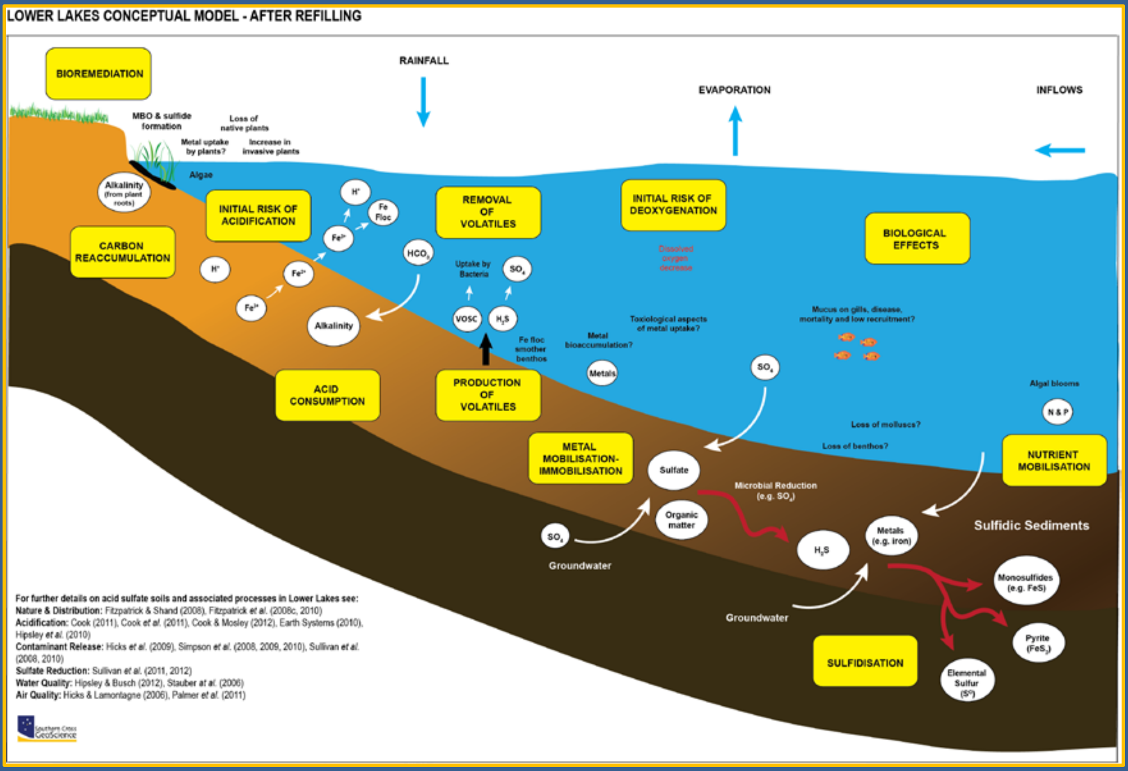
Lower Lakes Acid Sulfate Soil Detailed Conceptual Models

FINAL REPORT



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

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

Lower Lakes Acid Sulfate Soil Detailed Conceptual Models

Authors

N.J. Ward, L.A. Sullivan and R.T Bush

Centre for Acid Sulfate Soil Research
Southern Cross GeoScience
Southern Cross University
PO Box 157
Lismore NSW 2480

Permissive licence

Written requests for permission should be addressed to:
Coorong, Lower Lakes and Murray Mouth Program
Department of Environment, Water and Natural Resources
GPO Box 1047
Adelaide SA 5001

and:

Centre for Acid Sulfate Soil Research
Southern Cross GeoScience
Southern Cross University
GPO Box 157
Lismore NSW 2480

Disclaimer

This report has been prepared by consultants for the Department of Environment, Water and Natural Resources (DEWNR) and views expressed do not necessarily reflect those of the DEWNR. The DEWNR cannot guarantee the accuracy of the report, and does not accept liability for any loss or damage incurred as a result of relying on its accuracy.

Printed on recycled paper
July 2013

Citation

This report should be cited as:

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

Southern Cross University Disclaimer

Authors: Dr N.J. Ward, Prof. L.A. Sullivan and Prof. R.T. Bush

Reviewer: Dr L. Barnett

Approved by: Prof. L.A. Sullivan

Signed:

Date: 30th July 2013

Distribution: SA Department of Environment, Water and Natural Resources, Southern Cross GeoScience

Circulation: Public Domain

Acknowledgements

We would like to thank the various organisations that gave us permission to include their images in this report. The organisations include CSIRO, South Australian Water and Department of Sustainability, Environment, Water, Population and Communities.

Executive Summary

Detailed studies and monitoring of acid sulfate soils were undertaken in the Lower Lakes during the 2007-2010 drying event and following the reinundation of the exposed acidified Lower Lakes' sediments. The critical importance of acid sulfate soil associated processes to the ecological health of the Lower Lakes has become acutely apparent. These processes include: sediment and water acidification, interactions between surface waters and sediment pore-waters, ecotoxicological aspects of metal uptake, mineralogical controls of geochemical regime, the controlling effects of organic matter inputs by lacustrine vegetation on post re-inundation biogeochemistry, sediment erosion as a result of scalding during sediment exposure and post inundation, and metal mobilisation. The aim of this project was to detail the complexity of acid sulfate soil impacts arising from these processes through the development of conceptual models of the biogeochemical and physical processes involving acid sulfate soil that affect water quality and the ecology of the Lower Lakes.

Detailed conceptual models have been developed based on the current knowledge of acid sulfate soil processes in the Lower Lakes and where appropriate, the broader acid sulfate soil literature. These conceptual models include diagrammatic representations of processes and their relationships and interactions, as well as textual descriptions and interpretations. These conceptual models describe the key biogeochemical pathways within acid sulfate soil sediments and the main chemical, physical, biological and hydrological linkages to other inputs and exports.

The conceptualised modelling of acid sulfate soil processes in the Lower Lakes has been undertaken for three critical hydrological scenarios:

- *scenario 1)* under extended conditions where the lakes have been maintained in a relatively full condition;
- *scenario 2)* after extended drought conditions resulting in substantial drawdown of the lakes and the exposure of areas of the lake sediments, and;
- *scenario 3)* following refilling of the lakes immediately after *scenario 2*).

The conceptual models developed during this study have highlighted the complex interrelationships between the acid sulfate soil processes operating in the Lower Lakes especially during periods of hydrological change. These conceptual models contribute to our understanding of acid sulfate soils in the Lower Lakes, and of their management requirements especially in relation to wetting and drying cycles of decadal frequency. This increased understanding will assist managers to protect the environmental values of the Lower Lakes.

Whilst this study has described many of the main processes associated with acid sulfate soils, and mapped their interrelationships, these conceptual models have also highlighted significant gaps in our knowledge of how the lakes environments are affected by acid sulfate soil processes. For example, while the key processes controlling the release of metals from sediments into the surrounding water may be reasonably well understood, the long term impacts of metal release to the surrounding aquatic environment is largely unknown.

It is recommended that the conceptual models developed in this Phase 1 project be examined by an expert panel to continue to further address critical gaps in our understanding of the way that acid sulfate soils and their management impact on the environment and values of the Lower Lakes. Specifically, it is recommended that a workshop, attended by all scientific and management stakeholders, be held to assess the veracity and completeness of the conceptual models presented here, and prioritise the needs for future research and monitoring in the Lower Lakes in relation to acid sulfate soils.

It is also recommended that these conceptual models be updated as new information is received about acid sulfate soil processes in the Lower Lakes.

Contents

List of Figures

1.0 Project Overview

There have been many detailed research and monitoring studies into acid sulfate soils in the Lower Lakes over the past decade. The pace of these studies increased especially during the 2007-2010 drought that caused a substantial lowering of the levels of water in these lakes and the exposure of sediments that resulted in large-scale severe acidification caused by oxidation. From these studies the critical importance of acid sulfate soil processes to the ecological health of the Lower Lakes has become acutely apparent.

However, the findings of these studies usually addressed discrete aspects of the acid sulfate soil issues facing the Lower Lakes and there was not a clear mapping and description of the interrelationships between these studies. The lack of such a detailed understanding of the complex ways that acid sulfate soils can potentially affect the ecology of these lakes was considered to present a limitation to the effective management of these Lakes. This project was instigated to start Phase 1 to address this aspect by the collation and integration of the present knowledge detailed in the literature of acid sulfate soil processes in the Lower Lakes.

The aim of this project was to describe and map the complexity of acid sulfate soil processes in the Lower Lakes by the development of conceptual models on the biogeochemical, hydrological and physical processes that are affected by acid sulfate soils especially those that have a capacity to affect water quality and ecological health.

These conceptual models include diagrammatic representations of processes, and their relationships and interactions, as well as textual descriptions and interpretations of these processes. These conceptual models include a description of the key biogeochemical pathways within acid sulfate soil sediments and the main chemical, physical, biological and hydrological linkages to other pathways within the lakes. As well as detailing advances in our understanding of how acid sulfate soils affect lake processes these models can also be used to discern critical gaps in our understanding of these processes and of their relationships and interactions.

2.0 Objective

The objective of this project was to describe and conceptually map the interrelationships between the key processes related to acid sulfate soils and sediments in the Lower Lakes, especially in relation to wetting and drying cycles of decadal frequency.

3.0 Introduction

3.1 Background on acid sulfate soils

3.1.1. General

Acid sulfate soil materials are distinguished from other soil materials by having properties and behaviour that have either: 1) been affected considerably (mainly by severe acidification) by the oxidation of reduced inorganic sulfides (RIS), or 2) the capacity to be affected considerably (again mainly by severe acidification) by the oxidation of their RIS constituents.

A wide range of environmental hazards can be generated by the oxidation of RIS. These include: 1) severe acidification of soil and drainage waters (below pH 4 and often < pH 3), 2) mobilisation of metals (e.g. iron, aluminium, copper, cobalt, zinc), metalloids (e.g. arsenic), nutrients (e.g. phosphate), and rare earth elements (e.g. yttrium, lanthanum), 3) deoxygenation of water bodies, 4) production of noxious gases (e.g. hydrogen sulfide (H_2S)), and 5) scalding (i.e. de-vegetation) of landscapes. Some of these hazards are caused directly or indirectly by the severe acidification that can occur as a result of the oxidation of RIS, whereas some can also be the result of other simultaneous processes occurring in the environment.

Waters draining from sulfuric acid sulfate soil materials can be enriched in a wide range of potential toxicants, including metals and metalloids, endangering aquatic life and public health. Crops, trees, pastures and aquaculture can also be severely affected by acid sulfate soil materials. Acid sulfate soils can have detrimental impacts on their surrounding environments as well as on communities who live in landscapes containing these soils for many years.

Acid sulfate soil drainage waters can often have pH < 3.5 and can be the cause of massive fish kills, the death of invertebrates and benthic organisms, the development of chronic fish diseases, and impaired fish recruitment (Sammut *et al.* 1993).

Acid sulfate soils can also present health hazards to people living in landscapes containing these soils (Ljung *et al.* 2009). The human health issues relate mainly to the increased mobility of acid and metals from these soils affecting drinking water quality, food production and quality, but also to other issues such as increased dust generation causing respiratory health issues and acidic pools of surface water in acid sulfate soil landscapes providing suitable environments for mosquito breeding.

3.1.2 Characteristics and formation

It is useful to distinguish between sulfidic soil materials that, if disturbed sufficiently, will become severely acidified, and sulfuric soil materials that have already become severely acidic as a result of the oxidation of RIS minerals**.**

Sulfidic materials may be current or former marine and estuarine sediments, sediments in brackish lakes and lagoons, peats that originally formed in freshwater but which have been inundated subsequently by brackish water, or accumulations of sediment in water bodies such as drains or wetlands affected by salinity (especially when sulfate is an appreciable component of that salinity). The required conditions for the formation and accumulation of RIS are: (1) a supply of organic matter, (2) reducing conditions sufficient for sulfate reduction brought about by continuous waterlogging, (3) a supply of sulfate from tidewater or other saline groundwater or surface water, (the sulfate is reduced to sulfides by bacteria decomposing the organic matter), and (4) a supply of iron from the sediment for the accumulation of iron sulfides which make up the bulk of the RIS.

These conditions are found in tidal swamps and salt marshes where, over the last 10,000 years, thick deposits of sulfidic clay have accumulated in many locations around the globe (Pons and van Breemen 1982; Dent and Pons 1995). Sulfidic layers vary greatly in appearance but often have the gleyed colours typical of soil materials that are dominated by reduced waterlogged conditions.

Disturbance of sulfidic soils by, for example, drainage or excavation often causes dramatic changes in the properties of these soil materials and the draining waters. If there are insufficient effective neutralising materials (such as fine-grained calcium carbonate) in the sediment to neutralise the acidity generated by the oxidation of sulfides, extreme acidity can develop within weeks to months, resulting in sulfuric soil material. Sulfuric soil material is characterised by acidic pHs (e.g. pHs < 4), reddish brown iron oxides and/or yellow segregations of jarosite around pores and on ped faces.

3.1.3 Occurrence

Although acid sulfate soils are best known for their impacts in coastal areas, acid sulfate soils are also widely distributed in inland areas wherever the general conditions for RIS formation - a ready source of sulfate, iron, and organic matter in reducing waterlogged sediments - are met. The Australian Atlas of Acid Sulfate Soils (Fitzpatrick *et al.* 2008b) has greatly improved our understanding of the extent and distribution of acid sulfate soils within Australia. Recent studies have shown acid sulfate soils are widely distributed within the Lower Lakes region of South Australia (e.g. Fitzpatrick *et al.* 2008a; Simpson *et al.* 2008; Sullivan *et al.* 2008, 2010).

3.2 Introduction to this study

As a result of prolonged drought, combined with water extraction upstream in the Murray-Darling Basin, the Lower Lakes (Lake Alexandrina and Lake Albert) have recently experienced their first major drying phase since the introduction of barrages more than 70 years ago (Simpson *et al*. 2008; Sullivan *et al.* 2008). Concurrently, it was identified that the Lower Lakes were also being impacted by the presence of acid sulfate soil materials (Fitzpatrick *et al.* 2008a). As a consequence of unprecedented low water levels, extensive areas of acid sulfate soils were exposed in the Lower Lakes resulting in severe soil acidification (pH<4) over large areas and localised acidification of surface waters (DENR 2010).

To inform management, during this period an extensive research program was undertaken to fill critical knowledge gaps related to the risks posed by the exposure of acid sulfate soils in the Lower Lakes (DENR 2010). The research areas examined in this program included:

- an acid sulfate soil spatial heterogeneity/mapping survey;
- measurement of acid generation rates;
- assessment of the in-situ contaminant generation, transport and neutralisation processes;
- laboratory and field studies of the potential for mobilisation of contaminants following inundation with seawater compared to river water; and
- geochemical modelling of lake water quality.

The research and monitoring studies undertaken in that program have highlighted the critical importance of acid sulfate soils and associated processes to the ecological health of the Lower Lakes.

In this study, the relationships between many of the acid sulfate soil processes have been mapped to aid in our understanding of the broader view of how acid sulfate soils and their management affect the long-term ecology of the Lower Lakes.

Detailed conceptual models have been developed for the Lower Lakes based on the available knowledge of acid sulfate soil processes. The detailed acid sulfate soils conceptual models have been produced to describe the acid sulfate soil processes that would be expected to occur in and around the Lower Lakes under different water regimes.

4.0 Conceptual Models

4.1 General acid sulfate soil conceptual models

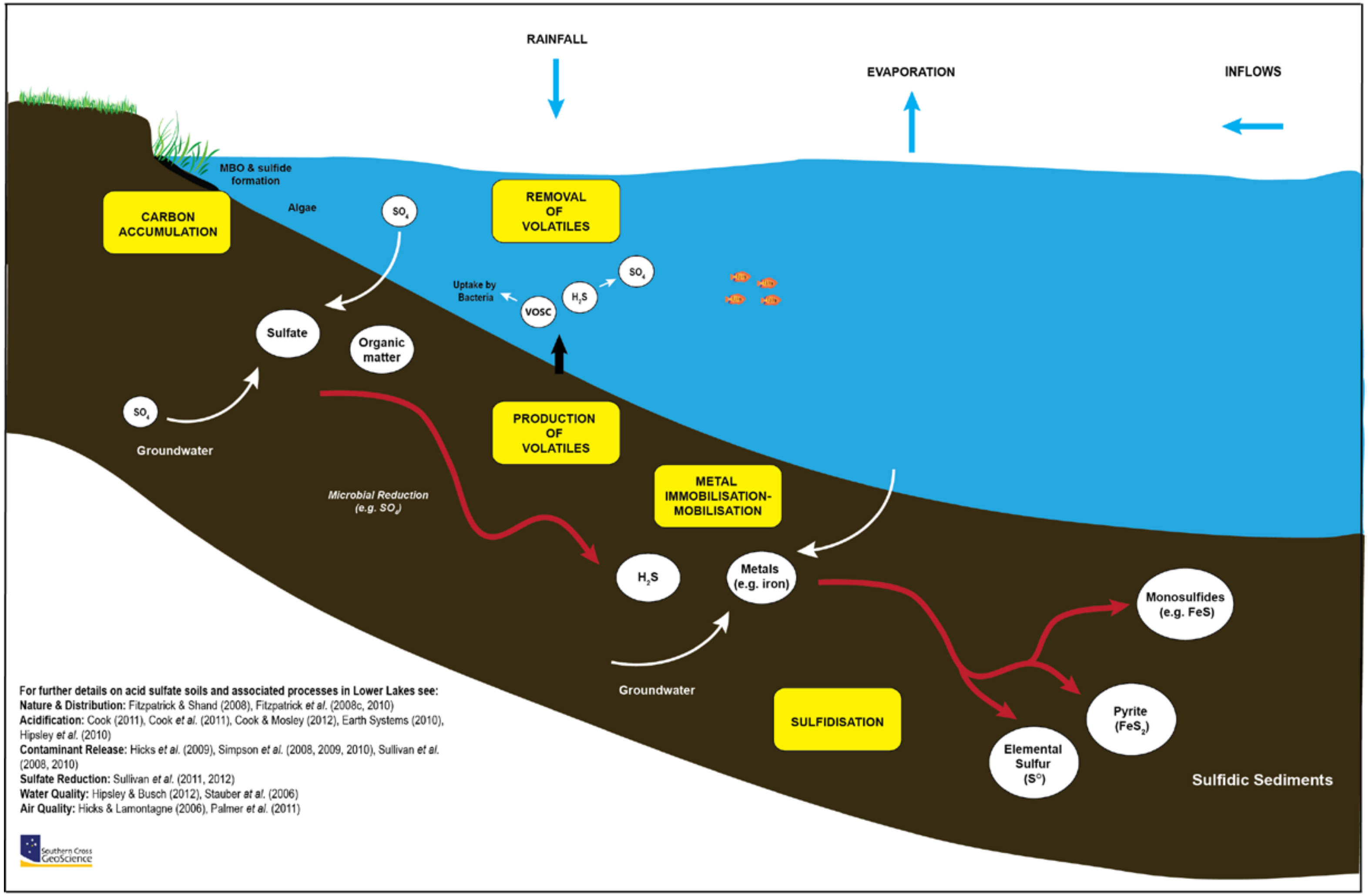
A review of the literature has provided a number of excellent existing conceptual models related to the processes operating in acid sulfate soil landscapes. For this study, these various conceptual models have been adopted and/or adapted to describe the acid sulfate soil processes that would be expected to occur in and around the Lower Lakes under three critical scenarios. These scenarios are 1) prior to a drought under extended lake-full conditions, 2) after extended drought conditions that result in lake drawdown and the exposure of considerable lake sediments, and 3) following refilling of the lakes after scenario 2. The findings of relevant recent acid sulfate soil research in and around the Lower Lakes have been incorporated into these conceptual models.

Conceptual models showing some of the fundamental processes that occur on both a landscape and mesoscopic scale in inland acid sulfate soil landscapes of the Murray-Darling Basin have recently been developed by EPHC and NRMMC (2011) (see Figures A-1 and A-2 in the Appendix). These conceptual models summarise: (i) the processes that occur during acid sulfate soil formation and accumulation, (ii) the oxidation processes that occur as a consequence of drying of an acid sulfate soil, and (iii) the processes that occur when an oxidised acid sulfate soil is rewetted. These general conceptual models were adapted as a starting basis for the development of broad conceptual models that describe the specific acid sulfate soil processes applicable to the Lower Lakes' situation.

Consequently three conceptual models have been developed here to illustrate the acid sulfate soil processes in and around the Lower Lakes and these are presented in Figures 4-1, 4-2 and 4-3. Figure 4-1 summarises the broad acid sulfate soil processes that occur under stable conditions. Figure 4-2 summarises the broad acid sulfate soil processes that occur under prolonged drought conditions sufficient to cause appreciable lake drawdown. Figure 4-3 summarises the broad acid sulfate soil processes that occur following lake refilling. The complexity of the acid sulfate soil processes operating in and around the Lower Lakes precludes the incorporation of all the information available into each conceptual model. This issue has been addressed by the provision of further details of the main processes (shown in yellow boxes in each conceptual model) operating under each of the three scenarios in Section 4.2 and include:

- sulfidisation (Section 4.2.1),
- acidification (Section 4.2.2),
- acid consumption (Section 4.2.3),
- metal immobilisation-mobilisation (Section 4.2.4),
- deoxygenation (Section 4.2.5),
- production of volatiles (Section 4.2.6),
- bioremediation (Section 4.2.7),
- carbon production and accumulation (Section 4.2.8),
- nutrient mobilisation (Section 4.2.9), and
- biological effects (Section 4.2.10).

Section 4.2 includes detailed flowcharts and descriptions to illustrate these acid sulfate soil processes. Additional relevant conceptual models of acid sulfate soil processes available in the literature and that have been adapted for use in the development of these Lower Lakes models are also presented in the Appendix.

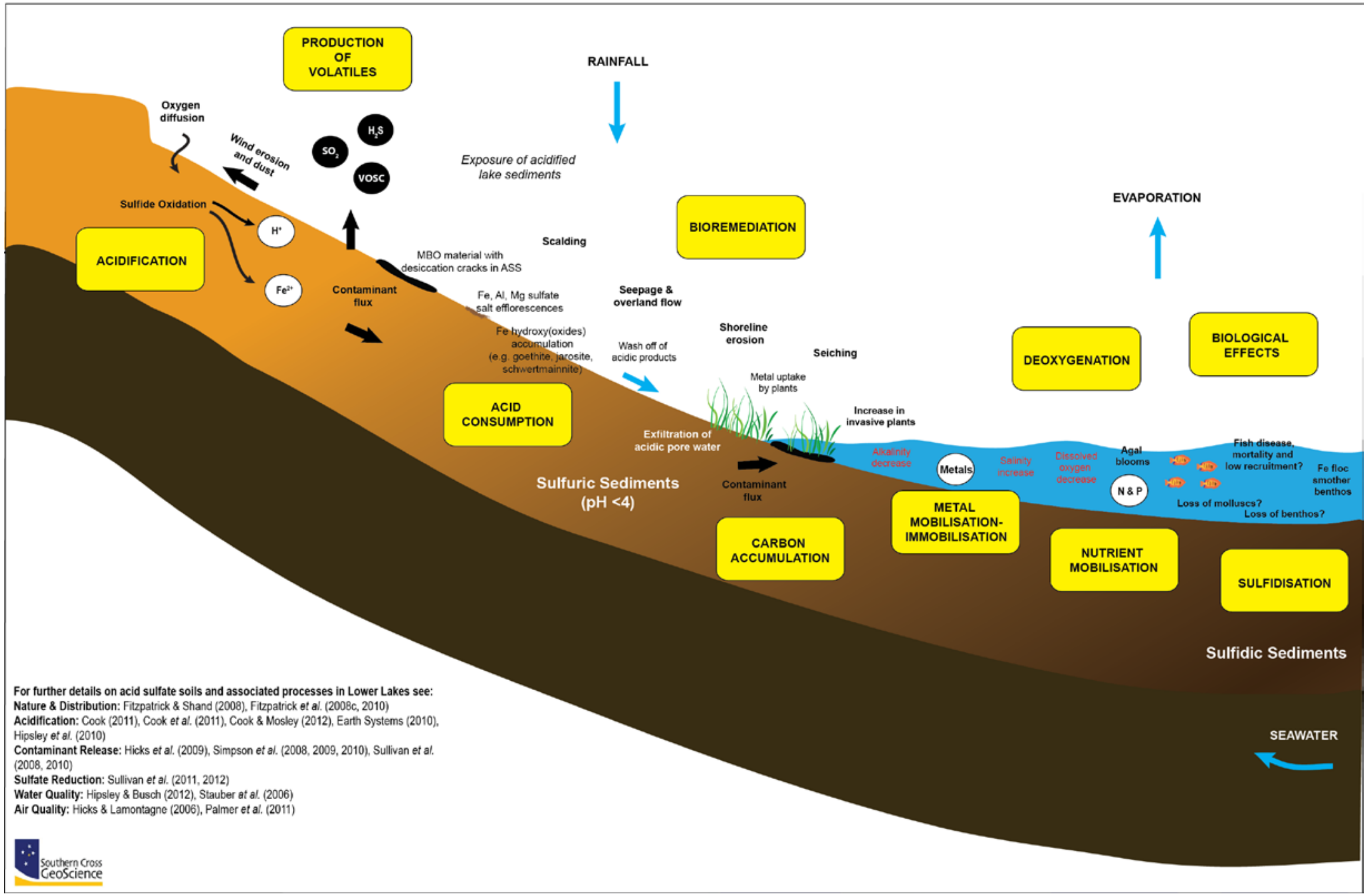


LOWER LAKES CONCEPTUAL MODEL - UNDER STABLE CONDITIONS

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

Figure 4-1. Conceptual model of the main acid sulfate soil processes in the Lower Lakes under stable conditions.

