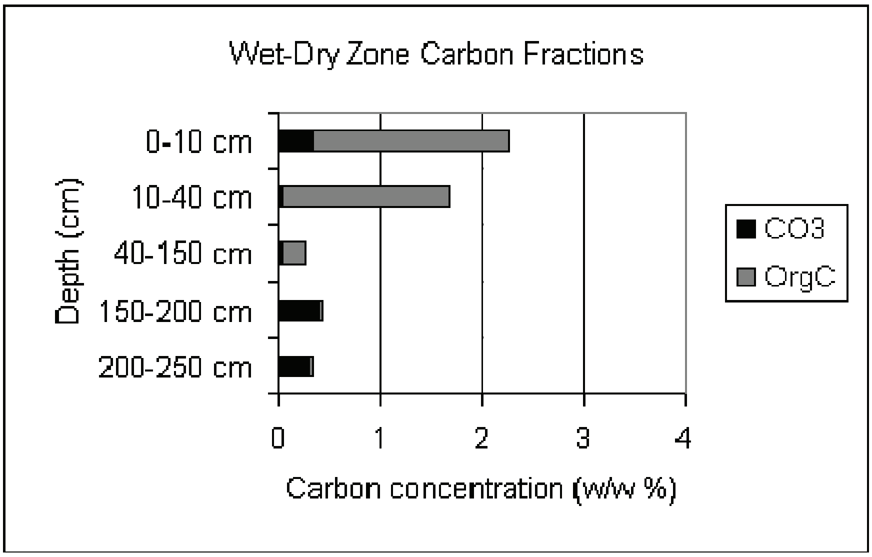


Figure 12. Wet_Dry Zone carbon concentrations

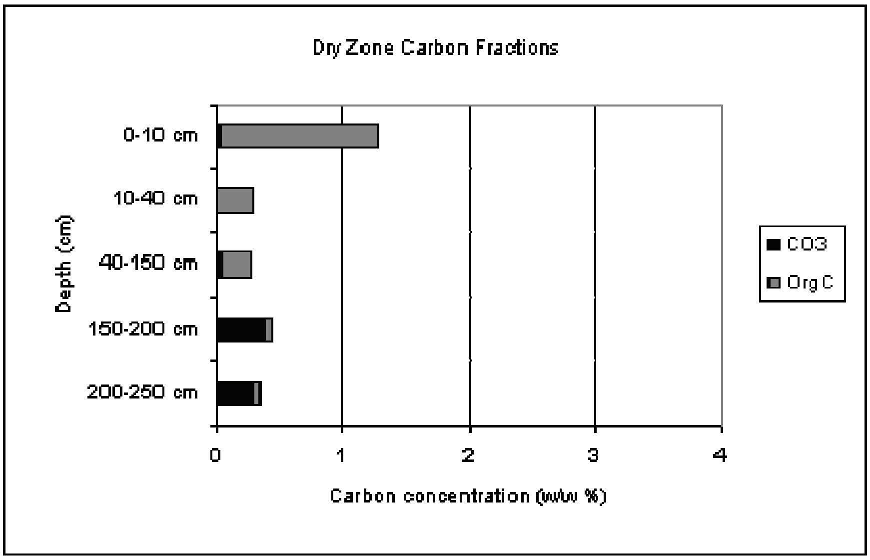


Figure 13. Dry Zone carbon concentrations

The concentrations of carbonate are spatially relatively consistent within the Wet and Dry Zones and, as for sulfate and sulfides, highly variable in the Wet-Dry Zone (Figure 14). The consistently low concentrations of carbonate in the Dry Zone are, like for sulfate, most likely related to the low salinity and infrequency of flooding events that reach these sediments. The consistently high concentrations of carbonate in the Wet Zone are most likely due to a combination of precipitation of carbonate from saline waters and mineralisation of organic carbon through sulfate reduction. The spatially variable carbonate concentrations of the Wet-Dry Zone are largely lower than those of the Wet Zone. This is unusual as carbonate, like sulfate, would be expected to have accumulated in the Wet-Dry Zone due to evaporation. The variable and considerably lower carbonate concentrations imply that wetting and drying of sediments has leached carbonate from the Wet-Dry Zone.

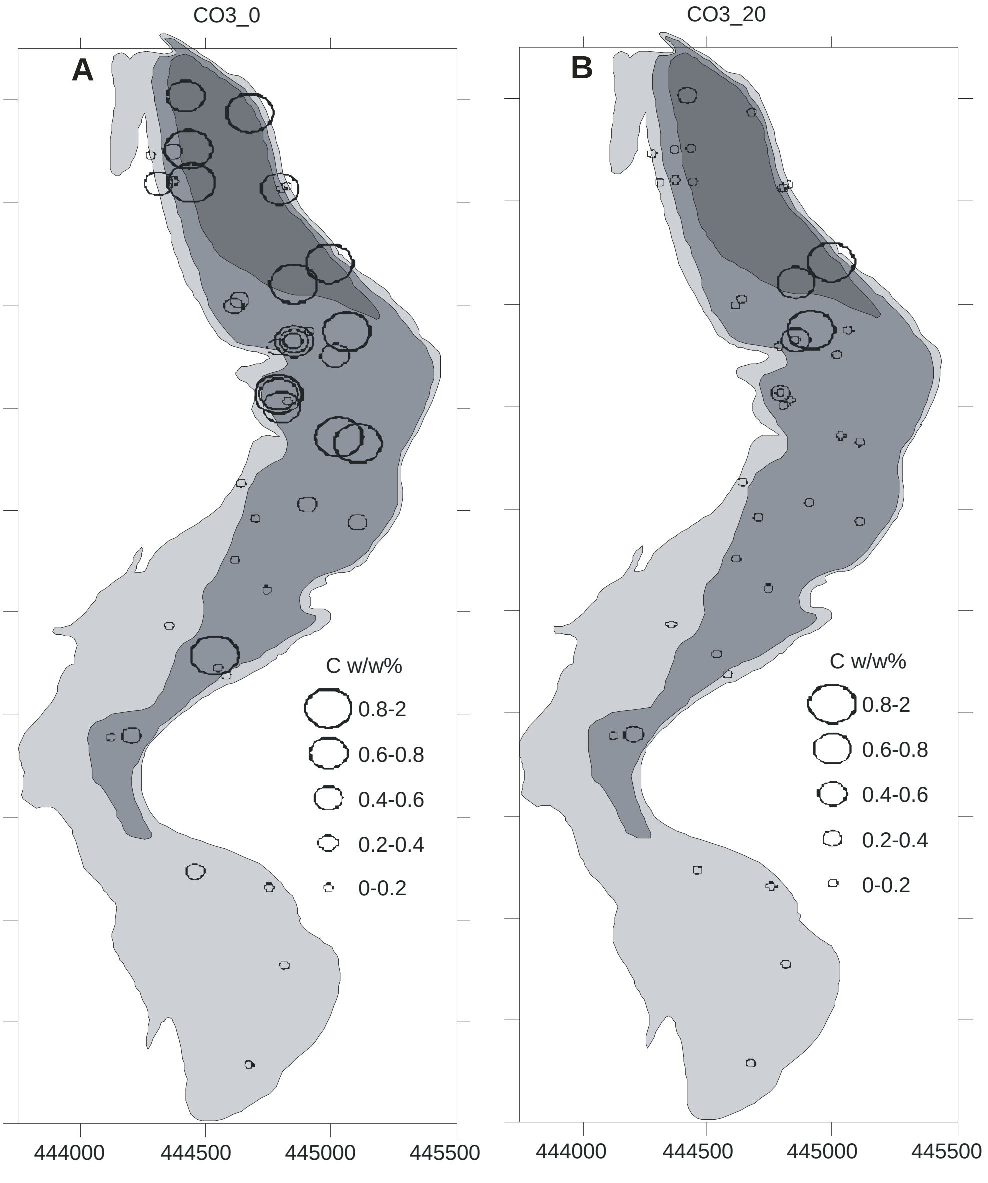


Figure 14

Carbonate concentrations of unit A (0-10 cm) and unit B (10-40 cm) through the Wet, Wet-Dry and Dry Zones.

ACIDIFICATION POTENTIAL

Distribution of sulfide versus carbonate

The spatial distribution of sulfide relative to carbonate controls the potential for the acidification of sediments (Dent 1986). The concentrations of sulfide against carbonate have been plotted for units A and B of the three water regimes (Figures 15 A-C) and for units C, D and E across the basin (Figure 15 D). The trigger value for sulfide concentrations in fine textured coastal ASS (0.1%S as sulfide) has been plotted as a dashed line. According to the coastal ASS guidelines, sediments with higher sulfide concentrations than this value would require further investigation. Plotted as a solid line is where the acid generation potential (AGP) of sulfides equals the acid neutralising capacity (ANC) of carbonate. Any value to the left of this solid line has greater AGP than ANC and may become acidic upon oxidation. The Loveday Basin sediments largely follow a trend of high sulfide concentrations matched with high carbonate concentrations. In units C, D and E and throughout the Dry Zone sulfide concentrations are consistently below the coastal ASS trigger value, with sufficient carbonate concentrations to counter any acidity (Figure 15 C and D). The Wet Zone has high sulfide concentrations but also proportionally high concentrations of carbonate (Figure 15 A).

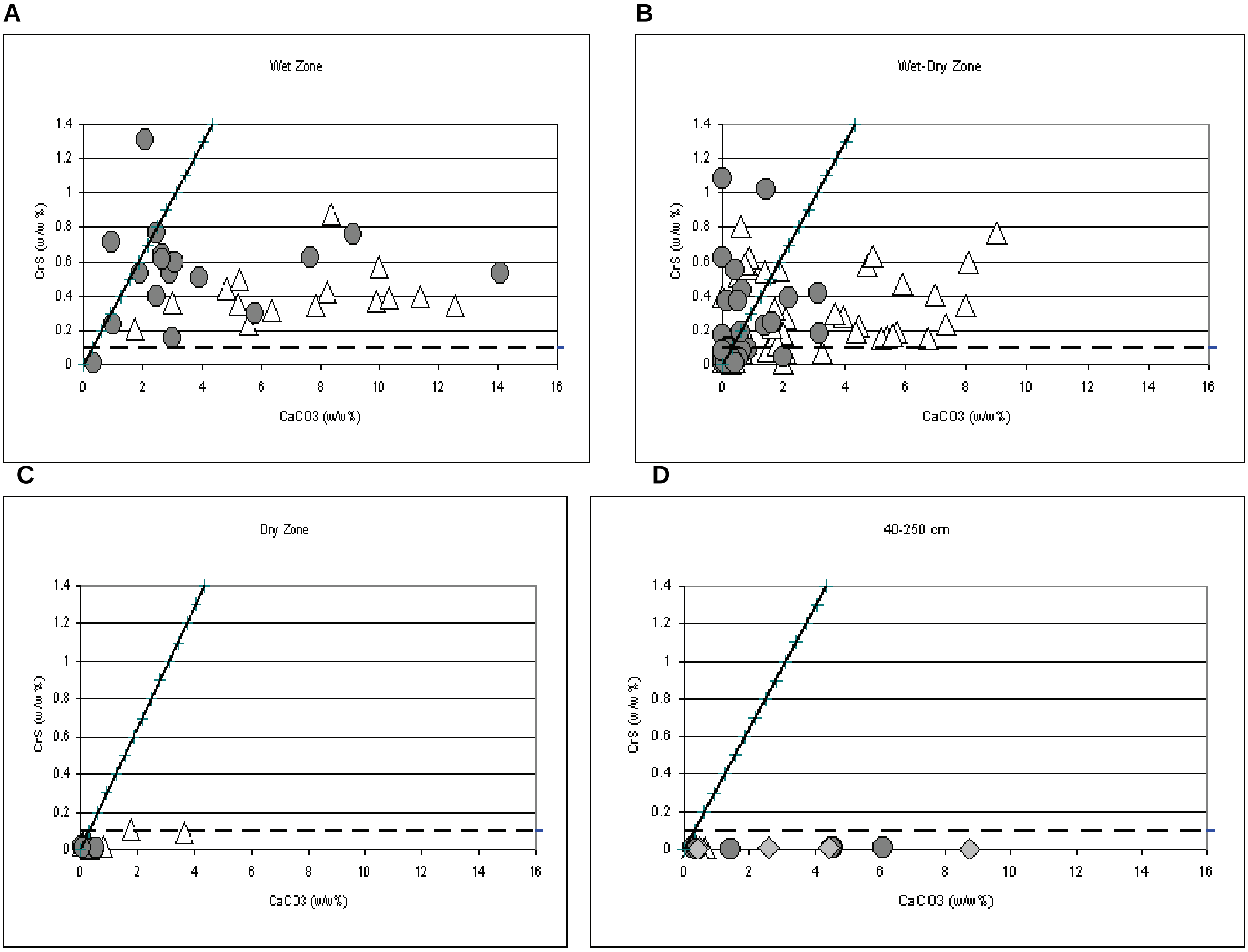


Figure 15. Concentration of sulfide (CRS) vs carbonate (CaCO3). A-C saline clay (triangles) and mottled clay (circles). D Coonambigual Clays (triangles), Monoman Sands (circles and dimands)
Coastal ASS triger value (0.1%S; Dashed line). AGP = ANC (Solid line).

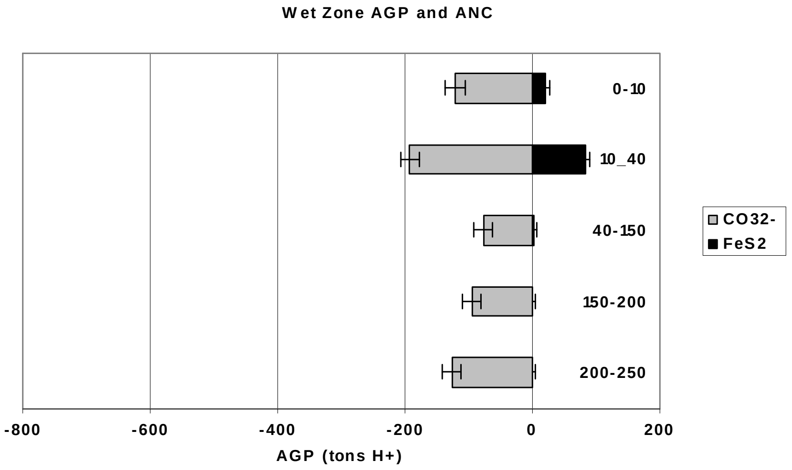
However, in the Wet-Dry Zone high sulfide concentrations are not always associated with high carbonate concentrations. In this zone, 61 out of the 105 samples measured have greater AGP than ANC, mostly from unit B, and have the potential to become acidic if oxidised (Figure 15 B). Although the majority of the basin's sulfidic sediments have high carbonate concentrations, some localised areas of the Wet-Dry Zone have high sulfide and low carbonate concentrations. These areas of the basin often contain localised acid ‘hot spots’ (pH 3-4) associated with mottles of jarosite, demonstrating that acidification, although only on a small scale, does occur in these sediments.

The lower concentrations of sulfides and carbonate of the Wet-Dry Zone compared with the Wet Zone indicate that the wetting and drying of sediments has removed sulfide and carbonate (discussed above). The difference in the distribution of sulfides and carbonate in the Wet-Dry Zone indicate they are removed by different processes or at different rates. Carbonate is readily solubilised in waters that are under-saturated in carbonate or at the mixing interface of two waters that are saturated with respect to carbonate (Gledhill and Morse 2006). These conditions for carbonate dissolution appear to be met during wetting and drying in parts of the Wet-Dry Zone sediments flushing carbonate from localised areas, principally from unit B. Sulfide as pyrite is highly insoluble in waters, even when under-saturated, but readily dissolves upon oxidation (Bierens De Haan 1991). The wetting and drying of the Wet-Dry Zone sediments has periodically exposed sediments to the oxidising atmosphere, when sulfide oxidation appears to occur locally. The difference in the processes of sulfide and carbonate dissolution under wetting and drying conditions appears to have locally separated sulfides and carbonate in the Wet-Dry Zone, leading to the current heterogeneity.

Net acid generation potential

The net acid generation potential (NAGP) has been estimated for each of the basin’s units by subtracting the AGP (calculated from the total amount of sulfide) from the ANC (calculated from the total amount of carbonate). All of the basin’s units, including the sulfide-rich upper 40 cm of sediments, are calculated to have no NAGP (Figure 16 A-H). The negative NAGP values for the basin are an indication of the potential alkalinity that would remain if sulfides where completely oxidised. The high AGP of the Wet Zone is matched with high ANC (Figures 16 A and B) whilst the low ANC of the Dry Zone is proportional to the low AGP (Figures 16 E and F). Conversely, the Wet-Dry Zone has high AGP and only moderate ANC in the mottled clay unit (10-40 cm), resulting in an overall NAGP of -0.89 t H^+ (Figure 16 C and D). Although this unit is calculated to be neutral, the net alkalinity is less than the standard error, indicating that these sediments may have the potential to become acidic if sulfides were completely oxidised. This demonstrates that the separation of sulfides and carbonate in localised areas may be significant enough to produce an NAGP in larger areas of sediment. However, combining the three zones together, the basin as a whole has excess ANC to counter the total AGP (Figure 16 G and H). Although the basin has a high level of internal variability, the basin overall has excess alkalinity, and basin-wide acidification is unlikely.

A



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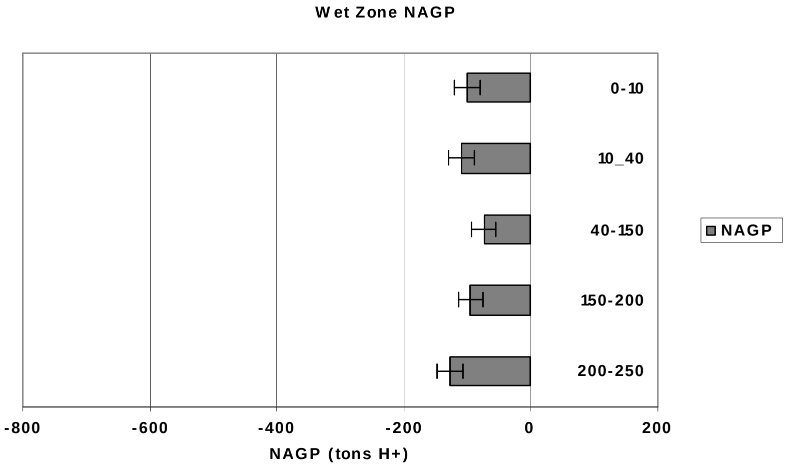

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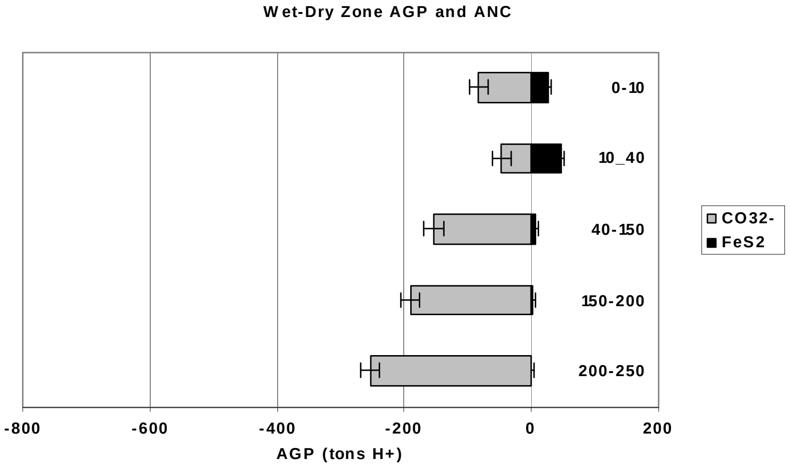

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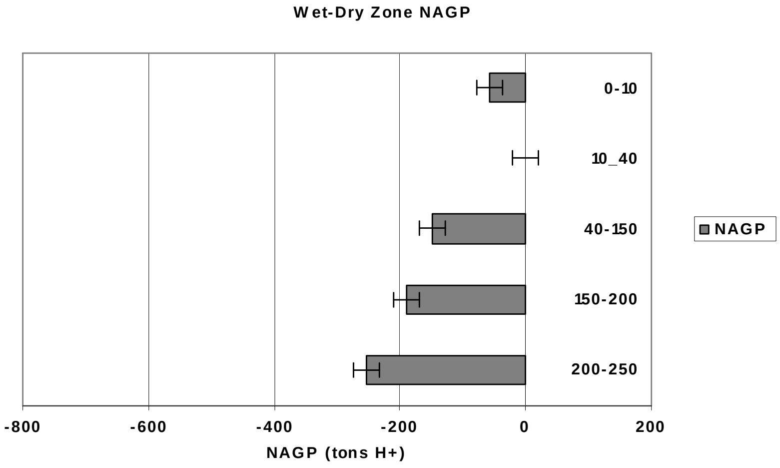
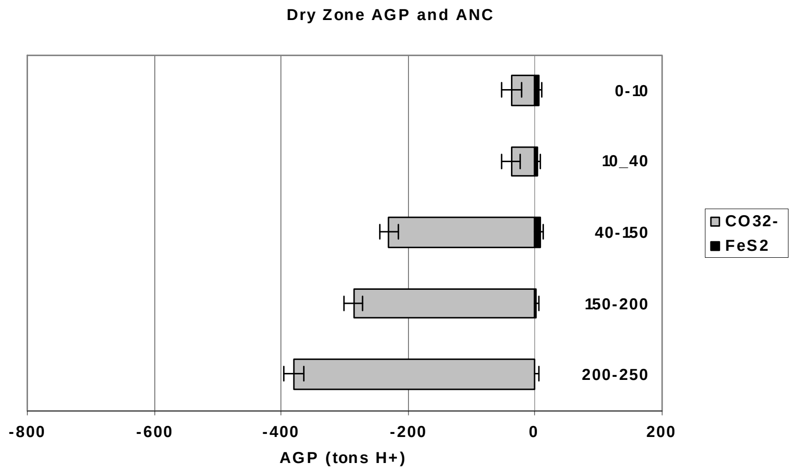
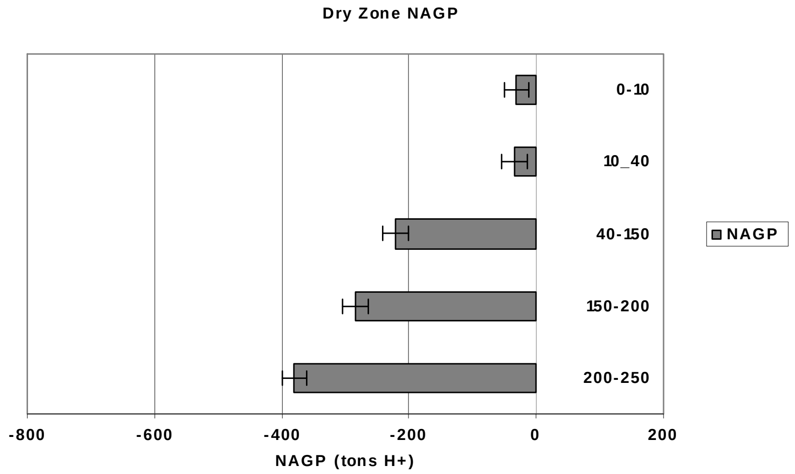


Figure 16 A-D. AGP and ANC (calculated from the amounts of sulfide and carbonate) and the resulting NAGP (AGP-ANC).

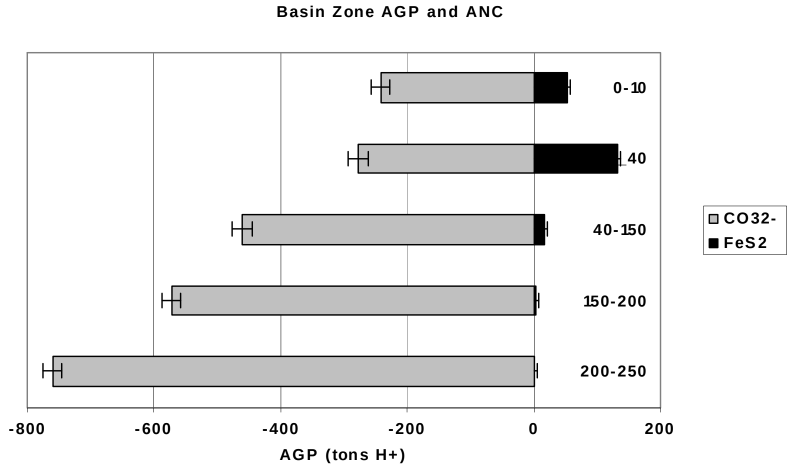
E


Dry Zone AGP and ANC
0-10
10_40
40-150
150-200
200-250
CO32-
FeS2
-800
-600
-400
-200
0
200
AGP (tons H+)

F


Dry Zone NAGP
0-10
10_40
40-150
150-200
200-250
NAGP
-800
-600
-400
-200
0
200
NAGP (tons H+)

G


Basin Zone AGP and ANC
0-10
40
40-150
150-200
200-250
CO32-
FeS2
-800
-600
-400
-200
0
200
AGP (tons H+)

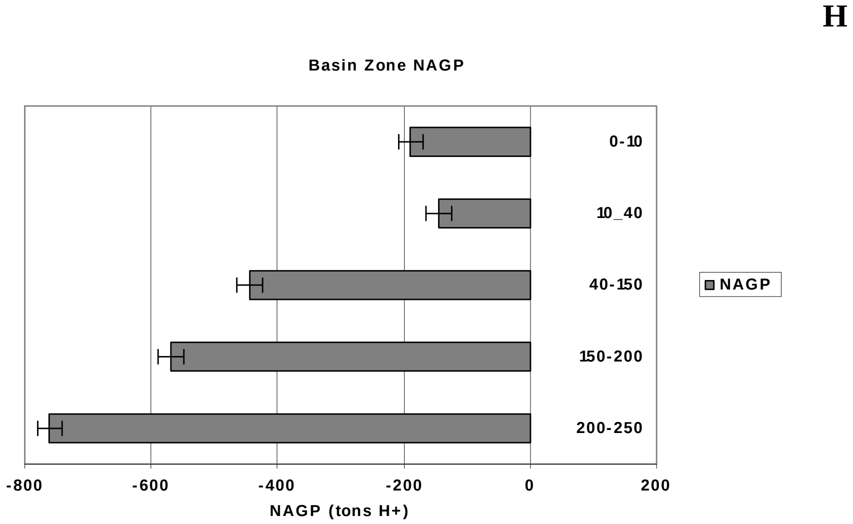


Figure 16 E-H. AGP and ANC (calculated from the amounts of sulfide and carbonate) and the resulting NAGP (AGP-ANC).

Acid sulfate soils

The sulfidic sediments/materials of the Loveday Basin, like other recent inland sulfidic sediments/materials, are intimately linked with sulfate-rich saline waters (Fitzpatrick *et al* 1996; Hall *et al* 2006; Lamontagne *et al* 2006a). Inland sulfidic materials/sediments typically form at the interface of sulfate-rich saline waters and organic-rich surface sediments. These sediments have high carbonate concentrations and, without sediment acidification, are characterised by schwertmannite rather than jarosite, characteristic of coastal ASS (Fitzpatrick *et al* 1996). Whilst the sulfidic sediments of the Loveday Basin have formed through similar processes to other inland sulfidic sediments, the basin has also developed acidic areas similar to coastal ASS. The oxidation of sulfides in carbonate-poor areas of the basin has resulted in the formation of acidic sulfuric horizons rich in jarosite (AASS) overlying un-buffered sulfidic sediments (PASS), which is a characteristic sediment profile of coastal ASS (Dent 1986). The principal difference between the basin sediments and coastal ASS is the spatial scale. Where coastal ASS have up to metres of sulfidic and sulfuric sediments (Fitzpatrick *et al* 1996) the basin's sulfur-rich sediments are restricted to 40 cm depth. Additionally, the basin's small acidic areas are surrounded by carbonate-rich sediments and the basin as a whole can not be classed as an ASS by the coastal ASS definition (Pons 1973). However, the development of acidic areas, although currently only small in the Loveday Basin, demonstrate that, under the correct conditions, there is the potential for ASS to develop from inland sulfidic sediments. This study has demonstrated an association between the wetting and drying of inland sulfidic sediments and the formation of acidic sediments. Other sulfidic wetlands and disposal basins along the Murray-Darling Basin floodplains may be disturbed by wetting and drying due to drought, increased irrigation efficiency or managed water level manipulation (i.e. for the mitigation of salinity or the reintroduction of 'natural' wetting and drying regimes) and could be at risk of forming ASS. The processes involved in the separation of sulfides and carbonate have not been investigated in this study but appear to be linked to the different solubilities of sulfides and carbonate during wetting and drying conditions.

CONCLUSIONS

After 35 years operating as a saline disposal basin, high sulfur and carbon concentrations are restricted to the surface 40 cm of the Loveday Basin. This accumulation is principally within organic-rich sulfidic wetland clays, the majority of which have been deposited over the same time period. The distribution and form of sulfur and carbon within the surface 40 cm of basin sediments show distinct trends between the basin’s dominant water regimes of predominantly dry (Dry Zone), predominantly wet (Wet Zone) and intermittent wetting and drying (Wet-Dry Zone). Due to infrequent flooding, the Dry Zone has not accumulated wetland clays and has low concentrations of organic carbon, carbonate and sulfur, principally as sulfate. In the Wet and Wet-Dry Zones, where water levels have remained high for around 30 years, the sedimentation of the organic-rich wetland clays and the concentration of sulfate by evaporation have produced a substrate for sulfate reduction, resulting in high sediment sulfide concentrations. Water levels have remained high in the Wet Zone and here the wetland clays have maintained consistently high concentrations of organic carbon, carbonate and sulphides, with low concentrations of sulfate. Wetting and drying of these sulfidic wetland clays in the Wet-Dry Zone since 2000 has produced highly variable concentrations of sulfur and carbon due to localised sulfide oxidation and the redistribution of sulfate and carbonate. Within the Wet-Dry Zone high sulfide concentrations are not always associated with high carbonate concentrations, most likely due to their different solubilities, resulting in small pockets of sediment with potential and actual acidity. However, as a whole, the Loveday Basin has excess ANP from carbonate to buffer the AGP from sulfides and, as long as the basin remains a closed system to carbonate, large scale acidification is unlikely. The distinct patterns between the three zones shown in this study demonstrate that the water regime controls not only the sediments’ texture but also the form and distribution of sulfur and carbon and the sediments’ NAGP. Management options for inland sulfidic sediments that incorporate water manipulations need to assess the potential for the separation of carbonate and sulfides and any resulting sediment acidification.

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CHAPTER 16

SULFUR AND CARBONATE MOBILITY DURING CHANGES IN WATER REGIME IN AN INLAND SULFIDIC WETLAND, LOWER MURRAY FLOODPLAINS, SOUTH AUSTRALIA

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INTRODUCTION

Inland sulfidic sediments are widespread in saline wetlands of the Murray-Darling Basin (Fitzpatrick *et al* 1996; Hall *et al* 2006; Lamontagne *et al* 2006a; Sullivan *et al* 2004). Wetlands most at risk of developing sulfidic sediments are those that have maintained a permanent water cover and high salinities for years to decades. As a consequence environmentally significant concentrations of sulfides have developed in saline disposal basins used for irrigation discharge (Lamontagne *et al* 2006a). Due to prolonged drought conditions and increased irrigation efficiency the water cover of some disposal basins are now being removed by evaporation, exposing sulfidic sediments to oxidising atmospheric conditions.

Pyrite is highly insoluble in water but readily oxidises in the presence of O_2 and Fe^{2+} (Bierens De Haan 1991). Bio-mediated sulfide oxidation proceeds rapidly under acidic conditions (Singer and Stumm 1970) and produce a range of sulfur and iron oxidation products (Fitzpatrick *et al* 1996; Luther *et al* 1982; Nordstrom 1982; Ritsema *et al* 1992; Ward *et al* 2004b). The complete oxidation of pyrite in acid sulfate soils (ASS) is often summarised by (Dent 1986):

$$FeS_{2\,(s)} + 15/4O_{2\,(aq)} + 7/2H_2O_{\,(l)} \rightarrow Fe^{III}(OH)_{3\,(s)} + 2SO_4^{2}{}_{(aq)}^{-} + 4H^+_{\,(aq)}$$

Here, 1 mole of pyrite (FeS_2) is decomposed in the presence of dissolved molecular oxygen (O_2) and water to produce ferric iron (Fe^{III}), sulfate (SO_4^{2-}) and 4 moles of acid (H^+). If the acid generation potential (AGP) of pyrite is greater than the sediments acid neutralising capacity (ANC), largely as carbonate, sediments can become acidified during oxidation. It is the production of acid during atmospheric exposure and sulfide oxidation in unbuffered coastal ASS which has led to the large scale degradation of soils and adjacent waterways (Astrom and Astrom 1997; MacDonald *et al* 2004; Sammutt and Lines-Kelly 1996; Sammut *et al* 1996; White *et al* 1997).

Inland sulfidic sediments of the Lower Murray are largely associated with high concentrations of carbonate. The production of acid during pyrite oxidation in these sediments is neutralised by reaction with carbonate minerals forming gypsum (Dent 1986):

$$CaCO_3 + 2H^+ + SO_4^{2-} + H_2O \rightarrow CaSO_4.2H_2O + CO_2$$

Here, acid (H^+) is neutralised by the decomposition of calcite ($CaCO_3$) to produce gypsum ($CaSO_4.2H_2O$) and carbon dioxide (CO_2), removing carbonate from the sediment profile. As an equal amount of ANC is produced, in the form of carbonate, to the amount of AGP during the formation of sulfides, sulfidic sediments will not become acidic upon oxidation unless carbonate has been removed. In coastal sediments the large disparity in the concentrations of pyrite and carbonate is due to the leaching of carbonate by tidal flushing during pyrite formation producing sediments with a net store of potential acidity (Dent 1986; Pons *et al* 1982). Carbonate is not removed from inland sulfidic sediments during formation and the undisturbed sediments have high concentrations of carbonate preventing acidification.

However, an association between the wetting and drying of inland sulfidic sediments and low carbonate concentrations has recently been demonstrated (Wallace *et al.* 2008; this volume). Sulfidic sediments of the Loveday Basin that had undergone wetting and drying contained low carbonate concentrations and small pockets of acidity and potential acidity whilst sulfidic sediments that had maintained permanent water cover also maintained high carbonate concentrations. Although the Loveday Basin as a whole had excess alkalinity from carbonate to neutralise all potential acidity, these observations indicate that during wetting and drying carbonate and sulfides can be separated in inland sulfidic sediments (Wallace *et al.* 2008; this volume). Inland sulfidic sediments are likely to undergo wetting and drying due to deliberate water manipulations to remove sulfides by oxidation or due to the decrease of wetland inputs as a consequence of drought and irrigation efficiency (Lamontagne *et al* 2006a). These recent findings indicate that there may be a risk of acidification associated with the wetting and drying of inland sulfidic sediments. The processes and rates of carbonate and sulfide separation in inland sulfidic sediments during wetting and drying are currently unknown.

In this study the distribution of sulfur and carbonate in sediments and waters of the Loveday Basin are used to establish the mobility of carbonate and sulfur under different water regimes. The aims of this study are to determine 1) if the wetting and drying of inland sulfidic sediments has separated sulfides and carbonate 2) what processes cause this separation and 3) over what time frames this can occur.

Site description

The Loveday Disposal Basin is a 3.3 km^2 hyper-saline wetland located in the lower Murray River floodplains, South Australia (34º15′S, 140º24′E; Figure 2.1). The climate is semi-arid having cool winters and hot dry summers with variable rainfall (100-500 mm y^{-1}) and a high potential evapo-transpiration (Hostetler and Radke 1994). Originally a stranded meander lake of the Murray River, the basin sits within the Coonabidgal Clays, a silty clay aquitard, that overlies the Monoman Sand aquifer and abuts the Parilla-Loxton Sand aquifer within the Murray floodplains (Hostetler and Radke 1994). The basin was disconnected from the Murray River via floodgates and converted into an evaporation basin in 1972 to dispose of saline irrigation water for nearby irrigation districts (Evans 1989). Additionally, the basin is inundated during flood events (Hostetler and Radke 1994) and may also receive saline groundwater discharge (Hostetler and Radke 1994). Over three decades the basin has been essentially a terminal site for salts, including sulfate, with the principal loss of water through evaporation (Hostetler and Radke 1994). In addition to sulfate the basin also contains significant accumulations of sulfides (Lamontagne *et al* 2006a). Basin sediments were partially dried in 2000 due to a reduction in irrigation discharge and lack of floods. The basin sediments have since remained partially dry with intermittent wetting and drying due to variable inputs of water from rain events and irrigation and groundwater discharge.

The Loveday Basin has developed three distinct water regimes of permanently wet (Wet Zone), intermittent wetting and drying (Wet-Dry Zone) and predominantly dry (Wallace *et al.* 2008; this volume). Due to infrequent flooding the Dry Zone has not accumulated high concentrations of sulfides or carbonate. The Wet Zone has accumulated high concentrations of sulfide and carbonate which are preserved under a permanent water cover. The Wet-Dry Zone has formed from the wetting and drying of sediments similar to the Wet Zone since 2000 and now has highly variable concentrations of sulfides and carbonate. Some areas of the Wet-Dry Zone have low carbonate and high sulfide indicating the removal of carbonate during wetting and drying.

METHODS

Sediments were sampled with PVC sediment corers for 7 depth profiles with samples taken at 5 cm increments from 0 cm to 40 cm. Samples were subsequently freeze-dried and milled for analysis.

The concentrations of reduced inorganic sulfur minerals (FeS and FeS_2) were analysed by the acid volatile sulfur (AVS; FeS) method and chromium reducible sulfur (CRS; FeS + FeS_2) method . AVS was conducted in the field on wet sediments as well as in the laboratory along with CRS on freeze-dried milled samples. These methods liberate the reduced inorganic sulfur fractions as H_2S, which is trapped in a zinc acetate solution as zinc sulfide and quantified from iodometric titration. The AVS fraction has commonly been assumed to represent the monosulfides (amorphous FeS, FeS_{1-x} and Fe_3S_4), but recent studies demonstrate that other sulfur fraction might be included in the extraction and that not all the monosulfides are removed. The limitations of this method are acknowledged but this fraction is referred to in this thesis as the “monosulfides” for comparison with other studies that have used this method. As the CRS method measures the total inorganic reduced sulfur (FeS + FeS_2), pyrite (FeS_2) has been calculated from the CRS fraction minus the AVS fraction, again for comparison with other studies that have used these methods.

Total sulfur was analysed on all samples by X-ray fluorescence (XRF) and total sulfur and total carbon analysed on a suite of 50 samples by LECO-CNS induction furnace analysis (conducted at CSIRO). Sediment sulfate concentrations where calculated from total sulfur minus the reduced sulfur fraction. Sediment carbonate was quantified by a manometric technique (conducted by CSIRO) on all samples, after removal of large shell fragments.

Pore waters were extracted by compression at 10 cm intervals from 7 sediment cores (0-40 cm depth) which were taken parallel to cores for sediment analysis. Pore waters and surface waters were acidified and analysed for Al, Ca, Fe, K, Mg, Mn, Na, Si and Sr by ICP-AES. Unacidified waters were analysed for Cl by IC and titrated for alkalinity (given as HCO_3 equivalents) with pH and temperature measured.

RESULTS

Sediment profiles

Sediments were sampled through the 40 cm thick sulfur-rich surface sediments of the Loveday Basin. The sediment depth profiles were taken along a transect that crossed the basin’s three dominant water regimes of the Wet Zone (predominantly wet), Wet-Dry Zone (intermittent wetting and drying) and Dry Zone (predominantly dry; Figure 1).

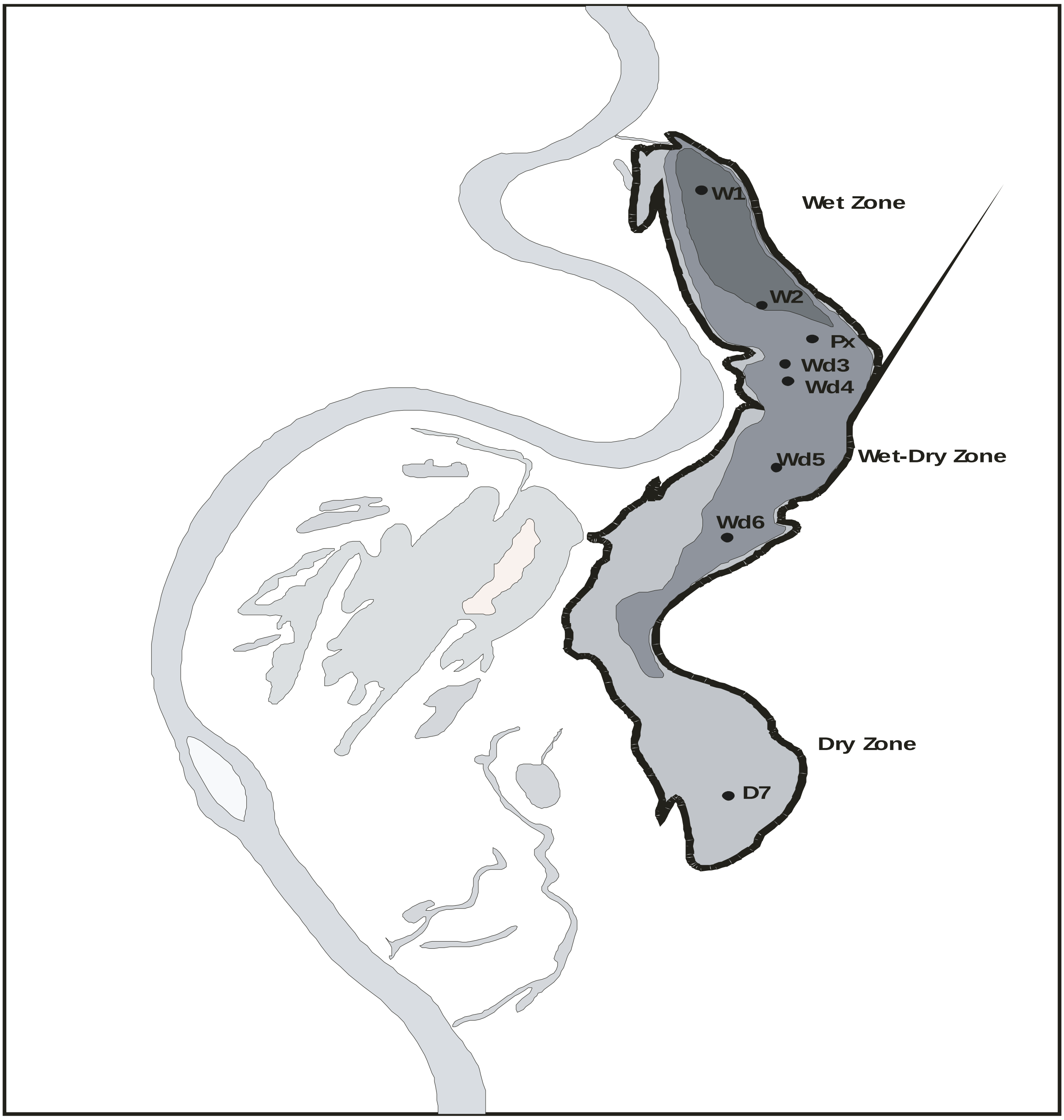


Figure 1 Loveday Basin sediment profile sample locations

Sediment profiles from the Wet Zone (W1 and W2) have relatively consistent total sulfur concentrations with depth ranging from 0.6-1.2 wt%S (Figure 2A) with an average total sulfur concentration of 0.79 wt%S. Below 5 cm depth sulfur is predominantly present as pyrite (0.4-0.9 wt%S; 70-90% of the total sulfur) in the Wet Zone (Figure 2B) with the slight increase in total sulfur in the surface 5 cm of the Wet Zone due to higher sulfate concentrations (0.5-0.9 wt%S; Figure 2C). Sulfate is more concentrated at the surface of the W2 profile (Figure 2C) which is closer to the waters edge adjacent to the Wet-Dry Zone (Figure 1). Monosulfides (0.02-0.07 wt%; Figure 2D) are restricted to these sulfate-rich sediments above 10 cm depth in the Wet Zone and only representing a small fraction of total sulfur. Associated with the high pyrite concentrations of the Wet Zone are high concentrations of carbonate (2.1-9.1 wt%$CaCO_3$; Figure 2E) which average 4.6 wt%$CaCO_3$. The consistently high concentrations of pyrite and carbonate indicate consistently high levels of sulfate reduction and sulfide preservation throughout the Wet Zone sediments.

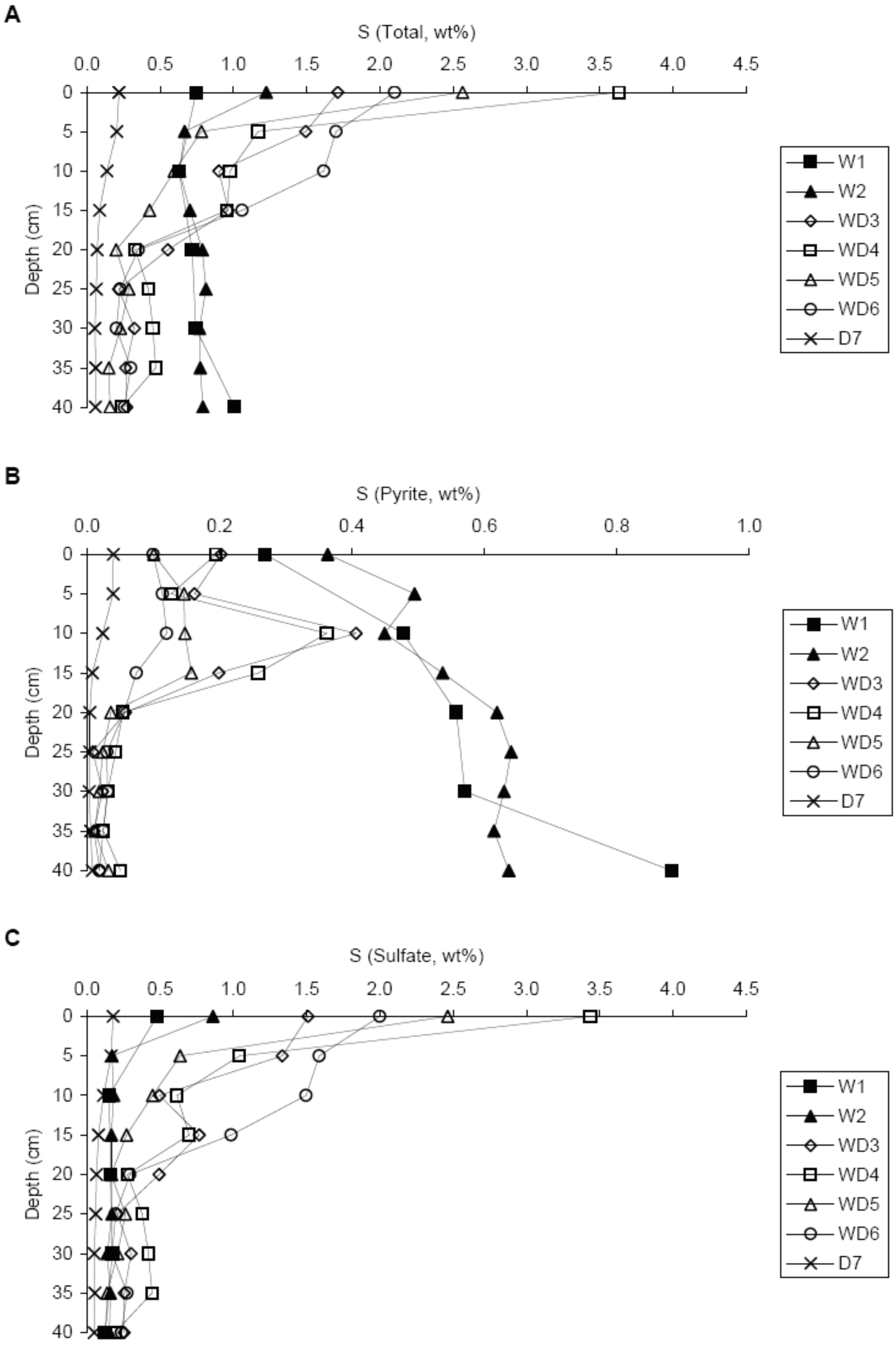


Figure 2 Depth profiles through upper 40 cm of basin sediments of the Wet Zone (W1 and W2), Wet-Dry Zone (WD 3-6) and Dry Zone (D7).

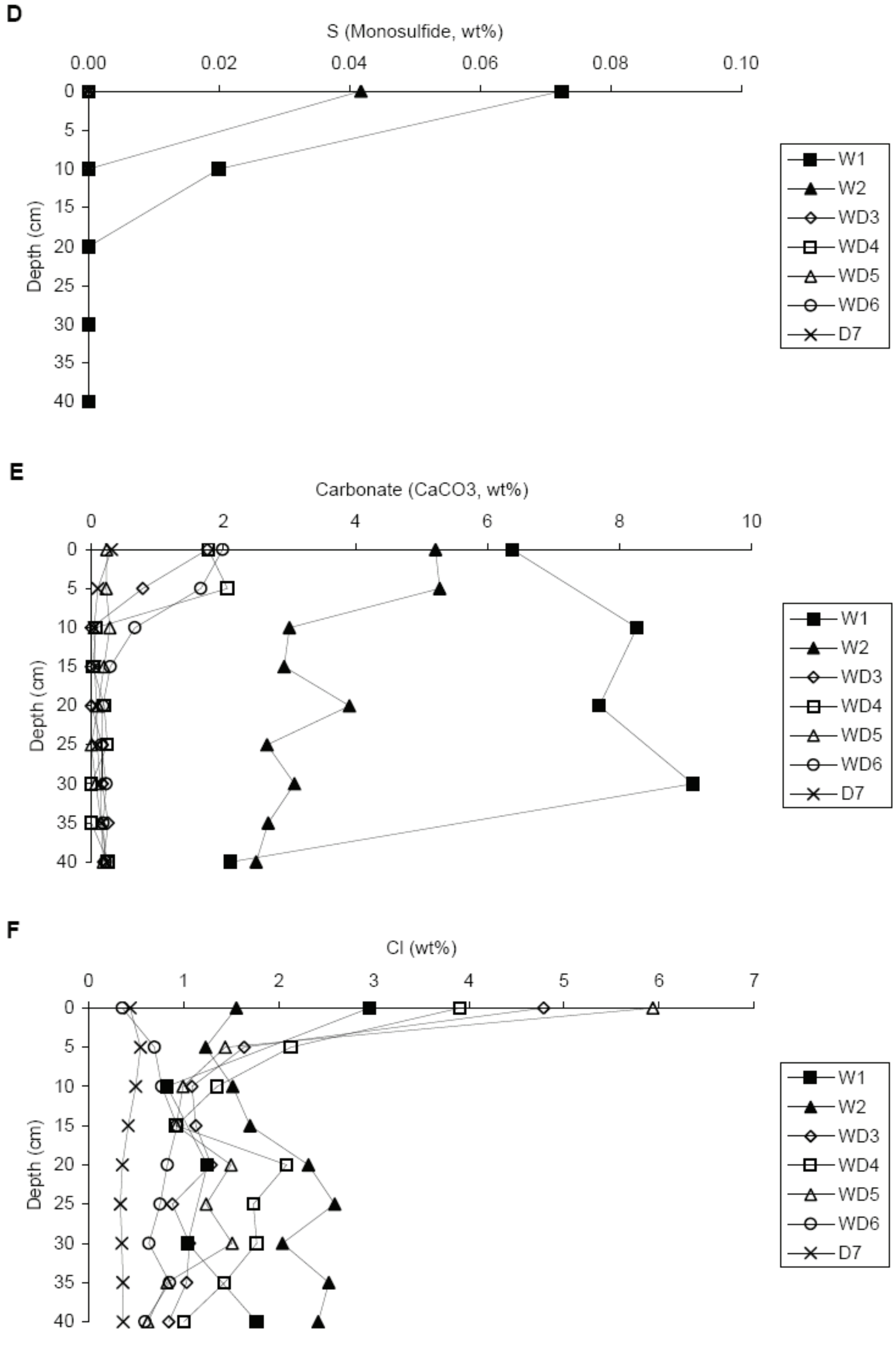


Figure 2 Depth profiles through upper 40 cm of basin sediments of the Wet Zone (W1 and W2), Wet-Dry Zone (WD 3-6) and Dry Zone (D7).

The Wet-Dry Zone sediment profiles (WD3-6) formed from the wetting and drying of sediments similar to the Wet Zone (Wallace *et al.* 2008; this volume). These profiles have high total sulfur concentrations above 5 cm depth (2.1-3.5 wt%S; Figure 2A) which decrease to 0.2-0.5 wt%S at 20 cm depth and below (Figure 2A). Although the surface of the Wet-Dry Zone has the highest total sulfur concentrations of the basin, the average total sulfur concentration of the Wet-Dry Zone is 0.74 wt%S, slightly lower than the Wet Zone. Unlike the Wet Zone, the Wet-Dry Zone does not have consistently high concentrations of pyrite and very little monosulfides (Figures 2B and 2D). In the Wet-Dry Zone pyrite is concentrated between 5 and 20 cm depth and increases towards the Wet Zone (Figure 2B). Total sulfur in the Wet-Dry

Zone is predominantly in the form of sulfate which increases in concentration above 20 cm depth to the surface (0.2-0.5 to 1.5-3.5 wt%S). Carbonate is concentrated at the surface of the Wet-Dry Zone with concentrations increasing towards the Wet Zone (Figure 2E). However, unlike the Wet Zone, carbonate is in much lower concentrations and is not directly associated with pyrite (Figures 2B and 2E). The average carbonate concentrations of the Wet-Dry Zone (0.4 wt%$CaCO_3$) are almost an order of magnitude lower than the Wet Zone. The Wet-Dry Zone sediment profiles show that the wetting and drying of sulfidic sediments has produced a wide range of sulfur and carbonate concentrations and that the high variability in the distribution of sulfur and carbonate is dependent on depth and distance form the Wet Zone.

The Dry Zone has much lower concentrations of sulfate, sulfides and carbonate throughout the profile (D6) compared with the Wet and Wet-Dry Zones (Figures 2A-E). Unlike the Wet and Wet-Dry Zones, the Dry Zone sediments have not formed under a sulfate-rich saline water cover or formed significant amounts of sulfides (Wallace *et al.* 2008; this volume).

Sediment chloride concentrations are not directly affected by sulfate reduction or sulfide oxidation like sulfur and carbon. The distribution of chloride throughout the basin’s sediment profiles can be used to separate these redox processes from salt precipitation and dissolution. Below 5 cm depth the sediment chloride concentrations (Figure 2F) are low in the Dry Zone (profile D6) and generally increase in the Wet-Dry Zone (profiles WD3-6; average of 1.4 wt%Cl) to the Wet Zone (average of 1.8 wt%Cl) where chloride concentrations are high near the waters edge (profile W2). The highest chloride concentrations of the basin are above 5 cm depth in the Wet-Dry Zone (4-6 wt%Cl). This trend of increasing concentrations at the surface of the Wet-Dry Zone is similar to sulfate and carbonate indicating that their concentrations are partly controlled by salt precipitation and dissolution. However, sulfate concentrations start increasing from 20 cm depth whilst carbonate concentrations are coparativly very low. The differences in chloride to sulfate and carbonate concentrations indicate that other processes such as sulfate reduction and sulfide oxidation may also be affecting concentrations.

Desiccation features

Sediments were sampled at a depth of 10 cm in a cross section from the centre to the edge of 4 desiccation features (PA-D) in the Wet-Dry Zone located near the edge of the Wet Zone between profiles W2 and WD3 (Figure 1). The trends of sulfur, carbon and chloride from the interior to the exterior of all the desiccation features are similar to the upper 10 cm of the Wet-Dry Zone depth profiles. The interior of the desiccation features are high in pyrite (5.6-6.4 wt%S, Figure 3A) whilst the surface of the desiccation features have high sulfate (2.4-4.1 wt%S, Figure 3C), monosulfides (0.03-0.07 wt%S, Figure 3D), carbonate (4.2-7.0 wt%$CaCO_3$, Figure 3E) and chloride (4.0-6.7 wt%S, Figure 3F). These observations demonstrate that desiccation features have strong zoning of sulfur and carbonate upward and outward from their interior and that this zoning is consistent throughout the Wet-Dry Zone. The concentrations of carbonate are also largely higher than the remainder of the Wet-Dry Zone which supports the trend of increasing concentrations towards the waters edge of the Wet Zone.

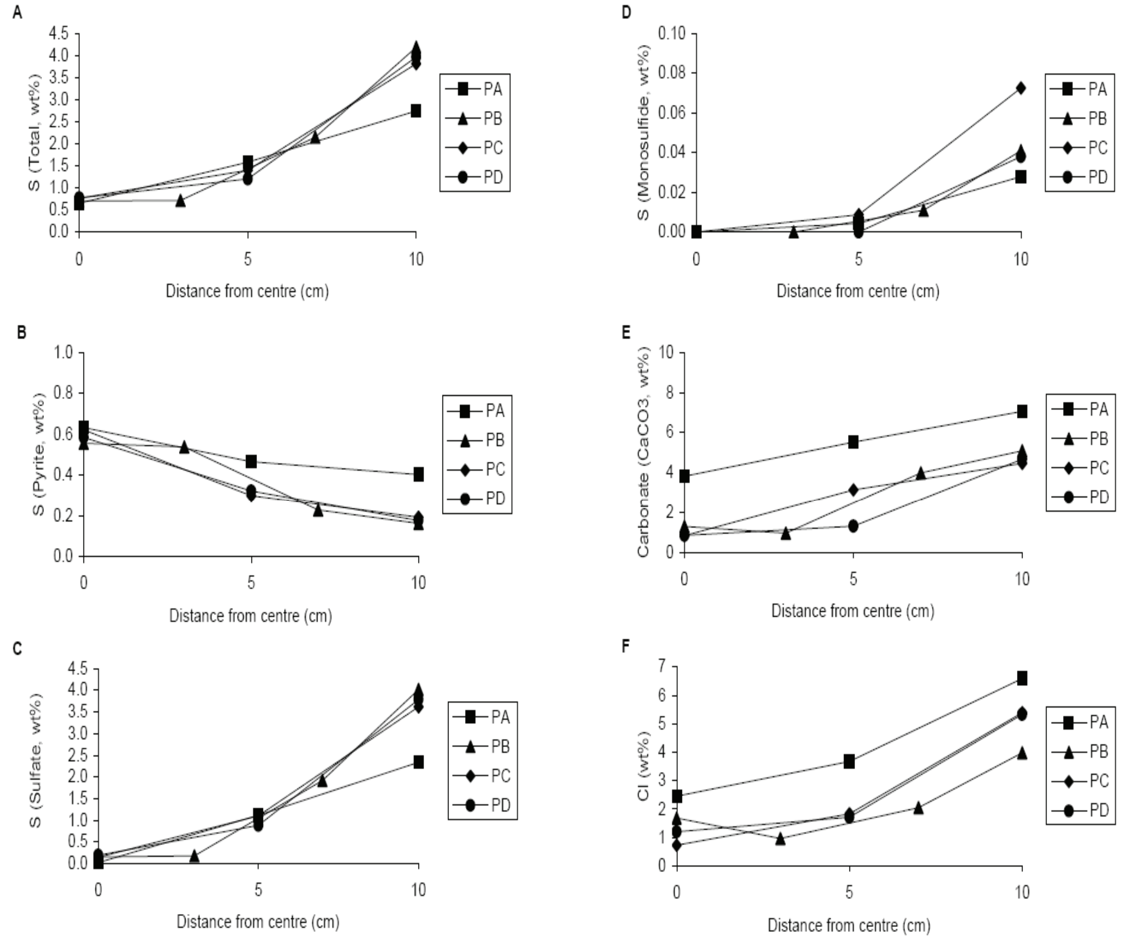


Figure 3 Horizontal profiles from centre (0cm) to exterior (10cm) of 4 peds in the Wet-Dry Zone.