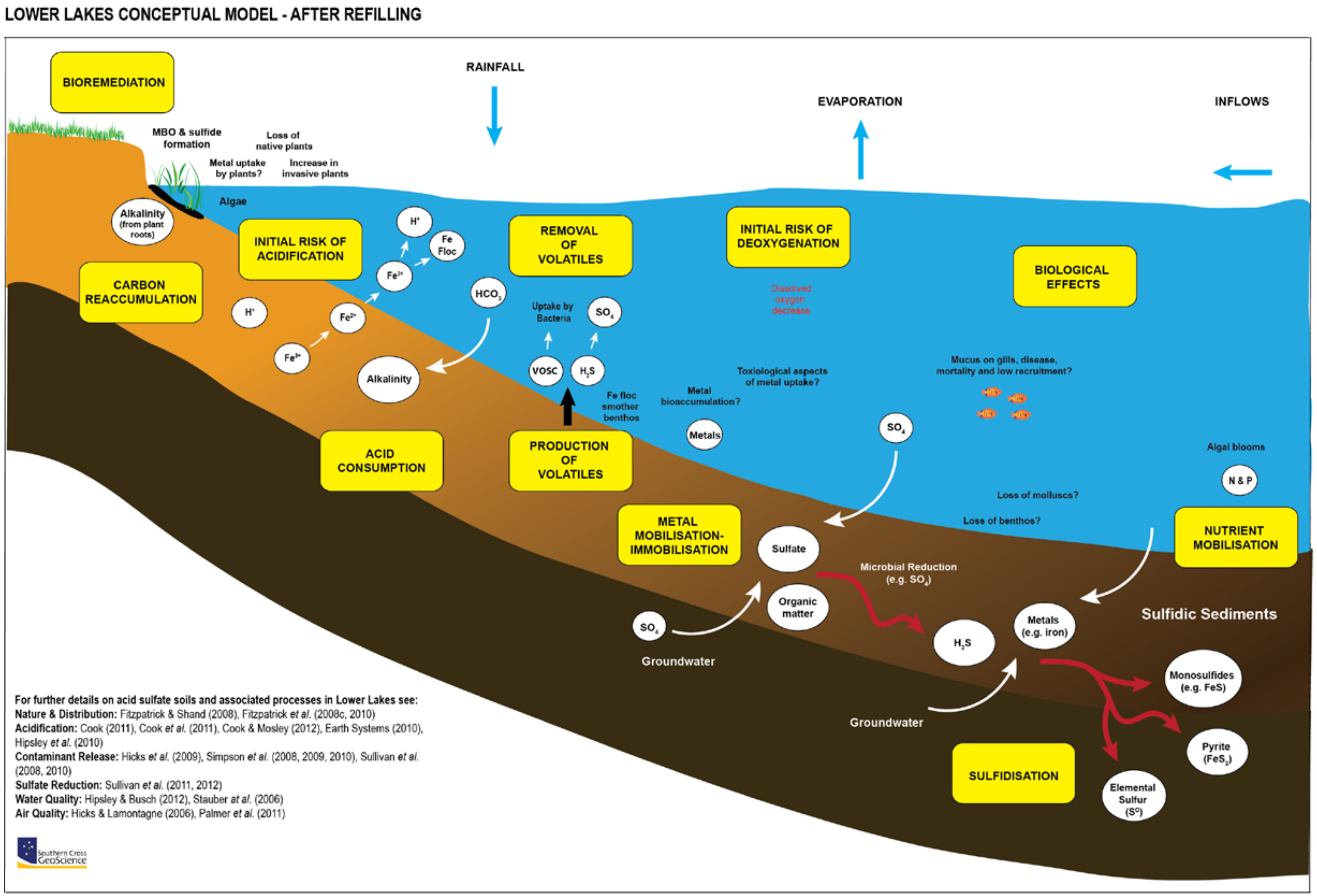
LOWER LAKES CONCEPTUAL MODEL - DROUGHT CONDITIONS



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

Southern Cross GeoScience

Figure 4-2. Conceptual model of the main acid sulfate soil processes in the Lower Lakes under drought conditions.



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

Figure 4-3. Conceptual model of the main acid sulfate soil processes in the Lower Lakes following lake refilling.

4.2 Acid sulfate soil processes conceptual models

4.2.1 Sulfidisation

A defining characteristic of sulfidic acid sulfate soils is the presence of significant concentrations of reduced inorganic sulfur (RIS). RIS include iron disulfides (most commonly pyrite (FeS_2) (Bloomfield and Coulter 1973; Pons 1973; van Breemen 1973), lower amounts of other minerals such as monosulfides (e.g. Georgala 1980; Bush *et al.* 2000), greigite (Fe_3S_4) (Bush and Sullivan 1997) and elemental sulfur (S_8) (Burton *et al.* 2006a,b). Sulfoxyanion intermediates (e.g. thiosulfate ($S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$)) have also been detected during the early stages of sulfide oxidation in acid sulfate soil materials (Ward *et al.* 2004).

The vast majority of RIS in sulfidic acid sulfate soil materials have formed at earth-surface temperatures and pressures under waterlogged, anoxic conditions. Under such conditions, accumulation of RIS species depends on microbially-mediated sulfate reduction, which is itself dependent on organic carbon availability, supply of sulfate, and on the amount of competing electron acceptors including reactive Fe^{III} minerals (Fanning *et al.* 2002). These variables influence the activity of dissimilatory sulfate-reducing microorganisms, which include phylogenetically diverse anaerobes that oxidise simple organic compounds or hydrogen-using sulfate as an electron acceptor. The overall process of dissimilatory sulfate reduction can be shown, for example, by:

$$CH_3COO^- + SO_4^{2-} + H^+ \rightarrow H_2S + 2HCO_3^- \qquad [4.1]$$

During this process, the sulfur in sulfate is reduced from the oxidation state of S^{6+} to S^{2-}. Conditions that are conducive to microbially-mediated sulfate reduction occur in organic-rich coastal and estuarine sediments, such as in tidal marshes and swamps. In inland systems, sulfate can be supplied by the same processes that cause salinization. In coastal areas, tidal exchange of pore-water supplies sulfate and removes the resultant HCO_3^- produced via the reaction in Equation 4.1. Tidal flushing thereby prevents the accumulation of pore-water alkalinity. In iron-deficient systems, this tidal flushing can also remove pore-water H_2S and lead to its subsequent oxidation to elemental S (and eventually to sulfate). However, in inland systems the lack of tidal flushing generally reduces the removal of HCO_3^- produced via the reaction in Equation 4.1 and can lead to the accumulation of carbonates in the sediments.

In contrast, in soils containing Fe^{2+}, often produced by the activity of ferric iron reducing microorganisms, H_2S may react rapidly to form monosulfide (FeS) precipitates as below:

$$H_2S + Fe^{2+} \rightarrow FeS + 2\,H^+ \qquad [4.2]$$

The initial FeS phase to form by reaction between H_2S and Fe^{2+} (Equation 4.2) has proved difficult to characterise, even in well-defined synthetic studies (Rickard and Morse 2005). Recently, such studies have shown that nanoparticulate mackinawite (tetragonal FeS) is the first condensed phase to form through this reaction. In acid sulfate soil materials the occurrence of mackinawite as 5 – 30 nm nanoparticles has been only recently demonstrated (Burton *et al.* 2009). The strong black colour seen in some of these acid sulfate soil materials is largely due to the presence of nanoparticulate mackinawite (Burton *et al.* 2009).

The H_2S produced by microbial sulfate reduction can also react with Fe^{III} contained in ferric oxide and oxyhydroxide minerals such as goethite, to produce elemental sulfur:

$$H_2S + 2\,FeOOH + 2\,H^+ \rightarrow S_8 + 2\,Fe^{2+} + 3\,H_2O \qquad [4.3]$$

The Fe^{2+} produced via this reaction may then feed into the reaction described by Equation 4.2 thus also resulting in mackinawite formation. This overall process, termed “sulfidisation” can be represented as:

$$3\,H_2S + 2\,FeOOH \rightarrow S_8 + FeS + 4\,H_2O \qquad [4.4]$$

In the presence of an oxidant, such as O_2, mackinawite is unstable and can transform readily via a solid-state process to greigite:

$$4\,FeS + 0.5\,O_2 + 2\,H^+ \rightarrow Fe_3S_4 + Fe^{2+} + H_2O \qquad [4.5]$$

Although frequently mentioned, there are only few studies (e.g. Bush and Sullivan 1997) that conclusively document the occurrence of greigite in acid sulfate soil materials. On the basis of the limited amount of field data it appears that greigite occurrence is limited to the oxidation front in mildly acidic soils that are subject to an oscillating groundwater table. Mackinawite and greigite are often described as “iron-monosulfide” minerals because they have an Fe:S ratio that is close to 1:1 (Rickard and Morse 2005). These mineral species are defined analytically by their dissolution in HCl to yield H_2S gas and described as acid-volatile sulfide (AVS).

Both mackinawite and greigite have long been implicated as precursors to the formation of iron-disulfides such as pyrite and marcasite. For example:

$$Fe_3S_4 + 2\,H^+ \rightarrow FeS_2 + Fe^{2+} + H_2 \qquad [4.6]$$

Pyrite can also form without the need for precursory greigite via (1) mackinawite oxidation by polysulfide species (Rickard 1975; Luther 1991) and (2) mackinawite oxidation by H_2S (Rickard 1997; Rickard and Luther 1997). These two pathways of pyrite formation, which involve an intermediate dissolved FeS cluster complex, can be represented overall as:

Polysulfide pathway: $FeS + S_n^{2-} \rightarrow FeS_2 + S_{n-1}^{2-}$ [4.7]

Hydrogen sulfide pathway: $FeS + H_2S \rightarrow FeS_2 + H_2$ [4.8]

Whilst iron monosulfides are a precursor to pyrite formation, this is not necessarily always the case. Pyrite can form quite rapidly in the presence of suitable reactive surfaces such as bacterial surfaces (Canfield *et al.* 1998) that serve to overcome a significant supersaturation threshold by providing heterogeneous nucleation sites. Other suitable reactive surfaces include pre-existing pyrite crystals or organic substrates, such as plant material. Accumulation of pyrite in soil can occur rapidly under suitable field conditions (Howarth 1979; Rosicky *et al.* 2004).

Pyrite is by far the most commonly observed RIS species in sulfidic acid sulfate soil materials. In these materials, pyrite occurs in a range of distinct crystal morphologies. The most remarkable of these morphologies are framboids (from the French term for raspberry – *frambois*). Pyrite framboids consist of spheroidal aggregates of densely packed, individual microcrystals. Earlier research into the origin of pyrite framboids in sediments pointed towards either a bacterial influence or the magnetic aggregation of precursor greigite crystals. However, while there have been many people fascinated by the source of these delicate geometric structures, there still is no consensus in the process for frambiodal morphology.

Whilst pyrite is normally the most abundant iron-disulfide in acid sulfate soil materials, marcasite (orthorhombic FeS_2) may occur under acidic conditions (pH < 6). Such conditions occur in waterlogged soils and sediments that are rich in dissolved organic acids, capable of buffering the low pH. For example, marcasite is a common iron sulfide in some peaty acid sulfate soil materials in eastern Australia (Bush *et al.* 2004a).

A conceptual model illustrating the major steps involved in the process of iron sulfide formation (and the reactions following disturbance) is shown in Figure A-3 in the Appendix. The process of sulfidisation following bioremediation has recently been examined in the surficial lake sediments in the Lower Lakes (Sullivan *et al.* 2011, 2012b). Sullivan *et al.* (2011) found that during the early stages of refilling (i.e. the initial 6 months) sulfate was reduced during organic matter decomposition (often in microsites around the roots of the plants). The sulfide (e.g. H_2S) released from this process was mainly converted to elemental sulfur ($S_8^o{}_{(s)}$), without the accumulation of sulfide minerals such as monosulfides and pyrite. However, a subsequent examination of the sulfidisation process by Sullivan *et al.* (2012b) at 19 months after lake re-filling showed considerable accumulation of both pyrite and monosulfide (as monosulfidic black ooze (MBO)) in the uppermost sediment layers at sites where a species tolerant to inundation (i.e. *Phragmites*) was used to bioremediate the sediments. A conceptual diagram by Sullivan *et al.* (2012b) of the sulfidisation processes operating in the upper layers of bioremediated sediments at the Lower Lakes following inundation is presented in Figure A-4 in the Appendix.

4.2.2 Acidification

The oxidation of iron-sulfide minerals (particularly pyrite) is the primary cause of the extreme acidification that characterises sulfuric acid sulfate soil materials. Sulfuric acid sulfate soils have a pH of less than 4 (or < 3.5 according to the particular soil taxonomy being employed), but values of pH < 3 in actively oxidising soils are frequently observed (e.g. Dent 1986; Fitzpatrick *et al.* 2008c). Such extreme acidification significantly alters the soil chemistry, render it hostile to plants and create a source of contamination to groundwater and surface waters. The acid produced can react with clay minerals and oxides to release silica and metal ions, principally aluminium, iron, potassium, sodium and magnesium (Nriagu 1978). Other metals and metalloids ions can also be released (van Breemen 1973; Sammut *et al.* 1996b; Åström 2000) (for further details see Section 4.2.4).

Pyrite and other iron-sulfide minerals can only persist in soils under anoxic, waterlogged conditions. If these conditions become oxic, as a consequence of exposure, the iron-sulfide components can undergo a series of oxidation reactions. For example, in the presence of oxygen (and water) pyrite oxidises to ultimately yield sulfuric acid and a poorly soluble Fe^{III} precipitate:

$$FeS_2 + {}^{15}/_4\, O_2 + {}^{7}/_2\, H_2O \rightarrow Fe(OH)_3 + 2\, SO_4^{2-} + 4\, H^+ \qquad [4.9]$$

While this reaction shows that exposure to oxygen under moist conditions is the driving force for pyrite oxidation, it neglects the complexity of reaction steps in the overall oxidation process. This complexity includes a number of possible final iron phases as well as the formation of intermediate sulfoxyanions and elemental S. Chemolithotrophic Fe- and S-oxidising bacteria play an important role in mediating various steps in the overall oxidation process, and in determining the formation and persistence of intermediate S species.

A wide variety of potential mineral phases play a role in determining the iron biogeochemistry following pyrite oxidation. Ferrous iron released in the initial stages of pyrite oxidation may precipitate as Fe^{II} hydroxysulfate minerals (Fanning *et al.* 2002), most importantly melanterite, rozenite and szomolnokite. While these phases are readily soluble and are rarely observed in acid sulfate soil materials, Fitzpatrick *et al*. (2008c) have identified a wide range of highly soluble sulfate-containing evaporite minerals (e.g. halotrichite, redingtonite) on the exposed sandy soil surfaces of sulfuric materials of the Lower Lakes.

Under continuous oxidation, the Fe^{2+} released by pyrite oxidation is also subject to oxidation to Fe^{3+} (Equation 4.10). Whilst the simple oxidation process consumes some acidity, the subsequent hydrolysis of the resulting Fe^{3+} leads to the liberation of acidity (Equation 4.11). At low pH (e.g. < 4), Fe^{3+} is sufficiently soluble that it may serve as a very effective electron acceptor driving further pyrite oxidation (Equation 4.12) (Moses *et al.* 1987). For this reason, it has been often suggested that the rate of Fe^{2+} oxidation to Fe^{3+} may be the rate-determining step in pyrite oxidation.

$$Fe^{2+} + {}^{1}/_4\, O_2 + H^+ \rightarrow Fe^{3+} + {}^{1}/_2\, H_2O \qquad [4.10]$$

$$Fe^{3+} + 3\, H_2O \rightarrow Fe(OH)_3 + 3\, H^+ \qquad [4.11]$$

$$FeS_2 + 14\, Fe^{3+} + 8\, H_2O \rightarrow 15\, Fe^{2+} + 2\, SO_4^{2-} + 16\, H^+ \qquad [4.12]$$

Partial oxidation of Fe^{2+} to Fe^{3+} can lead to precipitates of mixed valence Fe salts, such as copiapite which has been observed in the Lower Lakes region (e.g. Fitzpatrick *et al*. 2008c). This phase is one of the “soluble salts” that may form in acid sulfate soils under prolonged dry conditions (Fanning *et al.* 2002). Dissolution of these minerals during rainfall events may cause a first-flush of stored acidity.

The Fe^{3+} produced via pyrite oxidation also commonly precipitates as a range of Fe^{III} bearing minerals. In acid sulfate soil conditions at pH < 3, and/or in the presence of abundant K^+, jarosite appears to be the predominant Fe^{III} phase (Equation 4.13), whereas in the pH range of 3 – 4, schwertmannite is an important Fe^{III} phase in acid sulfate soil landscapes (Bigham *et al.* 1992; Sullivan and Bush 2004). The jarosite and schwertmannite may later slowly decompose with the hydrolysis of Fe^{III} and the liberation of acidity (e.g. Equation 4.14).

$$FeS_2 + {}^{15}/_4\, O_2 + {}^{5}/_2\, H_2O\ {}^{1}/_3\, K \rightarrow {}^{1}/_3\, KFe_3(SO_4)_2(OH)_6 + {}^{4}/_3\, SO_4^{2-} + 3\, H^+ \qquad [4.13]$$

$$KFe_3(SO_4)_2(OH)_6 + 3\, H_2O \rightarrow 3\, Fe(OH)_3 + 2\, SO_4^{2-} + 3\, H^+ + K^+ \qquad [4.14]$$

In addition to jarosite and schwertmannite, the widespread occurrence of the Fe^{III} mineral sideronatrite has been observed in the Lower Lakes region (Fitzpatrick and Shand 2008; Fitzpatrick *et al*. 2008c).

The type of minerals formed from the Fe released during pyrite oxidation governs to a large extent the amount of acidity expressed (Dold and Fontbote 2001). For example, if the released Fe precipitates as goethite or ferrihydrite from the Fe^{3+} produced by sulfide oxidation, then 3.0 moles of H^+ are formed for every mole of Fe^{3+} hydrolysed from pyrite. However, if hydrolysis is incomplete and jarosite is formed, only around 2 moles of H^+ is released for every mole of Fe^{3+} hydrolysed from pyrite (van Breemen 1976). If schwertmannite is formed then approximately 2.575 moles of H^+ is released for every mole of Fe^{3+} hydrolysed from pyrite (Piene *et al.* 2000). The 'stored' acidity in these two minerals is important as the Fe^{3+} in both jarosite and schwertmannite can undergo further hydrolysis and result in the release of acidity into the surrounding environment (Dold and Fontbote 2001; Sullivan and Bush 2004).

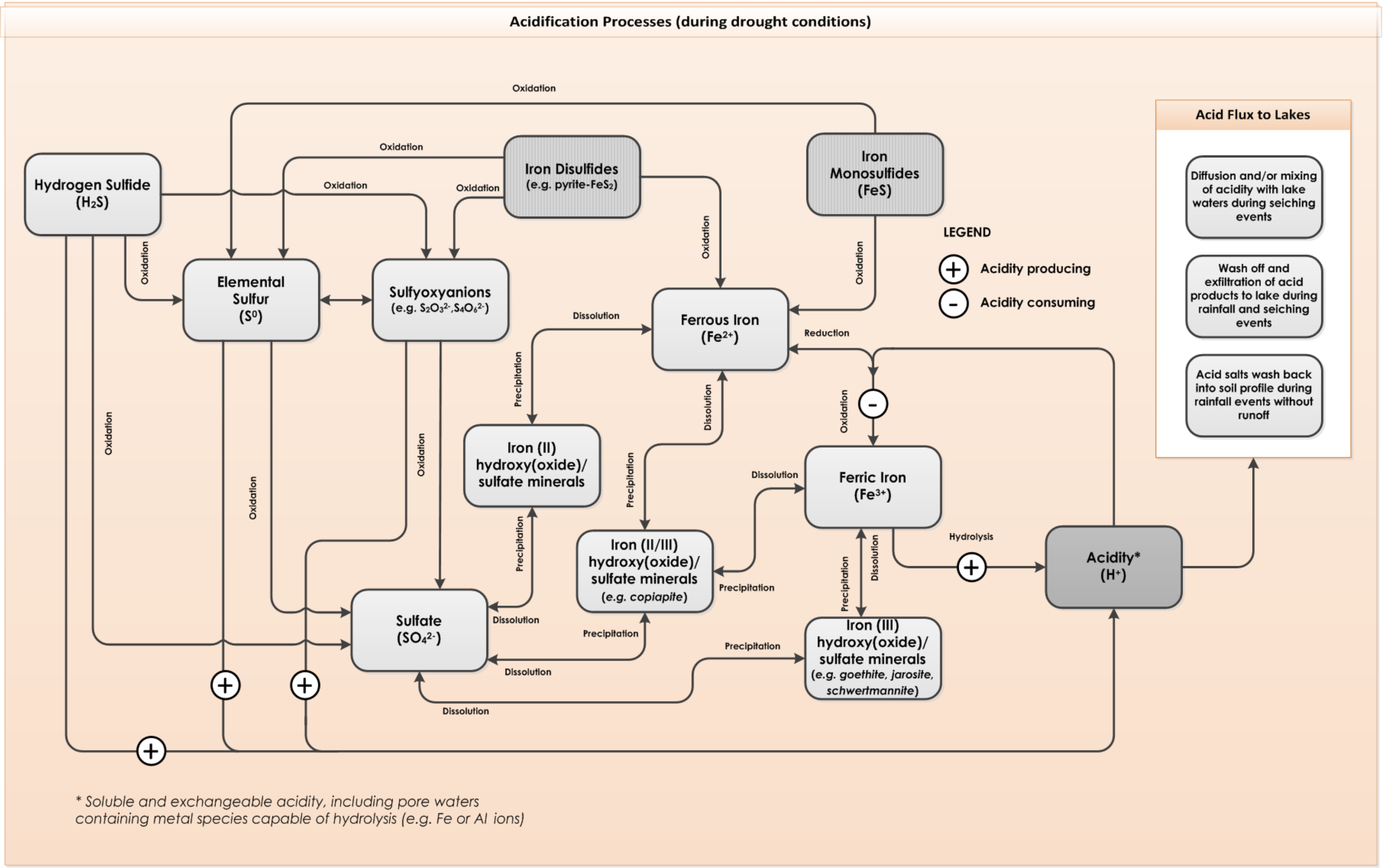
The oxidation of pyrite depends on factors including the supply of O_2, the availability of water, temperature and the physical properties of FeS_2. Pyrite oxidation generates acid and releases heat; consequently, the acidity and temperature of the surrounding solution will affect the overall reaction rates. The oxidation of FeS_2 in the environment is usually ultimately determined by the supply of O_2. Models describing FeS_2 oxidation are often based on the assumption that all other constituents required for the oxidation process are freely available except for O_2, which is supplied through the porous material from the atmosphere (Dent and Raiswell 1982; Davis and Ritchie 1986; Pantelis and Ritchie 1991; Bronswijk *et al.* 1993). Hipsley *et al.* (2010) modelled acidification processes as a result of pyrite oxidation in sediments from the Lower Lakes and provide further details on the O_2 diffusion controls on pyrite oxidation rates.

While the oxidation of pyrite is usually the main contributor to the acidification, the oxidation of iron monosulfides (in monosulfidic black oozes, MBO) may play an important role (see Section 4.2.5 for further details). In addition, H_2S oxidation may also be a potential minor source of acidity (see Figure A-4 in the Appendix).