Sediment depth profiles were also collected from the interior (P1) and edge (P2) of a desiccation feature between profiles W2 and WD3 after a rain event (46.6 mm over 3 days). Sulfur is concentrated at the surface of the desiccation crack (Figure 4A) whilst pyrite is most concentrated within the interior of the desiccation feature (Figure 4B). Pyrite in profile P1 (Figure 4B) has a similar trend to the other sediment depth profiles through the Wet-Dry Zone (Figure 2B) with pyrite preserved in the interior of desiccation features. Profile P1 is closer to the Wet Zone than profiles WD3-6 and has higher concentrations of pyrite demonstrating that, like carbonate, pyrite increase towards the Wet Zone. During the rain event salt efflorescence dissolved from the surface of the desiccation features and monosulfides rapidly formed within the desiccation cracks. This is reflected in the sediment profiles where sulfate, carbonate and chloride (Figures 4C, 4E and 4F) have been leached from the surface of desiccation features and concentrated within the desiccation cracks, along with monosulfides (Figure 4D). This shows that the surface salt efflorescence is highly mobile during inundation with rainwater accumulating in adjacent desiccation cracks.

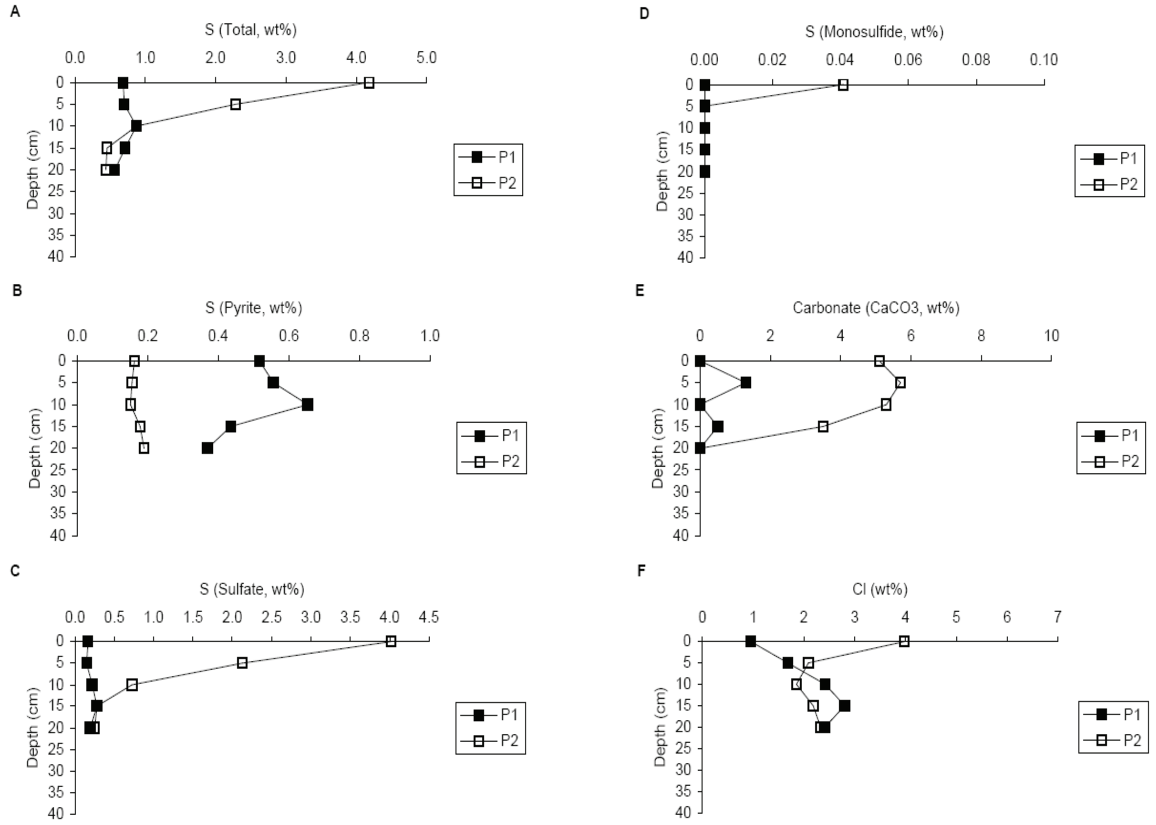


Figure 4 Vertical profiles of the centre (P1) and exterior (P2) of a ped in the Wet-Dry Zone.

Water chemistry

Water chemistries were analysed from the Wet Zone surface water cover and from pore waters of profile W1 (Wet Zone) and profiles WD3-6 (Wet-Dry Zone). In addition pore waters were analysed from profiles of the interior and exterior of a desiccation feature after a rain event P1 and P2 (Wet-Dry Zone). No waters could be extracted from the dry sediments of the Dry Zone.

The pore waters of the Wet Zone increase up profile in SO4 (2400-5000 mg/l) and Cl (13000-22000 mg/l) largely ranging between ground water (Kirste *et al*) and surface water (Figrues 5A and 5B). The pH (7-8) and alkalinity (600-850 mequiv) of Wet Zone pore waters also increase up profile below 5 cm depth (Figures 5C and 5D). However, above 5 cm depth, pH (7.5) and alkalinity (615 mequiv) decrease to values similar to surface waters. The upper pore waters appear to reflect surface water compositions. The pore water depth profiles most likely reflect the increase in the salinity of basin waters over time and indicate basin surface waters have recently had a decrease in alkalinity but maintain high pH.

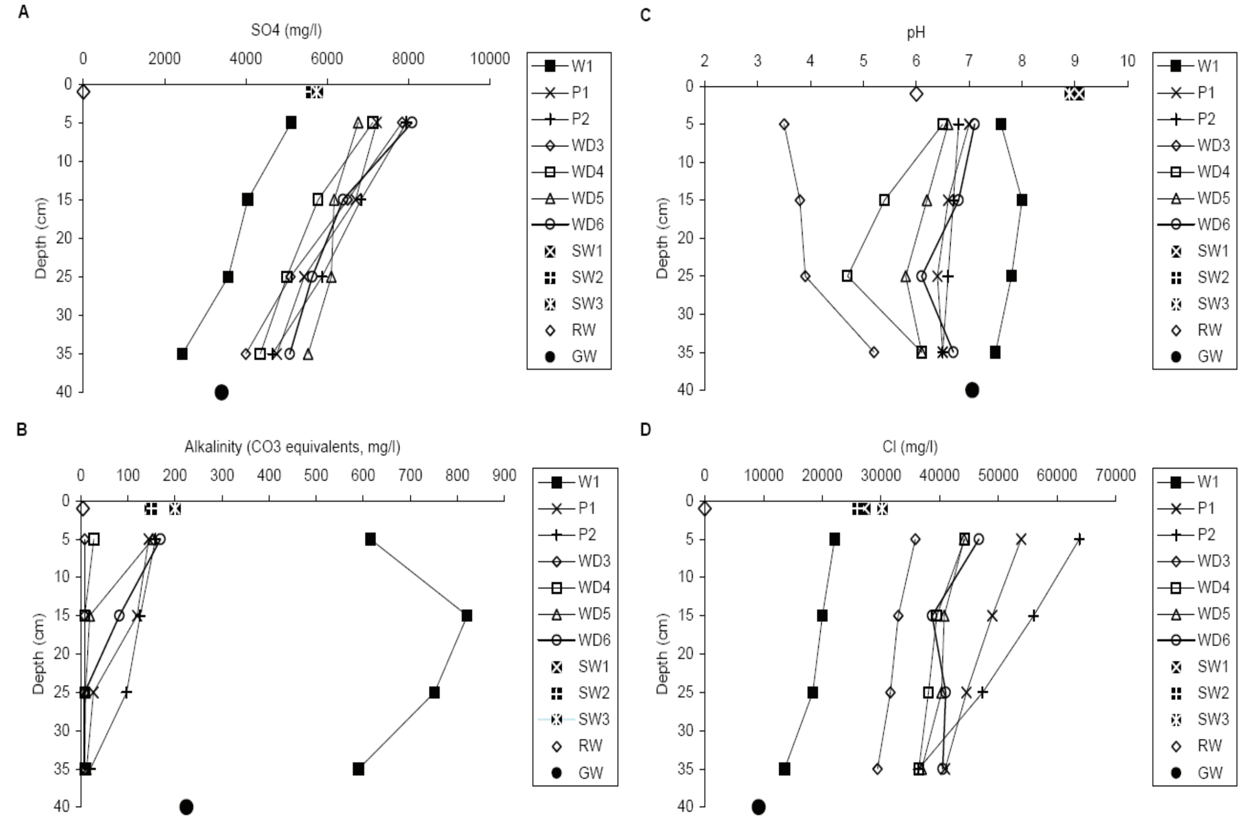


Figure 5 Dissolved concentrations in rainwater (RW), surface water (SW), groundwater (GW) and pore water of the Wet Zone (W1 and W2), Wet-Dry Zone (P1, P2 and WD 3-6) and Dry Zone (D7).

The Wet-Dry Zone pore waters have a range of sulfate and chloride concentrations (4000-8000mg/l SO_4 and 30000-64000 mg/l Cl respectively) that increase up profile above sulfate and chloride concentrations of the Wet Zone and of surface and ground waters (figures 5A and 5B). The Wet-Dry Zone pore waters range from pH 4-7 which generally increase towards the sediment surface. Pore waters with pH <6.5 have low alkalinities (<30 mequiv) and pore waters with pH >6.5 have alkalinities (80-200 meqiv) approaching surface waters of the Wet Zone (300mequivel; Figures 5C and 5D). The Wet-Dry Zone pore waters, relative to the Wet Zone, indicate that sulfate and chloride have been concentrated whilst alkalinity has decreased. Surface water sulfate, chloride and alkalinity concentrations largely sit between the Wet Zone and Wet-Dry Zone pore waters indicating they are influenced by both the Wet Zone and the Wet-Dry Zone waters.

DISCUSSION

Salt transport

The transport of salts in basin waters by diffusion and advection has been estimated using chloride rather than sulfate or carbonate concentrations. This is to discount sulfate reduction and sulfide oxidation which may affect sulfate and carbonate concentrations along flow paths.

Diffusive transport

The pore waters of the Wet-Dry Zone have high chloride concentrations that increase upwards towards the salt crust at the sediment surface. If the salt crust has formed due to the evaporation of surface water this concentration gradient is due to the inward diffusion of dissolved chloride. The mass flux of chloride by diffusive transport can be calculated from Fick’s first law as:

fd = D*dC/dz

Where fd is the diffusive mass flux of solute per unit area per unit time, D* is the sediment diffusion coefficient and dC/dz is the concentration gradient. The concentration gradient of chloride from the sediment surface to 40 cm depth in 7 profiles average 12.5-25 kg $m^{-3}m^{-1}$ (5000-10000 mg/l Cl). The profiles are all within a fine textured wetland clay unit and the diffusion coefficient is assumed to remain constant. The diffusion coefficient for chloride is dependent on the free diffusion of chloride in water and the porosity and permeability of sediments. This has been calculated in similar fine textured sediments to be around 3×10^{-10} m^2 s^{-1} (Price and Woo 1988). This gives a range in the average daily diffusive chloride flux from the surface salt crust into sediments of 3 - 6×10^{-4} kg m^{-2} d^{-1}.

Advective transport

The movement of water advect salts along the flow path. When surface waters of the Wet-Dry Zone fall below the sediment surface the fine clays remain wet due to capillary action, similar to other wetlands where the potential evaporation exceeds the input of waters (Casey and Lasaga 1987; Harvey and Nuttle 1995; Price and Woo 1988). The pore waters evaporated at the sediment surface are replaced by waters from the shallow water table producing vertical flow of water upward. This movement moves salts to the sediment surface by advection and could also account for the surface salt efflorescence. The water flux is controlled by the rate of evaporation and the hydraulic conductivity of sediments. As sediments do not dry out the supply of water from the water table must meet the output of water by evaporation demonstrating that evaporation is the limiting factor. With an average potential evaporation during summer months of 8 mm/d the water flux is estimated at 8×10^{-3} m d^{-1}. The advective flux of chloride (fa) will be (Price and Woo 1988):

$fa = cq$

Where c is the average concentration of advected chloride and q is the water flux. With the average concentration of chloride in surface pore water (40% moisture content) of 18 kg m^{-3}, the average daily chloride flux to the surface by advective transport is estimated at 0.14 kg m^{-2} d^{-1}. This is over two orders of magnitude greater than the inward diffusion of chloride demonstrating the high salt concentrations in the Wet-Dry Zone pore waters are formed by the outward vertical advection of salts from the shallow saline waters.

Salts may also be advected through the Wet-Dry Zone horizontally. During periodic inundation, input waters (irrigation discharge, river water and rainwater) flow towards the Wet Zone through the desiccation features of the Wet-Dry Zone. The lower concentration of these input waters relative to basin waters may displace or mix with the more saline waters and transport salts from the Wet-Dry Zone to the Wet Zone. However, recent studies at the Loveday Basin (Lamontagne *et al* 2006b) have shown that density stratification occurs during basin flooding with the lower density input waters sitting on top of the higher density basin waters for months. Due to the periodic nature of flow through events from input waters and the potential for incomplete mixing it is not possible to calculate the advective salt flux from the Wet-Dry Zone to the Wet Zone from pore waters. However, the amount of salts transported from the Wet-Dry Zone to the Wet Zone can be estimated from the difference in the average concentrations of sulfur, carbonate and chloride mineral salts in sediments (discussed below).

Salt precipitation and dissolution

Dissolved salts may be added to or removed from waters by mineral precipitation and dissolution. The saturation indices (SI) of sulfate, carbonate and chloride salts from the basins surface and pore water chemistry (Table 1) have been calculated with the software package ‘The Geochemist’s Workbench®’ (GWB; Figures 6A-C). Mineral SI are reported as log Q/K where Q is the reaction quotient and K is equilibrium constant of each mineral. Gypsum has SI between -1 and +1 (Figure 6A) indicating basin waters are in equilibrium with respect to gypsum and that increases in sulfate (by sulfide oxidation or evaporation) will result in gypsum precipitation whilst decreases in sulfate (by sulfate reduction or dilution by input waters) will result in gypsum dissolution (Le Chatelier’s principal). Waters throughout the Wet Zone and at the surface of the Wet-Dry Zone, where salt efflorescence is concentrated and pH is >6.5, are saturated with respect to calcite (SI ≈ >0) indicating carbonate mineral precipitation (Figure 6B). However, rainwater and pore waters below 15 cm depth in the Wet-Dry Zone with pH <6.5 are under saturated with respect to calcite (SI <0) indicating carbonate dissolution (Figure 6B). All waters measured are under saturated with respect to halite (SI <0) indicating, apart from in salt efflorescence, chloride is largely mobile (Figure 6C). The calculated SI of sulfate and carbonate and chloride minerals in basin waters indicate these salts may be both removed or added to solution by mineral precipitation and dissolution along vertical or horizontal flow paths.

Table 1 Summary of field observations and measurements of electrical conductivity and pH in 1:5 (sediment:water; sediment:30% hydrogen peroxide) slurries.

cm	Area (km^2)	Location	Clay features	Colour	1:5 EC (dS m$_{-1}$)	1:5 pH	1:5 pH (H_2O_2)
Wet 0-10	0.6	Under water	Sulfidic ooze	Black with yellow coating	6.1	7.0 - 8.2	6.9 - 7.8
Wet-Dry 0-10	1.1	Shallow water table	Salt efflorescence	White salts	21.4	6.3 - 8.4	6.0 - 7.8
Dry 0-10	1.7	Dry edge of basin	Flocculated clays	Light grey	17.3	6.8 - 8.1	6.0 - 7.5
Wet 10-40	0.6	Under water	Heavy clay	Dark grey with black mottles	5.5	7.0 - 8.6	7.0 - 8.0
Wet-Dry 10-40	1.1	Shallow water table	Ped - heavy clay	Grey with red, black and yellow mottles	9.9	3.2 - 8.0	1.9 - 7.2
Dry 10-40	1.7	Water table > 1 m deep	Heavy clay	Grey with red mottles	6.3	6.5 - 7.4	6.7 - 7.3
40-150	3.3	Across whole basin	Heavy clay	Grey homogeneous	2.3	6.8 - 7.5	6.2 - 7.2
150-200	3.3	Across whole basin	Silty clay	Light grey	2.8	6.9 - 7.2	6.8 - 7.0
200-250	3.3	Across whole basin	Sandy silt	Yellow with orange and black nodules	1.9	6.3 - 7.8	6.5 - 7.5

Ped = polygonal desiccation feature

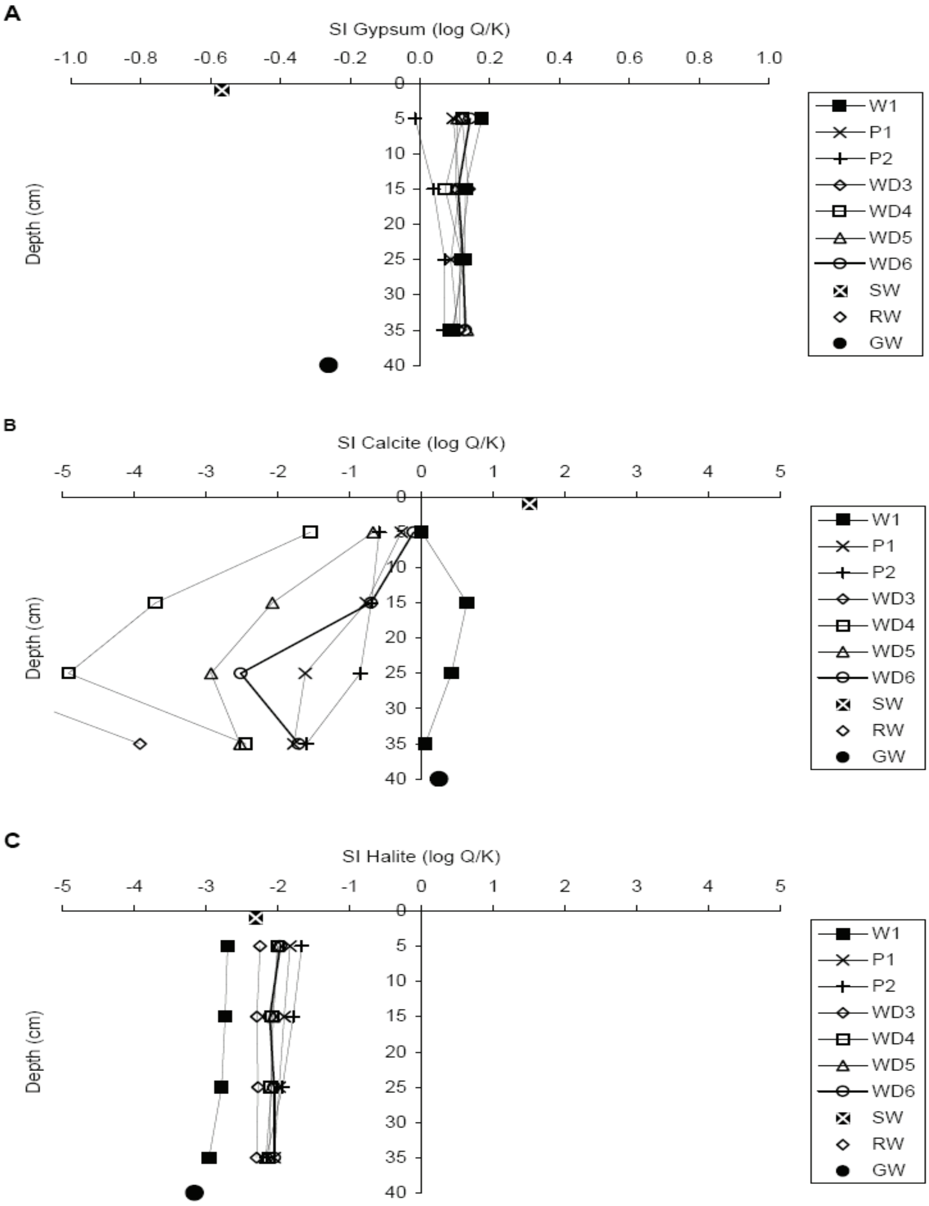


Figure 6 Saturation indices (SI) for rainwater (RW), surface water (SW), groundwater (GW) and pore water of the Wet Zone (W1 and W2), Wet-Dry Zone (P1, P2 and WD 3-6) and Dry Zone (D7).

Evaporation, which drives the vertical advection and concentration of dissolved salts in pore waters at the surface of the Wet-Dry Zone, produces salt efflorescence with high concentrations of gypsum (1.5-3.5 wt%S), calcite (0.2-2.1 wt%$CaCO_3$) and halite (0.3-6.0 wt%Cl, Figures 2C, 2E and 2F). This demonstrates that, as pore waters are drawn vertically upward and evaporated, these minerals all become saturated and dissolved sulfate, carbonate and chloride are removed from solution by mineral precipitation. The formation of salt efflorescence is rapid and the calculated advective chloride flux of 0.14 kg m^{-2} d^{-1} indicates that the observed range in salt efflorescence salt concentrations could form within 5-52 days. The salt crust can also be rapidly removed. The majority of salts were dissolved over 3 days during a rain event (46.6mm) with dissolved salts subsequently concentrated within adjacent desiccation cracks (Figures 4C, 4E and 4F). Within a day of the rain event, salt efflorescence started reforming at the tops of desiccation features as evaporation continued. This demonstrates that the salt crusts are not a permanent feature but are cyclically destroyed and reformed. Intermittent wetting and drying of the Wet-Dry Zone sediments results in the repeated formation and removal of salt efflorescence by the vertical redistribution of carbonate, sulfate and chloride salts.

Although the surface of the Wet-Dry Zone contains the basin's highest concentrations of salts, the average concentrations of chloride (as halite) through the Wet-Dry Zone sediment profile (1.43 wt%Cl) are slightly lower than those of the Wet Zone profile (1.84 wt%Cl). If the Wet-Dry and Wet Zones are assumed to have had the same average chloride concentrations prior to the partial draining of the basin this difference indicates a net loss of salts from the Wet-Dry Zone. This potential removal of chloride from the Wet-Dry Zone could be due to horizontal advection of salts by water inputs which flow through the Wet-Dry Zone (discussed above). If the difference in chloride concentrations between the Wet and Wet-Dry Zones is completely due to leaching by input waters the daily horizontal advective flux since 2000 would be 2.2 x 10^{-3} kg m^{-2} d^{-1}, significantly lower than the potential vertical advective chloride flux. The low horizontal salt flux suggests that the current intermittent nature of water input and incomplete mixing with saline basin waters does not move large amounts of salts. This shows that salts may be redistributed from the Wet-Dry Zone towards the Wet Zone by wetting and drying but that the maximum horizontal advection of salts is small compared to vertical advection within the Wet-Dry Zone.

Variations in the average sulfate and carbonate concentrations between the Wet and Wet-Dry Zone are different to the variation in average chloride concentrations. Average sulfate concentrations are higher in the Wet-Dry Zone (0.70 wt%S) than the Wet Zone (0.23 wt%S) whilst carbonate is concentrated in the Wet Zone (4.63 wt%$CaCO_3$) but largely absent from the Wet-Dry Zone (0.41 wt%$CaCO_3$). This difference from chloride indicate that sulfate and carbonate concentrations are not just controlled by salt precipitation and dissolution. The increase of sulfate and decrease of carbonate are an indication of sulfide oxidation (discussed below).

Sulfides

Pyrite is highly insoluble and remains concentrated within the interior of desiccation features (Figure 2B). However, pyrite is rapidly dissolved under oxidising conditions (Bierens De Haan 1991). The consistently high pyrite concentrations within desiccation features indicate that even after weeks of drying the interior of desiccation features do not undergo significant pyrite oxidation. This is because the interior of desiccation features remaining saturated with water, after water levels have dropped below the sediment surface, due to capillary action. This limits the amount of pyrite oxidation, which appears to be restricted to several centimetres into the surface of desiccation features and below 20 cm depth (Figures 2B and 3B). The preservation of pyrite concentrations in the middle of the desiccation features gives an indication of what pyrite concentrations would have been across the Wet-Dry Zone prior to sediment oxidation during the recent drying. The concentration of pyrite in the centre of desiccation features is similar to the concentration of pyrite in the relatively undisturbed Wet Zone sediments (Figures 2B and 3B). This indicates that prior to drying the Wet-Dry Zone had consistently high pyrite concentrations and have formed from sediments similar to the Wet Zone sediments.

Sulfide oxidation

The production of sulfate from sulfide oxidation has increased the amount of gypsum in sediments of the Wet-Dry Zone. This is demonstrated by comparing the sediment sulfate and chloride concentrations, as chloride is not produced by sulfide oxidation. Whilst chloride increases greatly toward the surface above 5 cm depth (Figure 2F) sulfate has relatively higher concentrations between 5 and 20 cm depth (Figure 2C). Sulfate concentrations are above what would be expected from vertical advection alone indicating sulfate is being added by active sulfide oxidation. This additional sulfate is precipitated as gypsum but also redissolved during wetting and drying. Dissolved sulfate may be transported both vertically and horizontally from the site of sulfide oxidation by advection (discussed above). However, the movement of sulfur is complicated by partitioning between sulfide and sulfate so the concentrations of total sulfur have been used to determine the overall movement of sulfur. The average total sulfur concentrations of the Wet-Dry Zone (0.72 wt%S) are only slightly lower than those of the Wet Zone (0.79 wt%S) indicating that potentially only a small amount of sulfur has been removed from the Wet-Dry Zone by horizontal advection. The similarity of the average total sulfur concentrations of the Wet Zone and Wet-Dry Zone demonstrate that the sulfate produced by sulfide oxidation is largely retained within the profile and concentrated at the sediment surface by vertical advection. These trends show that the highly variable concentrations of sulfate and sulfide within the Wet-Dry Zone are largely due to sulfide oxidation and the vertical redistribution of sulfate.

The oxidation of sulfides also produces acid which reacts with carbonate. The reaction of carbonate with acid can completely remove carbonate from sediments as CO_2 (Dent 1986). Comparing carbonate and chloride concentrations carbonate is almost completely absent below 5 cm depth indicating removal by acid during sulfide oxidation. However, the total removal of carbonate from the sediments below 5 cm depth cannot be explained by sulfide oxidation alone. If the Wet-Dry Zone sediments have formed from Wet Zone like sediments the acid produced from the complete oxidation of pyrite would not be sufficient to remove all carbonate minerals present as CO_2 (acid balance discussed below, section 5.4). This indicates additional removal of carbonate by advection. Although the advection of carbonate is limited due to the saturation of basin waters with respect to calcite (surface water, irrigation discharge, groundwater and pore waters of the Wet Zone), the solubility of carbonate is increased with small decreases in pH. Below 15 cm depth in the Wet-Dry Zone, where the majority of pyrite has been oxidised, pore waters have pH <6.5 and are under-saturated in respect to calcite. The advection (vertical and horizontal) of carbonate in these lower pH waters will be increased and could potentially remove calcite from the sediments. In addition rainwater is under-saturated with respect to calcite and flushing by rain events could also remove carbonate from the Wet-Dry Zone. This indicates that carbonate has been removed from the Wet-Dry Zone sediments, below 5 cm depth, by several processes including 1) direct removal of carbonate as CO_2 during sulfide oxidation, 2) increased solubility of carbonate in waters with pH <6.5 associated with sulfide oxidation, 3) vertical leaching of carbonate in under-saturated waters during evaporation, and 4) horizontal leaching of carbonate in under-saturated waters during rain events. The direct removal of carbonate by sulfide oxidation (1) also removes pyrite. However, the increased solubility of carbonate in basin waters with pH <6.5 combined with vertical and horizontal leaching (2, 3 and 4) remove carbonate without removing pyrite. This has produced sediments, largely between 5 and 20 cm depth, with high pyrite and low carbonate in the Wet-Dry Zone.

The majority of pyrite appears to have been removed from the Wet-Dry Zone. Whilst the concentrations of total sulfur between the Wet Zone and Wet-Dry Zone have remained similar the high concentrations of sulfide in Wet Zone sediments appear to have been largely replaced by high sulfate concentrations in Wet-Dry Zone sediments due to sulfide oxidation. If the Wet-Dry Zone had consistently high sulfide concentrations similar to the Wet Zone sediments, the sections of sediment profiles with low sulfides indicate the dominant sites of sulfide oxidation. The outward flow of water due to evaporation has kept the interior of desiccation features continually wet restricting the inflow of oxidants. This is demonstrated by low pyrite concentrations at the outer surface of desiccation features where sulfide oxidation has been limited to around 5 cm depth. The desiccation features of the Wet-Dry Zone also have low concentrations of pyrite between 20 and 40 cm depth (Figure 2B). This could represent an oxidation front from the shallow waters that are drawn up into the desiccation features. This indicates that as oxidising waters are drawn into the desiccation features oxidants are consumed by pyrite oxidation and sulfides are oxidised from the bottom up during vertical advection. The sulfate produced during sulfide oxidation is transported to the surface salt crust whilst acid produced lowers pore water pH and removes carbonate. Additionally, the decrease in pyrite and carbonate concentrations in the Wet-Dry Zone with distance form the Wet Zone indicate that areas that have had longer exposure time to dry conditions have undergone greater amounts of oxidation. These observations demonstrate that sulfide oxidation has been prevalent throughout the Wet-Dry Zone with remaining pyrite largely restricted to the interior of desiccation features where sediments remain wet. The oxidation of this large amount of pyrite has locally lowered the pH of waters slightly and produced small areas of sediment acidity but has not caused any large scale acidification. This indicates that sulfide oxidation, since the drying of the Wet-Dry Zone in 2000, has removed the majority of pyrite from sediments under bulk pH neutral conditions.

Sulfate reduction

During the wetting of the Wet-Dry Zone sulfate is partially reduced to sulfide. The wetting of the Wet-Dry Zone sediments is accompanied by the rapid (within hours) formation of algal mats and thin monosulfidic horizons. The formation of monosulfides on top of oxidised sediments and underneath an oxidising water column represents high redox gradients. This is most likely formed due to the localised consumption of oxidants by labile organic carbon within the algal mats and monosulfide formation is largely restricted to these areas. Sulfate reduction is most prevalent within desiccation cracks, where waters are present the longest, but these areas only form relatively thin coatings that contain a maximum of 0.1%S reduced sulfur. The subsequent drying of these Wet-Dry Zone sediments rapidly re-oxidises the monosulfides to sulfate replacing the thin layer of monosulfides with a thin horizon of iron oxides. The relatively short periods of sulfate reduction and rapid oxidation of monosulfides does not appear to significantly increase the amount of sulfides. The lower concentration of sulfides in the Wet-Dry Zone compared with the Wet Zone demonstrate that, in spite of periodic re-wetting and sulfate reduction events, wetting and drying of sulfidic sediments progressively removes sulfides.

NAGP

The net acid generation potential (NAGP) of the basins sediment profiles have been calculated from the acid generation potential (AGP) of pyrite minus the acid neutralisation capacity (ANC) of carbonate. A bulk NAGP balance for the basin has been calculated in Wallace *et al*/Chapter X, here the NAGP of individual profiles are used to determine where in the sediment profile NAGP occurs. The basin sediments have a wide range in NAGP but, like the distribution of pyrite and carbonate, show distinct trends between the three water regimes (Figure 7).

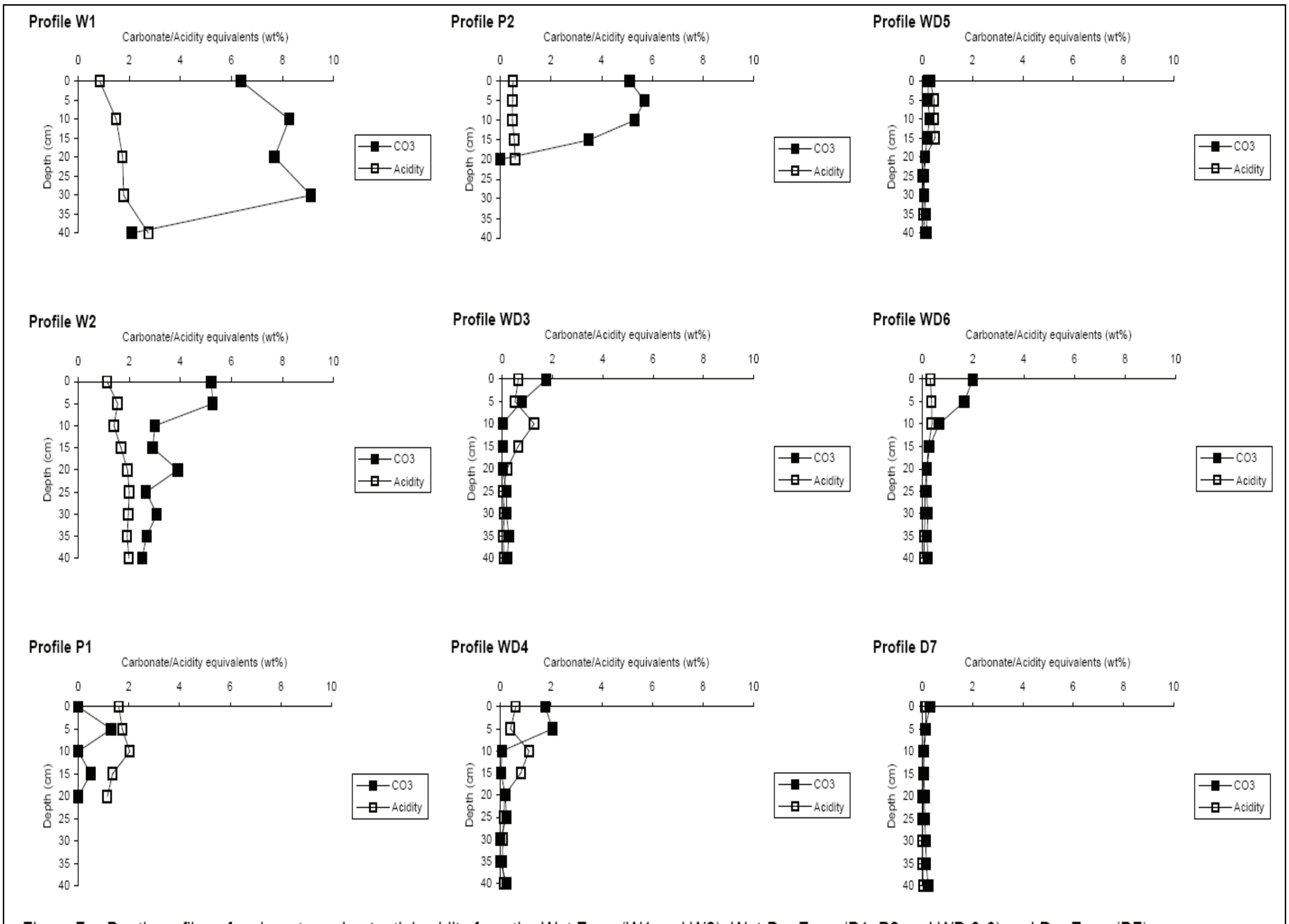


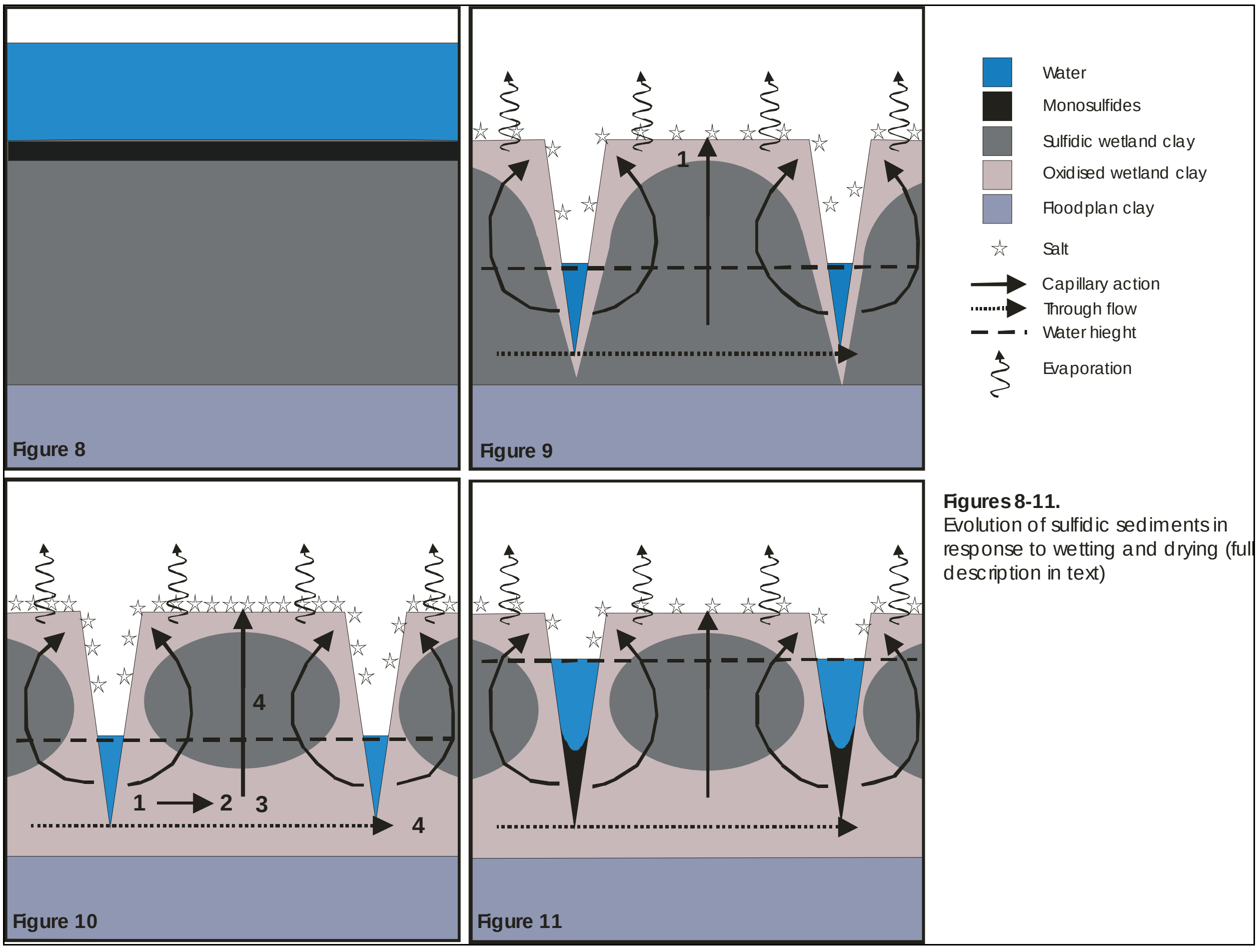
Figure 7 Depth profiles of carbonate and potential acidity from the Wet Zone (W1 and W2), Wet-Dry Zone (P1, P2 and WD 3-6) and Dry Zone (D7).

In the undisturbed sediments of the Wet Zone the ANC throughout profiles W1 and W2 in all but one sample exceeds the sediments AGP (Figure 7). The Dry Zone has little ANC but also low AGP and the slight NAGP is very low throughout profile D7 (Figure 7). In the Wet-Dry Zone the ANC is greatest at the surface of the desiccation features where carbonate is concentrated in salt efflorescence. The high AGP in the interior of desiccation features in the Wet-Dry Zone have low ANC resulting in high NAGP (profiles P1 and WD3-5, Figure 7). Where these high NAGP sediments have been oxidised in the field sediment profiles have become acidic. However, the high NAGP at the interior of desiccation features of the Wet-Dry Zone are largely matched by the negative NAGP of crack sediments resulting in no NAGP (profile P2, Figure 7). Although sediments have largely remained around pH neutral during the oxidation of pyrite in the Wet-Dry Zone the remaining pyrite has much less ANC to buffer the remaining AGP and some areas have the potential to become acidic. This localised separation of carbonate and pyrite appears to have produced sediments within desiccation features that have the potential to become acidic decreasing the overall buffering capacity of the sediments as a whole.

Conceptual model (wetting and drying)

The heterogeneous sulfur and carbonate distributions within desiccation features of the Wet-Dry Zone have formed from the wetting and drying of sediments chemically and texturally similar to the largely homogenise sulfidic Wet Zone (discussed above and in Wallace *et al.* 2008; this volume). This study has shown that the high variability in sulfur and carbonate concentrations of the Wet-Dry Zone can largely be explained by hydro-geochemical processes directly related to sediment wetting and drying. From this study it is now possible to construct the first detailed hydro-geochemical conceptual model for the wetting and drying of the recent inland sulfidic sediments of the lower Murray floodplains. This model explains the variability in the form and distribution of sulfur and carbon brought about by sediment wetting and drying. The consistency of desiccation feature chemistry throughout the Wet-Dry Zone of the Loveday Basin indicates that this model can be used to predict the response of similar sulfidic sediments to wetting and drying regimes.

Evaporation has concentrated salts forming highly saline basin surface waters and sulfidic sediments over a period of 30 years (Figure 8). Since 2000 evaporation has largely exceeded water input in the Wet-Dry Zone and saline waters have fallen below the surface of sediments producing prominent desiccation cracks upon drying of the smectite-rich wetland clays. The interior of the clay desiccation features remain predominantly wet due to the upward vertical movement of the shallow saline waters driven by capillary action and evaporation of pore waters. Sulfate and carbonate are concentrated by this vertical evaporation driven advection and precipitate at the surface of desiccation features as gypsum and calcite in salt efflorescence (Figure 9 [1]). Sulfides are preserved within the wet desiccation features (5-20 cm depth) but have been almost completely removed by oxidation around the outside of desiccation features (5 cm deep) and underneath desiccation features (20-40 cm depth) where oxidants are more prevalent (Figure 10 [1]). The majority of sulfides appear to have been removed from the Wet-Dry Zone, largely oxidised in bulk pH neutral sediments with only isolated areas of acidity. The oxidation of pyrite has produced additional sulfate which has largely been redistributed to the outsides of desiccation features by vertical advection (Figure 10 [2]). The production of acid during sulfide oxidation has removed carbonate directly from sediments as well as lowering the overall pH of sediments, increasing carbonate solubility (Figure 10 [3]). The vertical upward flow of these slightly lower pH waters, combined with periodic horizontal leaching by rainwater, appears to have removed carbonate from the interior of desiccation features (Figure 10 [4]). The preservation of pyrite and removal of carbonate within desiccation features have resulted in the formation of small areas of potential acidity that become acidic upon oxidation in the field, characterised by the presence of jarosite. Periodic wetting of sediments, by river water, irrigation and rainwater input, appears to have flushed only minor amounts of sulfur and carbonate from the Wet-Dry Zone increasing salt concentrations slightly towards the Wet Zone. The principal movement of sulfate and carbonate is the vertical redistribution within desiccation features where salts are concentrated at the sediment surface. Whilst periodic wetting of sediments rapidly dissolves salts and produces minor accumulations of monosulfides subsequent drying reforms salt crusts and oxidises monosulfides just as rapidly. The current heterogeneity observed within the Wet-Dry Zone is the result of cyclic wetting and drying of sediments (Figure 11). Wetting and drying has partially separated carbonate from pyrite but the majority of sulfides have been oxidised in largely bulk pH neutral sediments.



Figures 8-11.
Evolution of sulfidic sediments in response to wetting and drying (full description in text)

The process of sulfide oxidation in the lower Murray is distinct from sulfide oxidation in coastal ASS. In coastal sediment the carbonate produced during sulfide formation is subsequently removed by tidal flushing (Dent 1986; Pons *et al* 1982) resulting in large scale sediment acidification upon oxidation (Dent 1986; Dent and Pons 1995). The acidification of sulfidic sediments increases the rate of sulfide oxidation (Arkesteyn 1980; McKibben and Barnes 1986; Singer and Stumm 1970; Wang *et al* 2007) and produces many of the associated environmental problems (i.e. mobilisation of metals, soil structure decline and degradation of adjacent water ways; (Astrom and Bjorklund 1995; Cook *et al* 2000; MacDonald *et al* 2004; Osterholm and Astrom 2002; Rosicky *et al* 2004; Sammut *et al* 1996; Ward *et al* 2004a). The undisturbed sediments of the Loveday Basin have high carbonate associated with pyrite and the majority of pyrite within the Wet-Dry Zone has been oxidised between 2000 and 2005 without large scale sediment acidification. The localised areas of potential and actual acidity between 5 and 20 cm depth in the Wet-Dry Zone demonstrate that under the right conditions carbonate can also be separated from pyrite within inland sulfidic sediments. In the Loveday Basin this separation is largely vertical and the majority of sediment depth profiles with small pockets of potential acidity have no overall potential acidity. However, the separation of carbonate from pyrite and redistribution to the surface as salt efflorescence increases the potential for carbonate to be redistributed horizontally within the basin. Where carbonate has been removed from the profile small pockets of actual acidity have formed. The horizontal redistribution of carbonate appears to be limited in the Loveday Basin limiting acidification but this study has shown that increases in horizontal leaching of carbonate could have the potential to produce, on a small scale, coastal style ASS. By explaining the processes that separate carbonate and sulfides, the above model can be used to manage inland sulfidic wetlands of the lower Murray to reduce the risk of wetland acidification.

CONCLUSIONS

The wetting and drying of sulfidic sediments in the Loveday Basin has partially separated carbonate from sulfides. Wetting and drying over a period of 5 years has removed the majority of pyrite form sulfidic sediments without large scale acidification. The separation of carbonate from the remaining pyrite is a result of decreased pH, due to pyrite oxidation, and vertical advection driven by high evaporation rates. The combination of these processes in sediments undergoing wetting and drying has produced a sediment horizon (5-20 cm depth) with net acid generation potential. Carbonate, along with sulfur, largely remains within the sediment profile but are redistributed to the sediment surface and concentrated in salt efflorescence (0-5 cm depth) due to high upward vertical advection (0.14 kg m^{-2} d^{-1}) and low horizontal advection (2.2 x 10^{-3} kg m^{-2} d^{-1}). As the separation of carbonate from sulfides is only over relatively small distances the complete sulfidic profile (0-40 cm depth) has no net acid generation potential. This indicates the wetting and drying of well buffered inland sulfidic sediments is an effective way of removing pyrite from wetlands without large scale sediment acidification. However, in the small areas where carbonate has been completely removed form the sediment profile small pockets of sediment have become acidified during pyrite oxidation. This indicates that increasing the flushing of carbonate form the profile by horizontal advection could increase the risk of larger scale sediment acidification.

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CHAPTER 17

GEOCHEMISTRY AND MINERALOGY OF SULFIDIC DRAINS IN TILLEY SWAMP, SOUTH AUSTRALIA

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INTRODUCTION

To manage an expected increase in land area affected by dryland salinity and flooding in the upper South East of South Australia, an extensive system of drains has been constructed to intercept both saline ground water and fresher surface waters. Saline water is to be delivered to temporary storage in Morella Basin and nearby areas such as Tilley Swamp, or discharged to the Coorong. Fresher surface waters are expected to be directed to wetlands to improve environmental condition. Tilley Swamp is an interdune area running parallel to and just inland to the east of the Coorong (Figure 1). It trends approximately NNW-SSE and is approximately 40 km long and 4 km wide. A natural drainage course runs along the western side of the interdune. A drain that is about 2.5 to 3 m deep was constructed towards the eastern side of the interdune flat. It intercepts ground water and conveys saline waters and other surface waters from the extensive southern part of the network across the length of Tilley Swamp to Morella Basin. Vegetation of the area includes extensive areas of *Melaleuca halmaturorum* (coastal paperbark), pasture species, and *Gahnia* spp. (cutting grass) with samphire species in permanent saline areas along the natural drainage course.

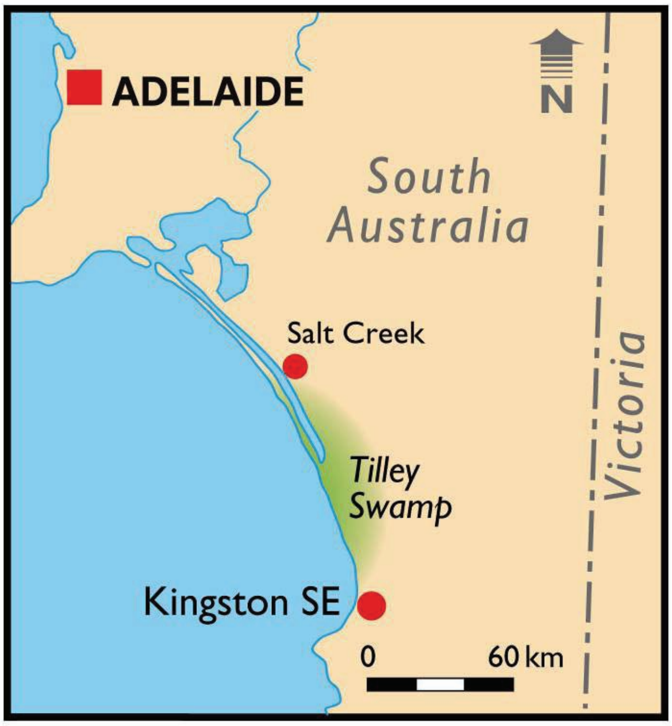


Figure 1: Locality of Tilley Swamp.

The drain constructed through Tilley Swamp provides an opportunity to observe the pedological, geochemical and mineralogical properties of materials within the drain, both recent (active acid sulfate soil weathering features) and relict (post-active acid sulfate soil weathering features; Fanning 2002), consider their value as environmental indicators and to evaluate the probable response of the soil materials to future inundation. Important materials that develop in the drains during periods of low flow are thin layers of sulfidic materials (Dent and Pons 1995; Isbell 2002), monosulfidic black ooze (MBO), salt efflorescences and iron oxyhydroxide minerals on drain walls.

The aim of this study is to use hydro-pedological, mineralogical and biogeochemical information to help understand the soil-water process in the open drains and assist in their management.

Materials and Methods

Samples were variously treated and fractionated (sub-samples). Specialised laboratory analyses were conducted on selected sub-samples from each site using X-ray fluorescence (XRF), ICP-MS, X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray Absorption Spectroscopy (S K-edge and Fe K-edge XAS) and laboratory chemistry to determine what biogeochemical and mineralogical processes were taking place in the drains.

RESULTS AND DISCUSSION

A detailed description of the field and laboratory analytical work is given in Merry and Fitzpatrick (2005) and Fitzpatrick and Merry (2005). A general view of a representative cross section through a drain in Tilley Swamp is shown in Figure 2. At each site the following materials were described and sampled: (i) monosulfidic black ooze (Sullivan *et al* 2002), (ii) sulfidic materials (Isbell 2002), (iii) yellowish Fe-rich mottles, (iv) white salt efflorescences and crusts on the walls of drain, (v) reddish–brown Fe-rich gels and precipitates and (vi) calcrete layers (Figure 2). These six materials were generally evident within the drains and were used to indicate six different geochemical process zones (Figure 2).

Tilley Swamp is a calcareous, saline environment with ground water commonly within 3 metres of the soil surface (Figure 2). Under conditions of low flow, sulfidic material (mottles) and monosulfidic black ooze (MBO) forms, but is not found in soils away from the drain (Figure 2). These sulfides remain benign in a reduced environment, but can quickly cause oxygen depletion of the water when re-suspended during periods of higher, turbulent flow.

The depletion of carbonate minerals in some soil layers due to acid formation has occurred over a long period of time (i.e. Post-active acid sulfate soil weathering conditions) but we have not yet observed sites where carbonate is totally removed. Under these circumstances, rapid acidification of remaining soil materials would be expected. High concentrations of As and P, observed in layers of iron oxyhydroxide accumulation are related to the layers with carbonate depletion on the eastern side of the interdune flats, and thought to have resulted from long-term scavenging by the iron oxyhydroxides. The common occurrence of salt efflorescences on drain surfaces provides a window on seasonal geochemical processes that could be used as environmental indicators.

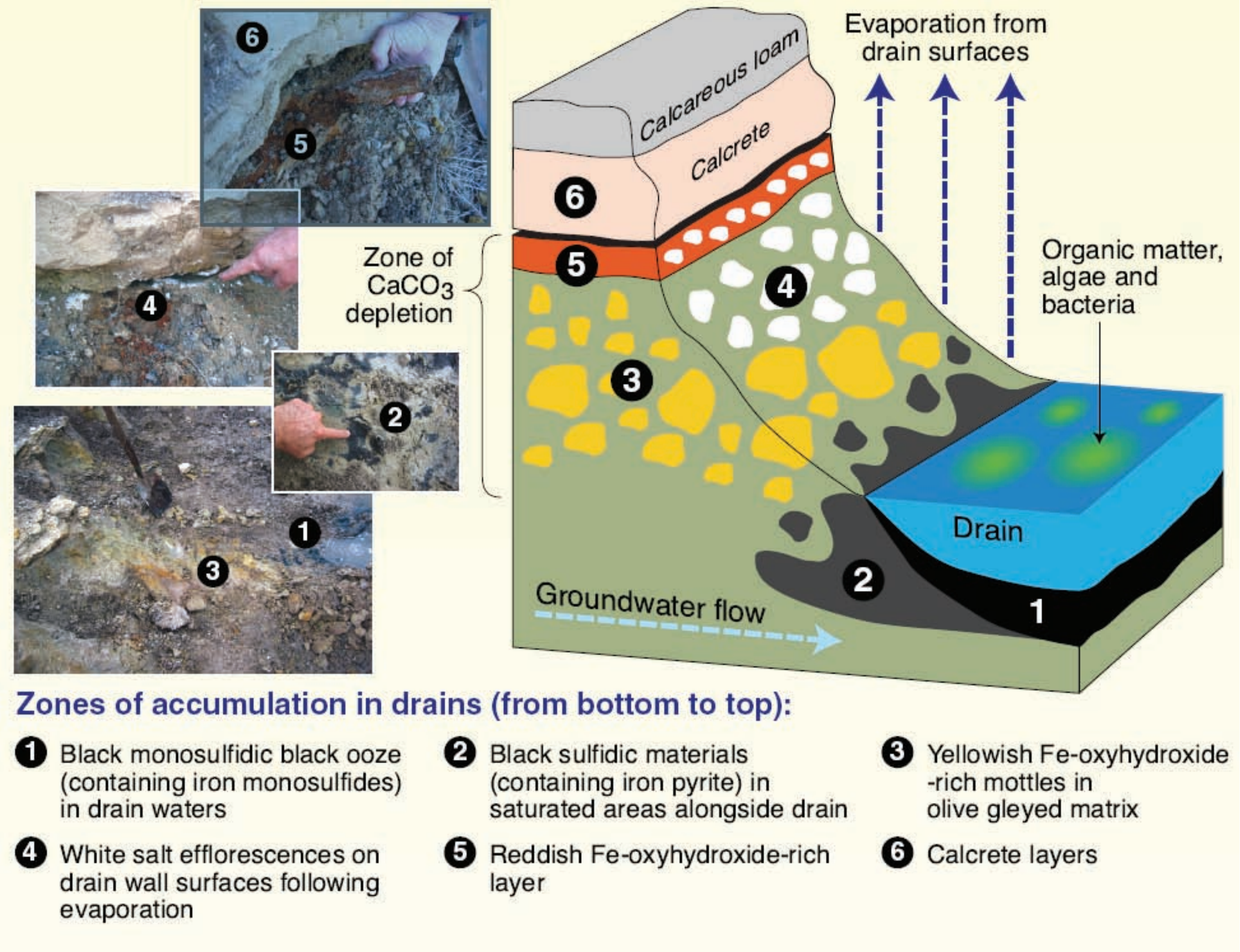


Figure 2. Schematic cross-section or hydro-toposequence through a drain showing six zones of accumulation in drains.

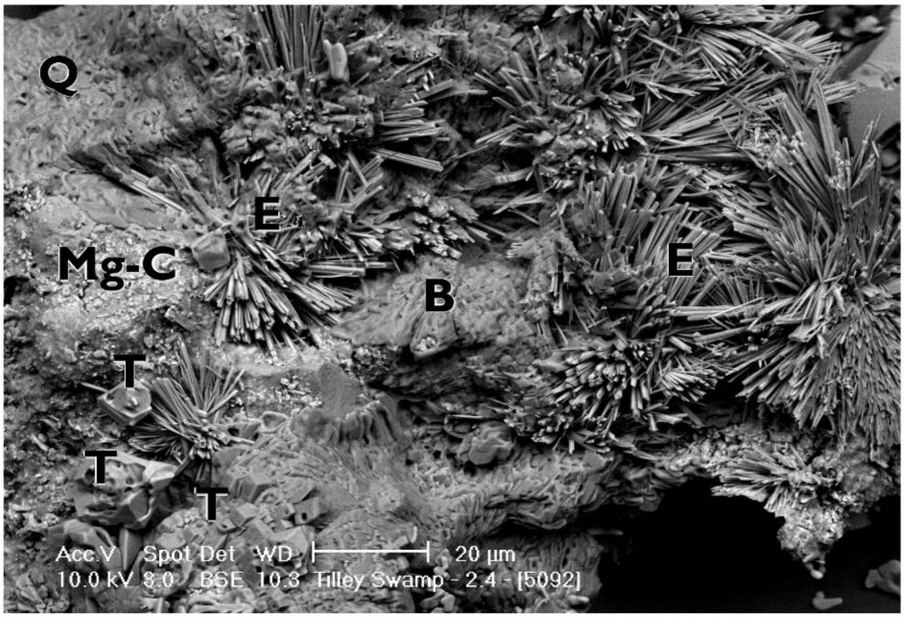
We have constructed 3D (Figure 2) and 4D mechanistic models of soil-regolith and water processes using the toposequence approach (soil landscape cross-sections; Fitzpatrick *et al* 1996), that explain and predict processes giving rise to the production, export and fate of leachate and minerals in the open drains. The main materials and key processes that these materials indicate are discussed and summarised for each of the six zones shown in Figure 2 as follows:

Zone 1: Oxidation of monosulfides in the monosulfidic black ooze causes oxygen depletion of drainage waters.

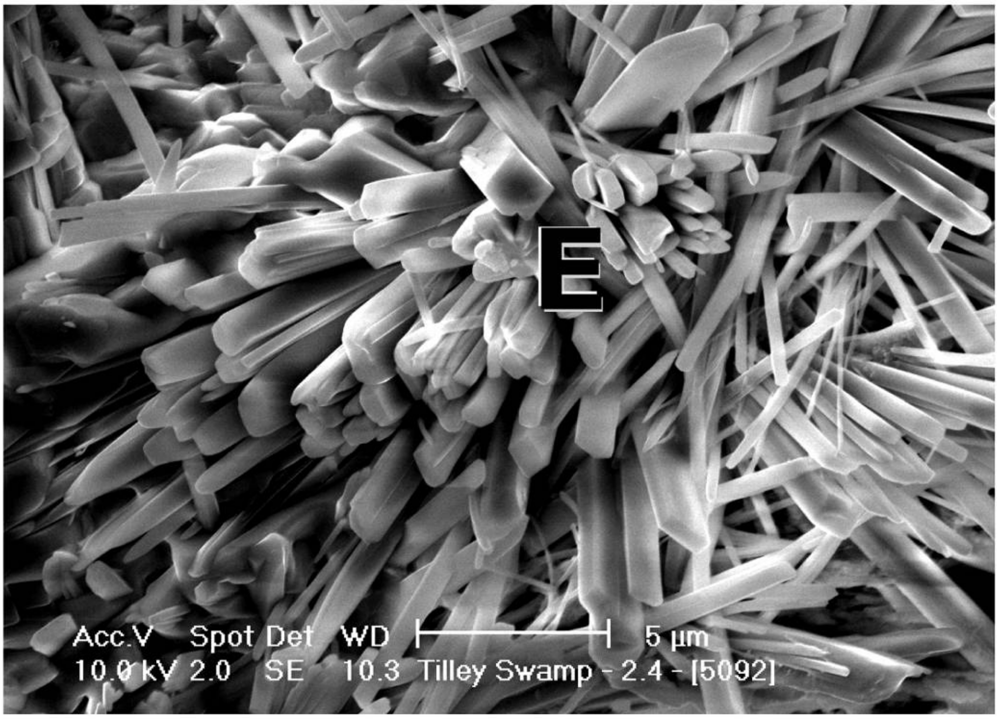
Zone 2 and 3: Oxidation of pyrite and ferrous iron within the zone of active watertable fluctuation forming:

- Sulfuric acid, which causes dissolution and removal of carbonates from soil layers
- Goethite-rich mottles in an olive gleyed matrix (post active acid sulfate soil materials).