No acidification of the lake waters as a consequence of acid sulfate soil processes would be expected during stable wet conditions illustrated in Figure 4-1. However, during drought conditions the oxidation of iron sulfide minerals (i.e. pyrite and iron monosulfides) would be the initial process resulting in acidification of the exposed sulfidic sediments, although any H_2S present also has the potential to produce some acidity (Figures 4-4 and A-4). Figure 4-4 shows the numerous potential processes and pathways that can be involved in the acidification process within acid sulfate soil materials.

As mentioned previously, not all the potential acidity is initially released when secondary iron minerals (such as jarosite and schwertmannite) are formed; over time these minerals may weather and release more acidity. Any acidity produced from sulfide oxidation that is not neutralised would be initially released into the sediment pore-waters; potential neutralisation processes are discussed in the next section (Section 4.2.3). The acidity released into the pore-water may then enter the lake by various mechanisms as shown in Figure 4-4. Acid fluxes from Lower Lakes' sediments to the water column of the lakes have been examined by several studies (e.g. Hicks *et al.* 2009; Simpson *et al.* 2009; Earth Systems 2010; Sullivan *et al.* 2010; Cook 2011; Cook *et al.* 2011; Cook and Mosley 2012).

Acidification processes following refilling are presented in Figure 4-5. The soluble and exchangeable acidity formed following sulfide oxidation under drought conditions, and the dissolution and/or hydrolysis of secondary iron and aluminium minerals would be the main potential sources of acidification immediately following lake refilling. Recent studies in the Lower Lakes indicate that the general changes in sediment redox status towards more reducing conditions and pH from acidic to neutral have begun to drive the reductive dissolution of iron minerals (such as jarosite) (Sullivan *et al.* 2012b).



** Soluble and exchangeable acidity, including pore waters containing metal species capable of hydrolysis (e.g. Fe or Al ions)*

Figure 4-4. Flowchart showing potential acidification processes that occur in the Lower Lakes during drought conditions (Acid flux to lake box after Cook 2011).

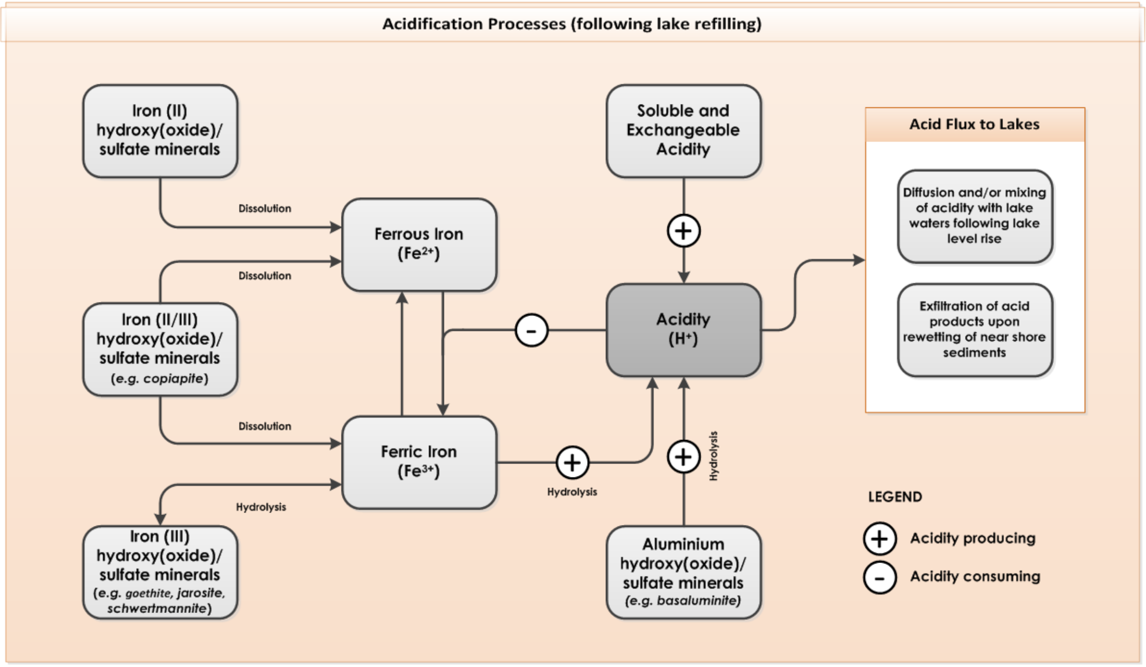


Figure 4-5. Flowchart showing potential acidification processes that occur in the Lower Lakes following lake filling (Acid flux to lake after Cook 2011).

4.2.3 Acid consumption

The acidity produced from the various processes discussed in Section 4.2.2 may be consumed by various mechanisms. Neutralisation processes may operate within the sediment, soil pore-water and surface water. Under anoxic conditions, microbial reduction processes (e.g. reduction of SO_4, and Fe^{III}, MnO_2 and NO_3) may consume acidity during the decomposition of organic matter. Acid neutralisation in the sediment can also be provided by processes such as the dissolution of calcium and/or magnesium carbonates (e.g. shell), cation exchange reactions, and by reaction with the organic and clay fractions (Ahern *et al.* 2004). In addition, other minerals can provide some acid neutralisation with the amount dependent on particle size and degree of weathering (Ahern *et al.* 2004).

Pore-waters and surface waters may neutralise any acidity produced as a result of buffering by dissolved carbonate species (e.g. HCO_3^-). Many of these acid neutralising processes have been modelled for the Lower Lakes' sediments (see Hipsley *et al.* (2010) for further details). Recent studies in the Lower Lakes have indicated two important sources of alkalinity including that derived from lake water and plant roots (Sullivan *et al.* 2011, 2012b).

As mentioned previously, under stable conditions acidification as a consequence of acid sulfate soil processes would not be expected. However, under these conditions the build-up alkalinity would be expected to occur within the sediment from microbial reduction processes using organic matter, often accompanied by the accumulation of potential forms of acidity, especially pyrite derived in part from sulfate reduction.

As water levels drop and sulfidic sediments become exposed to oxygen the acidity produced from the various processes shown in Figure 4-4 may be neutralised. A summary of the key acid consuming processes that may occur during drought conditions are presented below in Figure 4-6. In addition to the processes mentioned above, the oxidation of ferrous (a product of sulfide oxidation) to ferric iron is a well known acid sulfate soil process that consumes acidity (see Equation 4.10). However, as shown below in Figure 4-6 further hydrolysis of ferric iron will produce acidity (see Equation 4.11). A recent study by Sullivan *et al.* (2011) found the acid neutralising capacity (ANC) of the surficial sediment to be largely negligible in the latter stages of the recent drought, although the application of aglime prior to bioremediation was found to be an important source of ANC at selected sites.

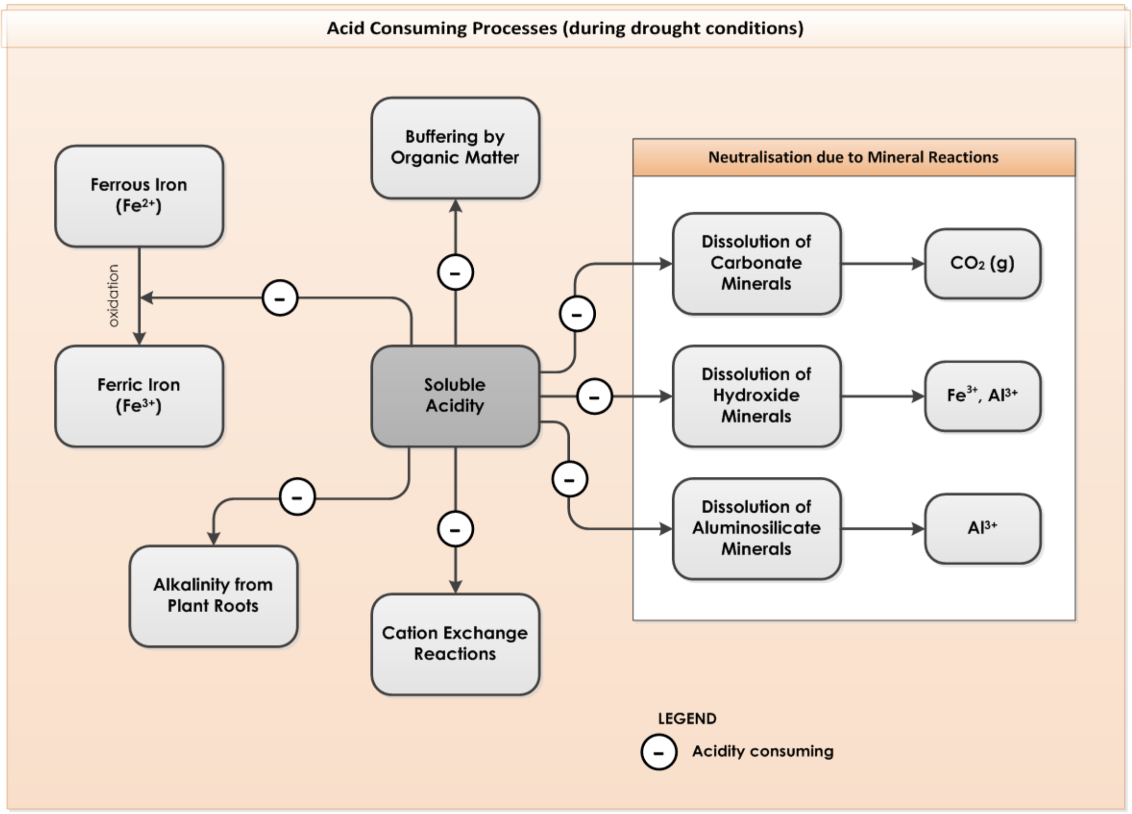


Figure 4-6. Flowchart showing potential acid consuming processes that occur in the Lower Lakes during drought conditions.

A summary of the key acid consuming processes that may occur following refilling are presented in Figure 4-7. Recent studies in the Lower Lakes have indicated that alkalinity derived from lake water as an important source of alkalinity (Sullivan *et al.* 2011, 2012b). The alkalinity in the lake water consumes acidity as the lake water enters the sediment profile via either convective or diffusive processes. The results of Sullivan *et al.* (2011) indicate that the diffusion of the substantial alkalinity in the lake waters was capable of causing appreciable increases in sediment pH down to approximately 30 cm depth within a few months. Further diffusion and acidity consumption was observed to continue over the following months (Sullivan *et al.* 2012b).

Plant roots may also be an important source of alkalinity as vegetation can increase sediment pH by the action of root exudation and nutrient uptake (Sullivan *et al.* 2011). While the microbial sulfate reduction can provide alkalinity, the results of a study by Sullivan *et al.* (2011) indicated that over the initial 6 months of inundation the alkalinity produced via this process was likely to be minimal. The two main constraints to sulfate reduction were observed to include the lack of organic matter and the severely acidified nature of the sediments. However, after 19 months of inundation Sullivan *et al.* (2012b) observed considerable sulfate reduction and production of alkalinity become important at sites where organic matter was continually replenished by the vegetation present (i.e. *Phragmites*). Further details of the acid consuming processes operating in the upper layers of the inundated Lower Lakes sediments associated with sulfate reduction are summarised in Figure A-4 in the Appendix.

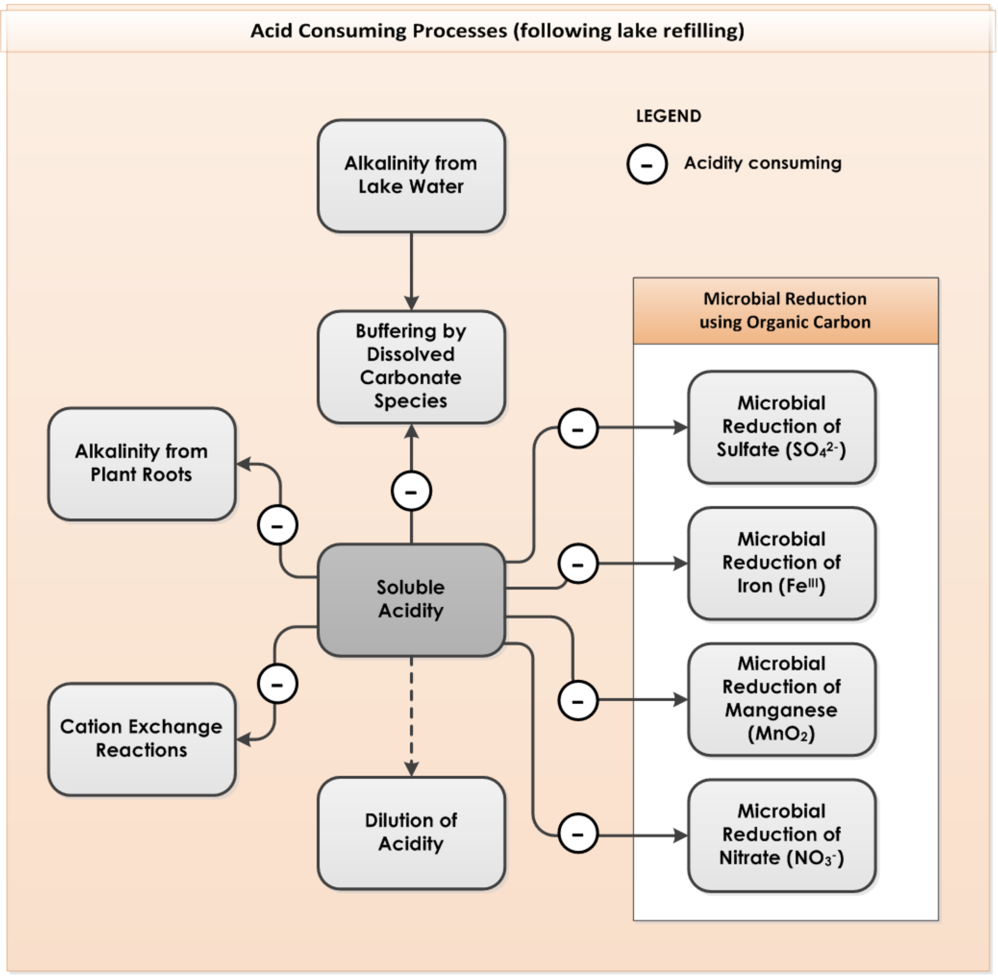


Figure 4-7. Flowchart showing potential acid consuming processes that occur in the Lower Lakes following lake filling.

4.2.4 Metal immobilisation-mobilisation

The oxidation and acidification of acid sulfate soils can lead to substantial changes in the mobility of metals (Claff *et al.* 2011). The mobilisation of metals and metalloids to soil pore-waters from acid sulfate soils can constitute a major environmental hazard (e.g. Åström *et al.* 2001; Burton *et al.* 2006c, 2008). Numerous metals and metalloids have been reported at levels exceeding accepted environmental protection thresholds in acid sulfate soil (e.g. Åström *et al.* 2001; Macdonald *et al.* 2004a; Burton *et al.* 2006c). Recent studies Lower Lakes acid sulfate soils have shown the capacity of these materials to mobilise elevated concentrations of metals and metalloids, with ANZECC/ARMCANZ (2000) guideline trigger values for the protection of aquatic ecosystems often being exceeded (e.g. Simpson *et al.* 2008, 2009, 2010; Sullivan *et al.* 2008, 2010; Hicks *et al.* 2009).

Metals in sediments occur within mineral phases or as charged ions or ionic complexes sorbed to reactive surfaces (Åström 1998; Fältmarsch *et al.* 2008; Claff *et al.* 2010). Trace metals are commonly associated with iron sulfides (Huerta-Diaz and Morse 1992), and the occurrence of iron monosulfides are well known to control the bioavailability of many metals (e.g. Simpson *et al.* 2005). Acidification can greatly enhance the solubility of metals, promoting their subsequent release from mineral phases by dissolution or cation exchange. The pH dependence of metal release has received considerable attention (Sammut *et al.* 1996b; Wilson *et al.* 1999; Åström 2001; Preda and Cox 2001; Macdonald *et al.* 2004a; Simpson *et al.* 2010). For example, Simpson *et al.* (2010) found that Al, Fe, Cu, Ni, V, and Zn may be rapidly mobilised (i.e. within 24 hours) by re-wetting exposed Lower Lakes sediments. The rate and extent of release of these metals depended strongly on the pH of those sediments, with the lower the pH the greater the release of metals.

While metal mobilisation is often observed under oxic-acidifying conditions, metals can also be mobilised when sulfuric acid sulfate soil materials are subject to prolonged inundation, resulting in the development of anoxic reducing conditions (e.g. Sullivan *et al.* 2010). Accumulations of iron minerals in acid sulfate soils are often concentrated at the ground surface and include goethite, ferrihydrite, jarosite and schwertmannite. These iron minerals often have a large surface area and are a significant sink for the sorption of metals. Under reducing conditions, these iron minerals are prone to microbial reductive dissolution (van Breemen 1973; Burton *et al.* 2007). Microbial iron reduction triggers three major changes that affect metal mobilisation. Firstly, it results in the dissolution of Fe^{3+} and transformation to Fe^{2+}, causing the co-release of other metals sorbed to the Fe mineral surfaces. Secondly, the microbial reduction process is proton-consuming and when accompanied by the formation of bicarbonate as a by-product of microbial respiration, can result in *in situ* neutralisation (Blodau 2006). The increase in pore-water pH generally reduces the solubility of divalent metals and aluminium. It also facilitates the recently identified Fe^{2+} catalysed transformation of poorly crystalline iron oxide minerals to more crystalline phases (e.g. rapid transformation of schwertmannite to goethite).

Although the overall consequences of these rapid mineral transformations on metal mobility are yet to be quantified (Burton *et al.* 2010), the mobility of some metals and metalloids can increase under these conditions. For example, arsenic is most soluble at around pH 5 and when associated with iron oxides in acid sulfate soil materials, is readily mobilised at the onset of microbially-mediated iron reduction (Burton *et al.* 2008).

In addition to the pH and redox potential, metal and metalloid mobilisation-immobilisation processes in sediments are affected by a number of other physical and chemical properties. These properties include texture, type of clay minerals, organic matter content, salinity, and the presence of inorganic chemical components such as carbonates and sulfides (Gambrell 1994). The mobility of metals in sediments also varies dependent on its chemical form. The chemical forms may include water soluble metals, exchangeable metals, metals precipitated as inorganic compounds, metals complexed with humic materials, metals adsorbed or occluded to precipitated hydrous oxides, metals precipitated as insoluble sulfides, and metals bound within the crystalline lattice structure of primary minerals (Gambrell 1994). A conceptual diagram by Claff *et al.* (2011) showing the metal mobilisation pathways and the dynamics between various metal pools commonly observed in acid sulfate soils is presented in Figure A-18 in the Appendix.

A summary of the key metal mobilisation-immobilisation processes that may occur under stable conditions in the Lower Lakes is presented in Figure 4-8. The pore-water metals derived from groundwater and surface water sources (i.e. lake and River Murray waters) can under reducing conditions be immobilised by precipitation or adsorption to sulfidic and/or non-sulfidic minerals, and may also be complexed with organic matter (Figure 4-8). While under these stable conditions it is expected there would be minimal flux of metals to the lake water from the sediments, bioaccumulation of metals by flora and benthic fauna may occur.

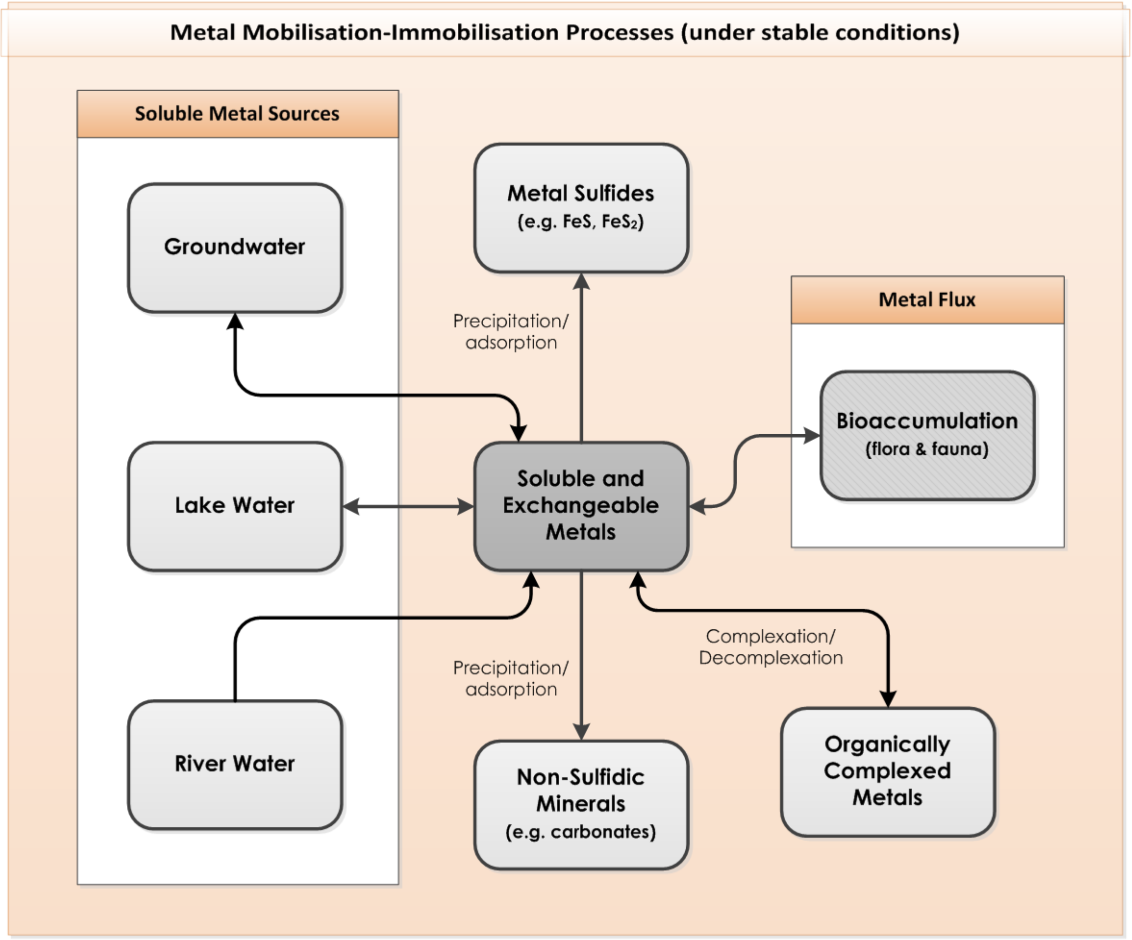


Figure 4-8. Flowchart showing potential metal mobilisation-immobilisation processes that occur in the Lower Lakes during stable conditions.

A summary of the key metal mobilisation-immobilisation processes that can occur during drought conditions is presented in Figure 4-9. Under drought conditions the oxidation of metal sulfides and the consequent acidification may result in substantial metal mobilisation. Ferrous iron (Fe^{2+}) is an initial iron sulfide oxidation product and trace metals associated with sulfides can also be released upon oxidation. The acidity produced during sulfide oxidation can lead to mineral dissolution (particularly clay mineral dissolution) and the associated mobilisation of metals. The oxidation of organic matter can also lead to the mobilisation of organically complexed metals. During drought conditions the precipitation of secondary oxidation products (e.g. iron hydroxy(oxide)/sulfate minerals) will lead to metal immobilisation. As mentioned previously, the secondary iron minerals formed following sulfide oxidation are also known to be a significant sink for the sorption of metals. Dissolved metals can be mobilised from the sediment into the lake by the flux processes indicated in the acidification flowchart during drought conditions (Figure 4-4). As indicated in Figure 4-9 metals may be bioaccumulated by flora and fauna.

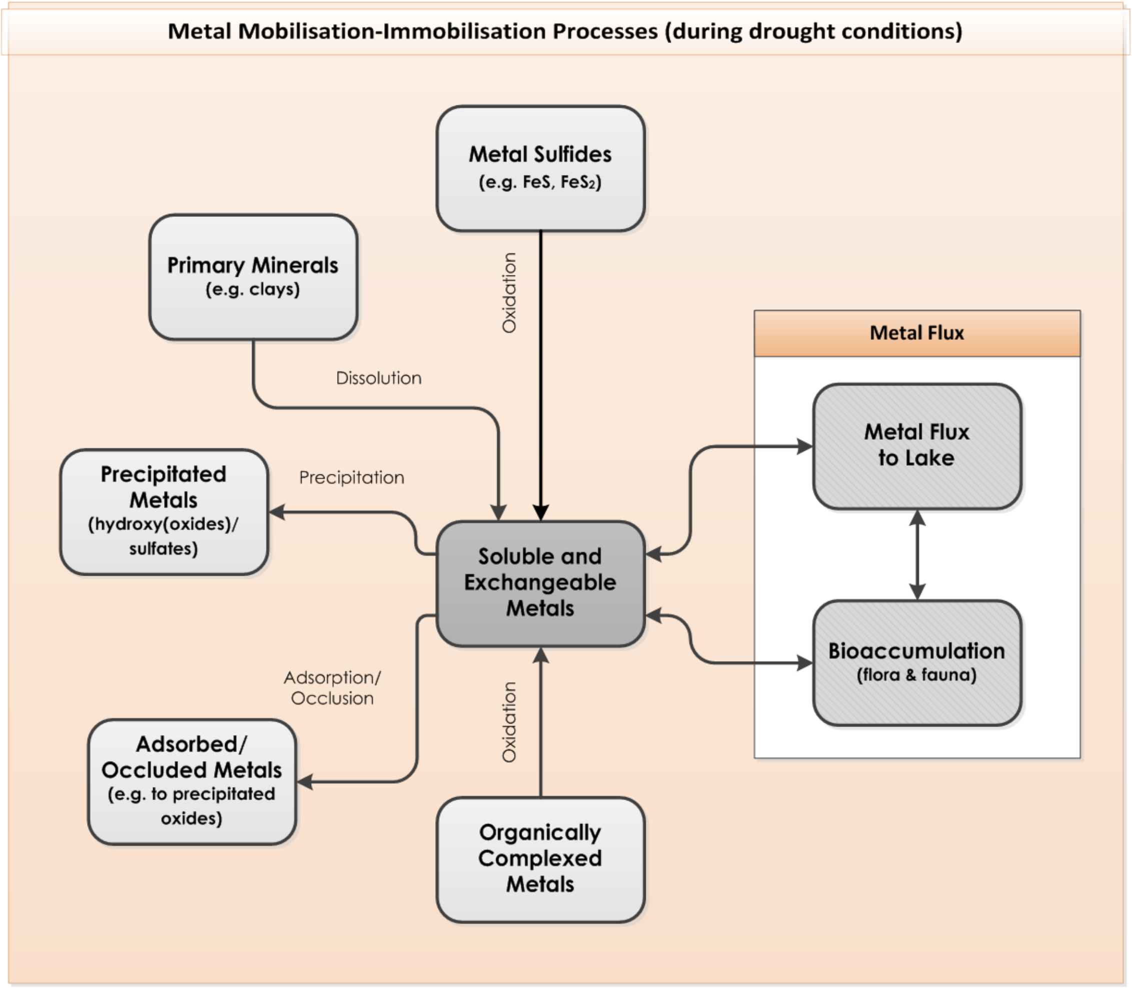


Figure 4-9. Flowchart showing potential metal mobilisation-immobilisation processes that occur in the Lower Lakes during drought.

The potential for the mobilisation of various metals and metalloids from acid sulfate soil materials following either freshwater or seawater inundation has been demonstrated in a number of studies on sulfuric and sulfidic Lower Lakes' sediments (e.g. Simpson *et al.* 2008, 2009, 2010; Sullivan *et al.* 2008, 2010; Hicks *et al.* 2009). A summary of the key metal mobilisation-immobilisation processes that may occur following lake refilling is presented in Figure 4-10. Sulfidisation processes will lead to the immobilisation of iron and other trace metals that become associated with sulfides. Metals can be released into solution from the dissolution of precipitated and adsorbed/occluded metals under reducing conditions (Figure 4-10). As discussed earlier, the reductive dissolution of iron minerals can lead to the release of Fe^{2+} and other metals adsorbed to Fe mineral surfaces. Precipitation and complexation reactions can result in metal immobilisation within the sediment. Alternatively, during and following lake refilling, dissolved metals can be mobilised into the lake by the flux processes indicated in the acidification flowchart following lake refilling (Figure 4-5). The bioaccumulation of metals in the sediment and lake water may also occur; a recent study in the Lower Lakes indicated metal uptake by vegetation (e.g. Sullivan *et al.* 2012a; see Section 4.2.7 for further details).

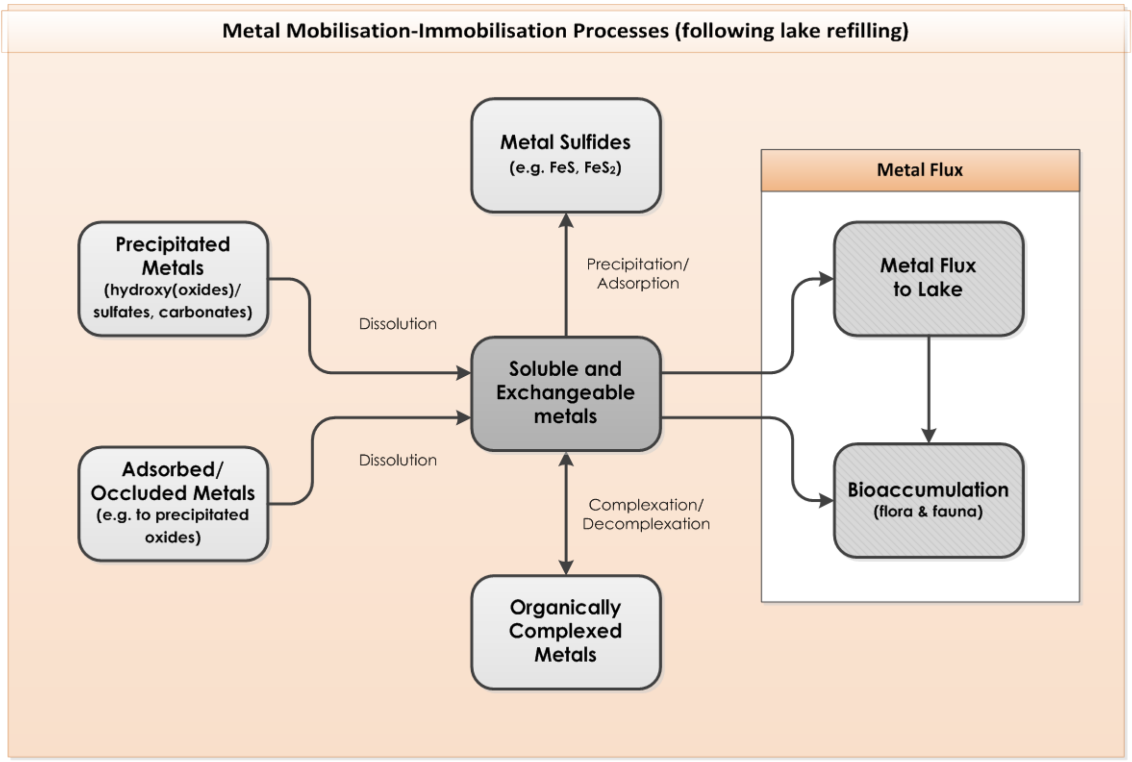


Figure 4-10. Flowchart showing potential metal mobilisation-immobilisation processes that occur in the Lower Lakes following lake filling.

4.2.5 Deoxygenation

Acute deoxygenation of estuaries, lakes, rivers and drainage channels is well known to be a major contributor to catastrophic fish kills (e.g. Johnston *et al.* 2003; Howitt *et al.* 2007; Hamilton *et al.* 1997). Many potential factors contribute to deoxygenation events, and they are known to impact a wide range of environments. Severe deoxygenation of waterbodies within acid sulfate soil landscapes has been linked directly to the behaviour of acid sulfate soil materials (e.g. Sullivan and Bush 2000).

Deoxygenation results when solids and aqueous compounds with a capacity to react with dissolved oxygen, enter water bodies and consume oxygen more rapidly than it can be replenished. The magnitude of deoxygenation depends on the spatial scale of the event, its persistence and its intensity. Aquatic ecosystems require dissolved oxygen concentrations generally greater than 85% saturation for lowland rivers (e.g. ANZECC/ARMCANZ 2000). Native fish and other large aquatic organisms are known to survive on dissolved oxygen concentration of as little as 2 mg L^{-1}, but may become stressed below 4 - 5 mg L^{-1} (Hladyz and Watkins 2009).

Anaerobic decomposition of vegetation can be a primary process leading to the deoxygenation of large volumes of waters in acid sulfate soil landscapes (e.g. Johnston *et al.* 2003; Wong *et al.* 2010). Decomposition of flood-intolerant vegetation in drained acid sulfate floodplains can lead to the formation of “blackwater” - a colloquial term used to describe anoxic stagnant floodplain water that develops a distinctive dark colour as a result of the accumulation of dissolved organic carbon compounds. Blackwater is typically anoxic, has a high chemical oxygen demand (COD) and high dissolved iron concentrations, and rapidly consumes dissolved oxygen when it discharges to main water bodies (Johnston *et al.* 2003).

The propensity for monosulfidic black ooze (MBO) to accumulate and be mobilised by floodwaters has also been identified as a contributing factor to deoxygenation in acid sulfate soil areas (Sullivan *et al.* 2002; Bush *et al.* 2004b,c; Burton *et al.* 2006b,d). The chemistry of estuarine waters during hypoxic events has indicated elevated concentrations of redox sensitive species associated with acid sulfate soil (e.g. Fe^{2+}, dissolved Mn, and elemental sulfur) (Wong *et al.* 2010), further implicating acid sulfate soil and MBO materials in deoxygenation events. Whether this chemistry also applies to MBOs mobilised into freshwater lakes is likely but yet to be determined.

The role of MBO in deoxygenation (and latter acidification) in acid sulfate landscapes has only been discovered relatively recently (Sullivan and Bush 2000; Sullivan *et al.* 2002). Since then Burton *et al.* (2006c) have described the oxidation dynamics of MBO when mobilised into oxygenated water. The oxidation of MBO follows a two-step process with oxygen consumption occurring with each step (after Burton *et al.* 2006c):

Step 1 $$FeS \left\{ \begin{array}{l} Fe^{2+} + 0.5O_2 + 1.5\,H_2O \rightarrow 2H^+ + FeOOH \\ S^{2-} + 0.5O_2 + 2H^+ \rightarrow H_2O + 0.125S_8 \end{array} \right. \qquad [4.15]$$

Step 2 $$0.125S_8 + 1.5\,O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \qquad [4.16]$$

The first step is a rapid chemical reaction of iron monosulfide minerals with oxygen, forming iron oxides and elemental sulfur. This initial oxygen-consuming step does not affect pH and is therefore non-acidifying. It is probably for this reason that the role of MBO in deoxygenation was overlooked until relatively recently. Acidification associated with MBO oxidation can result from the second step, the microbially-mediated oxidation of elemental sulfur, when oxygen is available.

Elevated elemental sulfur concentrations in deoxygenated waterways in acid sulfate soil landscapes may be a useful indicator of MBOs as a contributing cause to deoxygenation, although elemental sulfur can also form as a primary product of H_2S oxidation, and can be present within MBOs prior to flood events (Burton *et al.* 2006a,b).

The presence of MBO acid sulfate soil materials in the Lower Lakes has been identified in several reports (e.g. Fitzpatrick and Shand 2008; Fitzpatrick *et al*. 2008c; Sullivan *et al.* 2008, 2012b). It is very likely on the basis of the data available and given the shallow nature of these lakes that episodic localised deoxygenation events can occur in areas where MBOs are concentrated, due to mixing of these sediments with the waters of the lakes. It is expected that localised deoxygenation events will occur during drought conditions (particular as a consequence of disturbance due to seiching) and during lake refilling.

Flowcharts summarising the main processes resulting in deoxygenation events in the Lower Lakes during drought conditions and during lake refilling are presented in Figures 4-11 and 4-12, respectively. While it is expected that both the decomposition of organic matter and the chemical oxidation of iron monosulfides would be the major contributors to deoxygenation under both scenarios, during and following lake refilling, the oxidation of ferrous iron formed as a result of earlier sulfide oxidation may also contribute, especially to localised deoxygenation during lake refilling (Figure 4-12).

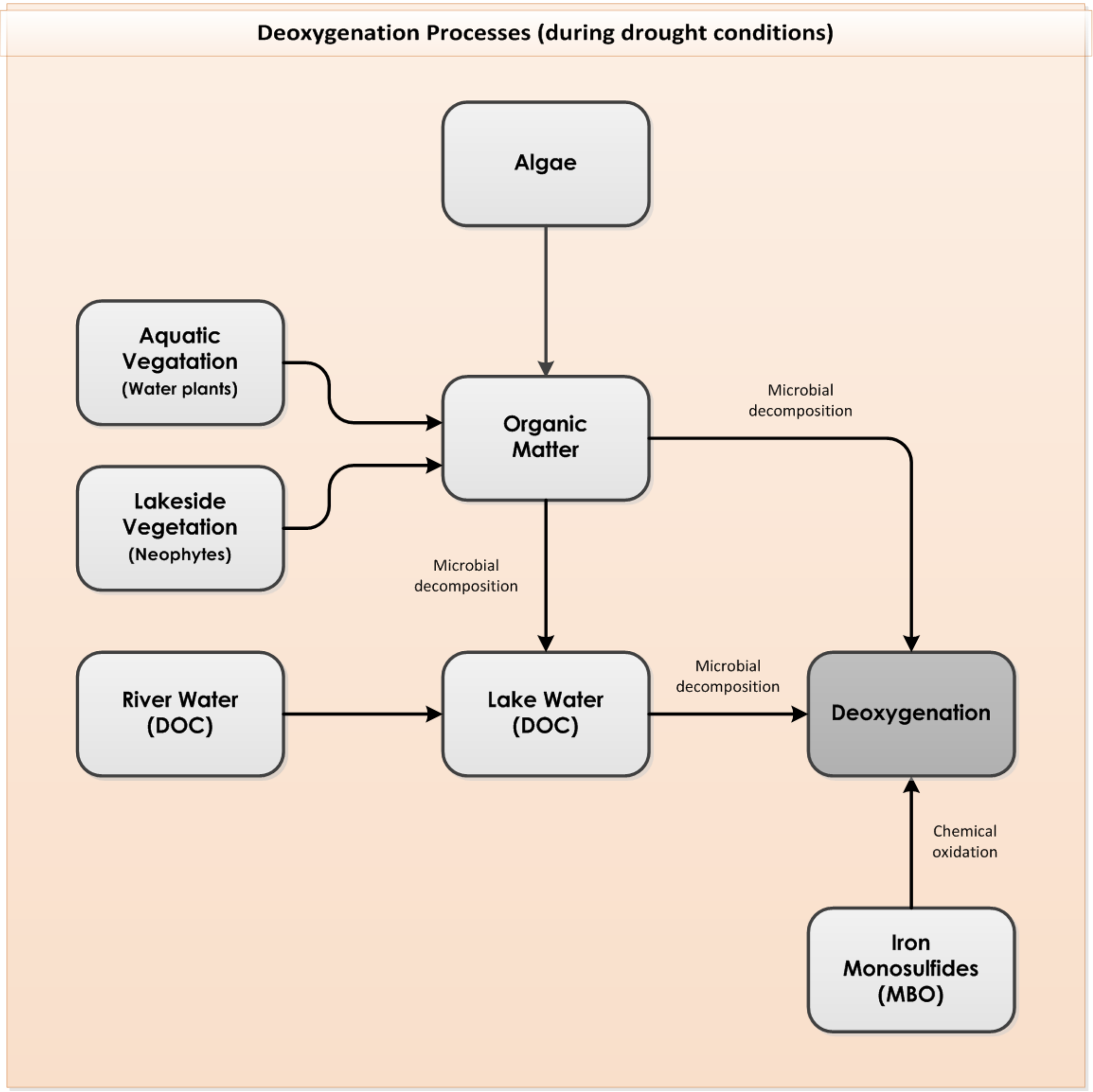


Figure 4-11. Flowchart showing potential deoxygenation processes that occur in the Lower Lakes during drought.

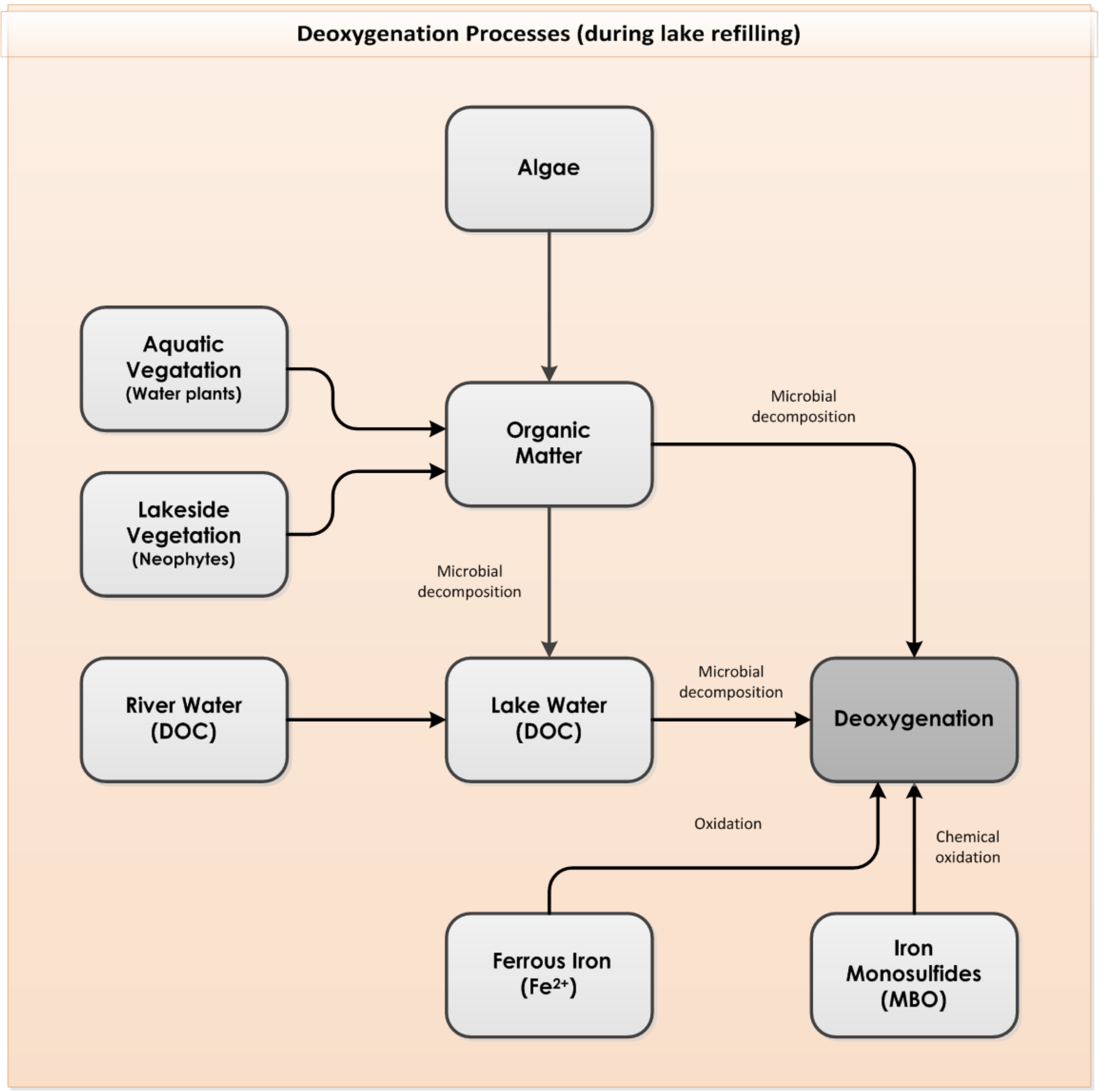


Figure 4-12. Flowchart showing potential deoxygenation processes that may occur in the Lower Lakes during lake filling.

4.2.6 Production of volatiles

Anthropogenic and biogenic sulfur-containing gases have important impacts on global climate change (Charlson *et al.* 1987; Lohmann and Feichter 2005), and atmospheric acid-base chemistry (Berresheim *et al.* 1995). Coastal estuarine and marine environments are major emitters of biogenic hydrogen sulfide (H_2S) (Aneja 1990; Bates *et al.* 1992), and it is likely that freshwater lakes with sufficient sulfate content to drive acid sulfate soil processes as is evident in the Lower Lakes similarly emit H_2S. Emissions of H_2S, and more recently sulfur dioxide (SO_2), from floodplains have been linked to acid sulfate soil management (Macdonald *et al.* 2004b). A wide variety of volatile organic sulfur gases are known to occur in the environment, and these gases are commonly referred to as volatile organic sulfur compounds (VOSC) (Hicks and Lamnontagne 2006).

Hydrogen sulfide is a highly noxious gas that causes distress to humans (Luther *et al.* 2003; EPA 2003) and threatens aquatic organisms (Diaz and Rosenberg 1995; Rabalais 2002). As described in Section 4.2.1 by Equation 4.1, H_2S is produced by sulfur-reducing bacteria under anoxic conditions. Even at small concentrations, H_2S can be detected by its characteristic rotten-egg odour. In acid sulfate soil landscapes, periodically inundated sediments, shallow waterways and field drains where stratified anoxic conditions can develop, are all situations conducive to sulfate reduction and the formation of H_2S (Dent 1986). However, H_2S is an unstable phase and its persistence in water and soil and ultimate gaseous emission is highly constrained by a wide range of oxidants in natural sediments and water bodies (Jørgensen *et al.* 1991). These oxidants include O_2, NO_3, Mn and Fe oxyhydroxides (Froelich *et al.* 1979; Luther *et al.* 1997). Due to their abundance in acid sulfate soil, iron oxides (Millero *et al.* 1987) are a particularly effective oxidant of H_2S, a process that can lead to the formation of iron sulfides as described previously. Hydrogen sulfide becomes a problem when the rate of its formation exceeds the catalytic oxidative capacity of the sediments and water bodies to eliminate its gaseous emission. An excess of labile carbon and stagnant water bodies create conditions that favour H_2S emissions in acid sulfate soil landscapes (Rozan *et al.* 2002).

Partially oxidised RIS-containing acid sulfate soil materials are a known source of SO_2. Macdonald *et al.* (2004b) quantified SO_2 flux from agricultural acid sulfate soils using both ground chamber and micro metrological methods. In this study, the rates of SO_2 emission from the soil were closely linked to soil moisture and evaporative flux, leading the authors to conclude that acidic dissociation of sulfite (SO_3^{2-}) occurring within the near-surface pore-water was probably the major source of SO_2. The precise mechanisms for SO_2 formation in acid sulfate soil require resolution: bacterial processes that utilise sulfate (Saltzman and Cooper 1989) or organo-sulfur compounds (Freney 1961) are both possibilities. From relatively few measurements, Macdonald *et al.* (2004b) estimated global SO_2 emissions from acid sulfate soils to be 3.0 Tg S yr^{-1}, ~ 3% of global anthropogenic emissions.

Hicks and Lamnontagne (2006) reviewed sulfur gas emissions from acid sulfate soil landscapes and developed conceptual models showing the major pathways under both wet and dry conditions (These models are shown in Figures A-19 and A-20 in the Appendix). Under stable wet conditions VOSC are produced from the decomposition of organic matter and H_2S is formed from the reduction of sulfate (Figure A-19). These gases are subsequently released into the water column where VOSC are taken up by bacteria and H_2S is oxidised to sulfate.

Under dry drought conditions VOSC and H_2S are still released by the same processes within the reduced sediments. However, VOSC are also produced from the aerobic decomposition of organic matter and SO_2 is a potential product of sulfide oxidation (Figure A-20). Under dry conditions all the gases produced are subsequently released into the atmosphere.

4.2.7 Bioremediation

Acid sulfate soil research in the Lower Lakes has shown the availability of organic carbon to be a major factor limiting sulfate reduction and the associated production of alkalinity (e.g. Sullivan *et al*. 2010). The Lower Lakes Bioremediation and Revegetation project began during the recent drought with the aim of removing acidity from the sediments (largely by increasing organic matter in soil in order to stimulate reduction processes) and also to reduce soil erosion (DEH 2009).

A recent study by Sullivan *et al.* (2012b) confirmed that bioremediation of the exposed acidified lake sediments by revegetation did produce substantial benefits in terms of reduced acidity of the surficial lake sediments due to the effects of vegetation. The findings indicated that the benefits were likely to have accrued from a combination of vegetation associated processes including the provision of alkalinity from plant roots, the provision of alkalinity indirectly from sulfate reductive processes enabled by the provision of organic matter from the bioremediating vegetation, as well as from the vegetation minimising soil erosion and hence preventing further exposure of severely acidic subsoils. Figure A-21 in the Appendix conceptualises the main changes in acidity and the associated key processes occurring in the sediments from: prior to the drought and during the various bioremediation scenarios upon and at 6 months after lake refilling.