Zone 4: Soluble sulfate/chloride-containing minerals in efflorescences (Figure 3) were also identified in localised areas in the drains. The salt efflorescences are produced by evaporation of ground and capillary waters. Pedogenic eugsterite [$Na_4Ca(SO_4)_3.2H_2O$] has been identified for the first time in Australia. These evaporite minerals reflect the unique geochemical reactions resulting from the combination of groundwater, drainage water and drained soils. Hence, under these more alkaline conditions (and also observed in the Iraq marshlands) where Na/Ca ratio >4, eugsterite, gypsum and thenardite (i.e. Na-Ca-sulfate salts) will form. In contrast, under acidic conditions (e.g. Western Australian wheatbelt drains) where Na/Ca ratio <4, bloedite and pentahydrite (i.e. Na-Mg-sulfate salts) form (Fitzpatrick *et al* 2005).



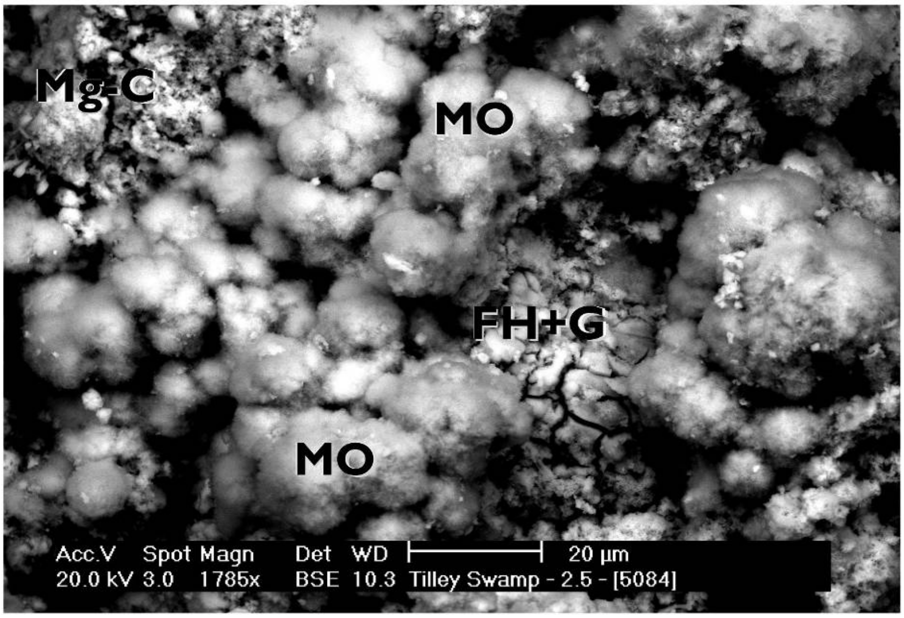
E Eugsterite - $Na_4Ca(SO_4)_3.2H_2O$
T Thenardite – Na_2SO_4
B Bloedite – $Na_2Mg(SO_4)_2.8H_2O$ **Q** Quartz - SiO_2
Mg-C Mg-Calcite - $CaCO_3$



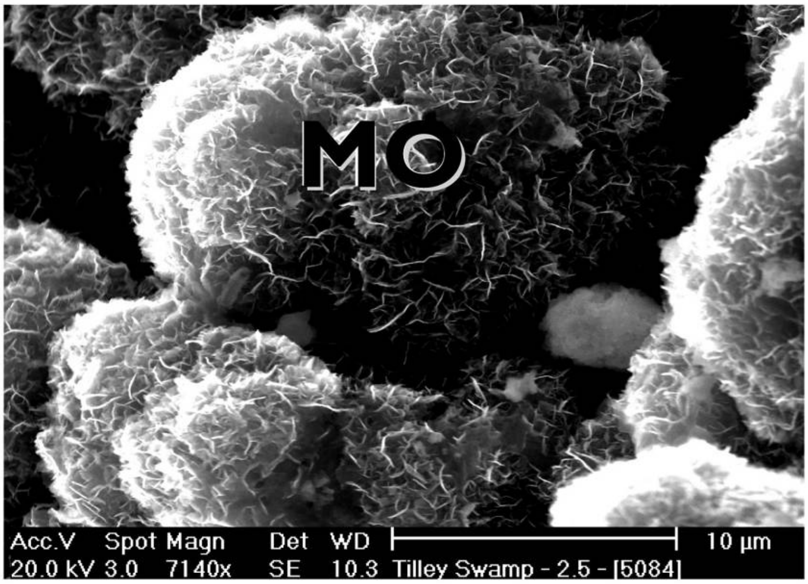
E Eugsterite - $Na_4Ca(SO_4)_3.2H_2O$

Figure 3. Scanning electron microscope (SEM) images of salt efflorescences from Zone 4 containing minerals with high levels of sodium, calcium, chloride and sulfate ions.

Zone 5: We identified various types of hydrated oxyhydroxides (ferrihydrite), oxyhydroxides (goethite), oxides (hematite, manganese oxides), Fe-sulfides and Fe-monosulfides (Figure 4) in various localities in the drains. Oxidation and concentration of ferrous iron in the upper ten centimetres of the capillary zone formed ferrihydrite, goethite and manganese oxides with ankerite and Mg-calcite. The Fe and Mn-oxides most likely scavenged high total concentrations of arsenic (5000 mg/kg) and phosphorus (1200 mg/kg). These oxides are ubiquitous in many soils and are known to take up arsenate and phosphate (Fordham and Norrish 1979).



MO Manganese Oxide
FH+G Ferrihydrite + Goethite
Mg-C Mg-Calcite



MO Manganese Oxide

Figure 4. Scanning electron microscope (SEM) images of reddish layer from Zone 5 containing ferrihydrite, goethite, ankerite, Mg-calcite and Mn-oxides with high concentrations of arsenic (5000 mg/kg) and phosphorus (1200 mg/kg)

CONCLUSIONS\

Minerals in efflorescences containing soluble sulfate and chloride play important roles in the transient storage of components (Na, Ca, Mg, Ba, Sr, Cl, Br, I and SO_4). They can detach soil during crystal growth and degrade drain walls. They will dissolve during rainfall and contribute to formation of saline monosulfidic black ooze in drains.

We conclude that the Fe-oxyhydroxide and Mn-oxide minerals, and sulfate/carbonate containing minerals in salt efflorescences, are indicative of changing local environments with variations in redox, pH and rates of availability of S and other elements. As such, they provide insight to the drain geochemistry and can be used as indicators of environmental change that can also be used to help understand and manage this system.

ACKNOWLEDGEMENTS

We are grateful to Adrian Beech and other staff at the CSIRO laboratories in Adelaide for soil analysis. This work was funded in part by the South Australian Department of Water, Land and Biodiversity Conservation.

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CHAPTER 18

INLAND ACID SULFATE SOILS OF THE SPRING ZONES ACROSS THE EASTERN DUNDAS TABLELAND, SOUTH EASTERN AUSTRALIA

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INTRODUCTION

Land degradation in the form of salinisation, acidic waters and associated soil erosion affects 5300 hectares, or seven per cent, of the Eastern Dundas Tablelands (EDT) (Figure 1) (Munroe 1998). Located within degraded zones are permanently flowing springs that are covered in iron precipitates and salt efflorescence. Within the discharge zones, conditions exist for formation of acid sulfate soils (ASS). The ASS identified are only located in discharge zones connected to the regional groundwater flow system that have been shown to be “primary discharge zones” (Fawcett 2004, Fawcett *et al* 2008) because these are know to have discharged prior to European land clearing. This case study outlines the hydrogeological and soil-landscape toposequence processes associated with springs that contain the ASS and illustrate the impact inland ASS have on soil degradation and water quality in this region.

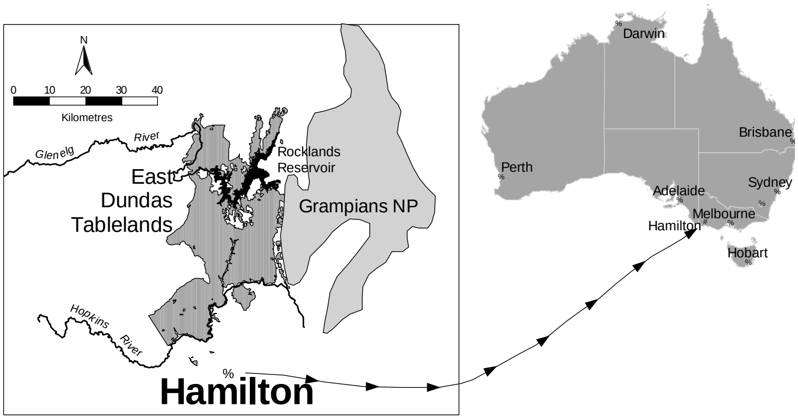


Figure 1. Location of the Eastern Dundas Tableland (EDT)

Description of the study area

The EDT is a slightly domed tableland with two acid-volcanic lava domes which creates a generally radial drainage pattern. Dissection of the plateau by rivers and streams has created shallow U-shaped valleys rarely deeper than 20 m. The present climate is Mediterranean. The district annual average rainfall is 628 mm (±114 mm), although the annual totals during the last 20 years have been predominantly below this average. Prior to European settlement the EDT was a well grassed, open forest of Eucalypt spp., Banksia spp. and Allocasuarina spp., with Banksia marginata the dominant tree species (Nathan 1998). By the 1900's, land clearing, sheep grazing and a variable climate changed the dominant tree species to River Red Gum (Eucalyptus camaldulensis) and the dominant native grasses were Wallaby Grass (Austrodanthonia spp.), Kangaroo Grass (Themeda triandra) and Spear Grass (Austrostipa spp.). Today, less than three per cent of the pre-European vegetation remains on the EDT.

Soils of the EDT comprise mainly brownish yellow texture contrast soils with ironstone gravels in well-drained areas, yellow sodic texture contrast soils in valleys and gradational soils along river flats (Land Conservation Council Victoria 1978). Frequently, texture contrast soil profiles have loamy A horizons, with distinct bleached A2 horizons overlying a mottled B horizon with well-structured peds, which are most conspicuous part way along and at the bottom of the slope. As a consequence of the multi-factorial genesis of these soils, the present landscape is pedologically complex (e.g. Gibbons and Downes, 1964; Dahlhaus *et al* 1999; Brouwer and Fitzpatrick 2002a, Fitzpatrick and Brouwer 2003, Fawcett 2004, Paine and Phang 2005).

Focus Site

Field measurements were conducted at the Merrifields research site located south of Balmoral, on the north side of Glenndinning Creek and east of Rocklands Reservoir (Figure 1). The 29 ha site encompasses a section of the northern half of the north-east running Glenndinning Creek valley (Figure 2), that eventually drains into Rocklands Reservoir (Figure 1). From west to east, Glenndinning Creek falls from 224 m AHD to 217 m AHD, a gradient of 0.7 per cent. The depth of the valley is between 17.0 and 18.5 metres. The pasture of the site comprises annual grasses and clovers, with barley grass (Hordeum leporinum) dominant on lower parts with scattered River Red Gums (E. camaldulensis) and some drooping She-oaks (A. verticillata) on higher ground. Irregular shaped scalds occur on the drainage flats at the breaks-of-slope and along valley walls, but never directly within the creek. These are dominant on the northern side of the creek. Downslope of barren scalds are areas of poor grass growth (soil salting class 1 and 2) occupied mainly by salt tolerant species. These salt indicator species include Buck's Horn Plantain (Plantago coronopus), Water Buttons (Cotula coronopifolia), Annual Beard Grass (Polypogon monspeliensis) and Sea Barley Grass (Critesion marinum). Distinct areas of Fog Grass (Holcus lanatus) are found directly upslope of degraded discharge zones. The degraded areas are generally separated by a change in the soil surface topography from concave to convex.

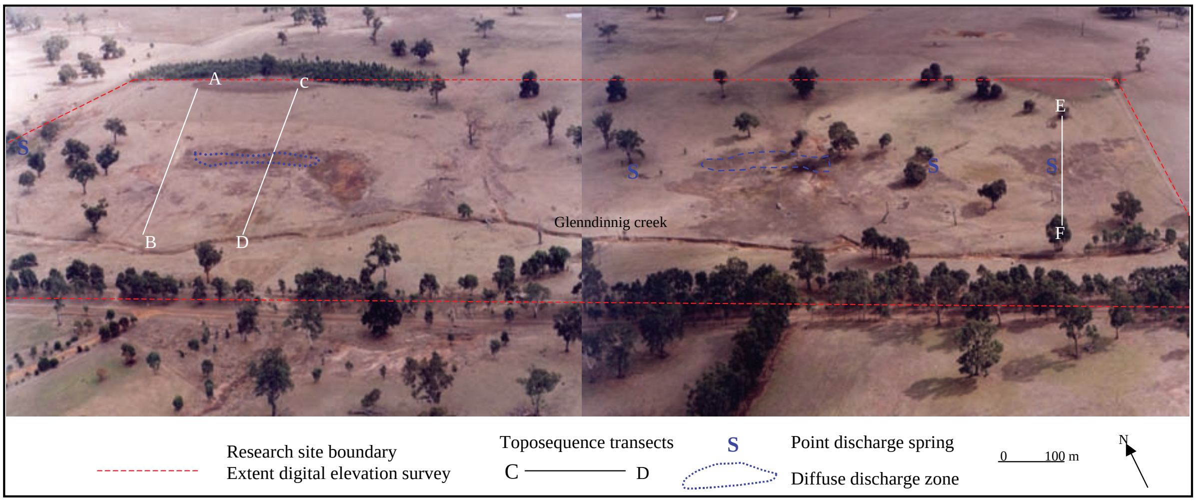


Figure 2. Aerial photograph of the Merrifields research site. The boundary of the research site is highlighted by the red dotted line; diffuse and point discharge springs are shown by the blue line with the three toposequence transects 1 (A-B), 2(C-D) and 3(E-F).

Localised point-discharge springs (Figure 3) and diffuse-discharge zones occur within and immediately above scalded areas. Groundwater discharge occurs between 222.5 m AHD and 224 m AHD. Relative to the creek level, these discharge zones occupy a progressively higher position in the landscape further down creek-lines. The location of the permanently flowing discharge zones are controlled by localised jointing and faulting within the underlying Ignimbrite (Fawcett *et al* 2008). There is no record, or recollection by the land owners, of the flow ever ceasing in the discharge zones which leads to the conclusion that these permanently flowing degraded springs are primary features of the landscape, and they existed prior to European land clearing (Nathan 1998; Fawcett 2004).

Figure 3. Permanent point spring during dry months. This discharge point is configured to enable monitoring of its flow rate

Background regional hydrogeology

The crystalline nature of welded ignimbrite and rhyolite, combined with joints and fractures formed during cooling, has created a fractured rock aquifer. Secondary jointing due to tectonic uplift has been documented in five pyroclastic units in the EDT (Jerinic 1993; Lewis 1985). The joints provide a pathway for water flow in all directions, allowing water to flow across the stratigraphic units of the Rocklands Volcanics (RV), effectively connecting the entire RV as one hydrological unit. Hydraulic connection of the relatively thick regolith to the underlying fractured rock aquifer was established by Woof (1994) based on similar ionic ratios in the groundwaters. Despite some local-scale heterogeneity imposed by the variable fracture spacing, the units within the RV are considered to be structurally similar (Simpson 1996) and can be described as homogeneous at the regional scale. Similarly, pumping tests carried out by Cossens (1999) indicated anisotropy at the local scale but isotropy at a regional scale where a continuum approach to groundwater flow can be applied (Cossens 1999). These assumptions are valid due to the small fracture spacing, high degree of fracture interconnectivity and the large size of the aquifer, resulting in a relatively small void ratio (Domenico and Schwartz 1990).

The groundwater flow system of the EDT is an example of the gravity-driven groundwater flow system within a regionally unconfined aquifer (Fawcett 2004, Fawcett *et al* 2008) first proposed by Tóth (1962) and later refined in Tóth (1999). The groundwater system is described as a series of nested flow systems increasing in flow length with depth, confined within a basin (Fawcett *et al* 2008). Within recharge areas, hydraulic heads will decrease with depth and water flow will be downward. Within discharge areas, hydraulic heads increase upwards resulting in the convergence of flow paths, as occurs along geological structures on the EDT (Figure 4). Within areas of through-flow, hydraulic heads are essentially equal so that water flow is lateral. Field mapping has identified the structural control on spring zones, with springs concentrated around areas of contact geology and faults. A total of 125 permanently flowing springs were located during this survey on the EDT. Spring locations are not evenly spaced across the EDT and 73% of springs are located within 1 km of major fault lines and the contact areas between different volcanic units. This implies that the location of groundwater discharge zones is structurally controlled rather than being a function of landscape position.

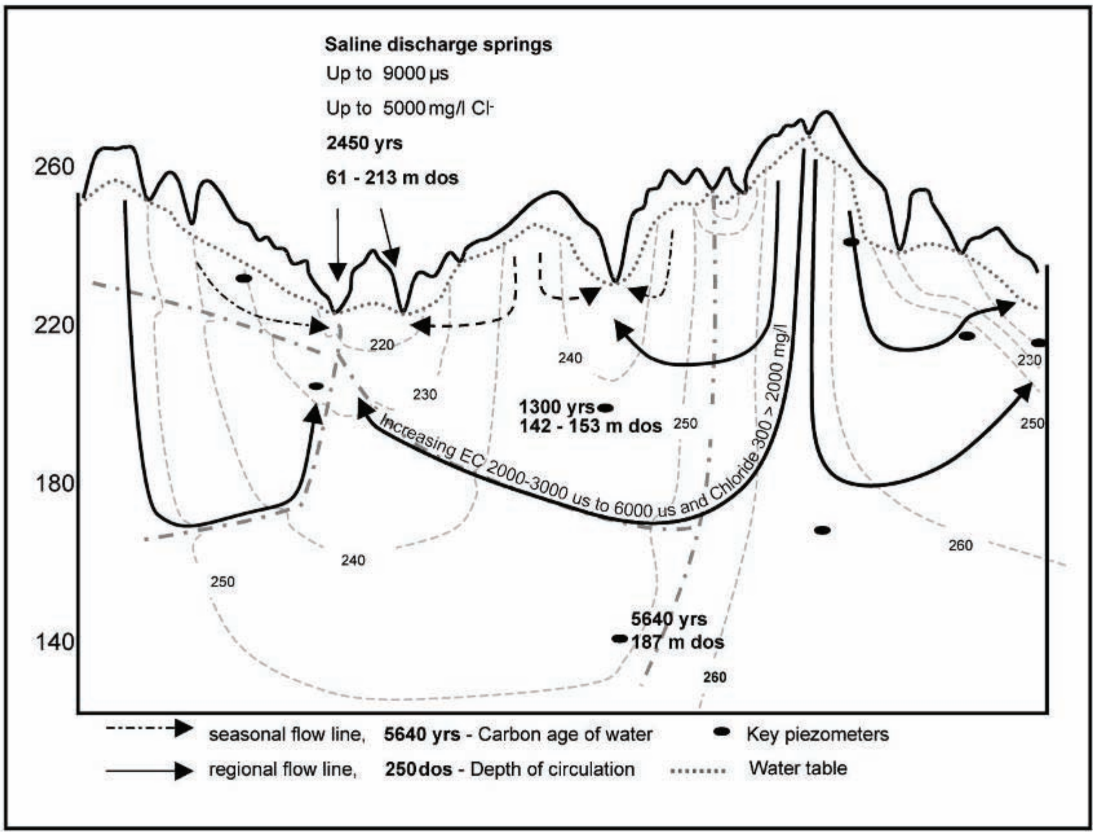


Figure 4. Sectional view of groundwater flow paths in the EDT. The dominant direction of deep groundwater flow, illustrated by increasing EC and chloride of selected piezometers, as shown.

The general chemistry of groundwaters of the EDT describes a groundwater system that has undergone similar wall rock alteration processes within different depths and locations. The lack of any significant difference in the composition of the groundwaters can, in part, be explained by a mixing of waters from different depths along the flow paths (Fawcett *et al* 2008).

Within discharge zones, groundwater depths of circulation can vary by 80 m within a year. The carbon age of spring water indicates some discharge water has been in the groundwater flow system for at least 2540 years.

Soil toposequence setting

In order to more easily understand the lateral linkages and relationships between soil profile features and water-flow patterns down landscape slopes, we used the systematic structural approach to characterise soil-regolith features at different parts down toposequences (e.g. Boulet *et al* 1982; Fritsch *et al* 1992; Fritsch and Fitzpatrick 1994; Fitzpatrick *et al* 1996; Brouwer and Fitzpatrick 2002a). The upper regolith of the Merrifields research site has been characterised in detail by constructing nine toposequences cross-sections along three transects that run parallel from the top of the slope towards, and perpendicular to, the Glenndinning Creek and through the degraded discharge zones. The toposequence models (Figure 5) interpret various soil characteristics: soil macromorphological features (top), soil EC and sodicity (middle); and soil pH (bottom) along transect 1 (Figure 2).

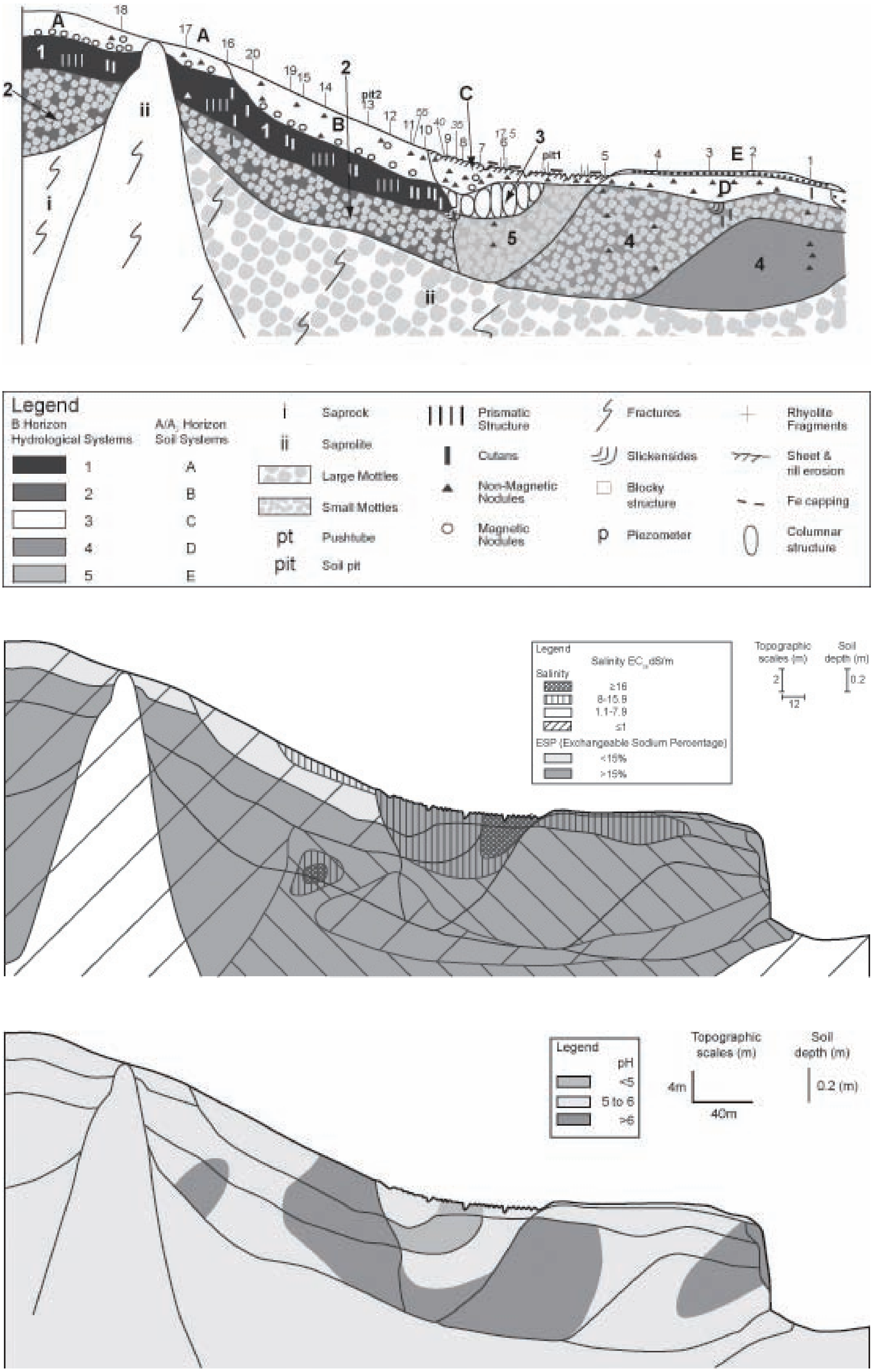


Figure 5. Topsequence for transect A_B (Figure 2), Hydrological soil systems toposequences–a, Soil salinity and sodicity toposequence - b and Soil sodicity toposequence – c. a b and c refer to the top, middle and lower toposequence respectively..

The presence of well-developed bleached A2 horizons within texture contrast soils directly below discharge areas suggests that lateral through flow and seasonal waterlogging of the topsoil occurs (Brouwer and Fitzpatrick 2002b; Fitzpatrick and Brouwer 2003). The water flow is consistent with monitored groundwater data (Fawcett *et al* 2009). The yellow/orange mottles within the tabletop and mid-slope positions indicate a well drained environment, where vertical unsaturated flow down to the water table will dominate. The presence of reduced mottle colours within the discharge areas indicates prolonged saturation of the regolith (Bigham *et al* 2002) as would be expected because the discharge zones are permanently saturated.

The absence of strong, horizontally-orientated mottling patterns within discharge zones suggests the area has remained saturated and has not undergone changing groundwater levels, which have been thought to cause horizontal mottling patterns (Brouwer and Fitzpatrick 2002; Fitzpatrick and Brouwer 2003, Paine and Phang 2005). This supports the proposal that these discharge zones on the EDT are permanent features, rather than seasonal or a development since land clearing. The presence of strongly reduced mottles alongside brighter coloured red mottles in hydrological soil systems 5 and 6, is indicative of more oxidising conditions and suggests reduction of the subsoil may be localised. It is proposed that the zones of intense reduction exist mainly along groundwater flow paths.

Salt accumulation and distribution

Areas of high salinity (more than 8 EC_{se}) create a teardrop shape that extended downslope (Figure 3) from the regional groundwater discharge zones and these spread downslope as a consequence of seasonal discharge. This process enlarges the area affected by soil salinity and generates some salt wash-off into waterways. Areas of high salinity (8–15.9 EC_{se}) extended upslope of the immediate area of groundwater discharge within all toposequences. Salts accumulate as a result of evapotranspiration above scalded zones during periods of high seasonal watertables.

Soil acidity and sodicity

In general, the soils of the site were in the pH range of 5 to 6. Extremely acid soils were confined to the immediate area of diffuse and point flowing discharge zones. The soil chemical processes that drive the acidity are presumably also confined to discharge zones. The majority of the soils within the transects were classified as sodic (ESP >15%). It would be expected within acidic soils available aluminum would be present and cause an overestimation of the CEC of the soils. Soils that disperse completely occur across a range of pH values while they were confined to soil EC_{se} of less than 2 ds/m. Of the 267 soil samples taken from transects across a degraded discharge zone and analysed for pH, EC and dispersion, EC had a significant effect on preventing dispersion ($p<0.001$) as expected, but there was no significant effect of pH on dispersion ($p>0.14$).

Identifying Inland Acid Sulfate Soils (ASS)

Acid sulfate soils with predominantly sulfidic materials (i.e. potential ASS materials) and minor sulfuric materials as defined by Isbell (2000) occur within spring zones of the EDT but are not as obvious as those identified in coastal or large scale wetland settings. The conditions for their formation only exist within discharge zones associated with the regional groundwater system, which may only be several meters in size (Figure 3). Field observations and the following laboratory analyses using Isbell (2000) were used to identify the presence of sulfidic materials (potential acid sulfate soil materials or PASS material) and sulfuric material (actual ASS material) at the Merrifields research site: (i) pH before and after incubation of moist samples for 8 weeks and treatment with hydrogen peroxide, (ii) mineralogical identification of various iron sulfide and iron oxyhydroxide minerals and (iii) detailed measurements of discharge water chemistry. Water chemistry of surface water within scalded regions was sampled via a series of surface drains, with groundwater chemistry sampled via a series of shallow piezometers and drain inserted into a 6 m deep trench within and around degraded springs. Detailed redox, pH and EC measurements of spring discharge water were taken along two transects through a disturbed discharge zone (Figure 6). Run one, is where discharge water evaporated and iron scalding was present and Run two is where the discharge rate was sufficient to enable water to freely drain away from the scalded zone.

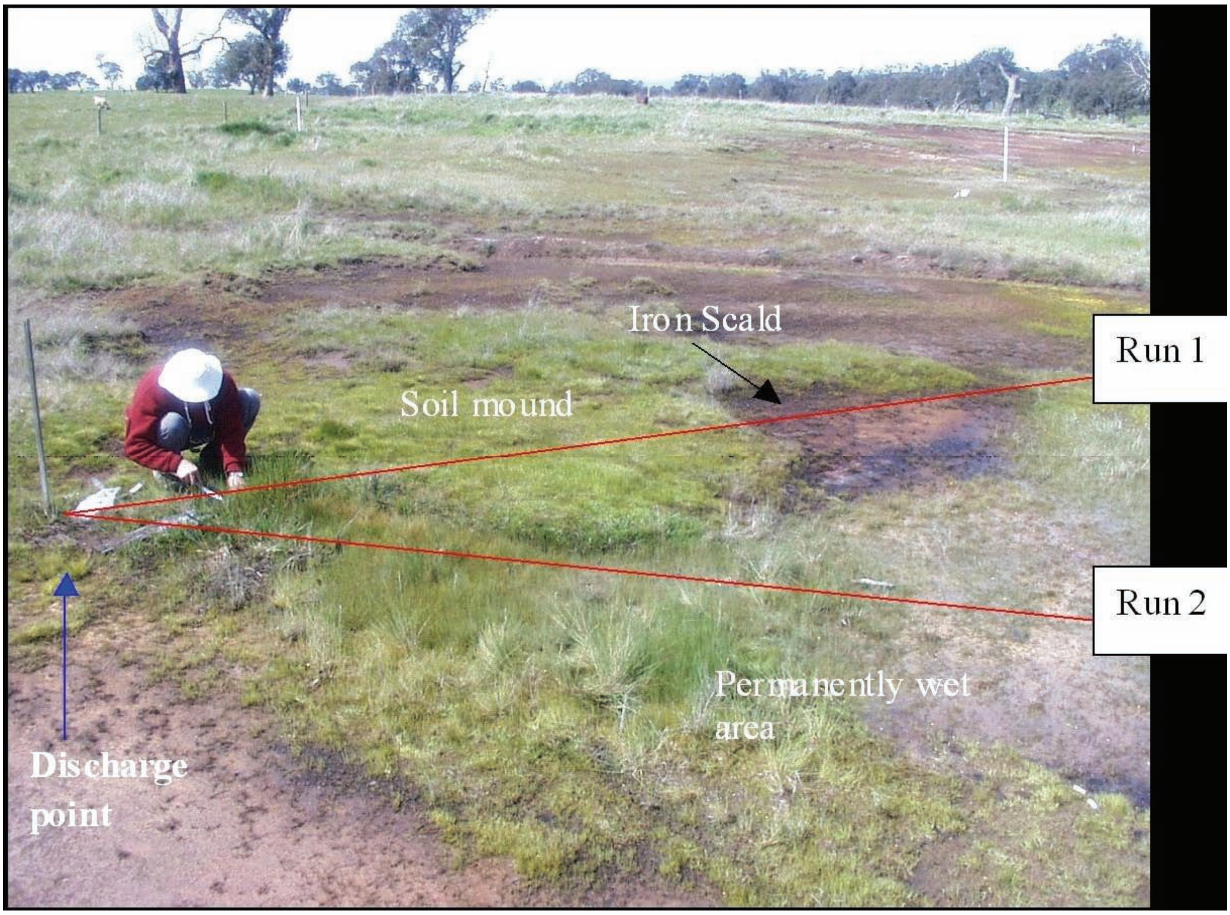


Figure 6. Location of sampling point runs from artificially created discharge point for redox, EC and pH.

Field observations

A summary of observations taken from 1998 to 2004 at the Merrifields site associated with the degraded discharge zones helped identify the presence of redox process that suggest the presence of iron reducing bacteria and these observations are summarised in Table 1.

Table 1. Summary of field observations on Acid Sulfate Soils at the Merrifields site on the Eastern Dundas Tablelands.

	Permanent diffuse discharge zones	**Seasonal discharge zones**	**Permanent point discharge zones**
Wet periods	Sealing and clogging of soil pores by illuviated material and iron precipitants, erosion of highly sodic soils along exposed sections	Erosion of highly sodic soils, waterlogging of low-lying areas and sealing and clogging of soil pores by illuviated layer silicates and iron oxide-rich materials	Little evidence of active degradation during wet periods
Dry periods	Accumulation and concentration of salts, salt efflorescence on soil surfaces driven by evaporation. Periodic sealing and clogging of soil pores by illuviated layer silicates and iron oxide-rich materials. Erosion of the sodic top soil during storm events	Accumulation and concentration of salts combined with salt efflorescence, loosening of surface soil by the expansion of thernaldite and wind and water erosion of highly sodic soils during storm events	Accumulation and concentration of salts combined with minor salt efflorescences. The periphery of the discharge zone may erode during storm events.

The thin oil-like substance observed on the surface of water, reflecting light and giving a distinct oil-slick appearance, is formed by iron oxidising bacteria (Fitzpatrick *et al* 1996; Fitzpatrick and Self 1997). The red-yellow gelatinous material consists of ferrihydrite within filaments of iron oxidising bacteria (*Gallionella and Leptothrix*). Ferrihydrite is held within the *Gallionella* and *Leptothrix* bacteria growing on discharge waters (Fitzpatrick *et al* 1996) and is altered to less complex iron minerals as the gelatinous material dries. Subsequently, yellow coloured goethite and red coloured haematite deposits form on the soil surface (Fitzpatrick *et al* 1996; Fitzpatrick and Self 1997; Bigham *et al* 2002). This process is repeated as wet and dry periods occur from winter through to spring, with the iron rich layers accumulating.

When the iron deposits are subjected to anaerobic conditions in the presence of organic matter, they may be remobilised and deposited further downslope which enlarges the iron rich scald. Thin iron rich crusts form where permanent diffuse discharge water evaporates and the soil surface dries (Fitzpatrick *et al* 1996). Ferrous iron must exist in the discharged waters for the bacteria to grow. The iron deposits appear to be most abundant after a period of high rainfall followed by several weeks of dry weather. This is likely to be due to an increase of ferrous ions in discharge waters as ferrous sulfide, which is oxidised and made available to bacteria to be recrystallised.

Chemical and Laboratory results

The average pH of the deep trench discharge and shallow groundwater varied from 4.6 to 5.9, which is the general pH range of groundwaters across the Eastern Dundas Tableland (Fawcett 2004). The pH of the surface waters ranged from very acidic (pH<3.2) to almost neutral (pH 6.2). In general, the surface waters were more acidic than the deep trench water discharge. This observation suggests that processes within the soil of the discharge zones caused a drop in the pH of groundwater discharge.

The concentration of salts generally increased along away from the main discharge point (Figure 7) although the concentrations within the permanently wet zone, soil mound, and the edge of the soil mound (see Figure 4) ranged from 6.6 dS/m to 10.4 dS/m across the three monitoring periods. The highest EC concentrations for each monitored period were consistently along the iron scalded section of run 1, with 20 of the 32 measurements over 11 dS/m and 15.9 dS/m being the highest concentration.

The pH of discharge waters ranged from 2.8 to 6.8 (Figure 7). Values less than 4 occurred mainly along scalded sections of run 2, ranged from 4 to 6 along the permanently wet sections, and were greater than 5 to 7 within the soil mound and the edge of the soil mound. Along the end of the scalded section of run 1, no pH values above 4 were measured (Figure 7). The redox potential of the discharge waters during the monitoring period (i.e. the winter months) ranged from 81 to 614 mV (Figure 7) and there appeared to be no trend within different surface locations, unlike the EC and pH measurements.

These observations show that the highest salt concentrations and the most acidic discharge water measured from the disturbed discharge zone were where water flowed through a soil mound at a rate insufficient to maintain surface saturation (Figure 7). In contrast, where water was able to pond and flow freely down slope away from the scalded region, iron scalding did not occur. Salinities were lower and waters were less acidic.

The low pH measurements at this site occurred within a sandy loam soil with high sodicity (>6 % ESP). Within Australia, Rengasamy (2002) identified 86% of sodic soils have an alkaline pH but in this location, high ESP is associated with more acid pH. Fitzpatrick and Self (1997) concluded that the formation of sulfide minerals is dependent on soil Eh and pH. The pH and Eh data collected were plotted onto stability diagrams for ferrous and ferric minerals for each period that was measured (Fawcett 2004). Along the soil mound within the discharge area and the permanently wet region, the surface environment occurred mainly within the stability field of ferric oxides and we identified ferrihydrite in this region using combined SEM images and powder X-ray diffraction analysis. However, several measurements of the permanently wet area plot were within the stability field of ferric sulfate and ferrous sulfate. It is therefore apparent that the Eh and pH conditions of the discharge zone do support the production of sulfate rich iron minerals.

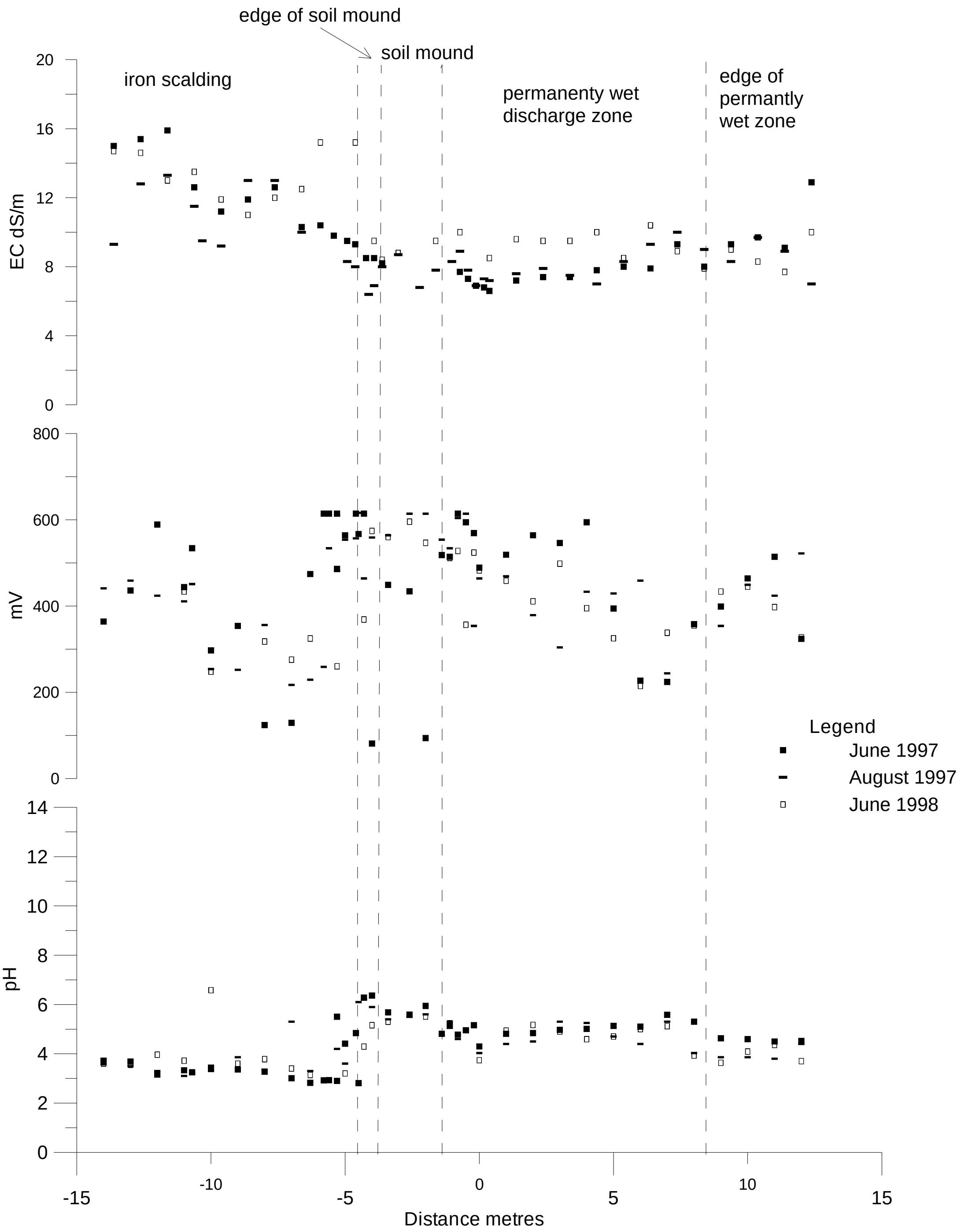


Figure 7. EC, Eh and pH of discharge waters of explosion experiment. Run 1 is indicated by negative distances, run 2 indicated by positive distances. Main discharge point occurs at 0 metres

The pH drop, as seen in run 1 (Figure 7) and measured in surface drains, must be a consequence of the oxidation of the iron sulfide materials. These ranges of pH and redox measured indicate a non-tidal saline-sulfidic seep, as described and detailed by Fitzpatrick *et al* (1996) in the Adelaide Hills. Those authors developed a conceptual model that described the nature of these environments, the observations of saline and sulfidic features, the local hydrogeology, and surface and sub-surface Eh, pH and EC. Conditions at the Merrifields research site are compatible with those in that model, and we conclude that these degraded discharge zones are in fact areas consisting of acid sulfate soils with sulfidic materials. It also appears the break down of soil structure and subsequent erosion within the discharge sites can be attributed to the development of sulfidic material with no or very little soil structure (e.g. Fitzpatrick and Skwarnecki 2003), high salinities, the formation of salt efflorescences and the production of high acidity.

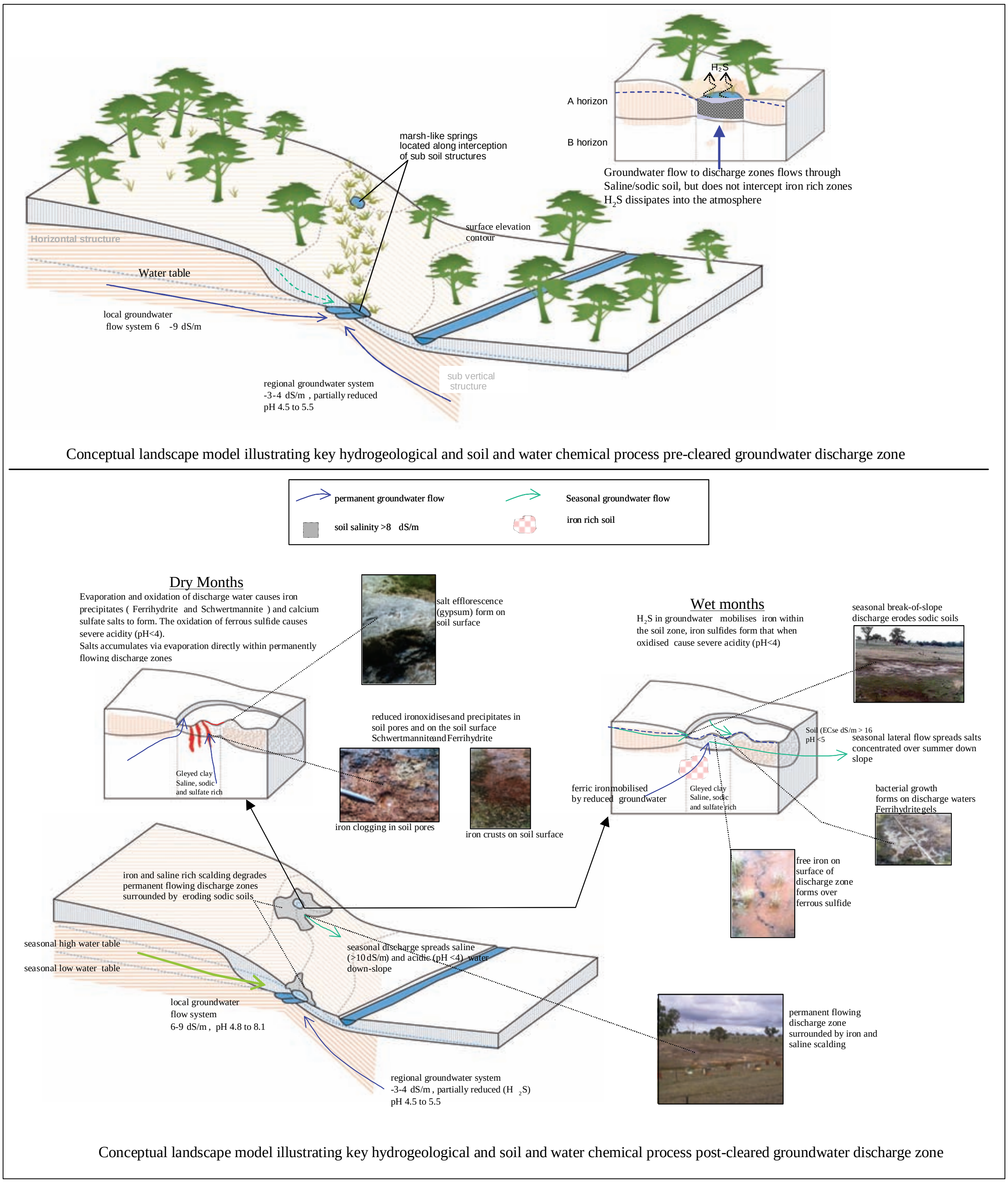
CONCLUSIONS

The evidence presented here shows that suitable conditions exist for the formation of inland ASS within discharge zones on the EDT. It has also shown that degradation is in part caused by the altered surface environment within these primary groundwater discharge zones that cause sulfidic materials to transform to sulfuric material. It is also apparent that the process of acidity and iron precipitation is halted if the discharge area is permanently saturated, which prevents the oxidization of iron sulfides. Therefore, remediation is in part achieved by promoting a stable permanently saturated wet-land environment. The direct implication of the identification of sulfidic and sulfuric materials within these degraded discharge zones is that land management options aimed at lowering water tables, are impacting on part of the hydrogeological cycle that is not a driver of the degradation processes observed on the EDT.

The conclusion of this research enables the construction of conceptual models (Figure 8), which explains how land clearing causes severe degradation of primary groundwater discharge zones on the EDT that contain ASS with both sulfidic and sulfuric materials. The major process and assumption used in the model are:

- Groundwater discharge is a primary process, and occurred prior to land clearing
- Groundwater discharge occurred into wet-land like environments where hydrogen sulfide was able to dissipate into the atmosphere
- Land clearing following European settlement caused discharge zones to be exposed and adversely impacted by agriculture
- Land clearing caused an increase in the magnitude of the local nested flow system.

In the model presented in Figure 8, a stable discharge environment exists. As the area is cleared and impacted by agriculture, the discharge environment is altered. Salts accumulate within the discharge zone, exposed sodic soils are eroded by increased activity of the local groundwater flow systems. The interaction of hydrogen sulfide in the groundwater and the iron in the soils causes the formation of inland acid sulfate soils with both sulfidic and sulfuric materials. Land degradation occurs without any measurable change to the regional groundwater system. Groundwater discharge and shallow water tables existed prior to and after European settlement. The driving cause of the degradation is the exposure of the discharge zone.



Groundwater flow to discharge zones flows through Saline/sodic soil, but does not intercept iron rich zones H_2S dissipates into the atmosphere

Conceptual landscape model illustrating key hydrogeological and soil and water chemical process pre-cleared groundwater discharge zone

Dry Months

Evaporation and oxidation of discharge water causes iron precipitates (Ferrihydrite and Schwertmannite) and calcium sulfate salts to form. The oxidation of ferrous sulfide causes severe acidity (pH<4).
Salts accumulates via evaporation directly within permanently flowing discharge zones

Wet months

H_2S in groundwater mobilises iron within the soil zone, iron sulfides form that when oxidised cause severe acidity (pH<4)

Conceptual landscape model illustrating key hydrogeological and soil and water chemical process post-cleared groundwater discharge zone

Figure 8. Conceptual model

ACKNOWLEDGEMENTS

This research has been supported by the Dame Elisabeth Murdoch Trust, Mr Geoff Handbury, CSIRO Land and Water and The Balmoral Landcare Group. The authors would like to recognize the contribution of the Smith family at Merrifields for providing the field site and the input of Dr William Gardner into the project development.

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CHAPTER 19

ACID SULFATE SOIL MATERIALS AND SALT EFFLORESCENCES IN SUBAQUEOUS AND WETLAND SOIL ENVIRONMENTS AT TAREENA BILLABONG AND SALT CREEK, NSW: PROPERTIES, RISKS AND MANAGEMENT

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INTRODUCTION

In April 2007, Tareena Billabong (south-west NSW) was isolated by sandbagging from Salt Creek and the River Murray as an option to generate water savings and help mitigate drought-related problems in the Murray-Darling Basin. Because evaporation from the billabong surface is approximately 1GL per annum, it has been estimated that environmental flow savings of about this amount can be achieved at Tareena Billabong by preventing inflow from the Murray River. In addition, the proposed works will also direct flows down the Murray in order to maintain the Lock 6 weir pool, through restricting flows within Salt Creek.

Previous work by CSIRO Land and Water and others in subaqueous soil (lakes/rivers) and wetland environments in this region have identified various occurrences of sulfidic, sulfuric and monosulfidic black ooze materials (i.e. acid sulfate soils; e.g. Baldwin *et al* 2007; Fitzpatrick *et al* 2006, Fitzpatrick *et al* 2007; Hicks and Lamontagne 2007; Lamontagne *et al* 2004). Occurrences of these ASS materials would have serious environmental consequences relating to soil and water acidification, de-oxygenation of water, foul smelling (H_2S, organo-S compounds) and possible heavy and trace metal mobilisation – especially if these wetlands are to be slowly evaporated and experience wetting-drying cycles. Hence, characterisation of a range of representative subaqueous soils and sediments in the billabong and adjacent Salt Creek would allow identification of ASS hot-spots and contaminant types, and development of specific management options and contingency plans.

This chapter presents a summary of findings (Fitzpatrick *et al* 2008) and subsequent of Murray Darling Basin Commission actions on:

- The properties, extent, potential severity and management of the various subtypes of acid sulfate soils (ASS) currently present in Tareena Billabong and adjacent Salt Creek, based on field sampling (Figure 1), morphological descriptions and laboratory data
- Provide predictive capability when the area continues to be drained, partially drained and reflooded
- Recommendations for the sustainable management of ASS subtypes and identify mitigation strategies, especially their suitability for drying to generate water savings.

Field sampling of soils

Field work was carried out at Tareena Billabong and adjacent Salt Creek from 13th to 15th September 2007. Sampling sites are shown in Figures 1 to 3. Samples of soil profiles and salts (efflorescences) were taken from 21 sites at Tareena and 8 sites on Salt Ck (for detailed information see Fitzpatrick *et al* 2008).

We collected and analysed 80 samples from 29 sites for morphological, chemical, mineralogical and physical properties. These samples provided a comprehensive database to develop a user-friendly "Soil Identification Key" to allow the easy identification of the various subtypes of ASS in Tareena Billabong and Salt Creek areas. Identification of the various subtypes of ASS enabled us to assess soil condition across Tareena Billabong and Salt Creek. An understanding the properties, distribution, evolution and interrelationships of the seven subtypes of ASS identified has been vital for effective selection of appropriate management strategies.

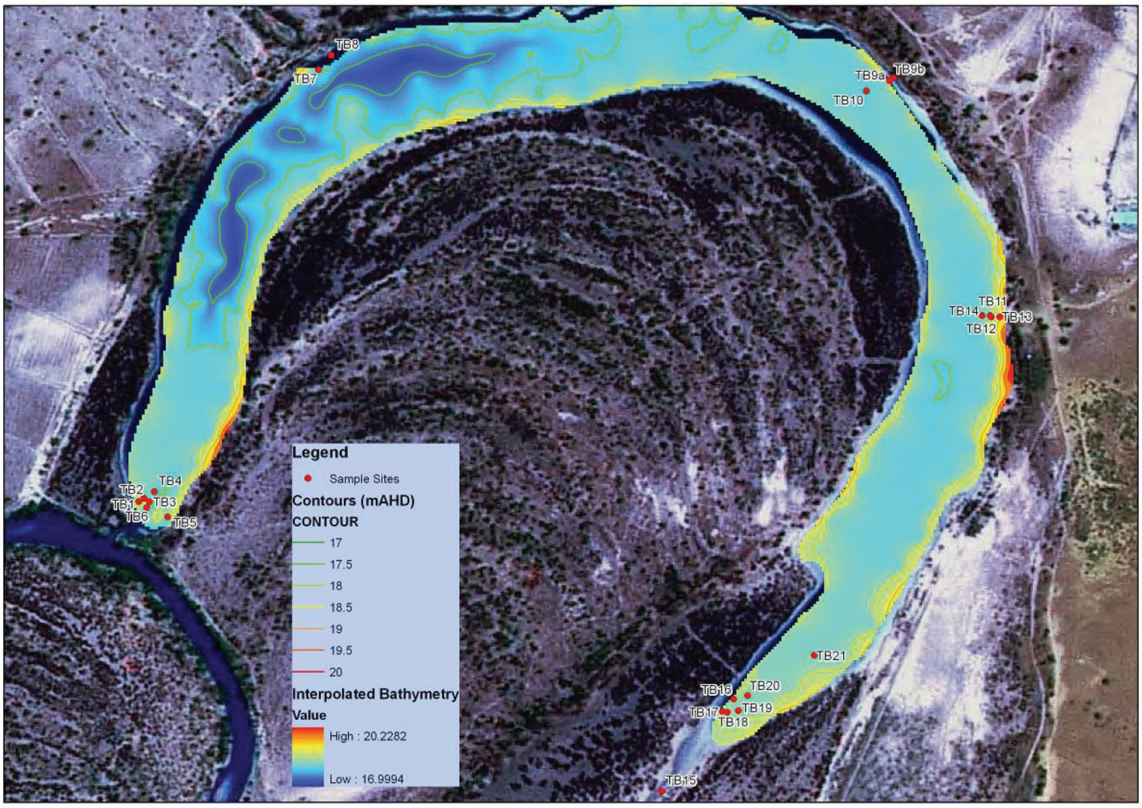

Figure 1. Sites sampled at Tareena Billabong.

Figure 2 . Sites sampled at Salt Creek. Tareena Billabong is on the right.

Figure 3. Detail of sampling sites SC3 to 6 on Salt Creek.

Results and discussion

We examined 29 sites for the occurrence of ASS. We found a wide range of ASS subtypes at these sites (Fitzpatrick *et al* 2008). We inspected 29 profiles and sampled 87 soil horizons/layers, which were stored in plastic chip trays to facilitate detailed soil morphological descriptions and mineralogical analyses. Eighty samples were analysed for chemical, mineralogical and physical properties.

These samples provided a comprehensive database to develop a user-friendly “Soil Identification Key” to allow the easy identification of the various subtypes of ASS in Tareena Billabong and Salt Creek areas. The key is based on the comprehensive data set of soil properties acquired in a range of subaqueous and wetland environments. The soil identification key essentially uses non-technical terms to categorise ASS subtypes in terms of attributes that are important for characterising soil and water degradation. Identification of the various subtypes of ASS enabled us to assess soil condition across Tareena Billabong and Salt Creek. An understanding the properties, distribution, evolution and interrelationships of the 7 subtypes of ASS has been vital for effective selection of appropriate management strategies.

Tareena Billabong

A range of subaqueous and wetland acid sulfate soil (ASS) subtypes with sulfidic and monosulfidic black ooze (MBO) materials are present in Tareena Billabong (ASS and non-ASS soils in subaqueous, waterlogged and drained soils). Sulfidic materials are expected, on oxidation, to result in pH values less the 4, measured in water (Isbell 2002). Although soil layers may be identified as sulfidic, acid generation on exposure to oxygen may be locally neutralised by carbonate minerals or by bicarbonate in the billabong and ground waters which can reach exposed soils by wind or wave action. On oxidation, MBO materials in soils do not usually produce a pH value lower than 4, the critical pH value for sulfuric material, unless other sulfidic minerals are also present. No sulfuric material (soil pH in water less than 4) was identified because the pH of most soil materials was alkaline, between pH 7 and 8.

Subaqueous ASS subtypes include:

1. Sulfidic subaqueous clayey soil with MBO (wet, soft, clayey MBO material overlying wet, heavy clay sulfidic material; Figure 4**Figure 4.**).

Figure 4. Sulfidic subaqueous clayey soil with MBO, in shallow water in the south east end of the billabong (Site TB21). This subtype has a thin surface layer (10 to 15 cm) of soft clayey monosulfidic black ooze (MBO) material, which overlies wet heavy clay sulfidic material.

2. Sulfidic subaqueous clayey soil (wet, soft, clayey sulfidic material overlying wet, heavy clay sulfidic material; Figure 5)

Figure 5 . Site TB5 sampled in water (subaqueous) near the sand-bagged outlet to the billabong (Left side). Sulfidic subaqueous clayey soil (wet, soft clayey sulfidic material overlying wet heavy clay sulfidic material) (Right side).

3. Sulfidic subaqueous soil (wet, soft sandy sulfidic material overlying wet sandy to loamy sulfidic material). The upper layers often contain fine or medium sand of varying thickness, probably of aeolian origin.

In middle sections of the billabong (e.g. from Sites TB 7 to TB 10 to TB 13, Figure 1), the dominant subaqueous ASS subtype comprises mostly a thin layer (10 to 20 cm thick) of sandy to loamy sulfidic material overlying a heavy clay matrix with prominent slickensides and bluish or greenish diffuse mottles (Figure 6).

Figure 6. Sulfidic subaqueous soil (wet, soft, sandy sulfidic material overlying wet, heavy clay sulfidic material). This site, Site TB7, was sampled in water 20 cm deep.

3. Sulfidic subaqueous soil (wet, soft, sandy sulfidic material overlying wet, heavy clay sulfidic material). The upper layers often contain fine or medium sand of varying thickness, probably of aeolian origin.

Wetland (undergoing drying) ASS subtypes include:

4. Sulfidic cracking clay soil with MBO (dry to moist, hard to soft clayey MBO material overlying wet, heavy clay sulfidic material).

At the south-east terminal end of the billabong, as drying has proceeded for a much longer time period, the sulfidic heavy clays are overlain, above the shallow water table (Figure 7), by profiles with hard to friable cracked clayey MBO layers, which are surrounded by a brown hardened oxidised surface coating (Figure 8) with surface salt crusts (moist through capillarity or groundwater seepage) and dry, ‘fluffy’ surface with salt efflorescences. All of these materials show some evidence of accumulation of what we believe to be wind-blown fine sands and other materials.

Figure 7. Sulfidic cracking clay soil with MBO (Dry to moist, hard to soft clayey MBO material overlying wet, heavy clay sulfidic material). Site TB16 (left) is a groundwater seep surrounded by very thin (< 1 cm) dried surfaces with extensive cracking and salt efflorescences on edges of cracks. More extensive drying (0-10 cm) at TB 19 (right) displays hard crust.

Figure 8. Close-up view of a fractured piece of the dried and hardened surface material at site TB19 showing a brownish, platy surface layer (2 to 10 mm thick) abruptly surrounding the inner, black sulfidic-like material.