In addition to ameliorating acidification and reducing erosion, bioremediation may also enhance carbon sequestration in the lake sediments (e.g. Sullivan *et al.* 2012a), and provide a refuge and food source for lake biota. It is also likely that bioremediation will result in the uptake of both metals and nutrients by vegetation. Sullivan *et al.* (2012a) recently assessed the uptake of some metals by the bioremediating vegetation, and found the concentration of nickel was high in some of the vegetation samples assessed. Previous studies have also shown that in the pore-water in acidic sediment layers can have nickel concentrations that greatly exceed the Australian water quality guidelines for ecosystem protection (e.g. Sullivan *et al.* 2011). The uptake of metals by vegetation around the Lower Lakes is currently being further examined (Sullivan *et al.* In preparation). While bioremediation may uptake nutrients and remove them from the system, unless eth bioremediation biomass is removed, the bioremediating vegetation will inevitably also be a source of nutrients upon decomposition.

A flowchart summarising the effects of bioremediation processes in the Lower Lakes is presented in Figure 4-13.

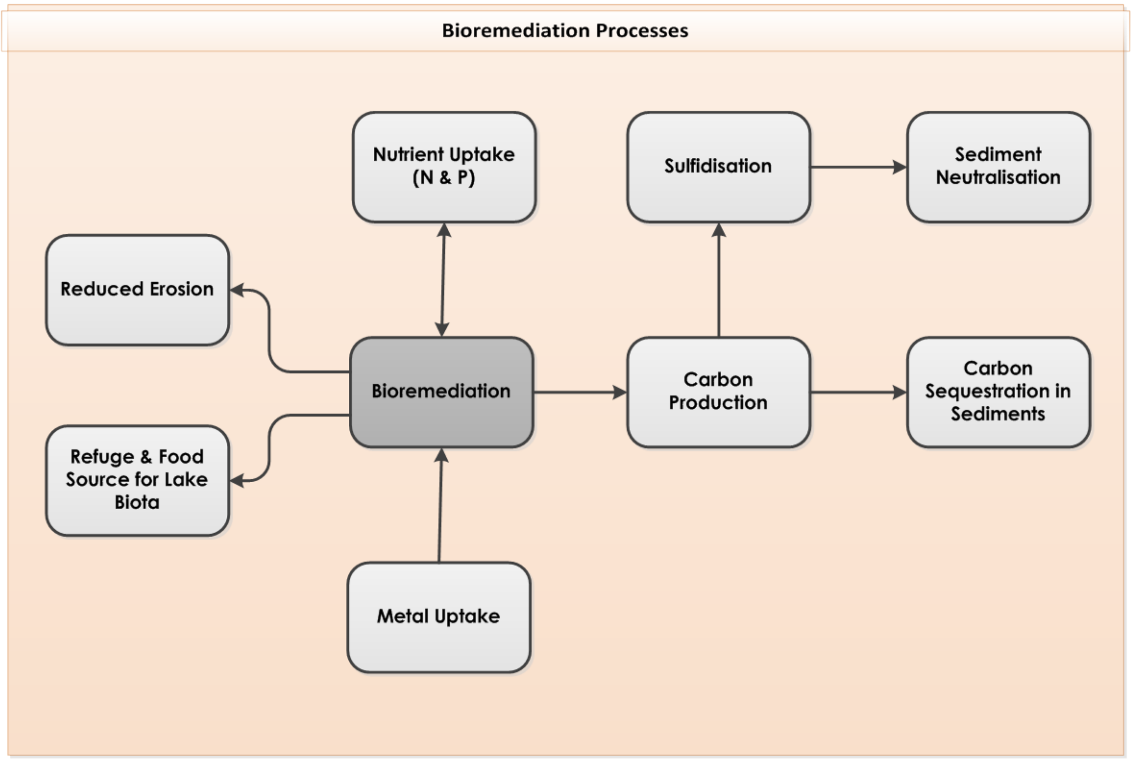


Figure 4-13. Flowchart showing potential effects of bioremediation processes in the Lower Lakes.

4.2.8 Carbon production and accumulation

A simple conceptual model showing the major fluxes involved in carbon production and accumulation in Lower Lakes sediments is shown in Figure 4-14. Under stable wet conditions and following refilling the decomposition of organic matter would largely be a result of anaerobic processes, whereas under drought conditions aerobic processes will also play an important role.

There is little information currently available on the size of these fluxes. A recent study of vegetation in the Lower Lakes showed the accumulation of organic matter ranged between 670 and 903 C ha^{-1} yr^{-1} in sediments post lake refilling (Sullivan *et al.* 2012a). The usual low organic matter levels in sandy lake fringe sediments (e.g. Sullivan *et al.* 2010) indicates that the magnitude of decomposition processes generally equal those responsible for organic matter production.

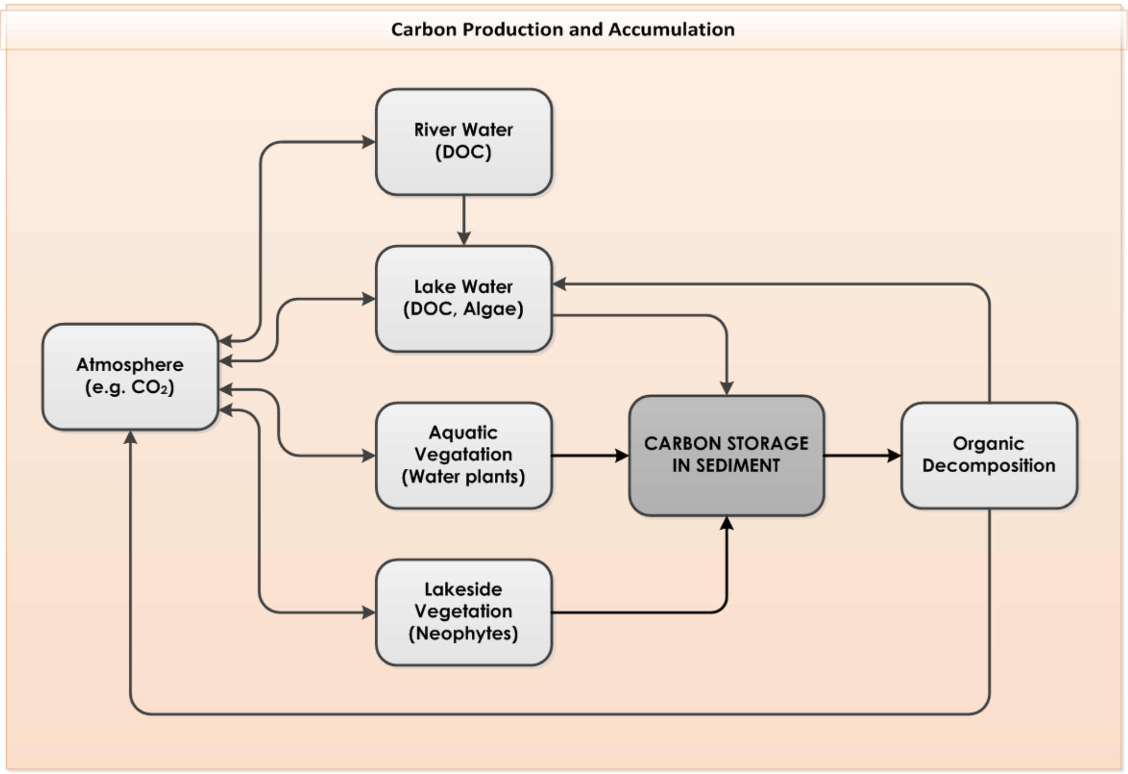


Figure 4-14. Flowchart showing the major flows and fluxes involved in carbon production and accumulation in Lower Lake sediments.

4.2.9 Nutrient mobilisation

The 2007-10 drought resulted in substantial changes to both the flow regimes and biochemical cycling of the Lower River Murray, which led to changes in the water quality of the Lower lakes including the concentration of nutrients (Hipsley *et al.* 2010). The factors controlling the nutrient concentrations in the Lower Lakes are reasonably well understood and predicted by recently developed water quality models (see Hipsley *et al.* 2010; Hipsley and Busch 2012). Some acid sulfate soil processes are known to affect the uptake and/or release of nutrients.

Previous research has shown the presence of sulfate in appreciable concentrations can greatly increase the rate of organic matter decomposition and nutrient mineralisation in sediments (Jørgenson 1982). Caraco *et al.* (1989) proposed that phosphorus release from freshwater sediments correlates with the sulfate concentration of the overlying water. The work of Lamers and co-workers (e.g. Lamers *et al.* 2002) confirmed this for sulfate-polluted freshwater wetlands. Therefore, it is likely that sulfate reduction within the Lower Lakes' sediments can also increase the release of phosphates (and other nutrients) from sediments.

In addition, the uptake and release of phosphate in sulfidic sediments is known to be strongly linked to the cycling of iron. A conceptual diagram of the coupled phosphate and iron and during early diagenesis in marine sediments is presented in Figure A-22 in the Appendix. Ferric oxyhydroxides (FeOOH) precipitated at the sediment-water interface and in the water column scavenge phosphate (PO_4^{3-}) (Ruttenberg *et al*. 2003). This adsorbed phosphate may be later released into pore-waters upon the decomposition of organic matter and reductive dissolution of the ferric oxyhydroxides. Non-precipitated phosphate or phosphate that is not readsorbed can then be subsequently released from the sediment.

Laboratory studies by Simpson *et al.* (2008, 2010) found the release of nutrients immediately following rewetting of acid sulfate soils from around the Lower Lakes was generally low. However, other recent laboratory and field studies have shown that prolonged inundation of sulfuric and sulfidic soil materials from the Lower Lakes with freshwater was capable of mobilising high concentrations of nutrients (e.g. Sullivan *et al.* 2008, 2010; Hicks *et al.* 2009). Sullivan *et al.* (2008) showed the inundation of sulfuric soil materials and oxic suspensions of MBOs from the around the Lower Lakes mobilised high concentrations of both ammonium and nitrate. Sullivan *et al.* (2010) also showed the potential for the release of ammonium into the overlying waters at selected sites following inundation; concentrations exceeded the ANZECC and ARMCANZ (2000) guideline trigger value for the protection of aquatic ecosystems. A field experiment by Hicks *et al.* (2009) observed the ANZECC and ARMCANZ (2000) trigger values for various nutrients (i.e. NH_4-N, NO_x-N and PO_4-P) were exceeded for both surface and pore water following inundation.

Recent research by Sullivan *et al.* (2012b) at 19 months after lake re-filling has observed two strong trends in nutrient mobility at a site under *Phragmites*. This includes: (i) large decreases in ammonia concentrations in the pore-waters of the deeper sediment layers, and (ii) greatly increased phosphate concentrations in the pore-waters of the surface sediments. It is therefore likely the *Phragmites* is uptaking ammonium and that sediments under *Phragmites* are a potential source of soluble phosphate to the overlying lake waters.

A summary of the potential nutrient mobilisation processes expected to occur in the Lower Lakes under stable conditions, during drought and following lake refilling is presented in Figure 4-15.

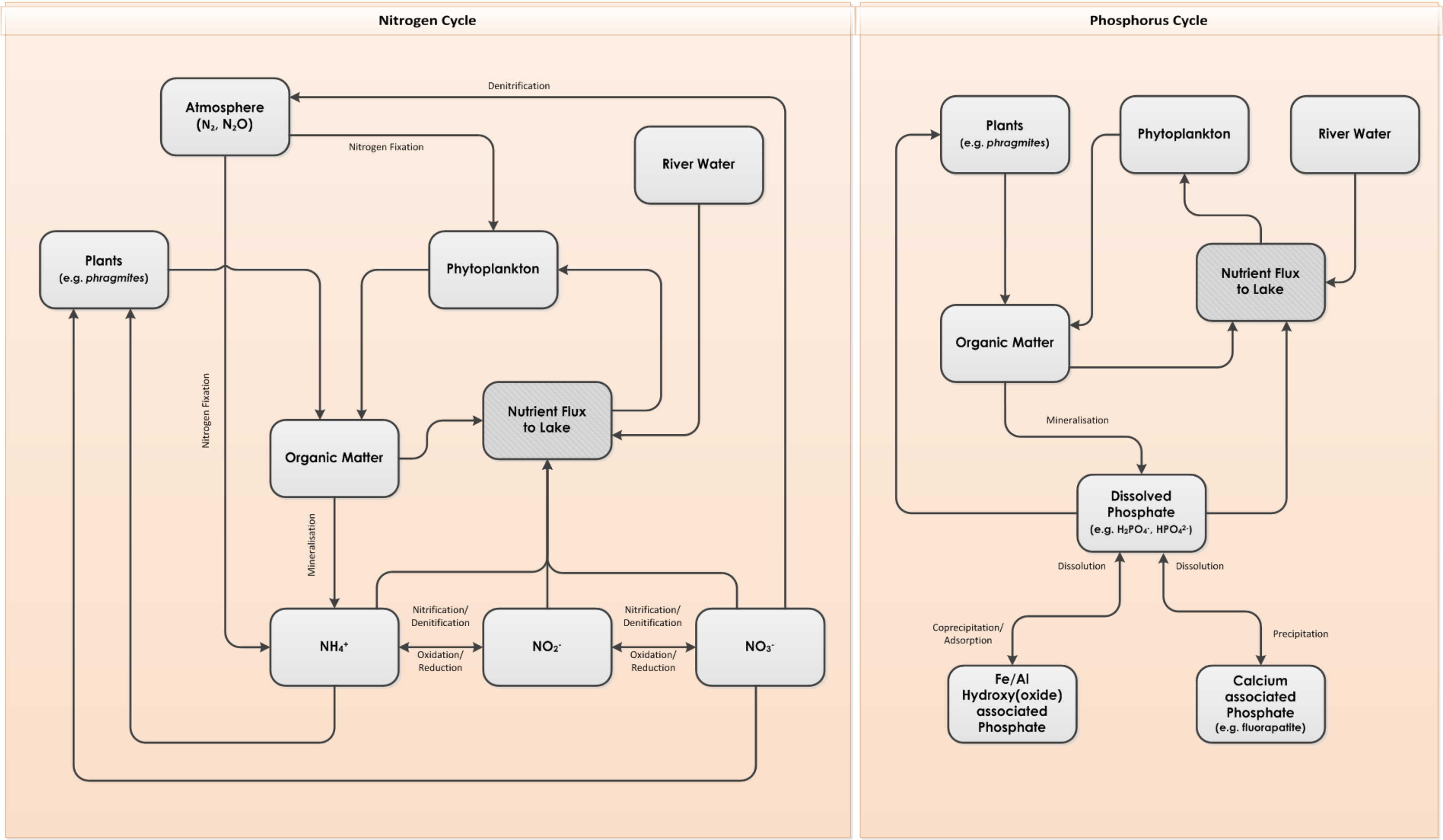


Figure 4 -15. Flowchart showing key potential nutrient mobilisation pathways (Nitrogen cycle adapted from Andrews *et al.* 2004).

4.2.10 Biological Effects

A wide range of environmental hazards can result from acid sulfate soils processes, and the processes involved with the development of many of these hazards have been discussed in earlier sections of this report. As mentioned in the introduction, environmental hazards commonly associated with acid sulfate soils include: 1) severe acidification of soil and waters, 2) mobilisation of metals, metalloids, nutrients, and rare earth elements, 3) deoxygenation of water bodies, 4) production of noxious gases, and 5) scalding of landscapes.

Numerous studies have documented the impacts of severe acid sulfate soil acidification and the often associated mobilisation of metals on agricultural crops (e.g. Dent 1986), terrestrial habitats (e.g. van Breemen 1973), and aquatic environments (e.g. Sammut *et al.* 1996a,b; Wilson *et al.* 1999; Callinan *et al.* 2005). The ecological impacts of acid sulfate soil acidification in waterbodies can include fish kills (Sammut *et al.* 1996a,b; Callinan *et al.* 2005), loss of native aquatic macrophytes and fauna followed by invasion by acid tolerant species (Sammut *et al.* 1996a), mass mortality of crustaceans and shell fish (Simpson and Pedini 1985), and loss of benthic communities (Corfield 2000). Sub-lethal exposure of fish to acidity has also been linked to an increased susceptibility to skin diseases (Callinan *et al.* 2005), whereas depletion of alkalinity has been linked to poor shell development in crustaceans (Dove and Sammut 2007).

Aluminium toxicity has been identified as a significant issue linked to acid sulfate soil acidification. The solubility of aluminium is critically dependent on pH, only becoming soluble at environmentally significant levels at approximately pH < 5. Soluble aluminium affects plant growth primarily by disrupting root function, and severe environmental impacts can occur when acidic aluminium-rich leachate from acid sulfate soil enters waterbodies. Iron precipitates in the form of iron flocs also are known to directly affect gilled organisms, smother benthic communities and aquatic flora (Sammut *et al.* 1996a,b).

Gilled organisms are particularly vulnerable to soluble metals and metal mobilisation can lead to rapid mortality rates in these species (Simpson and Pedini 1985; Sammut *et al.* 1995; Sammut *et al.* 1996a,b). Studies of the effects of metals on shellfish (oysters) revealed longer term, more chronic impacts on their growth and survival (Dove and Sammut 2007). However, the longer term impacts of metal release from acid sulfate soils to surrounding aquatic environments are poorly understood. Elevated metal concentrations can be toxic to both aquatic flora and fauna. However, the consequences of elevated metal concentrations to algal and phytoplankton production and the potential for their bioaccumulation are largely unknown (Macdonald *et al.* 2004a).

The range of potentially longer term impacts on aquatic ecosystems arising from acid sulfate soil leachate include: disturbance to fish reproduction and recruitment, acidity barriers to fish migration, decline of primary food web, reduction of species diversity, and long term habitat degradation (Sammut *et al.* 1996a,b). A summary of some of the impacts of acid sulfate soils on fish and aquatic life is illustrated in Figure A-23 in the Appendix.

Acid sulfate soil processes can contribute towards the deoxygenation of waterbodies (see Section 4.2.5 for further details). Acute deoxygenation of waterbodies is well known to be a major contributor to catastrophic fish kills (e.g. Johnston *et al.* 2003; Howitt *et al.* 2007; Hamilton *et al.* 1997). Hydrogen sulfide toxicity may also be an issue for aquatic ecosystems impacted by sulfidic sediments (e.g. Koch *et al.* 1990).

During the recent drought in the Lower Lakes there were concerns about possible human health risks associated with the metals in the dust blown off the acidic lake beds (Palmer *et al*. 2011). However, studies showed that all the metals analysed (except for chromium which was confirmed to be in the low toxicity form (Cr III) were found to be below the guidelines for metals in air, and indicated that the metals in the dust did not represent a significant risk to public health (Palmer *et al*. 2011).

Stauber *et al.* (2008) developed a conceptual model of the potential acid sulfate soil impacts in the Lower Lakes (Figure A-24 in the Appendix). This conceptual model has been used as a basis for the flowchart of the potential biological effects in the Lower Lakes presented in Figure 4-16. Figure 4-16 shows the potential biological effects from five of the acid sulfate soil processes that may have an impact including acidification, metal mobilisation, nutrient mobilisation, deoxygenation and production of volatiles. However, it is important to note that whilst Figure 4-16 shows there is a complex interaction between the potential biological effects, the actual biological effects of acid sulfate soil processes within the Lower Lakes, particularly in the long term, are currently poorly understood.

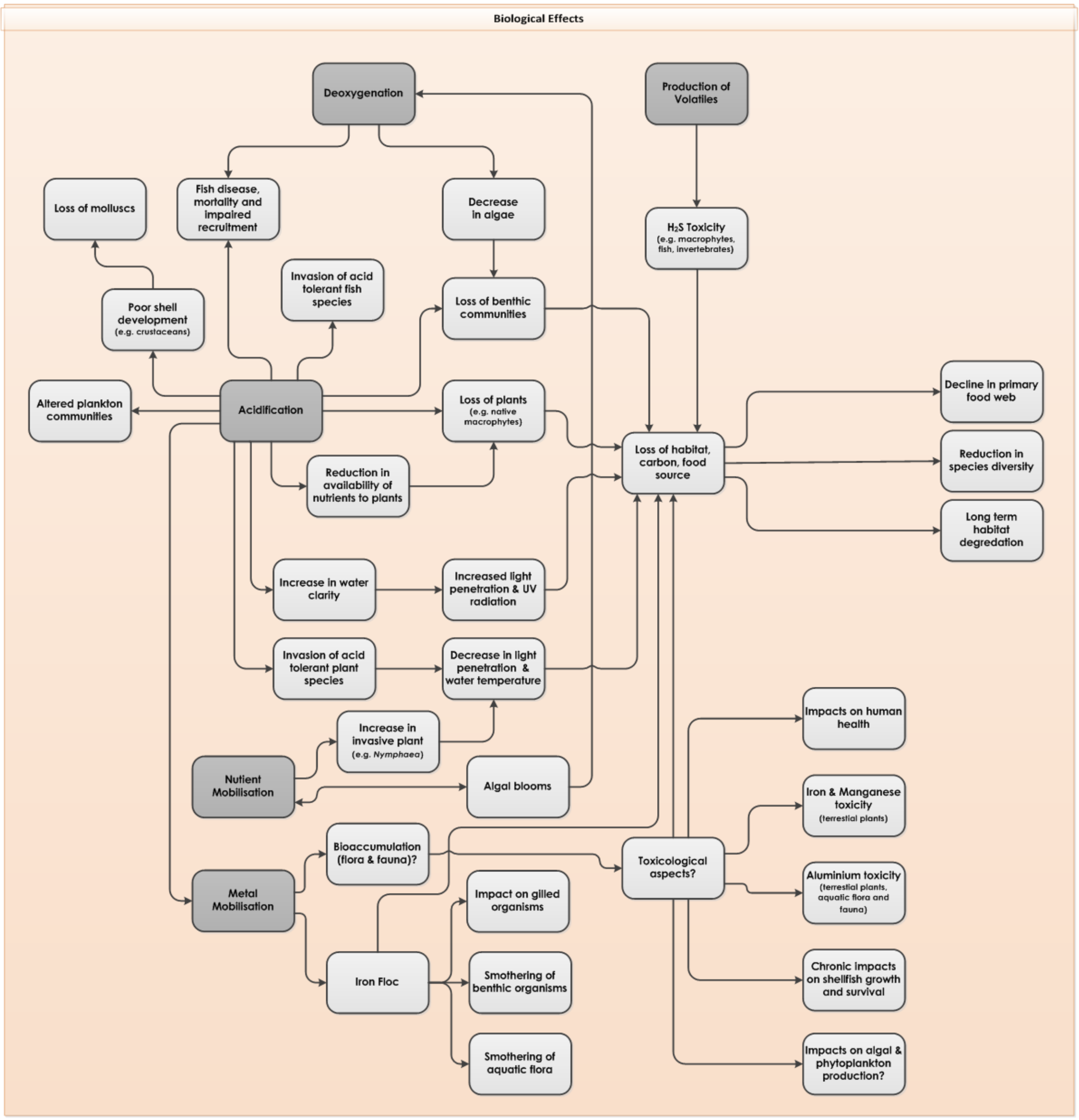


Figure 4-16. Flowchart showing potential biological effects arising from acid sulfate soil processes in the Lower Lakes. There are numerous relationships and interrelationships between these effects, but for clarity many of these interrelationships have been omitted from this diagram.

5.0 Conclusions

The conceptual models developed during this study have highlighted the complex interrelationships between the acid sulfate soil processes operating in the Lower Lakes especially during periods of hydrological change. These conceptual models contribute to our understanding of the acid sulfate soils in the Lower Lakes, and of their management requirements especially in relation to wetting and drying cycles of decadal frequency. This increased understanding will assist managers to protect the environmental values of the Lower Lakes.

Whilst this study has described many of the main processes associated with acid sulfate soils, and mapped their interrelationships, these conceptual models have also highlighted significant gaps in our knowledge of how the Lower Lakes environments are affected by acid sulfate soil processes. For example, while the key processes controlling the release of metals from sediments into the surrounding water may be reasonably well understood, the long term impacts of metal release to the surrounding aquatic environment are largely unknown.

By mapping the current state of our understanding of the acid sulfate soil processes affecting the Lower Lakes, the conceptual models developed during this study will provide a valuable management tool that can help guide prioritisation of future studies in the Lower Lakes to ensure that essential knowledge gaps are filled. Finally the use of these conceptual models will allow value adding of previous studies by the recognition of synergies between future studies and the existing knowledge as well as the avoidance of duplication.