5. Sulfidic cracking clay soil (dry to moist, hard to friable clayey sulfidic material overlying wet heavy clay sulfidic material).

In the partly dried and evaporated area near the sand-bagged connection to Salt Creek (SW end; (site TB 4)) of the billabong, dry to moist, sulfidic cracking clay ASS subtypes occur with no MBO but with a thick, 'fluffy' surface with salt efflorescences.

Figure 9. Sulfidic cracking clay soil near Site TB4 at the south-western end of Tareena Billabong. The top 5 cm has potential to acidify significantly, depending on drying.

6. Sulfidic soil with MBO (dry to moist, soft to friable sandy MBO material overlying wet heavy clay sulfidic material). The upper layers often contain fine or medium sand of varying thickness, probably of aeolian origin.

Adjacent (5 to 10 m) to shoreline in the middle sections of the billabong (e.g. from Sites TB 8 to TB 13, Figure **Figure 1.**11, the dominant ASS subtypes comprise mostly a thin layer (10 to 20 cm thick) of sandy to loamy MBO material abruptly overlying a heavy clay matrix with prominent slickensides and bluish or greenish diffuse mottles (Figure 10).

Figure 10. Sulfidic soil in sandy MBO matrix, site TB9, 6 m from shoreline near the Telephone Station.

7. Sulfidic soil (dry to moist, soft to friable, sandy to loamy (thick 0 to 50 cm) sulfidic material overlying wet clayey sulfidic material).

On the upper shorelines (>10 m from shoreline at time of sampling), especially in the middle sections of the billabong (e.g. from Sites TB 8 to TB 13), the dominant ASS subtype comprises a thick layer (10 to 50 cm thick) of sandy to loamy sulfidic material overlying a heavy clay matrix with prominent slickensides and bluish or greenish diffuse mottles (Figure 11).

Figure 11. Sulfidic soil at site TB 8 (on the upper shoreline) on the north-west side of the billabong. The dark bands at about 7 – 15 cm are sulfidic material and are likely to acidify on drying.

We also identified a sandy podsol soil with some ASS properties overlying a bluish-grey clay (site TB 11) on the upper shoreline with beach-line features (Figure 12). These are beach-like features - some of long standing in that they have experienced palaeo-environmental conditions where the climate was considerably wetter and suitable to develop a podsol (i.e. 'Podosol' according to the Australian Soil Classification: Isbell 2002). This soil may date from the earliest times of the billabong (Gell *et al* 2005) when it was a freshwater lagoon. Sand accumulation may also be a feature of where dry creek lines abut the billabong.

Figure 12. Sandy podsol soil overlying bluish-grey clay (site TB 11) on the upper shoreline with beach-like features.

Salt efflorescences containing mainly Na, Mg and Ca sulfate salts

The presence of several groundwater seepages with associated salt efflorescences containing mainly Na, Mg and Ca sulfate salts are most obvious at the south-eastern end of the billabong. However, some groundwater seepage is also evident at other places where dry gullies meet the billabong and near the sand-bagged connection to Salt Creek (SW end), with salt efflorescences containing significant concentrations of Mg and Na sulfate salts. These take the form of clearly defined seepages up to a few metres across, or much more extensive areas at some height above the billabong water level at the time of sampling, which may be kept moist by capillarity from the subsoil water table.

The pH of some soils at both ends of the billabong - which have likely been drained for the longest period - have pH values that are slightly acidic, about pH 6, similar to the groundwater in pits dug in these soils. Some localised, ‘spot’ pH measurements made in the field on naturally oxidised layers also showed pH values between 5.6 and 6. Soil pH after peroxide treatment, a quick measure of potential for acidification that simulates oxidation of sulfides on drying, indicates that there is acid neutralising capacity for most materials to maintain pH values above about 5.

More than 60% of samples exceed the highest trigger value for reduced inorganic sulfur concentrations (chromium reducible sulfur) for fine grained (clayey) soils. However, only around 40% of samples have a net acid generation potential (NAGP). Fourteen of eighteen profiles analysed had at least one horizon with a reduced inorganic sulfur concentration above the highest trigger value for fine grained soils. However, only five profiles have a net acidity (positive NAGP), although within profiles individual samples and the sum at shallower depths may have small net acidity.

Hence, we conclude that oxidation of the sulfides present are unlikely to produce very acidic soil profiles (pH less than 4) to a depth of 50 cm. Some limited layers in the upper 20 to 30 cm have potential to acidify more significantly, especially if the materials are sulfidic sands.

Two environmental features are likely to help mitigate acidification:

1. the evapo-concentration of alkalinity in the billabong water, and
2. the entry of alkaline groundwater to the surface soils.

The alkalinity of the billabong water is not known, but its pH is increasing as the billabong dries (ongoing MDBC Tareena Monitoring Reports). The alkalinities of the groundwaters are also not known, but the subsoils in seep areas are alkaline (pH > 8) and should be in equilibrium with the groundwater. The presence of groundwater leakage is also significant as it should maintain at least some areas of the billabong soils in a moist or wet state, and this will slow or prevent oxidation by excluding air. Any residual water that can be retained in the billabong will help this process as the heavy clays will wet up by capillarity (but not the sandy materials).

The rapid drying of the sulfidic material, especially the heavy clays, which cracks and lifts away from the moist, clayey subsoil and breaks the capillarity, slows the biological processes, which are responsible for oxidation of sulfides and thus the formation of acid.

White salt efflorescences containing Na, Mg and Ca-rich sulfate minerals have formed directly over the drying monosulfidic black ooze and sulfidic materials, with higher abundances of salt efflorescences occurring on the edges of cracks. The dominant salts are konyaite ($Na_2Mg(SO_4)2.5H_2O$), halite (NaCl), gypsum ($CaSO_4.2H_2O$) and thenardite (Na_2SO_4) with minor (trace) epsomite ($MgSO_4.7H_2O$), eugsterite ($Na_4Ca(SO_4)3.2H_2O$) and hexahydrite ($MgSO_4.6H_2O$). Salt efflorescences have potential for aerial transport and to be dissolved in surface flow waters. There is a need to prevent stock from ingesting these salts (e.g. similar to Epsom salts) because this is likely to lead to scouring in sheep and cattle. Magnesium salts are toxic when ingested in high levels.

Fine granular surface flakes containing “dried” sulfidic material may also form when the soils material dries. This material is also highly susceptible to wind erosion, especially on the extensive flat area of the bare, salty lake beds.

The concentrations of major and minor (or trace) elements determined using X-ray fluorescence spectroscopy (XRF) are considered to be in the normal range for most, if not all samples. Several elements – notably mercury (Hg), cadmium (Cd) and selenium (Se) – were present at concentrations below the lower limits of detection for the XRF method used. Evaluation of the potential toxicity of these and a few other elements requires other, more advanced techniques and, probably, the determination of the different species present in aqueous systems.

We recommend that the following steps be taken:

- The upper layers of soil materials be allowed to dry as quickly as possible
- The state of the drying billabong initially be monitored weekly for a period of three months – if there is little change in water pH (e.g. they remain in the range 6 to 9) reduce monitoring frequency to fortnightly
- People and farm animals be excluded as far as possible
- Develop a strategy for re-wetting based on the likely possibilities presented below.

Salt Creek

Salt Creek was sampled at five sites in the vicinity of Tareena Billabong. Mostly the banks are steep sided, with occasional reed beds and depositional areas with reduced soils and shallow water depth. Sampling and laboratory analyses of these subaqueous and near shore wetland soils indicate that the materials differ considerably from those in Tareena Billabong.

The subaqueous soils in Salt Creek mainly occur on steep sided banks (Figure 13) The dominant soil materials are grey clay to heavy clays with greenish or bluish diffuse mottles overlain by grey (sometimes yellowish grey) gel or ‘ooze’, or silty clay. In places where there are side channels, the layers may be silty or contain fine sand or grit. However, Site SC4 differed in having sand bars with rushes and reeds (Phragmites) (Figure 14). The heavy clays may show structure (lenticular or parallelepiped) and slickensides at depth. Where there was subaqueous weed, orange brown mottles are evident in the soils around the roots. Some of the heavy clays contained medium to fine sand.

Figure 13. Salt Creek near site SC1 with its steep sided banks.

Figure 14. Sulfidic subaqueous soil with thick (0 to 50 cm) soft, sandy, sulfidic material overlying wet clay. Site SC6 was sampled from the stream bed of Salt Creek mid way between the near bank and the reeds on the far side.

Subaqueous ASS subtypes include: Sulfidic subaqueous clayey soil (wet, soft, fine or medium, sandy or silty, sulfidic material overlying wet bluish grey, heavy clay sulfidic material with slickensides).

pH measurements show that these materials are mostly already acidic (pH less than 7 and lacking carbonate minerals) and that they contain sufficient sulfide, which, when oxidised, is likely to result in significant further acidification.

Wetland ASS subtypes include: Sulfidic cracking clay soil (wet, soft, fine or medium, sandy or silty, sulfidic material overlying wet, bluish grey, heavy clay sulfidic material with slickensides).

The alkalinity of the water in Salt Creek is not currently known but the low levels thought to be present may partially neutralise the subaqueous soils if they are exposed to drying. Otherwise, any acidity developed will be partially neutralised by the acidification and decomposition of the soil mineral matter. This may be effectively irreversible. Since the river water would also be expected to flush soluble sulfate salts from the system, the production of alkalinity by reduction processes that re-form sulfides may not be significantly retained for neutralising the soils. Water quality issues are also likely. Neutralisation by applying lime along the banks of the creek is not considered practical.

Management options based on subtypes of ASS

We developed the user-friendly “Soil Identification Key” to allow the easy identification of the various subtypes of ASS in Tareena Billabong and Salt Creek areas. The key is based on the comprehensive data set of soil properties acquired in a range of subaqueous and wetland environments. The soil identification key essentially uses non-technical terms to categorise ASS and other soils in terms of attributes that are important for charactering soil and water degradation. The key also describes practical, surrogate methods to assist managers and engineers to estimate hazard classes for the subtypes of ASS (High, Moderate, Low and Very Low).

Management strategies should to be based on adequate characterisation and mapping of the seven identified ASS subtypes. Understanding the distribution, evolution, nature and interrelationships of the seven subtypes of ASS is vital for effective planning of agricultural management and selection of appropriate remediation options. We recommend that the steps outlined below be taken.

Strategies for re-wetting based on likely possibilities

The results of investigations suggested that re-establishing the billabong to full capacity should result in the exclusion of oxygen to much of the cracked dry soils and the re-establishment of the more benign subaqueous acid sulfate soils with clayey or sandy monosulfidic black ooze overlying the clayey sulfidic materials that currently exist under water. Formation of sulfide minerals produces alkalinity (derived from organic matter) that may partially offset some of the acid formed, but only if this alkalinity is retained in the system. Re-flooding should manage potential acid formation of all soil types indentified in the billabong.

Management options for re-flooding and re-wetting dry wetlands

A strategy for re-wetting was prepared and implemented. For example, flood waters were held in Tareena Billabong for some weeks to permit anaerobic conditions to develop. This created reducing conditions for the oxidised sulfate to transform back to sulfide. Once this has occurred, and water quality is acceptable, then water can be allowed to flow back into Salt Creek.

A careful approach will be needed when re-wetting the adjacent Salt Creek to manage the increased salt loads and potential mobilisation of acidity and metals. Management to enable periodic flushing of the salts is recommended long-term, if possible, as this will decrease the sulfur load in Salt Creek and Murray River wetlands.

Monitoring of Salt Creek and adjacent wetlands was recommended and implemented as the wetting and re-filling occurs. It provided an opportunity to learn for future drought recovery programs.

Proposed monitoring strategy

For future work, it is strongly recommended that a detailed monitoring strategy be developed at the representative monitoring sites in the Billabong and Salt Creek for key field indicators and laboratory tests. The strategy will be to determine key trigger values to identify the onset of acidification and other ASS related problems (e.g. changes in pH, alkalinity, presence of indicator minerals, etc.), which needs to be site specific. Preliminary trigger values for pH of 6.5 is suggested since at pH values below this, significant impacts are likely for many natural ecosystems. However, part of the monitoring exercise should assess in detail site specific indicators for key indicator elements e.g. sulfur species.

A monitoring strategy should be based on data from the current ASS investigations, especially the identification of the sandy ASS “hot spots”.

CONCLUSIONS

Tareena Billabong

Field and laboratory investigations led to the conclusion that significant acidification is unlikely to occur and become a problem if Tareena Billabong continues to evaporate to dryness, although minor local acidification within soil layers is likely. Acidity is likely to be neutralised by carbonate minerals present in the soils, by the entry of alkaline groundwater, wind and wave action on alkaline billabong water and by the accession of alkaline components of wind-borne dusts.

Salt efflorescences containing Na, Mg, Ca sulfate salts, their transport by wind (e.g. aerial transport of fine granular surface flakes containing sulfidic material) or water, and malodorous problems may become serious issues, though the latter is somewhat negated by its remote location. These efflorescences are mostly highly water soluble and can be expected to be easily entrained in and contribute to degraded quality of river water.

Monitoring of soils and waters for pH was recommended and implemented as the water in the disconnected billabong receded to confirm the expected course of acidification or alkalinisation (in this case, the latter). Murray Darling Basin Commission staff monitored the system, initially weekly for three months and subsequently fortnightly because pH levels remained alkaline. A similar monitoring program is recommended during reflooding of the billabong.

Finally, we also recommended:

- Removal of sandbags and installation of a floodgate and manual mini-sluice gate to enable controlled exchange of water between Tareena Billabong and Salt Creek
- Installation of a one-way hinged flap gate (floodgate) to regulate billabong water entering Salt Creek and the Murray River system, especially during reflooding of Tareena Billabong. The flood waters must be held in Tareena Billabong for some weeks to permit anaerobic conditions to develop. This will create reducing conditions for the oxidised sulfate to transform to sulfide
- Once anaerobic conditions have been re-established in the reflooded billabong, then water exchange with Salt Creek should be allowed, provided the water is of suitable quality. Self-regulating or manual mini-sluice gates allow better control of water exchange than raising floodgates.

Salt Creek

Field and laboratory investigations indicate that acidification is more likely to be a serious problem if the river bed of Salt Creek continues to be exposed. The higher quality river water contains relatively low alkalinity, as do the soils adjacent to the creek and in its bed. Generally these soils are already mildly acidic. Receding river water levels may allow significant entry of alkaline ground waters that should introduce alkalinity.

Should water levels decline further exposing more creek bed and bank, a monitoring program should be instigated and an assessment made of risks.

ACKNOWLEGEMENTS

This work was funded through the Murray-Darling Basin Commission (MDBC). We acknowledge Dean Ansell, River Murray Channel Coordinator (MDBC) for his assistance in project management. Thanks also to: Steve Marvanek, CSIRO Land and Water (CLW), for preparing the map figures; Warren Hicks, CLW for preparing the Acid Base Accounting figures; Benn Britton CLW for undertaking the x-ray fluorescence (geochemical) analyses, Ms Nilmini Jayalath for preparing samples for x-ray analyses and Mrs Alison Fitzpatrick for assistance in the field.

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CHAPTER 20

CASE STUDY: ACID SULFATE SOILS OF THE MAGELA CREEK PLAIN, EAST ALLIGATOR RIVER, N.T.

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INTRODUCTION

Ranger Uranium Mine is located about 40 km inland from the East Alligator River and separated by it by the flood plain of Magela Creek (Fig. 1). Detailed work on acid sulfate soils (ASS) were made there in the late 1980s as part of environment and geomorphic studies concerned with prediction of the fate of potential pollutants, in the form of mine tailing or in water, should discharges from the mine site ever occur. At that time ASS research was in its infancy in Australia. Before the mid-1990s there seemed to be a form of collective denial by land managers, and even research managers, of the existence and environmental consequences of ASS. The soil and geomorphology research in the Magela Plain was undertaken by CSIRO in collaboration with the laboratory that is now the Environmental Research Institute of the Supervising Scientist (ERISS), at Jabiru, N.T. Most of the research concerning the ASS was published in reports of the Supervising Scientist for the Alligator Rivers Region (Wasson 1992), and only specific aspects concerning details of chemical and micro-morphological transformations during controlled oxidation, and the chemical behaviour of heavy metals, uranium and radium were published in the mainstream literature (Willett *et al* 1992, 1994).

The Plain is a fresh water system, which is underlain by sulfidic material (potential acid sulfate soil material). The entire flood plain with sulfidic substrata extends to nearly 40 km, from the East Alligator River to the upper plain just north of Ranger Uranium Mine. Their distance from the present coast, the current fresh water ecosystem rather than the mangroves of current marine systems, and their significance to inland mining activities suggests that they be included with this compilation of inland ASS. The purpose of this chapter is to briefly summarise information on the nature and distribution ASS of the Magela Plain.

Physical setting

The Magela Plain (Fig. 1) is a low-lying flood plain of about 220 km^2 downstream of the point where Magela Creek emerges from sandy upland country. The flood plain is confined to a valley by upland areas in the upper reaches in an area designated as the Mudginberri Corridor. Upper and lower basins are separated by a slightly elevated landform (“central topographic high” in Fig. 1). At the northern end the flood plain merges with that of the larger East Alligator River.

Billabongs up to 4 m deep occur upstream of the central topographic high. The billabongs and channels have narrow depositional levees that are higher, by up to a few metres, on the downstream ends of billabongs. Surface expressions of acid sulfate soils are most obvious in backslopes leading from billabongs and in marginal flood basin areas (Fig. 1).

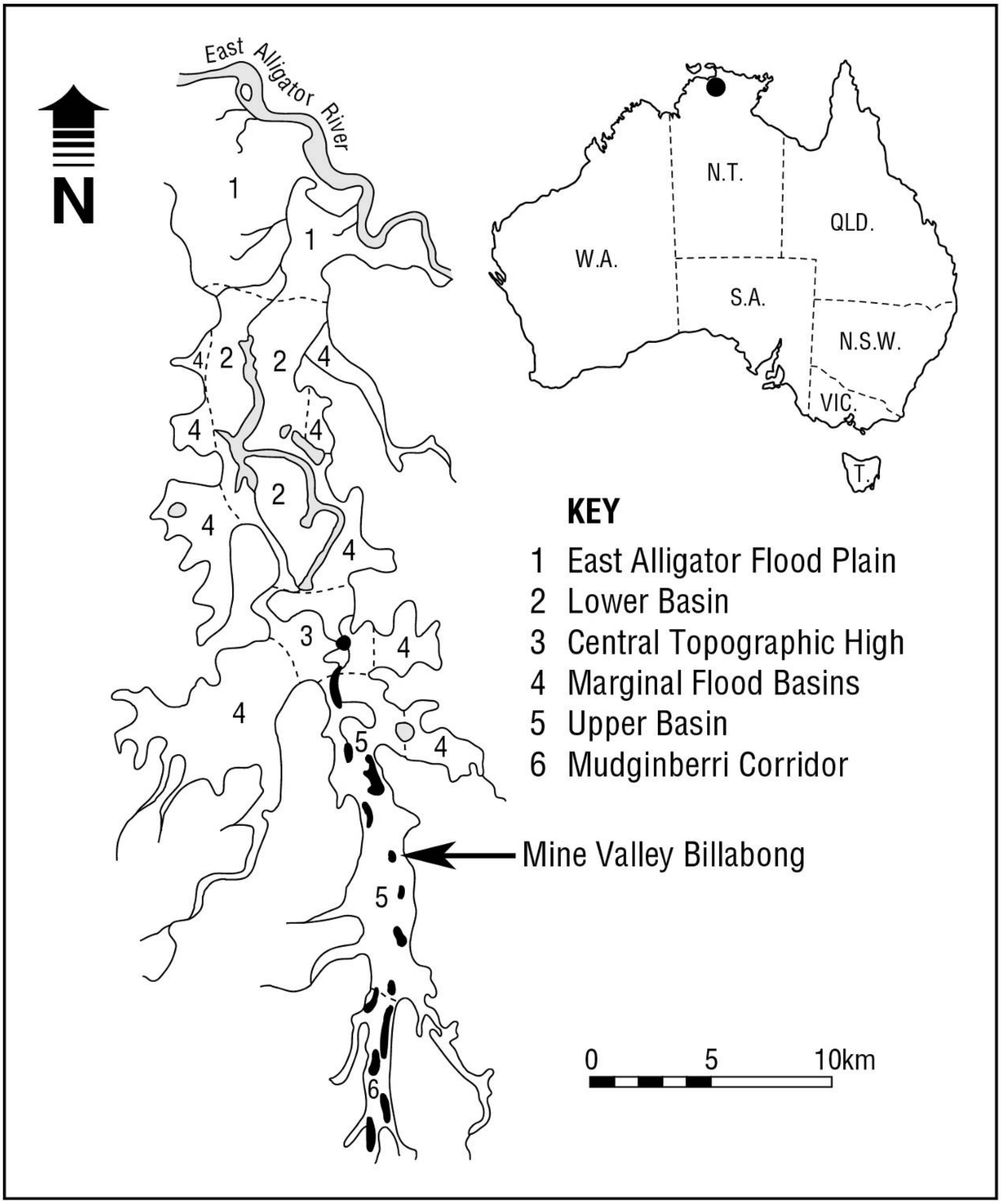

Figure 1. Geomorphic map of Magela Plain showing the main topographic units.
Dashed lines show drilled transects (Wasson, 1992).

A substratum of distinctive blue-grey sulfidic clay underlies most of the Plain. Pollen and radiocarbon dating studies reported in Wasson (1992) showed that the lower strata of the Plain were formed by deposition in a large mangrove forested estuary. This material contains thick deposits of peat often with preserved mangrove wood. The pyrite occurs as framboids usually associated with organic matter, as fossilised plant materials (Fig 2.), and occasionally as individual micro-crystals. After a transitional period represented by sediments that contain pollen of mangrove and fresh water plants, the surface materials are dominated by fresh water pollen and have chemical properties corresponding to fresh water deposition.

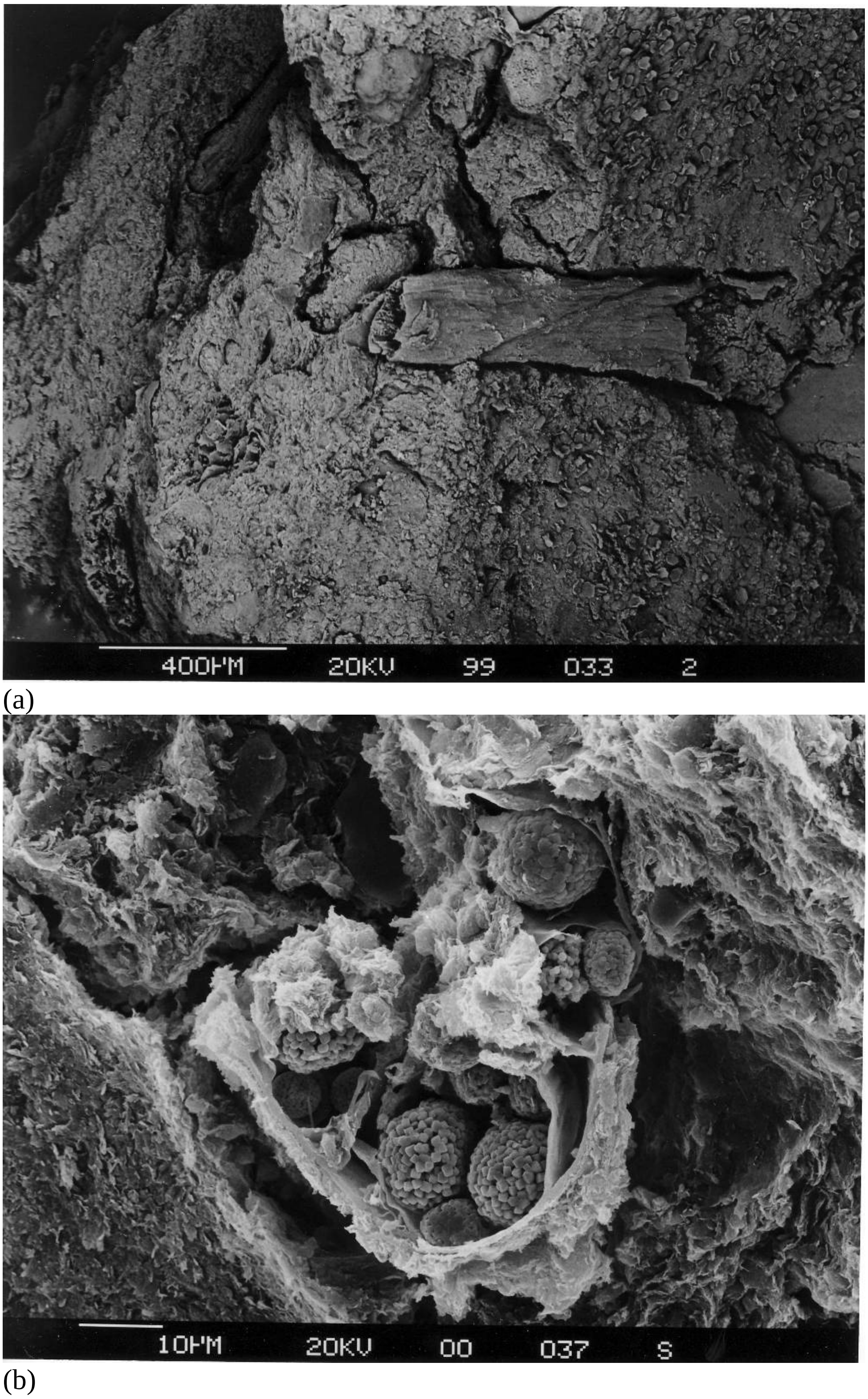

Figure 2. Pyrite in blue-grey clay substratum of Magela Plain. Unoxidised samples from near Mine Valley Billabong, dated ca. 4,000 years B.P. (a) pyritised fossil plant remains, probably a root, (b) pyrite framboids in organic capsules, surrounded by a clay matrix. SEM photographs, CSIRO, unpublished.

Soils

Fifty-two soil profiles, drilled on transects shown in Fig. 1, were dug or drilled down to the blue-grey clay substratum. The unoxidised sulfidic samples were oven-dried at 80 ˚C within two days of collection to minimise oxidation. The samples were analysed by conventional methods and pyrite-sulfur estimated from the difference in S extracted in hydrogen peroxide and that extracted by EDTA (Willett and Walker 1982).

The soils materials could all be described in terms of 9 horizons:
Ao: brown to black organic surface mat, usually less than 5 cm deep
A2: dark organic surface, sometimes rich in biogenic silica
B: B horizon of uniform colour, light to dark grey, light to heavy clay
Mr: Grey clay with abundant orange and/or red mottles
My1: Grey clay with occasional yellow oxide mottles
My2: Grey clay with abundant yellow oxide mottles
J: Grey clay with abundant yellow jarosite mottles, or jarosite on ped surfaces, root channels
S: Slightly oxidised pyritic clay, occasional jarosite in channels
G: Unoxidised pyritic clay, usually blue-grey clay

The unoxidised G material, and the derived S and J materials are former marine sediments. The mottled horizons Mr, My1 and My2 correspond with deposits when the Plain was transitional from marine to fresh water, whilst the surface Ao, A2 and B horizons are derived from alluvium. The chemical properties of each horizon are shown in Table 1, as average values for all samples of each horizon from throughout the Plain. There was a clear distinction between the ASS layers J, S and the unoxidised G horizon. It is clear that there was a loss of pyrite-S and which was replaced by jarosite- and sulfate-S, and depressed pH values, as the pyritic G horizon oxidised. The ASS horizons J and S indicate the lowest points that the watertable reached, presumably during extended dry periods. In general, the mottled (M) horizons have accumulations of free iron and manganese oxides, whereas the surface A horizons are richer in organic-C than the other horizons.

Table 1. Summary of the chemical properties of morphologically-defined soil horizons of the Magela Plain

Horizon	Ao	A1	B	Mr	My1	My2	J	S	G
pH	4.7	5.6	6.3	6.9	7.8	6.8	4.1	4.7	6.8
EC, mS cm^{-1}	0.43	0.50	0.87	0.80	2.26	2.01	2.59	3.57	3.3
Cl, mg kg^{-1}	182	274	714	614	2783	1339	1191	1749	3190
Mn-CDB* mg kg^{-1}	13	120	145	220	215	206	27	90	135
Fe-CDB , %	0.45	0.97	0.71	0.85	0.80	0.95	0.85	0.60	0.49
Org-C, %	7.17	3.30	1.41	0.73	0.36	0.62	1.33	2.64	1.89
EDTA-S**, mg kg^{-1}	1151	821	751	377	533	1392	3870	7128	2250
Jarosite-S, mg kg^{-1}	20	20	51	20	28	23	3868	1240	256
Pyrite-S, %	0.02	0.03	0.03	0.05	0.04	0.04	0.16	0.69	0.62

*CDB – citrate dithionite bicarbonate extraction - total free iron or manganese as oxides
** EDTA extractable sulfur - water soluble and adsorbed sulfate, and gypsum

A selection of three transects to show the distribution of soils in relation to local landscape features are shown in Figures 3, 4 and 5. At Jabiluka and Nankeen Billabongs, the underlying G horizon is overlain with ASS in the form of S and J horizons. The absence of J and S horizons beneath the levee banks may be due to continuous anoxic conditions as these billabongs retain water all year round. In general the horizons strongly reflect the sedimentary history - from marine, transitional and, now, fresh water. The ASS layers are closer to the surface with distance away from the billabongs, in a manner similar to those found in backslopes of rivers in coastal NSW (Willett and Walker 1982). There has been less oxidation of the sulfidic G horizon nearer the East Alligator River, which is wetter all year round and still salt affected.