6.0 Recommendations

As well as detailing our existing knowledge of key acid sulfate soil processes the development of these conceptual models for the Lower Lakes has highlighted that there are significant gaps in our knowledge of some of these processes. These gaps include:

- the processes by which metals mobilised by the severe acidification of sediments may impact on the water quality and biota in the lakes,
- the carbon budget and carbon fluxes within the previously exposed lake sediments,
- the pattern and kinetics of the accumulation of sulfide minerals and potential acidity in the previously exposed lake sediments,
- The kinetics of many of these processes are poorly defined,
- the development of appropriate threshold values for risk and hazard assessment,

It is recommended that the conceptual models developed in this project be examined by an expert panel to both establish the critical gaps in our understanding of the way that acid sulfate soils and their management impact on the environment and values of the Lower Lakes, and then to prioritise these knowledge gaps. Specifically, it is recommended that a workshop, attended by all scientific and management stakeholders, be held to assess the veracity and completeness of the conceptual models presented here, and prioritise the needs for future research and monitoring in the Lower Lakes in relation to acid sulfate soils.

Finally, it is recognised that future studies of the Lower Lakes and acid sulfate soils will provide a clearer focus of the processes that occur. Consequently the conceptual models presented here should be regarded as frameworks that should be periodically reviewed to enhance their utility further as a result of the incorporation of the new knowledge and understanding that develops from future studies.

7.0 References

Ahern C.R., L.A. Sullivan and A.E. McElnea. 2004. Laboratory methods guidelines 2004 - acid sulfate soils. In: 'Queensland Acid Sulfate Soil Technical Manual'. (Department of Natural Resources, Mines and Energy: Indooroopilly, Queensland).

Andrews J.E., P. Brimblecombe, T. D. Jickells, P.S. Liss and B. Reid. 2004. An introduction to environmental chemistry. 2nd Ed., Blackwell Publishing, Oxford, UK.

Aneja V.P. 1990. Natural sulfur emissions into the atmosphere. JAPCA J. Air Waste Manag. 40: 469-76.

ANZECC/ARMCANZ. 2000. 'Australian and New Zealand guidelines for fresh and marine water quality.' (Australian and New Zealand Environment and Conservation Council, Agricultural and Resource Management Council of Australia and New Zealand: Canberra). http://hermes.erin.gov.au/pls/crg_public/!CRGPPUBLIC.PSTART?strAction=SearchByChemical

Åström M. 1998. Partitioning of transition metals in oxidised and reduced zones of sulphide-bearing fine-grained sediments. App. Geochem. 13: 607-617.

Åström M. and N. Corin. 2000. Abundance, source and speciation of trace elements in humus-rich streams affected by acid sulfate soils. Aquat. Geochem. 6: 367-383.

Åström M. 2001. Effect of widespread severely acidic soils on spatial features and abundance of trace elements in steams. J. Geochem. Explor. 73: 181-191.

Bates T.S., B.K. Lamb, A. Guether, J. Dignon and R.E. Stoiber. 1992. Sulfur emissions to the atmosphere from natural sources. J. Atmos. Chem. 14: 315-37.

Berresheim H., P.H. Wine and D.D. Davis. 1995. Sulfur in the atmosphere. p. 251-307. In: Composition, chemistry, and climate of the atmosphere. Singh, H.B. (Ed.). New York: Van Nostrand Reinhold.

Bigham J.M., U. Schwertmann and L. Carlson. 1992. Mineralogy of precipitates formed by the biogeochemical oxidation of Fe(II) in mine drainage. p. 219-232. In: Biomineralization Processes of Iron and Manganese – Modern and Ancient Environments (Eds. HCW Skinner and RW Fitzpatrick), Catena Supplement 21.

Blodau C. 2006. A review of acidity generation and consumption in acidic coal mine lakes and their watersheds. Sci. Total Env. 369: 307-332.

Bloomfield C. and J.K. Coulter. 1973. Genesis and management of acid sulfate soils. Adv. Agron. 25: 265–326.

Burton E.D., R.T. Bush and L.A. Sullivan. 2006a. Elemental sulfur in drain sediments associated with acid sulfate soils. Appl. Geochem. 21: 1240–1247.

Burton E.D., R.T. Bush and L.A. Sullivan. 2006b. Reduced inorganic sulfur speciation in drain sediments from acid-sulfate soil landscapes. Env. Sci. Tech. 40: 888-893.

Burton E.D., R.T. Bush and L.A. Sullivan. 2006c. Acid-volatile sulfide oxidation in coastal floodplain drains: iron-sulfur cycling and effects on water quality. Env. Sci. Tech. 40: 1217-1222.

Burton E.D., R.T. Bush and L.A. Sullivan. 2006d. Sedimentary iron geochemistry in acidic waterways associated with coastal lowland acid sulfate soils. Geochim. Cosmochim. Acta 70: 5455-5468.

Burton E.D., R.T. Bush, L.A. Sullivan, R.K. Hocking, D.R.G. Mitchell, S.G. Johnston, R.W. Fitzpatrick, M. Raven, S. McClure and L.Y. Jang. 2009. Iron-Monosulfide Oxidation in Natural Sediments: Resolving Microbially Mediated S Transformations Using XANES, Electron Microscopy, and Selective Extractions. Env. Sci. Tech. 43: 3128-3134.

Burton E.D., R.T. Bush, L.A. Sullivan, S.G. Johnston and D.R.G. Mitchell. 2008. Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. Chem. Geol. 253: 64-73.

Burton E.D., R.T. Bush, L.A. Sullivan and D.R.G. Mitchell. 2007. Reductive transformation of iron and sulfur in schwertmannite-rich accumulations associated with acidified coastal lowlands. Geochim. Cosmochim. Acta 71: 4456 - 4473.

Burton E.D., S.G. Johnston, K. Watling, R.T. Bush A.F. Keene and L.A. Sullivan. 2010. Arsenic effects and behaviour in association with the Fe(II)-catalysed transformation of schwertmannite. Env. Sci. Tech. 44: 2016–2021.

Bush R.T., R. McGrath and L.A. Sullivan. 2004a. Occurrence of marcasite in an organic-rich Holocene mud. Aust. J. Soil Res. 42, 617–622.

Bush R.T., D. Fyfe and L.A. Sullivan. 2004b. Occurrence and abundance of monosulfidic black ooze in coastal acid sulfate soil landscapes. Aust. J. Soil Res. 42: 609-616.

Bush R.T. and L.A. Sullivan. 1997. Morphology and behaviour of greigite from a Holocene sediment in eastern Australia. Aust. J. Soil Res. 35: 853–861.

Bush R. T., L.A. Sullivan, D. Fyfe and S.J. Johnston. 2004c. Redistribution of monosulfidic black oozes by floodwaters in a coastal acid sulfate soil floodplain. Aust. J. Soil Res. 42: 603-607.

Bush R.T., L.A. Sullivan and C. Lin. 2000. Iron monosulfide distribution in three coastal floodplain acid sulfate soils, eastern Australia. Pedosphere 10: 237–246.

Callinan R.B., J. Sammut and G.C. Fraser. 2005. Dermatitus, bronchitis and mortality in empire gudgeon Hypseleotris compressa exposed naturally to run-off from acid sulfate soil. Dis. Aquati. Organ. 63: 247-253.

Canfield D.E., B. Thamdrup and S. Fleischer. 1998. Isotope fractionation and sulfur metabolism by pure and enrichment cultures of elemental sulfur-disproportionating bacteria. Limnol. Oceanogr. 43: 253–264.

Caraco N.F. 1989. Evidence for sulphate-controlled phosphate release from sediments of aquatic ecosystems. Nature 341: 316-318.

Charlson R.J., J.E. Lovelock, M.O. Andreae and S.G. Warren. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. Nature 326: 655-61.

Claff S.R., L.A. Sullivan, E.D. Burton and R.T. Bush. 2010. A sequential extraction for acid sulfate soils: Partitioning of iron. Geoderma 155: 244-230.

Claff S.R., E.D. Burton, L.A. Sullivan and R.T. Bush. 2011. Metal partitioning dynamics during the oxidation and acidification of sulfidic soil. Chemical Geology 286: 146-157.

Cook F.J. 2011. Lake Alexandrina and Lake Albert: Analysis of groundwater measurements and estimation of acid fluxes. Prepared by CSIRO Water for a Healthy Country National Research Flagship for the Department of Environment and Natural Resources' Lower Lakes and Coorong Recovery program.

Cook F.J., G. McLachlan, E. Leyden and L. Mosley. 2011. Physical properties of soils/sediments of Lower Murray Lakes and modelling of acid fluxes. Prepared by CSIRO Water for a Healthy Country National Research Flagship for the Department of Environment and Natural Resources' Lower Lakes and Coorong Recovery program.

Cook F.J. and L. Mosley. 2012. Modelling of acidic solute fluxes from sediments to the water column in the Lower Lakes of South Australia. Prepared by Freeman Cook and Associates Pty Ltd. & South Australia Environmental Protection Agency for the SA Department of Environment, Water and Natural Resources, Adelaide.

Corfield J. 2000. The effects of acid sulfate soil run-off on a subtidal estuarine macrobenthic community in the Richmond River, NSW, Australia. ICES J. Mar. Sci. 57: 1517-1523.

Davis G.B. and A.I.M. Ritchie. 1986. A model of oxidation in pyritic mine wastes: Part 1. Equations and approximate solution. Appl. Math. Model. 10: 314–322.

DEH. 2009. Growing a healthy future for the Lower Lakes. Lower Lakes bioremediation and revegetation project. Department of Environment and Heritage, Adelaide.

DENR. 2010. Acid sulfate soils research program summary report. Prepared by the Lower Lakes Acid Sulfate Soils Research Committee for the SA Department of Environment and Natural Resources, Adelaide.

Dent D.L. 1986. Acid sulfate soils: A baseline for research and development. ILRI Publ. 39. International Institute for Land Reclamation and Improvement, Wageningen, Netherlands.

Dent D.L. and L.J. Pons. 1995. Acid sulphate soils: A world view. Geoderma 67: 263–276.

Dent D.L. and R.W. Raiswell. 1982. Quantitative models to predict the rate and severity of acid sulphate development. p. 73–95. In: H. Dost, and N. van Breemen. 1982. Proceedings of the Bangkok Symposium on Acid Sulfate Soils. ILRI Pub. 31. International Institute for Land Reclamation and Improvement, Wageningen, Netherlands.

Diaz R.J. and R. Rosenberg. 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna. Oceanography and Marine Biology: An Annual Review 33: 245 - 303.

Dold B. and L. Fontbote. 2001. Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, and mineral processing. J. Geochem. Exploration 74: 3-55.

Dove M.C. and J. Sammut. 2007. Impacts of estuarine acidification on survival and growth of Sydney rock oysters Saccostreaglomerata (Gould, 1850). J. Shellfish Res. 26: 519–527.

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

EPA. 2003. Toxicological Review of Hydrogen Sulfide. http://www.epa.gov/ iris/toxreviews/0061-tr.pdf.

EPHC and NRMMC. 2011. National guidance for the management of acid sulfate soils in inland aquatic ecosystems. Canberra.

Fanning D. S., M.C. Rabenhorst, S.N. Burch, K.R. Islam and S.A. Tangren. 2002. Sulfides and sulfates. In: Soil Mineralogy with Environmental Applications (Eds. J. B. Dixon, D. G. Schulze and W. L. Daniels). Soil Science Society of America, Madison, WI.

Fältmarsch R.M., M.E. Åström and K-M. Vuori. 2008. Environmental risks of metals mobilized from acid sulphate soils in Finland: a literature review. Boreal Env. Res. 13: 444-456.

Fitzpatrick R.W., S.P. Marvanek, P. Shand, R.H. Merry, M. Thomas and M.D. Raven. 2008a. Acid sulfate soil 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. CSIRO Land and Water Science Report Number 46/08. CSIRO Land and Water, Glen Osmond, SA.

Fitzpatrick R.W., G. Grealish, A. Chappell, S. Marvanek and P. Shand. 2010. Spatial variability of subaqueous and terrestrial acid sulfate soils and their properties, for the Lower Lakes South Australia. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.

Fitzpatrick R.W., B. Powell and S. Marvanek. 2008b. Atlas of Australian Acid Sulfate Soils. p. 90–97. In: Fitzpatrick, R.W. and Shand, P. (Eds.) ‘Inland Acid Sulfate Soil Systems Across Australia’ CRC LEME Open File Report No. 249. (Thematic Volume), CRC LEME, Perth, Australia.

Fitzpatrick R.W. and P. Shand. 2008. Inland Acid Sulfate Soils in Australia: Overview and Conceptual Models. p. 6–74. In: Fitzpatrick, R.W. and Shand, P. (Eds.) ‘Inland Acid Sulfate Soil Systems Across Australia’ CRC LEME Open File Report No. 249. (Thematic Volume), CRC LEME, Perth, Australia.

Fitzpatrick R.W., P. Shand, S. Marvanek, R.H. Merry, M. Thomas, M.D. Raven, S.L. Simpson and S. McClure. 2008c. Acid sulfate soils in subaqueous, waterlogged and drained soil environments in Lake Albert, Lake Alexandrina and River Murray below Blanchetown (Lock 1): properties, distribution, genesis, risks and management. Report prepared for Department of Environment and Heritage SA. CSIRO Land and Water Science Report Number 46/08. CSIRO Land and Water, Glen Osmond, SA.

Fitzpatrick R.W., P. Shand and R.H. Merry. 2009. Acid Sulfate Soils. p. 65-111. In: Jennings, J.T. (Ed.) ‘Natural History of the Riverlands and Murraylands’. Royal Society of South Australia (Inc.) Adelaide, South Australia.

Freney J.R. 1961. Some observations on the nature of organic sulfur compounds in soils. Aust. J. Agric. Res. 12: 424-432.

Froelich P.N., G.P. Klinkhammer, M.L. Bender, N.A. Luedtke, G.R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman and V. Maynard. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta 43: 1075 - 1090.

Gambrell R.P. 1994. Trace and toxic metals in wetlands. J. Environ. Qual. 23: 883-891.

Georgala D. 1980. Paleoenvironmental Studies of Post-glacial Black Clays in Northern Sweden. PhD Thesis, University of Stockholm, Sweden.

Hamilton S.K., S.J. Sippel, D.F. Calheiros and J.M. Melack. 1997. An Anoxic Event and Other Biogeochemical Effects of the Pantanal Wetland on the Paraguay River. Limn. Oceanog. 42: 257-272.

Huerta-Diaz M.A. and J.W. Morse. 1992. Pyritisation of trace metals in anoxic marine sediments. Geochim. Cosmochim. Acta 56: 2681-2702.

Hicks W. and S. Lamontagne. 2006. A guide to sulfur gas emissions from wetlands and disposal basins: Implications for salinity management. Science Report 37/06; CRC LEME Open File Report 208. CSIRO Land and Water.

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

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

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

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

Hladyz S. and S. Watkins. 2009. Understanding blackwater events and managed flows in the Edward-Wakool River system. Fact Sheet p. 2. (Murray-Darling Freshwater Research Centre: Wodonga, Vic).

Howarth R.W. 1979. Pyrite: its rapid formation in a salt marsh and its importance in ecosystem metabolism. Science 203: 49–51.

Howitt J.A., D.S. Baldwin, G.N. Rees and J.L. Williams. 2007. Modelling blackwater: Predicting water quality during flooding of lowland river forests. Ecol. Modelling 203: 229-242.

Johnston S.G., P.G. Slavich, L.A. Sullivan, and P. Hirst. 2003. Artificial drainage of floodwaters from sulfidic backswamps: effects on deoxygenation in an Australian estuary. Marine Freshwater Res., 54: 781-795.

Jørgenson B.B. 1982. Mineralisation of organic matter in the sea bed - the role of sulphate reduction. Nature 296: 643-645.

Koch M.S., I.A. Mendelssohn, K.L. McKee. 1990. Mechanism for the hydrogen sulfide-induced growth limitation in wetland macrophytes. Limn. Oceanog. 35: 399-408.

Lamers L.P.M., S. Falla, E.M. Samborska, I.A.R. van Dulken, G. van Hengstum and J.G.M. Roelofs. 2002. Factors controlling the extent of eutrophication and toxicity in sulfate-polluted freshwater wetlands. Limn. Oceanogr. 47: 585-593.

Lamontagne S., W.S. Hicks, R.W. Fitzpatrick and S. Rogers. 2004. Survey and description of sulfidic materials in wetlands of the Lower River Murray floodplains: Implications for floodplain salinity management. CSIRO Land and Water Technical Report No. 28/04. CRC LEME Open File Report 165. CRC for Landscape Environments and Mineral Exploration, Bentley, Western Australia.

Ljung K., F. Maley, A. Cook and P. Weinstein. 2009. Acid sulfate soils and human health: A Millennium Ecosystem Assessment. Env. Int. 35: 1234-1242.

Lohmann U. and J. Feichter. 2005. Global indirect aerosol effects: a review. Atmos. Chem. Phys. 5: 715-37.

Luther III G.W. 1991. Pyrite synthesis via polysulfide compounds. Geochim. Cosmochim. Acta 55: 2839–2849.

Luther III G.W., B. Glazer, S. Ma, R. Trouwborst, B.R. Shultz, G. Drushcel and C. Kraiya. 2003. Iron and sulfur chemistry in a stratified lake: evidence for iron-rich sulfide complexes. Aquatic Geochem. 9: 87 - 110.

Luther III G.W., B. Sundby, B.L. Lewis, P.J. Brendel, and N. Silverberg. 1997. Interactions of manganese with the nitrogen cycle: alternative pathways to dinitrogen. Geochim. Cosmochim. Acta 61: 4043-4052.

Macdonald B.C.T., J. Smith, A.K. Keene, M. Tunks, A. Kinsela and I. White I. 2004a. Impacts from runoff from sulphuric soils on sediment chemistry in an estuary lake. Sci. Total Environ. 329: 115-130.

Macdonald B.C.T., O.T. Denmead, I. White, and M.D. Melville. 2004b. Natural sulfur dioxide emissions from sulfuric soils. Atmos. Env. 38: 1473-1480.

Millero F.J., S. Hubinger, M. Fernandez and S. Garnett. 1987. Oxidation of H_2S in seawater as a function of temperature, pH and ionic strength. Env. Sci. Tech. 21: 439 - 443.

Moses C.O., D.K. Nordstrom, J.S. Hermann and A.L. Mills. 1987. Aqueous pyrite oxidations by dissolved oxygen and by ferric iron. Geochim. Cosmochim. Acta 51: 1561–1571.

Nriagu J.O. 1978. Biogeochemistry of Lead in the Environment, Ecological Cycles, Elsevier, Amsterdam.

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

Pantelis G. and A.I.M. Ritchie. 1991. Macroscopic transport mechanisms as a rate-limiting factor in dump leaching of pyrite ores. Appl. Math. Model. 15: 136–143.

Piene A., A. Tritschler, K. Kusel and S. Peiffer. 2000. Electron flow in an iron-rich acidic sediment-evidence for an acidity-driven iron cycle. Limnol. Oceanogr. 45: 1077-87.

Pons L.J. 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In: Dost, H. (Ed.) ‘Acid Sulphate Soils. Proceedings of the International Symposium on Acid Sulphate Soils 13-20 August 1972, Wageningen, The Netherlands. I. Introductory Papers and Bibliography.’ pp. 3-27. Publication No.18, International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands.

Pons L.J. and N. van Breemen. 1982. Factors influencing the formation of potential acidity in tidal swamps. p. 37–51. In: H. Dost and N. van Breemen. 1982. Proceedings of the Bangkok Symposium on Acid Sulfate Soils. ILRI Pub. 31. International Institute for Land Reclamation and Improvement, Wageningen, Netherlands.

Preda M. and M.E. Cox. 2001. Trace metals in acid sediments and waters, Pimpama catchment, southeast Queensland, Australia. Environ. Geol. 40: 755-768.

Rabalais N.N. 2002. Nitrogen in aquatic ecosystems. Royal Swedish Academy of Sciences. Ambio 31: 102 -112.

Rickard D.T. 1975. Kinetics and mechanisms of pyrite formation at low temperatures. Am. J. Sci. 275: 636–652.

Rickard D. 1997. Kinetics of pyrite formation by the H_2S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125°C: the rate equation. Geochim. Cosmochim. Acta 61: 115–134.

Rickard D. and G.W. Luther. 1997. Kinetics of pyrite formation by the H_2S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125°C: the mechanism. Geochim. Cosmochim. Acta 61: 135–147.

Rickard D. and J.W. Morse. 2005. Acid volatile sulfide (AVS). Mar. Chem. 97: 141–197.

Rosicky M.A., L.A. Sullivan, P.G. Slavich and M. Hughes. 2004. Soil properties in and around acid sulfate soil scalds in the coastal floodplains of New South Wales, Australia. Aust. J. Soil Res. 42: 587-594.

Rozan T.F., M. Taillefert, R.E. Trouwborst, B.T. Glazer, B.T., S. Ma, J. Herszage, L.M. Valdes, K.S. Price and G.W. Luther III. 2002. Iron, sulfur and phosphorus cycling in the sediments of a shallow coastal bay: implications for sediment nutrient release and benthic macroalgal blooms. Limn. Oceanography 47: 1346 - 1354.

Ruttenberg K.C., H.D. Holland, K.K. Turekian. 2003. The global phosphorus cycle. In: Schlesinger, W.H. (Ed.), Treatise on Geochemistry. Pergamon, Oxford, pp. 585-643.

Saltzman E.S. and W.J. Cooper. 1989. Biogenic sulfur in the environment. American Chemical Society, Washington DC.

Sammut J. 2000. An introduction to acid sulfate soils. National Heritage Trust, Australia.

Sammut J., R.B. Callinan and G.C. Fraser. 1993. The impact of acidified water on freshwater and estuarine fish populations in acid sulphate soil environments. In: 'Proceedings National Conference on Acid Sulphate Soils'. Coolangatta, Qld. 24-25 June 1993. (Ed. RT Bush) pp. 26-40. (CSIRO, NSW Agriculture, Tweed Shire Council).

Sammut J., R.B. Callinan, and G.C. Fraser. 1996a. An overview of the ecological impacts of acid sulfate soils in Australia. p. 140–143. In: R.J. Smith (Ed.) Proc. 2nd Nat. Conf. Acid Sulfate Soils. R.J. Smith & Associates and ASSMAC, Alstonville, Australia.

Sammut J., I. White, and M.D. Melville. 1996b. Acidification of an estuarine tributary in eastern Australia due to drainage of acid sulphate soils. Marine Freshwater Res. 47: 669-684.

Simpson S.L., G.E. Batley, A.A. Chariton, J.L. Stauber, C.K. King, J.C. Chapman, R.V. Hyne, S.A. Gale, A.C. Roach and W.A. Maher, 2005. Handbook for sediment quality assessment. CSIRO, Bangor, NSW.

Simpson S., R. Fitzpatrick, P. Shand, B. Angel, D. Spadaro, R. Merry and M. Thomas. 2008. The acid, metal and nutrient mobilisation following rewetting of acid sulfate soils in the Lower Murray. Prepared for the South Australian Environmental Protection Agency. CSIRO Land and Water Bangor, NSW.

Simpson S.L., R.W. Fitzpatrick, P. Shand, B.M. Angel, D.A. Spadaro and L. Mosley. 2010. Climate-driven mobilisation of acid and metals from acid sulfate soils. Marine Freshwater Res. 61: 129-138.

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

Simpson H.J. and M. Pedini. 1985. Brackishwater aquiculture in the tropics: the problem of acid sulfate soils. Rome, Italy: Food and Agriculture Organisation of the United Nations.

Stauber J., A. Chariton, M. Binet, S. Simpson, G. Batley, M. Durr, R. Fitzpatrick and P. Shand. 2008. Water quality screening risk assessment of acid sulfate soil impacts in the Lower Murray, SA. Prepared for the South Australia Environmental Protection Authority. CSIRO Land and Water Science Report No. 45/08. CSIRO Land and Water, Lucus Heights, NSW.

Sullivan L., E. Burton, R. Bush, K. Watling and M. Bush. 2008. Acid, metal and nutrient mobilisation dynamics in response to suspension of MBOs in freshwater and to freshwater inundation of dried MBO and sulfuric soil materials. Final Report. A report for "The acid, metal and nutrient mobilisation following rewetting of acid sulfate soils in the Lower Murray Project”. Prepared for the South Australian Environmental Protection Agency. Centre for Acid Sulfate Soil Research, Southern Cross GeoScience, Southern Cross University, Lismore, NSW.

Sullivan L.A., E.D. Burton, N.J. Ward, R.T. Bush, J. Coughran, M.D. Cheetham, D.M. Fyfe, P.J. Cheeseman and T. McIntyre. 2011. Lower Lakes sulfate reduction study. Prepared for South Australian Department of Environment and Natural Resources. Southern Cross GeoScience Technical Report No. 711, Southern Cross University, Lismore, NSW. 312 pp.

Sullivan L.A. and R.T. Bush. 2000. The behaviour of drain sludge in acid sulfate soil areas: some implications for acidification of waterways and drain maintenance. In: 'Proceedings of Workshop on Remediation and Assessment of Broadacre Acid Sulfate Soils'. (Ed. P Slavich) pp. 43-48. (Acid Sulfate Soil Management Advisory Committee (ASSMAC): Southern Cross University, Lismore).

Sullivan L.A. and R.T. Bush. 2004. Iron precipitate accumulations associated with waterways in drained coastal acid sulfate landscapes of eastern Australia. Marine Freshwater Res. 55: 727-736.

Sullivan L.A., R.T. Bush, and D. Fyfe. 2002. Acid sulfate soil drain ooze: distribution, behaviour and implications for acidification and deoxygenation of waterways. p. 91-99. In: Acid sulfate soils in Australia and China. (Eds. C. Lin, M. Melville and L.A. Sullivan), Science Press, Beijing, China .

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

Sullivan L.A., J.F. Parr, N.J. Ward, R.T. Bush, D.M. Fyfe, M. Bush and R. Hagan. 2012a. Lower Lakes carbon project. Prepared by Southern Cross GeoScience for the SA Department of Environment and Natural Resources, Adelaide.

Sullivan L.A., N.J. Ward, R.T. Bush, M.D. Cheetham, P.J. Cheeseman, D.M. Fyfe, T. McIntyre, M. Bush and R. Hagan. 2012b. Lower Lakes Phase 1 sulfate reduction monitoring project. Prepared by Southern Cross GeoScience for the SA Department of Environment, Water and Natural Resources, Adelaide.

Sullivan L.A., N.J. Ward**,** M.A. Rosicky, S. Li, R.T. Bush, D.M. Fyfe, M. Bush, and N. Toppler. (In preparation). Recovery of acid sulfate sediments in the Lower Lakes. Prepared by Southern Cross GeoScience for the SA Department of Environment, Water and Natural Resources, Adelaide.

van Breemen N. 1973. Soil forming processes in acid sulphate soils. In: 'Proceedings of the International Symposium on acid sulphate soils. 13-20 August 1972, Wageningen, The Netherlands'. (Ed. H Dost), Wageningen, The Netherlands. pp. 66-129. (International Institute for Land Reclamation and Improvement).

Ward N.J., L.A. Sullivan, D.M. Fyfe, R.T. Bush and A.J.P. Ferguson. 2004. The process of sulfide oxidation in some acid sulfate soil materials. Aust. J. Soil Res. 42: 449-458.

Wilson B.P., I. White and M.D. Melville. 1999. Floodplain hydrology, acid discharge and changing water quality associated with a drained acid sulfate soil. Marine Freshwater Res. 50: 149-157.

Wong V.N.L., S.G. Johnston, R.T. Bush, L.A. Sullivan, C. Clay, E.D. Burton and P.G. Slavich. 2010. Spatial and temporal changes in estuarine water quality during a post-flood hypoxic event. Estuarine, Coastal and Shelf Sci. 87: 73–82.

8.0 Appendix

Additional conceptual models

The conceptual models of the acid sulfate soil processes in this project were developed using information from a variety of sources. A number of additional conceptual models were used to inform the development of the Lower Lakes acid sulfate soil conceptual models presented previously. Some models have been designed for inland waterways in general and these are presented in Section A1. Additional models have been developed specifically for the acid sulfate soil processes in the Lower Lakes and some models for acid sulfate soils in general are presented in Sections A2 and A3, respectively.

A1. Acid sulfate soil processes in inland waterways

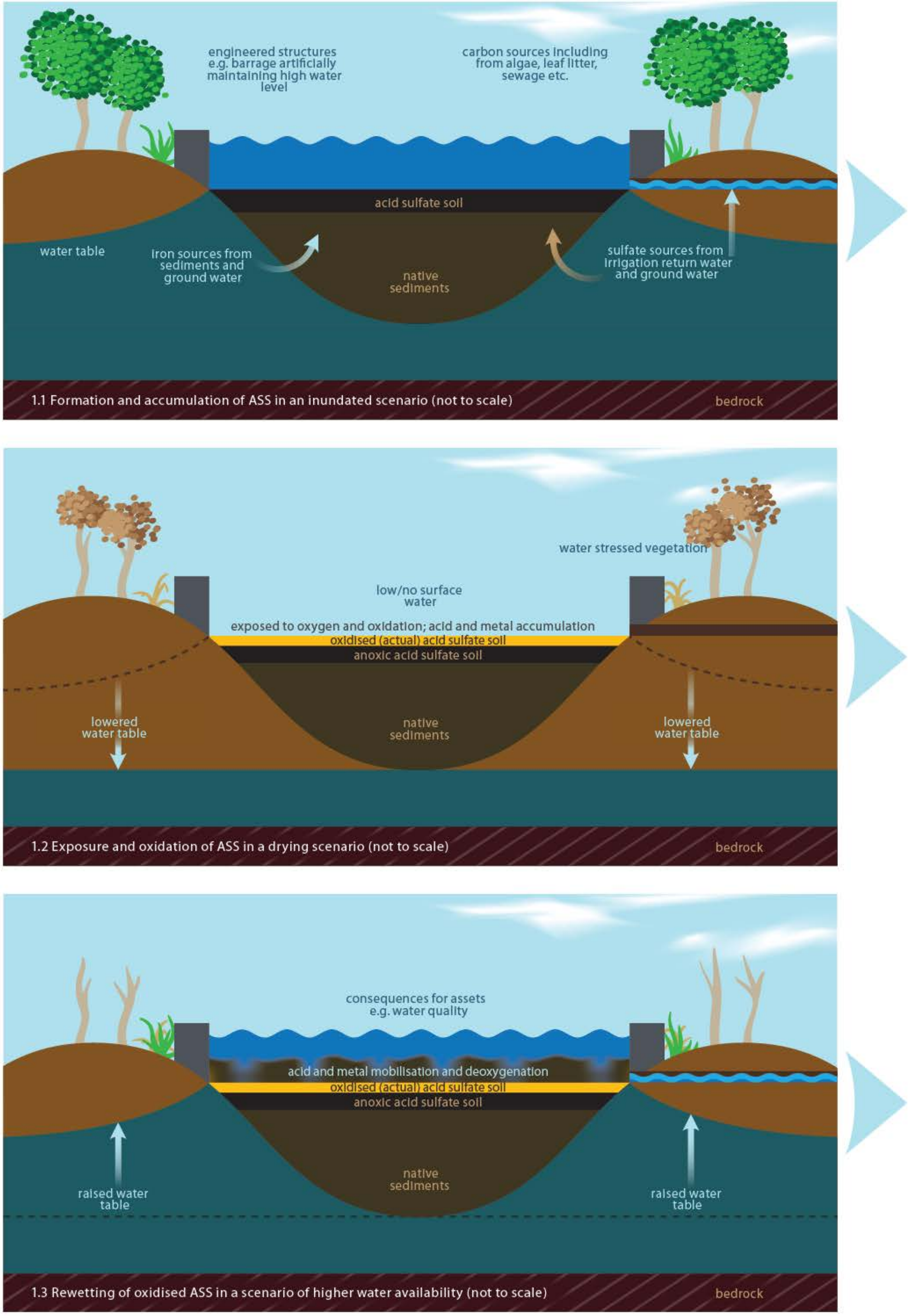


Figure A-1. Conceptual model of an inland aquatic ecosystem (source: EPHC and NRMMC 2011).

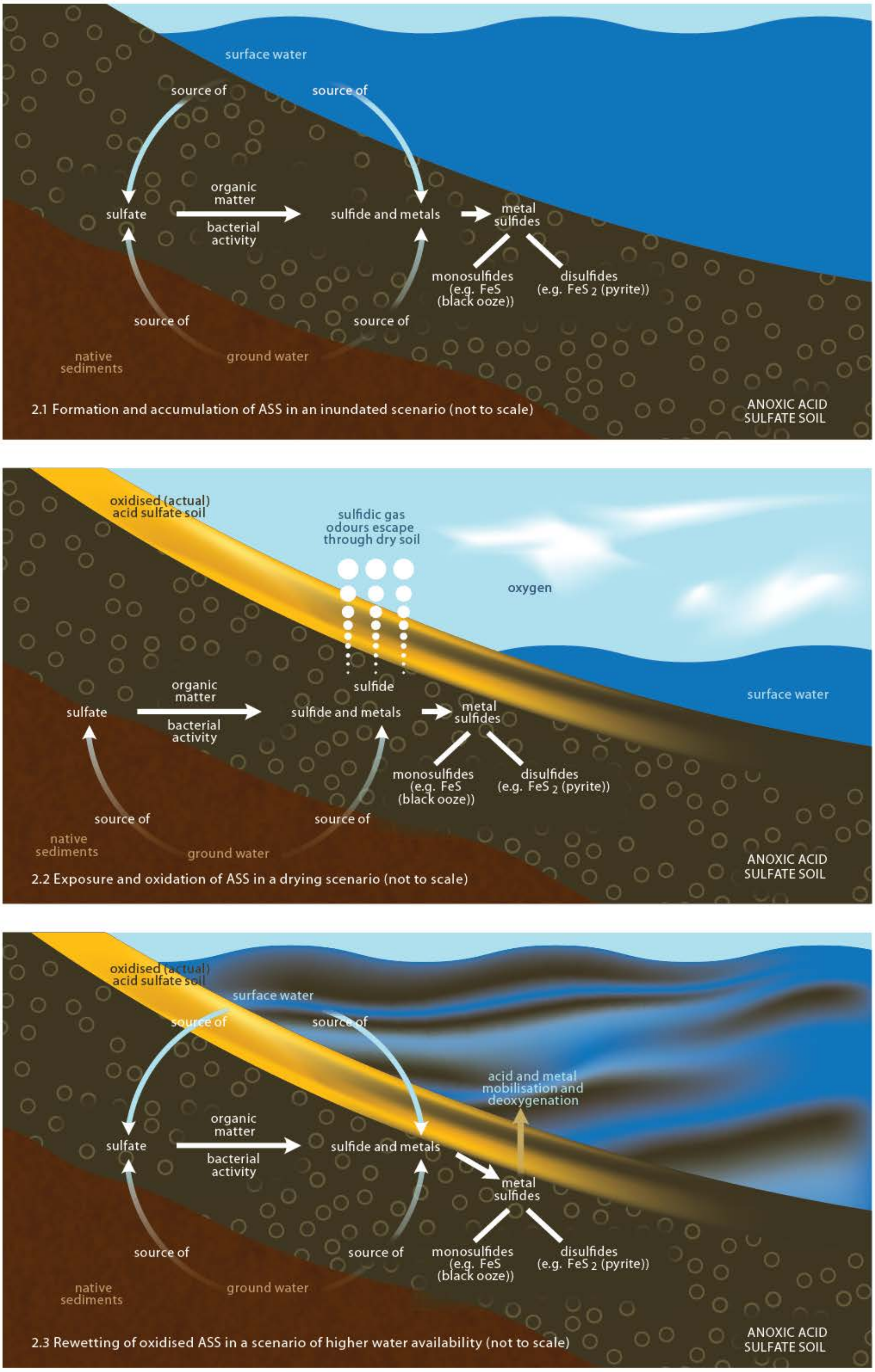


Figure A-2. Conceptual model of an inland aquatic ecosystem (mesoscopic scale) with acid sulfate soil in a consecutive sequence (source: EPHC and NRMMC 2011).

A2. Acid sulfate soil processes in the Lower Lakes

Lamontagne *et al.* (2004) produced a conceptual model of sulfide formation in the River Murray wetlands and the potential reactions following disturbance (Figure A-3).

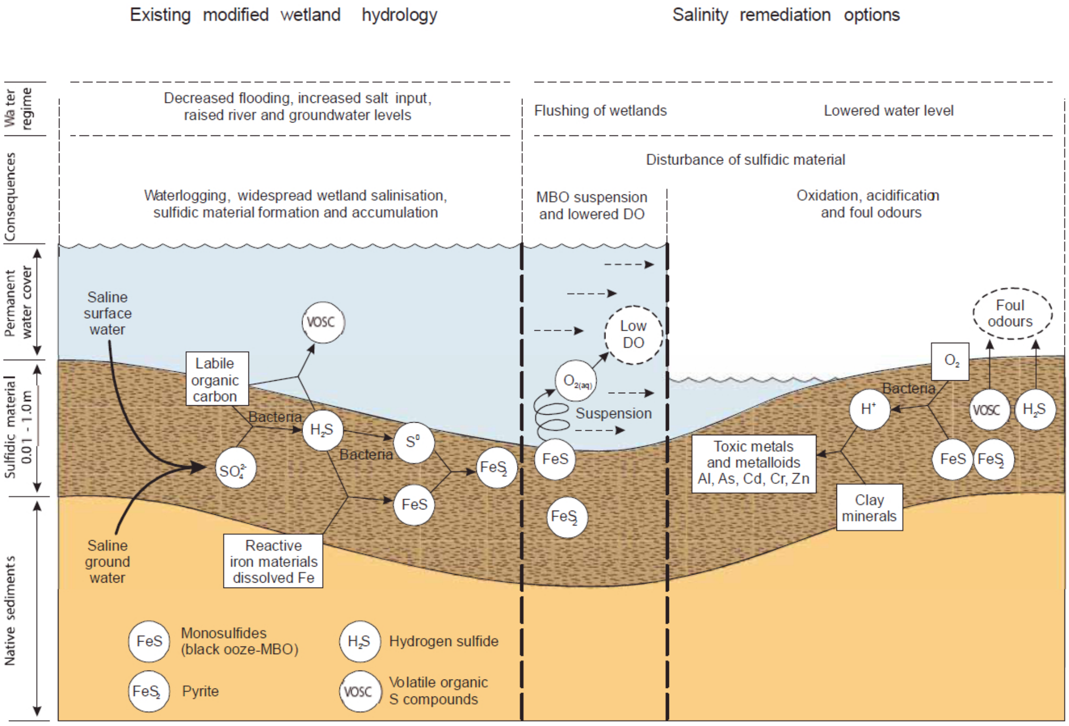


Figure A-3. Conceptual model of sulfide formation in the River Murray wetlands and the potential reactions following disturbance (source: Lamontagne *et al*. 2004. Copyright CSIRO).

Sullivan *et al.* (2012b) developed a conceptual diagram of the sulfur cycle operating in the upper layers of the bioremediated inundated Lower Lakes sediments (Figure A-4).

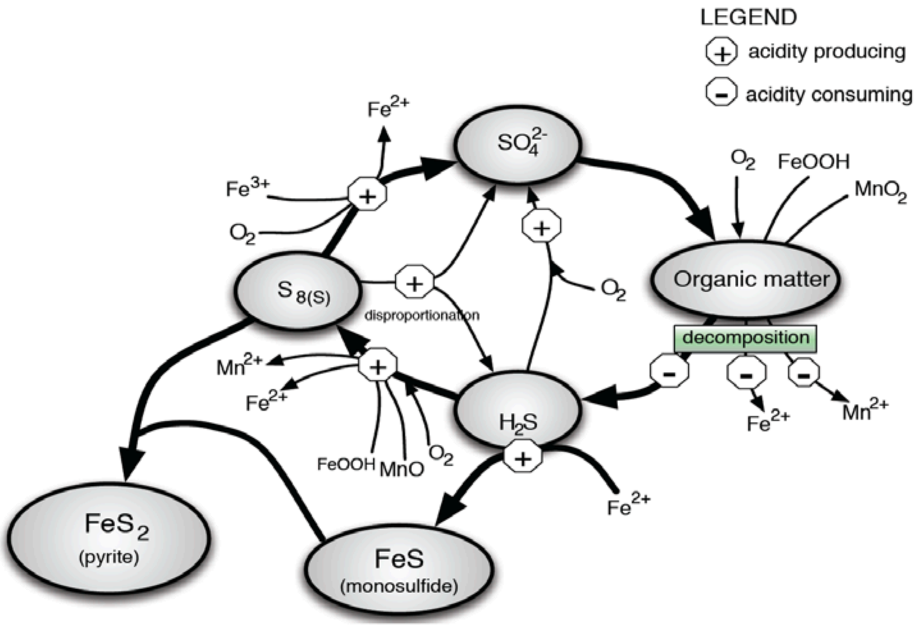


Figure A-4. Conceptual diagram of sulfur cycle operating in the upper layers of the bioremediated inundated Lower Lakes sediments (source: Sullivan *et al.* 2012b).

Fitzpatrick *et al.* (2008c, 2009) produced a series of conceptual models for Lake Albert to illustrate acid sulfate soil (ASS) properties prior to and during the recent drought (Figures A-5 – A-8).

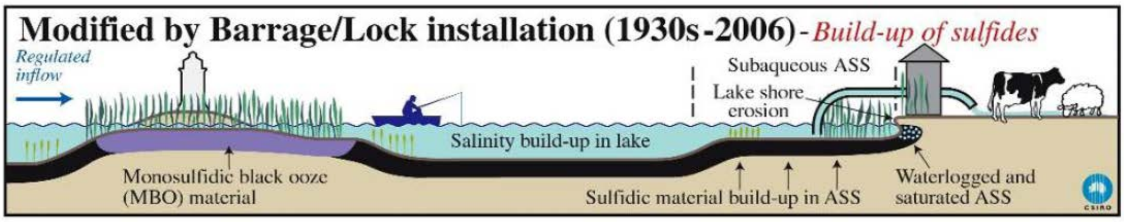


Figure A-5. Generalised schematic cross section model for Lake Albert; illustrating modification of water flows by barrage (and lock) installations causing the build up of sulfides under continuous subaqueous ASS conditions from 1930s-2006 (source: Fitzpatrick *et al.* 2008c. Copyright CSIRO).

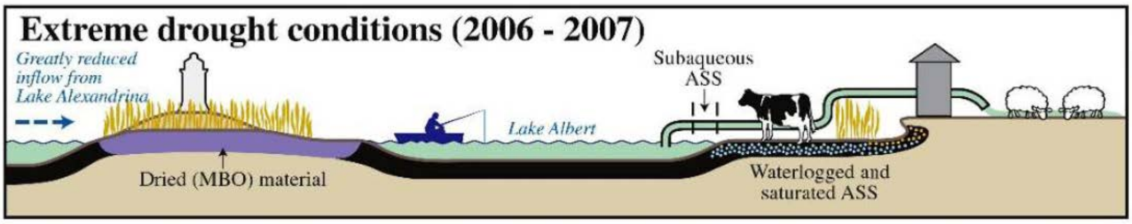


Figure A-6. Generalised schematic cross section model for Lake Albert, illustrating extreme drought conditions in 2006 – 2007 where subaqueous ASS transform to waterlogged ASS (i.e. ASS that are wet or saturated long enough to produce periodically anaerobic conditions, thereby influencing the growth of plants: e.g. hydric soils with sulfidic material) (source: Fitzpatrick *et al.* 2008c. Copyright CSIRO).

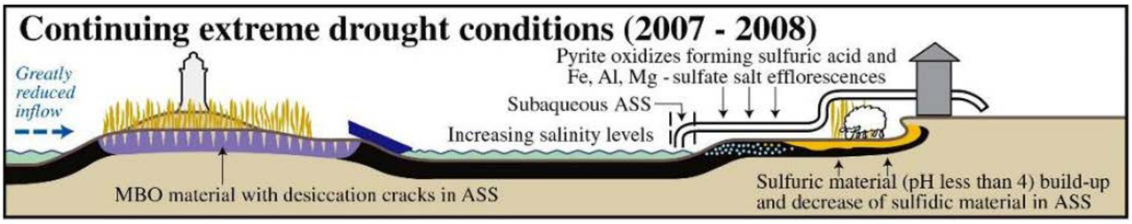


Figure A-7. Generalised schematic cross section model for Lake Albert; illustrating the formation of: (i) sulfuric material (pH <4) by oxidation of sulfides present in sulfidic material, (ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued lowering of water levels under persistent extreme drought conditions during 2007 – 2008 (source: Fitzpatrick *et al.* 2008c. Copyright CSIRO).

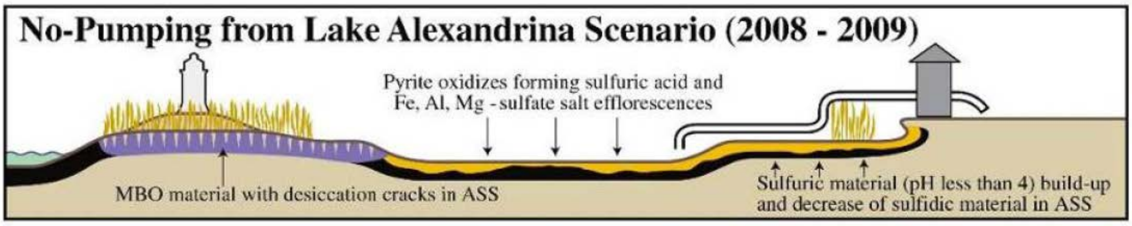
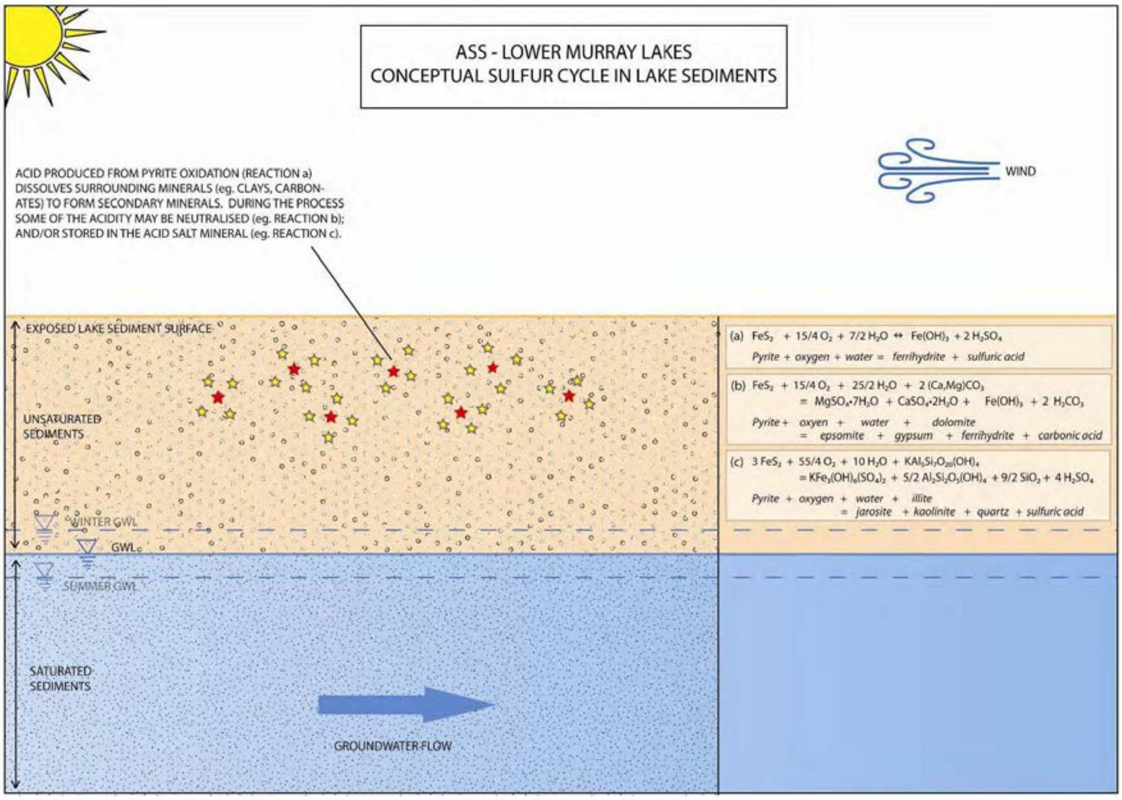


Figure A-8. Generalised schematic cross section model predicted for Lake Albert under a no-management scenario (e.g. no water pumping from Lake Alexandrina); illustrating the widespread formation of: (i) sulfuric material (pH <4) by oxidation of sulfides in sulfidic material, (ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued lowering of water levels under persistent extreme drought conditions during 2008 – 2009 (source: Fitzpatrick *et al.* 2008c. Copyright CSIRO).