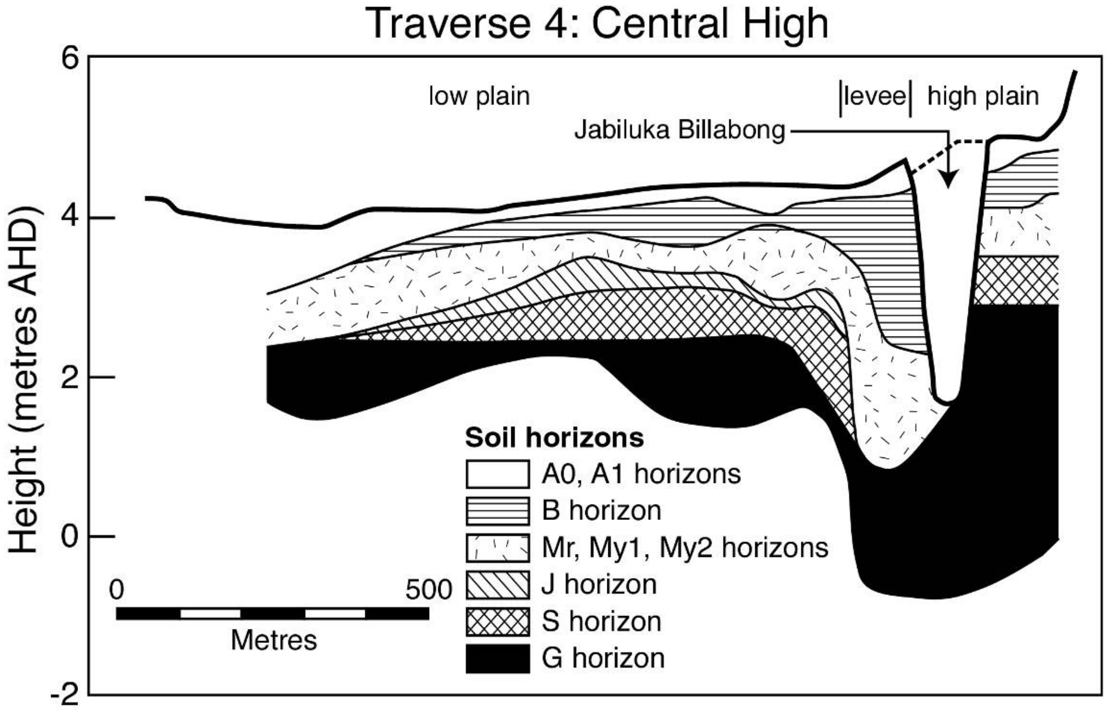

Figure 3: Soils along transect (Traverse 4) of the central topographic high billabong areas and East Alligator River Flood Plain.

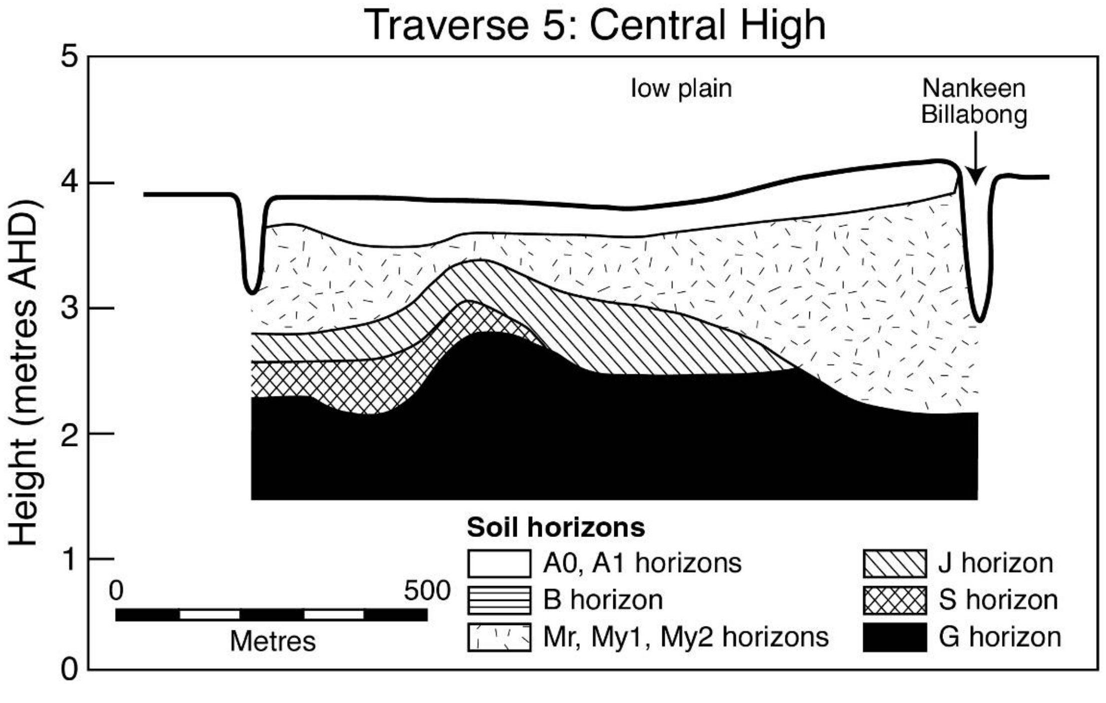

Figure 4: Soils along transect (Traverse 5) of the central topographic high billabong areas and East Alligator River Flood Plain.

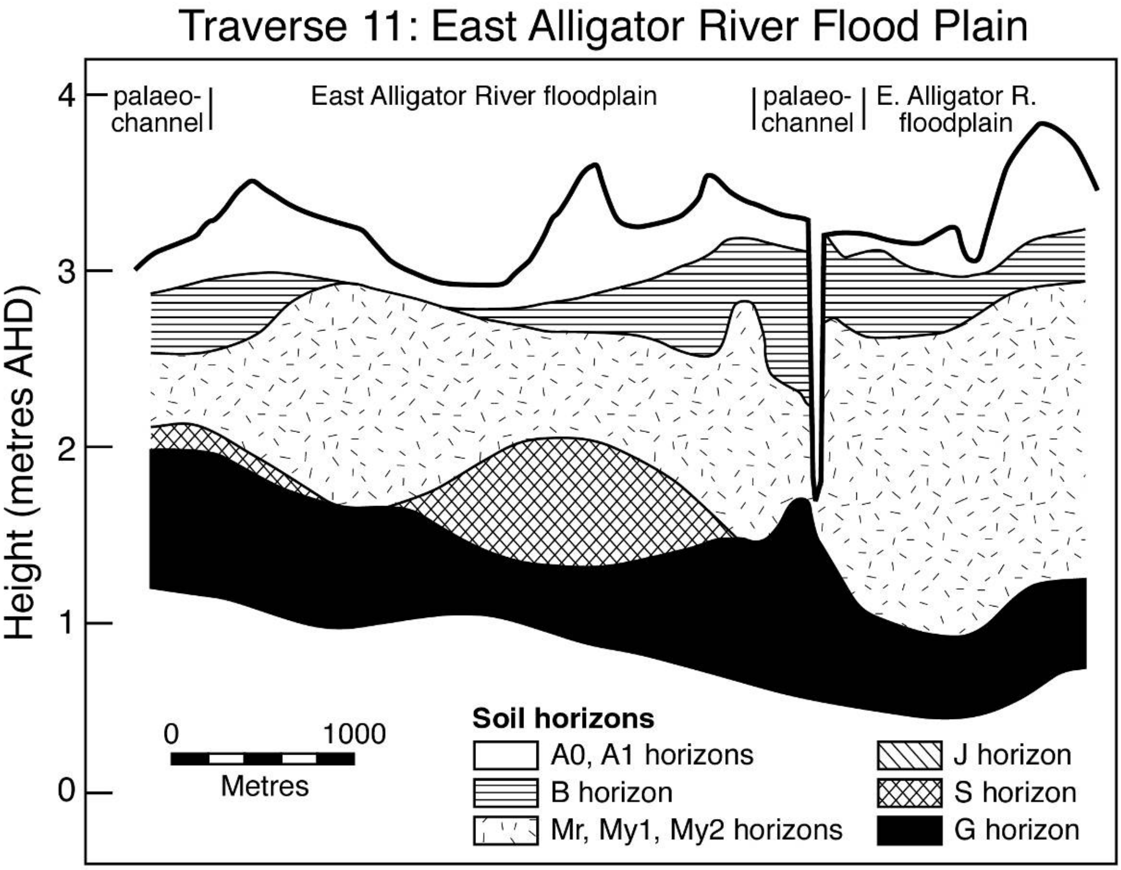

Figure 5: Soils along transect (Traverse 11) of the central topographic high billabong areas and East Alligator River Flood Plain.

The Magela Plain is protected within Kakadu National Park and should be subjected to minimal disturbance by human activities. The removal of Asian buffaloes, which had the capacity to expose buried sulfidic materials, has already been achieved. The recognition of ASS extending about 40 km from the East Alligator River has been important in understanding some natural phenomena such as the extremely acidic "first flush" water that has been observed moving on the Plain after the first heavy monsoonal rains after the dry season. Should tailings from Ranger Uranium Mine ever escape their containment structures they could be exposed to extremely acid soils of the Magela Plain. The tailings are enriched in heavy metals and radionuclides of the thorium-230 and radium-226 series in comparison with soils of the region, particularly in Pb-210 and Ra-226. However, the heavy metals, including uranium, occur in very stable forms in the tailings (Willett *et al* 1994). When a pyritic soil of the Plain was oxidised there were marked increases in the extractability (and by implication also increases in mobility and bioavailability) of Fe, Mn, Cu and U, even from soils to which tailings had not been added. In contrast the extractability of Pb and Ra decreased, perhaps because of $PbSO_4$ and $RaSO_4$ formation.

ACKNOWLEDGEMENTS

The research summarised here was part of a larger study of sedimentation and late quaternary evolution of the Magela Creek Plain, led by R J Wasson and T J East, and funded by the Office of the Supervising Scientist. B N Noller contributed to the soil chemistry work.

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CHAPTER 21

BRUNEI: SUMMARY OF ACID SULFATE SOILS

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INTRODUCTION

Negara Brunei Darussalam is a small country of 5765 square kilometres located on the north of Borneo Island bordering the South China Sea and the Malaysian state of Sarawak (Figure 1). Rainforest covers about 80 percent of Brunei’s land mass and its capital city, Bandar Seri Begawan is located next to the Brunei River. A recent survey and characterisation of soils in Negara Brunei Darussalam was conducted as part of the project “Soil Fertility Evaluation/Advisory Service in Negara Brunei Darussalam”. The survey was carried out on twenty-nine separate development areas totalling around 4422 hectares. These development areas were either existing agricultural areas or areas under consideration for agricultural development. The distribution of the survey areas provided a reasonable baseline for the range of soils that occur throughout the country. The classification, morphology and extent of the soils are described in Grealish *et al*. (2007a, 2007b).

Acid sulfate soils were identified in nine of the twenty-nine areas studied and are widespread throughout the country. They occur adjacent to tidal rivers in mangrove and peat areas and inland they occur on terraces and down slope from where sedimentary shale containing sulfides have been exposed. Their properties, problems associated with them, suitability for agricultural development and recommendations for the sustainable management and mitigation strategies for identified hazards are described in Fitzpatrick *et al*. (2008). In the nine areas where acid sulfate soils were occurred, twenty-seven sites were inspected and a wide range of acid sulfate soil types identified. Seven of these sites were chosen for detailed analysis and thirty samples were collected and analysed for chemical, mineralogical and physical properties.

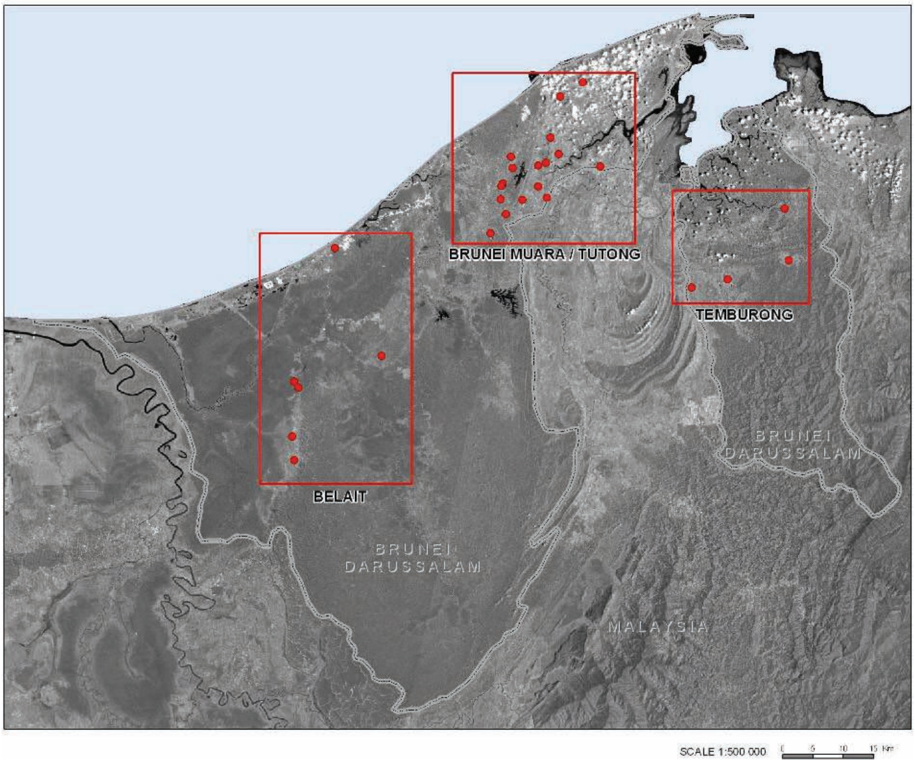

Figure 1: Location of the Surveyed Areas in Negara Brunei Darussalam (identified by the red dots).

Classification

Soils were described and classified according to Soil Taxonomy (Soil Survey Staff 2003). Seven soil Orders were identified leading to twenty-four Subgroups. Acid sulfate soils are represented in four of these Orders and ten Subgroups (Table 1).

Table 4. Soil Taxonomy classifications of surveyed Agricultural Development Areas in Negara Brunei Darussalam. Non acid sulfate soils are in grey font type. The soil marked *, while not acid sulfate, has pH <4.5 resulting from oxidation of sulfides.

Order	Suborder	Great Group	Subgroup
Histosols	Saprists	Sulfosaprists	Terric Sulfosaprists
			Typic Sulfosaprists
		Sulfisaprists	Terric Sulfisaprists
			Typic Sulfisaprists
Spodosols	Aquods	Epiaquods	Ultic Epiaquods
			Umbric Epiaquods
Vertisols	Aquerts	Sulfaquerts	Sulfic Sulfaquerts
		Dystraquerts	Typic Dystraquerts*
Ultisols	Humults	Kandihumults	Aquic Kandihumults
			Typic Kandihumults
		Palehumults	Aquic Palehumults
			Oxyaquic Palehumults
			Typic Palehumults
		Haplohumults	Oxyaquic Haplohumults
			Typic Haplohumults
	Udults	Paleudults	Arenic Paleudults
Alfisols	Aqualfs	Epiaqualfs	Aeric Epiaqualfs
			Typic Epiaqualfs
Inceptisols	Aquepts	Sulfaquepts	Hydraquentic Sulfaquepts
			Typic Sulfaquepts
Entisols	Aquents	Sulfaquents	Haplic Sulfaquents
			Thapto-Histic Sulfaquents
		Fluvaquents	Sulfic Fluvaquents
		Endoaquents	Humaqueptic Endoaquents

To assist users identify these soil classes a user-friendly soil identification key was developed to more readily identify the various acid sulfate soils and other soils of Brunei found in the survey (Grealish *et al.* 2007a). The soil identification key uses non-technical terms to categorise acid sulfate soils and other soils in terms of attributes that are important for charactering the soils and their fertility. The key describes practical, surrogate methods to assist extension officers and farmers to recognise and manage soils. The key is designed for people who are not experts in soil classification systems such as Soil Taxonomy. Hence it has the potential to deliver soil-specific land development and soil management packages to advisors, planners and engineers.

The key consists of a systematic arrangement of soils and a collection of plain language soil type and subtype names was developed to correspond to the major Soil Taxonomy Suborder and Subgroup classes found in the survey. These names are intended to provide some assistance in understanding the intent and general nature of the soils classified using the Soil Taxonomy classification. The four acid sulfate soil types in the Key are: (i) Organic Soils, (ii) Cracking Clay Soils, (iii) Sulfuric Soils and (iv) Sulfidic Soils. These are further sub-divided into eleven subtypes based on depth to sulfuric/sulfidic horizon; firmness; and drainage (waterlogging).

CHARACTERISATION

Morphology

Soil colour, structure, texture and consistency along with field pH are the most useful properties for soil identification and appraisal. Soil colour, structure and consistency provide practical indicators of soil redox status and existing acidity. This relates directly to soil aeration and organic matter content in the soils of Brunei. Consequently, these field indicators were used to help develop a user-friendly soil identification key to categorise the various acid sulfate soils and other soils.

Soil pH and Electrical Conductivity

The floodplain soils and sediments generally have low pH values ranging from 2.5 for the sub-surface (80–180 cm) of the Soft poorly drained sulfuric soil at Limpaki (06 0002) to 6.2 in the surface (0–5 cm) of the Mineral sulfuric organic soil from Labi Lama (23 0001), indicating that acid neutralising capacity is already exhausted. Electrical Conductivity values ranged from 0.02 dS m^{-1} at 20–70 cm in the Organic poorly drained moderately deep sulfidic soil at site 2 Melayan A (22 0002) to 8.6 dS m^{-1} for the sub-surface (80–180 cm) of the Soft poorly drained sulfuric soil at Limpaki (06 0002).

Sulfur

Total sulfur values in samples, range from 0.04% below 30 cm at Tungku (09 0015) to 4.4% in the sub-surface (80–180 cm) at Limpaki (06 0002). Chromium reducible sulfur values range from below the detection limit (0.005%) throughout the soil profile at Tungku (09 0015) to 3.4% in the sub-surface (150–200 cm) at Betumpu (01 0015). Generally, chromium reducible sulfur concentrations are lower to around 50 cm (<0.05%) and higher below 100 cm (>1%). In the limited number of analysed profiles the exception is Limpaki (ADA 06) where the top 40 cm contains chromium reducible sulfur concentrations >0.2%. The soft poorly drained sulfuric soil at Tungku is also an exception, but here the acid originates in adjacent outcrops of weathering pyritic shale and not in the soil profile.

Carbon

Carbonate minerals in a soil are a component of its acid neutralising capacity (ANC). However, in the low pH, highly leached Brunei environment carbonate levels are expected to be low. The exceptions would be soils in proximity to carbonate rich sedimentary rocks or in soil profiles containing shell. In Brunei acid sulfate soils, pH values were too low for measurable carbonate, shells were absent from the profiles and none of the acid sulfate soil profiles occurred near carbonate rich sedimentary rocks. While shell may be present in soils closer to the coast, it should be noted that carbonate from shell material is usually not a good source of neutralising capacity, as it can become unreactive when acidic waters result in the shell fragments becoming coated with iron and/or gypsum. Repeated wetting and drying cycles in wetlands may similarly armour carbonates with unreactive coatings. Detailed discussion of the precautions and factors recommended when using carbonate values as a measure of ANC can be found in manuals and technical documents published for coastal acid sulfate soils (e.g. Dear *et al.* 2002). None of the soils examined had measurable acid neutralising capacity (i.e. carbonate minerals in the soil).

In the Organic soils, organic carbon concentrations are (by definition) at least 12% in at least half of the top 80 cm. In the organic soil class, the maximum concentration was 59% organic carbon at 60–80 cm in a Sulfuric organic soil at Meranking (21 0007) and 0.35% at 70–150 cm in a Mineral sulfidic organic soil at Labi Lama (23 0004). Sulfuric soils have a range in carbon concentrations from 0.18% in the Soft poorly drained sulfuric soil from site 15 at Tungku (09 0015) to 17% in a poorly drained sulfuric soil at site 11 in Betumpu (01 0011). The range in organic carbon found in Sulfidic soils was from 0.14% at 20–70 cm to 24% at 130–200 cm, both in the Organic poorly drained moderately deep sulfidic soil at Melayan A (22 0002). Cracking clay soils contain between 0.94% organic carbon between 20–70 cm at Si Tukak, Limau Manis B (03 0001) and 6.5% between 0–10 cm of the same soil (see Fitzpatrick *et al.* 2008) for the complete set of results.

ACID-BASE BUDGET

Total Actual Acidity

Actual acidity is a measure of the existing acidity in acid sulfate soils that have already oxidised. The method measures acidity stored in a number of forms in the soil such as iron and aluminium oxyhydroxides and oxyhydroxysulfate precipitates (e.g. jarosite, schwertmannite and alunite) which dissolve to produce acidity. Because some samples thawed in transit and potentially oxidised before analysis for total actual acidity, this measure as a stand alone variable to assess the current level of acidity in Brunei acid sulfate soils is not reliable. However, it can be applied to the acid–base budget, which uses the total of actual and potential acidity to assess the acid generation potential of a soil. All sites had existing acidity, which ranged from 49 moles $H^+ t^{-1}$ in the sub-surface (30–50 cm) of the Soft poorly drained sulfuric soil at Tungku (09 0015) to 760 moles $H^+ t^{-1}$ in the sub-surface (80–150 cm) of the Sulfidic organic soil at Betumpu (01 0015).

Acid Neutralising Capacity (ANC)

By definition any soil with a pH <6.5 has a zero ANC. All acid sulfate soils examined had pH values of <6.5 throughout the profile.

Acid Generation Potential (AGP)

This parameter is calculated from the concentration of reduced sulfur in the sample. Methods for analysing soil samples to assess AGP are given in Ahern *et al.* (2004), which includes the chromium reducible sulfur (CRS or SCr) (Method Code 22B) and its conversion to AGP.

Net Acid Generation Potential (NAGP)

NAGP is calculated by subtracting the ANC from the AGP and is a measure of the overall acidification risk of a soil. A positive value indicates an excess of acid and the likelihood of sulfuric materials (or an actual acid sulfate soil material) forming in the soil when it is disturbed and oxidised:
NAGP = AGP – ANC.

Net Acidity

The net acidity of a soil where there is existing acidity includes both NAGP and the existing or titratable actual acidity (TAA) so that:
Net Acidity = TAA + AGP – ANC

or

Net Acidity = TAA +NAGP.

All soils sampled had positive net acidities. Net acidities ranged from 49 moles H+ t^{-1} in the sub-surface (30–50 cm) of the Soft poorly drained sulfuric soil at Tungku (09 0015) to 2,900 moles H^+ t^{-1} in the sub-surface (150–200 cm) of the Organic sulfidic soil at Betumpu (01 0015). The soil at Limpaki (ADA 06) had a high acid generating potential, being >500 moles H^+ t^{-1} throughout the profile and >2000 moles H^+ t^{-1} below 80 cm.

Arsenic and Cadmium

Arsenic concentrations in the acid sulfate soils analysed ranged from 0.1 to 20 mg kg^{-1}. Cadmium concentrations in these soils ranged from less than the detection limit of 0.2 mg kg^{-1} to 1.8 mg kg^{-1}. Both arsenic and cadmium were below the serious risk concentrations in soil for human and ecotoxicological protection set in soil standards for the Netherlands (576 and 85 mg kg^{-1} respectively for As and 28 and 13 mg kg^{-1} respectively for Cd; Lijzen *et al.* 2001) and below the soil investigation levels set in Australia (100 mg kg^{-1} for As and 20 mg kg^{-1} for Cd; Imray and Langley 1999). The highest levels of cadmium were found at Labi Lama (23 0001) and may reflect fertilisation of the orchard. There is evidence of over-fertilisation in some intensively used areas, which carries with it the risk of elevated concentrations of cadmium in soil and produce. Such areas may need further investigation. Another difficulty in assessing levels of arsenic and cadmium in the soil of Brunei is the low pH, compared with the soil pH values assumed in developing the standards (pH 7.0 and 6.0 respectively for the Netherlands and Australia). The low pH values (3.9–4.2) of the Brunei soils may increase metal availability and uptake by crops.

DISTRIBUTION

Brunei contains a wide range of different types of acid sulfate soils in various physical settings, which occur because of changing hydrological and biogeochemical conditions. There are two broad situations in which various organic matter fractions (mostly sapric) and minerals (e.g. pyrite, jarosite and schwertmannite) form acid sulfate soils via various micro-scale weathering pathways:

i) Drained conditions, which develop during the excavation and construction of drains; buildings and other infrastructure; or when erosion of sulfide-rich sediments or weathered pyritic sedimentary rocks occurs
ii) Undrained/partly drained conditions, which develop in natural tidal, intertidal and supratidal zones; and fluvial floodplains

In general terms, these acid sulfate soils occur in association with lowland peat domes where specific characteristics such as clay and organic carbon contents depend upon their topographic setting within the peat dome (Figure 2). Exceptions are acid sulfate soils in which the sulfuric horizon has been formed as a result of acid leachate from the weathering of pyritic shale (Figure 3).

Figure 2. Recently cleared land and excavated drains in the Betumpu Agricultural Development Area showing: (a) good pineapple growth on the higher mounded areas and stunted growth on the lower areas adjacent to the drains with precipitates of iron oxyhydroxysulfate minerals (schwertmannite) on the edges of the drain / wetland margin (pH 3.5–4.2), and (b) close-up view of a sulfuric horizon in spoil bank of a drain showing bright yellow jarosite mottles (pH 3.5) and clear reddish coloured water in the drain (pH 3) with patches of oil-like bacterial surface films.

Figure 3. Damage to road infrastructures by erosion and corrosion of concrete and road material (pH 3.5 - 4.2) from the exposure (oxidation) of pyrite contained in the pyrite-rich shale at Tungku.

Acid Sulfate Soils Hazard Maps

Acid sulfate soils of the flat terrace areas are already acidic, and appear to have been so for a long period of time. Much of this condition may be attributable to a lowering of the shallow water table by drainage. The key to management and sustainable production on these lowland soils both for soil fertility and environmental protection is an understanding of their complex hydrology so that the water table can be managed appropriately (Melling *et al.* 2002). Unless properly managed the economic usefulness of these soils will be short lived.

Management of acid sulfate soils is but one facet of this management. Poor management of the water table will result in increased acidification, poor production, environmental degradation and ultimately the loss of the soil resource itself. Acidification or occurrence of sulfuric materials is considered to be a risk because all the sulfide containing wetland soils we examined have little acid neutralising capacity. In soils, acid neutralising capacity is provided by carbonate minerals and clays. In Brunei, as in all high rainfall, highly leached acid tropical soils, carbonate contents are low; however many locations in Brunei have high (>30%) clay contents which provide some buffering.

The main risks to the development of acid sulfate soils for agricultural production are:

- Lowering the water table and exposing the remaining sulfidic material to further oxidation and acidification
- Subsidence due to oxidation of the organic soils (peats) and loss of the soil resource

Unless well managed and controlled, the development of acid sulfate soils will result in decreased production due to the toxicity and plant nutrition effects of the low pH. The discharge of acid drainage water will cause offsite environmental degradation from acidic discharges into waterways affecting aquatic life and fisheries. There will also be cumulative global effects due to greenhouse gas emissions from the release of fossil carbon currently stored in the soils.

Grealish *et al.* (2007b) prepared maps of the acid sulfate soils hazard for each area. These maps are derived from the soil maps shown in the same report. The acid sulfate soils hazard class of each soil map unit is based on the estimated proportion of the map unit area occupied by soil types with sulfidic material or a sulfuric layer. These soil types are those with the ‘c’ attribute in the Fertility Capability Classification (Sanchez *et al.* 2003) that indicates the presence of sulfidic/sulfuric material as discussed in Wong *et al.* (2007) and Grealish *et al.* (2008). The acid sulfate soils hazard classes are defined in Table 5.

Table 5: Acid Sulfate Soil Hazard Classes

	Class	Proportion of area with sulfidic material or a sulfuric layer
1	Negligible	≤5%
2	Low	>5% and ≤25%
3	Moderate	>25% and ≤50%
4	High	>50% and ≤75%
5	Very high	>75%

These acid sulfate soils hazard classes indicate the likelihood of a site being an actual or potential acid sulfate soils. They do not indicate the severity of problem when encountered, which is given by the ‘Treatment class’ of Fitzpatrick *et al.* (2008).

Hazard subclasses are defined by the most common depth to the sulfidic material or sulfuric layer sometimes with the minimum depth in brackets. For example, “3 / 40cm [15cm]” means there is a moderate likelihood (i.e. Class 3 in Table 2) of sulfidic material or a sulfuric layer, which is most commonly at 40 cm depth but can be as shallow as 15 cm.

The maps show that the greatest problem with actual or potential acid sulfate soils are in surveyed areas in the low-lying areas of Brunei-Muara and, to a lesser extent, Belait. Their occurrence in Tutong and Temburong is negligible. Several patterns of acid sulfate soils occurrence can be identified. In Brunei-Muara, six areas (Betumpu, Si Tukak Limau Manis, Si Bongkok Parit Masin, Lumapas, Limpaki and Pengkalan Batu) are almost entirely covered by actual or potential acid sulfate soils (very high hazard). Only in the elevated part of Si Tukak Limau Manis A are the acid sulfate soils negligible. In addition, the areas are dominated by Organic soils that mostly require very high levels of treatment with smaller areas of Sulfuric soils requiring high levels of treatment, and Sulfidic soils requiring moderate levels.

Wasan also has extensive areas of acid sulfate soils (if the Acid poorly drained cracking clay soils are included), but because they are Cracking clay soils they require only low to moderate treatment. The pattern of acid sulfate soils in Tungku is rather different, with acid sulfate soils being only moderately extensive in most of the area. Soft poorly drained sulfuric soils occur in the lower parts of the landscape and require moderate levels of treatment.

In Belait, four survey areas (Tungulian, Melayan A, Labi Lama and Km26 Jalan Bukit Puan Labi) have parts of very high acid sulfate soils hazard in the lowland parts of their areas associated with the AN (be) map unit. This map unit is dominated by Organic soils requiring very high levels of treatment. In Km26 Jalan Bukit Puan Labi there are also pockets of Organic poorly drained moderately deep sulfidic soils that require a high treatment level. Within these four areas, much of the area with very high acid sulfate soils hazard is currently undeveloped for agriculture. Given that very high levels of treatment are necessary to successfully develop these areas, consideration should be given to leaving them undeveloped.

Merangking Bukit Sawat has isolated pockets of acid sulfate soils, accounting for only a small part of its total area. If this survey area s developed for agriculture, these areas of organic soil would best be left undeveloped, since they require a very high treatment level.

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