Earth Systems (2010) produced a series of conceptual models to illustrate various aspects of sulfur cycling in the Lower Lakes sediments (Figures A-9 – A-12).



ACID PRODUCED FROM PYRITE OXIDATION (REACTION a) DISSOLVES SURROUNDING MINERALS (eg. CLAYS, CARBONATES) TO FORM SECONDARY MINERALS. DURING THE PROCESS SOME OF THE ACIDITY MAY BE NEUTRALISED (eg. REACTION b); AND/OR STORED IN THE ACID SALT MINERAL (eg. REACTION c).

(a) $FeS_2 + 15/4\,O_2 + 7/2\,H_2O \leftrightarrow Fe(OH)_3 + 2\,H_2SO_4$

Pyrite + oxygen + water = ferrihydrite + sulfuric acid

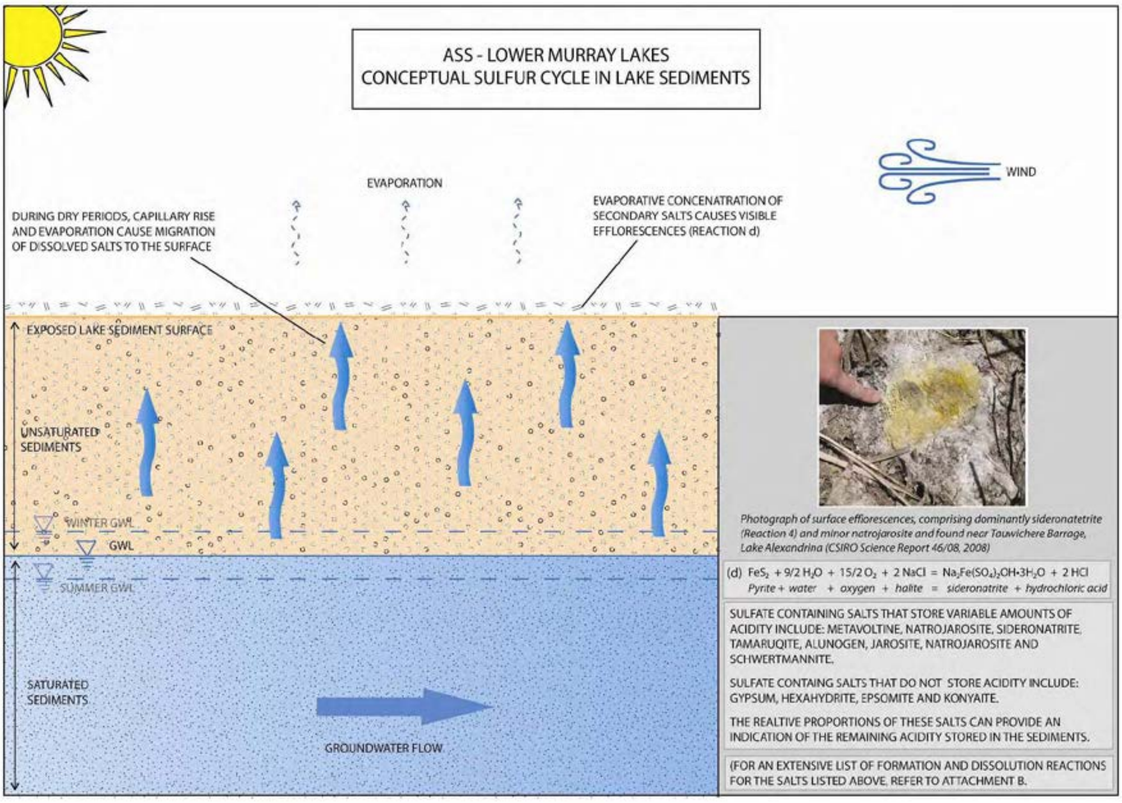
(b) $FeS_2 + 15/4\,O_2 + 25/2\,H_2O + 2\,(Ca,Mg)CO_3$
$= MgSO_4{\cdot}7H_2O + CaSO_4{\cdot}2H_2O + Fe(OH)_3 + 2\,H_2CO_3$

Pyrite + oxyen + water + dolomite
= epsomite + gypsum + ferrihydrite + carbonic acid

(c) $3\,FeS_2 + 55/4\,O_2 + 10\,H_2O + KAl_5Si_7O_{20}(OH)_4$
$= KFe_3(OH)_6(SO_4)_2 + 5/2\,Al_2Si_2O_5(OH)_4 + 9/2\,SiO_2 + 4\,H_2SO_4$

Pyrite + oxygen + water + illite
= jarosite + kaolinite + quartz + sulfuric acid

Figure A-9. Conceptual diagram of sulfur cycle operating Lower Lakes sediments (1 of 4) (source: Earth Systems 2010).



DURING DRY PERIODS, CAPILLARY RISE AND EVAPORATION CAUSE MIGRATION OF DISSOLVED SALTS TO THE SURFACE

EVAPORATIVE CONCENATRATION OF SECONDARY SALTS CAUSES VISIBLE EFFLORESCENCES (REACTION d)

Photograph of surface efflorescences, comprising dominantly sideronatetrite (Reaction 4) and minor natrojarosite and found near Tauwichere Barrage, Lake Alexandrina (CSIRO Science Report 46/08, 2008)

(d) $FeS_2 + 9/2\,H_2O + 15/2\,O_2 + 2\,NaCl = Na_2Fe(SO_4)_2OH{\cdot}3H_2O + 2\,HCl$
Pyrite + water + oxygen + halite = sideronatrite + hydrochloric acid

SULFATE CONTAINING SALTS THAT STORE VARIABLE AMOUNTS OF ACIDITY INCLUDE: METAVOLTINE, NATROJAROSITE, SIDERONATRITE, TAMARUQITE, ALUNOGEN, JAROSITE, NATROJAROSITE AND SCHWERTMANNITE.

SULFATE CONTAING SALTS THAT DO NOT STORE ACIDITY INCLUDE: GYPSUM, HEXAHYDRITE, EPSOMITE AND KONYAITE.

THE REALTIVE PROPORTIONS OF THESE SALTS CAN PROVIDE AN INDICATION OF THE REMAINING ACIDITY STORED IN THE SEDIMENTS.

(FOR AN EXTENSIVE LIST OF FORMATION AND DISSOLUTION REACTIONS FOR THE SALTS LISTED ABOVE, REFER TO ATTACHMENT B.

Figure A-10. Conceptual diagram of sulfur cycle operating Lower Lakes sediments (2 of 4) (source: Earth Systems 2010).

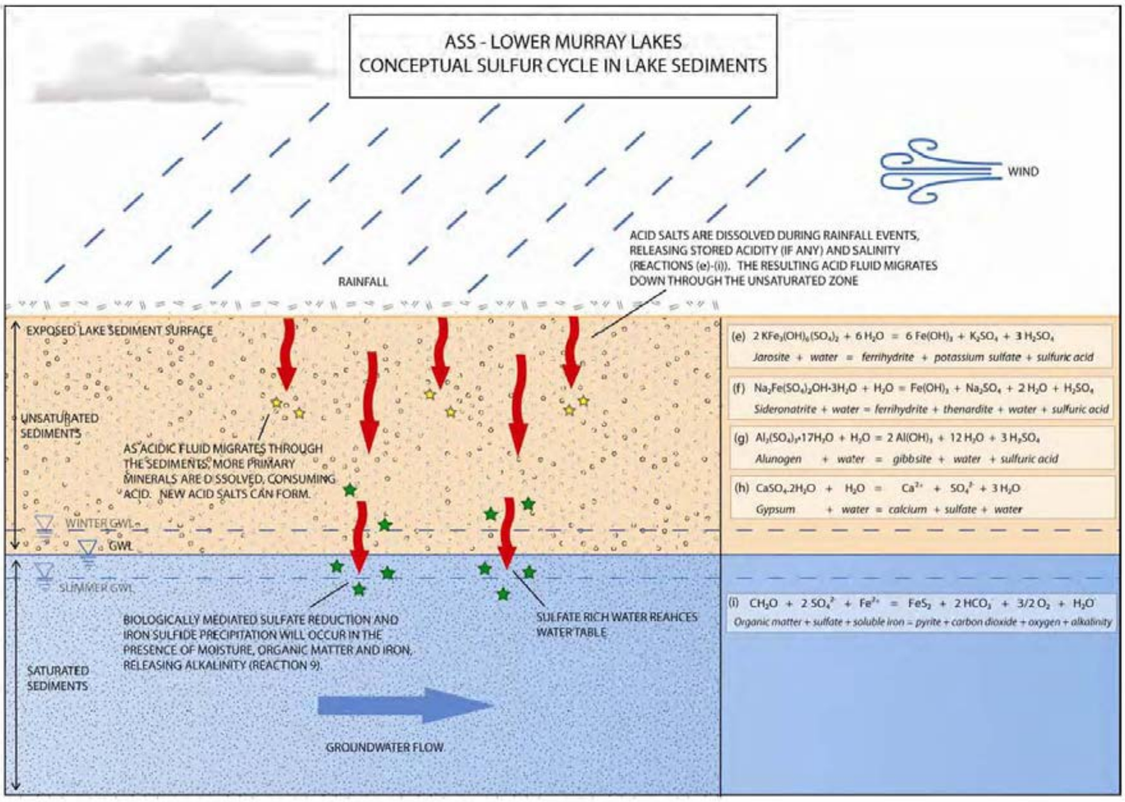


Figure A-11. Conceptual diagram of sulfur cycle operating Lower Lakes sediments (3 of 4) (source: Earth Systems 2010).

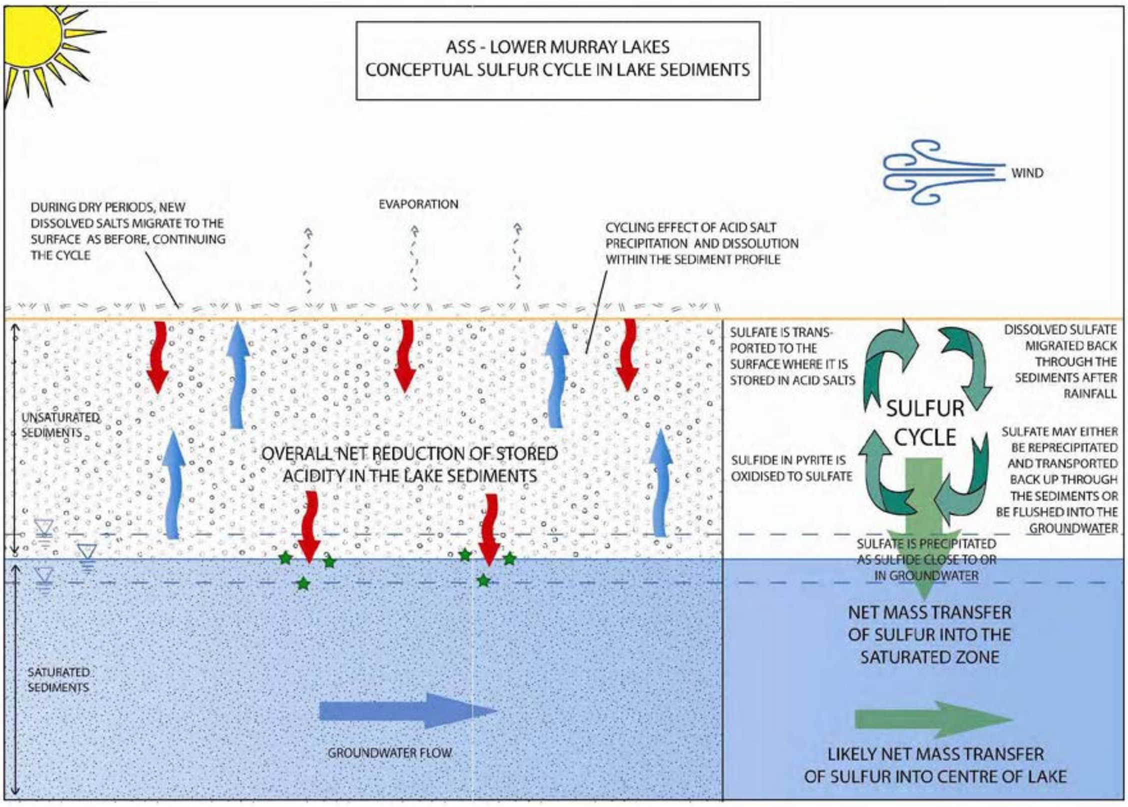


Figure A-12. Conceptual diagram of sulfur cycle operating Lower Lakes sediments (4 of 4) (source: Earth Systems 2010).

Hipsey *et al.* (2010) presented a conceptual overview of the main factors contributing to acidity in the Lower Lakes system (Figure A-13).

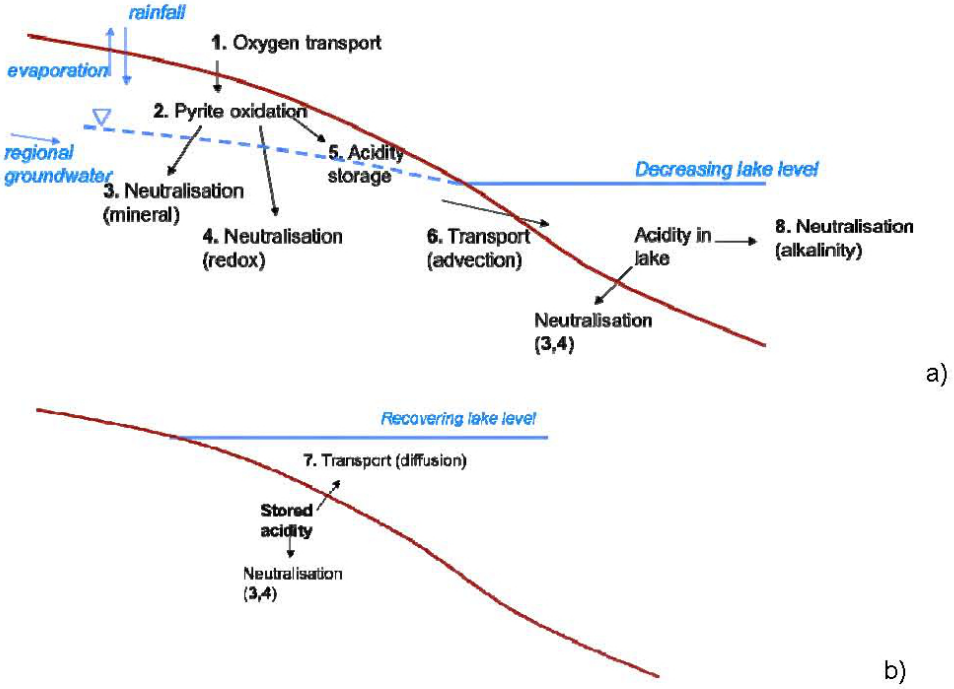


Figure A-13. a) Processes involved in acid generation and fate as lake water levels recede, b) additional process upon re-wetting of previously exposed sediments: diffusive transport of stored acidity back into the water column (source: Hipsey *et al.* 2010).

Hipsey *et al.* (2010) produced a conceptual model of acid generation and transport processes for the drying phase and the wetting phase (Figure A-14).

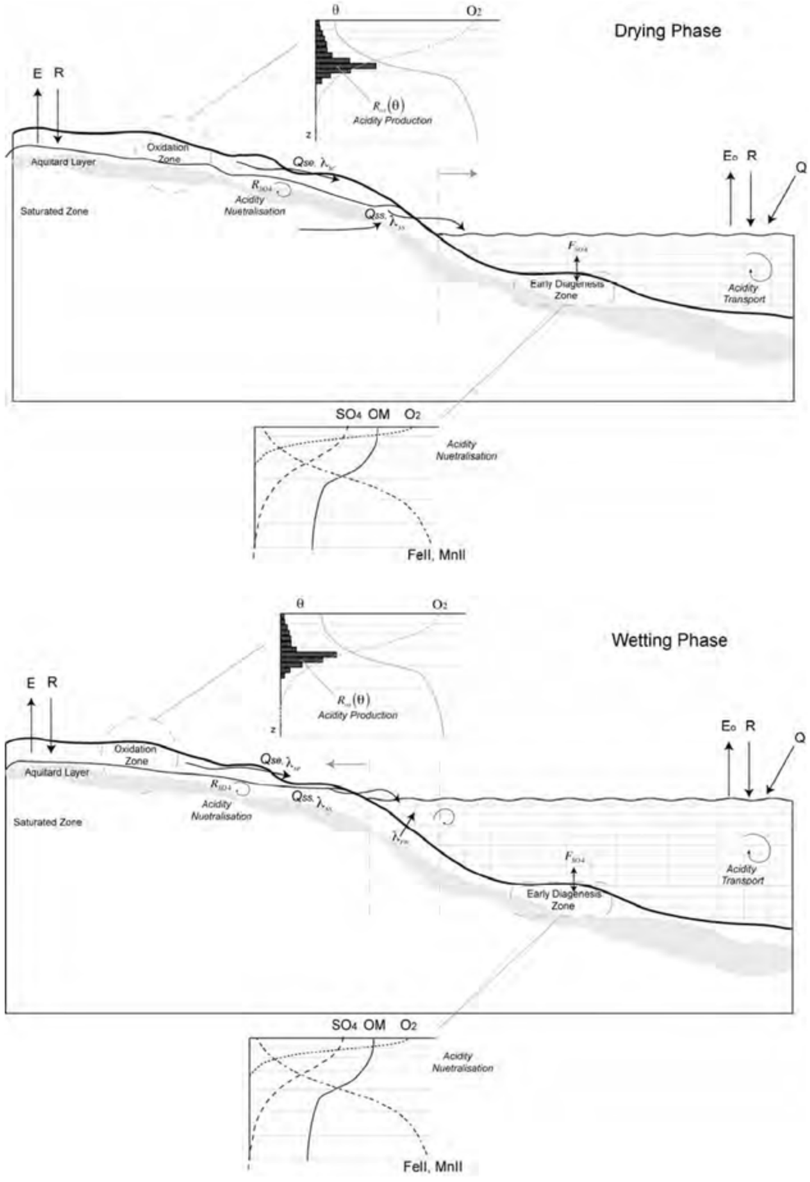


Figure A-14. Conceptual model of acid generation and transport processes for the drying phase (top) and the wetting phase (bottom). Notation: E = evaporation; R = rainfall; Q = general inflows coming to the lake; SO_4 = dissolved sulfate concentration; OM = organic matter; FeII = dissolved iron; MnII = dissolved manganese; Θ = soil moisture; O_2 = oxygen concentration; Qse= saturation excess flow; Qss= seepage flow; RSO_4= acidity consumption via SO_4 reduction; Rox= pyrite oxidation; FSO_4= acidity consumption by SO_4 reduction in lake sediments; R*rw*= flux of acidity from acidified sediment following rewetting (source: Hipsey *et al.* 2010).

Hipsey *et al.* (2010) produced a conceptual outline of the coupled hydrodynamics-biogeochemical-acid sulfate soil model as configured to the Lower Lakes simulations (Figure A-15).

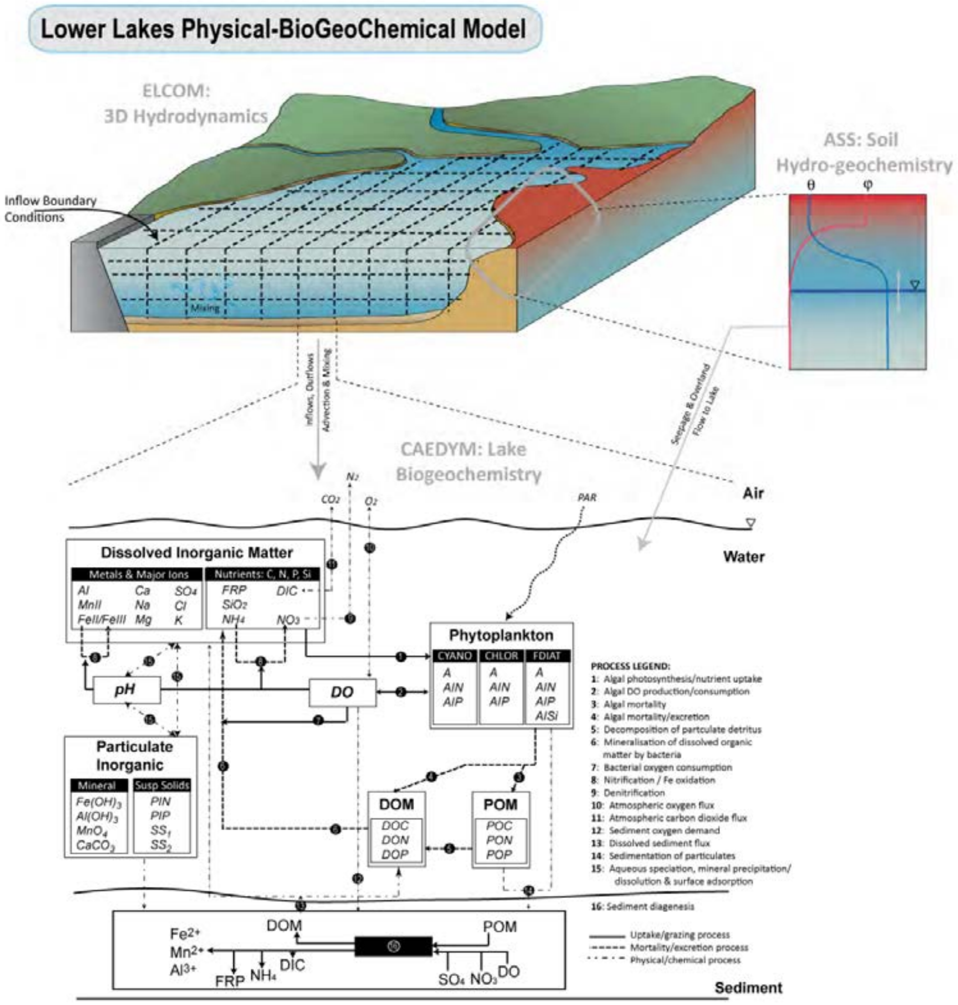


Figure A-15. Conceptual outline of the coupled hydrodynamics-biogeochemical-acid sulfate soil model as configured to the Lower Lakes simulations (source: Hipsey *et al.* 2010).

A3. General acid sulfate soil conceptual models

A geochemical conceptual model summarising the sedimentary iron transformations observed in coastal lowland acid sulfate soil associated waterways has been developed by Burton *et al.* (2006d) (Figure A-16). This model shows the pathways to the formation of a variety of minerals which are also commonly found in inland acid sulfate soil landscapes, including schwertmannite ($Fe_8O_8(OH)_6(SO_4)$), goethite ($\alpha FeOOH$), mackinawite (FeS), siderite ($FeCO_3$) and pyrite (FeS_2) (e.g. Fitzpatrick and Shand 2008). Mackinawite (FeS) is commonly found associated with monosulfidic black oozes (MBO).

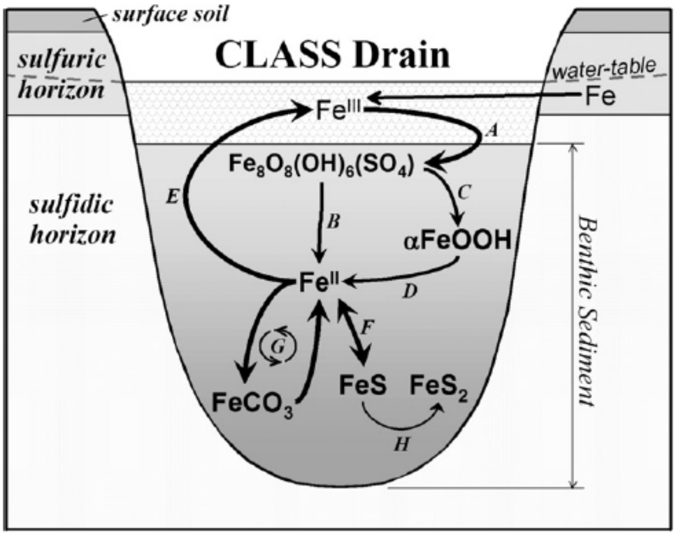


Figure A-16. Conceptual model of in-situ iron transformations in accreting coastal lowland acid sulfate soil drain sediments. (A) precipitation of schwertmannite ($Fe_8O_8(OH)_6(SO_4)$), (B) reductive dissolution of schwertmannite, (C) transformation of schwertmannite to goethite ($\alpha FeOOH$), (D) reductive dissolution of goethite, (E) upward diffusion and oxidation of Fe^{II}, (F) precipitation-dissolution of disordered mackinawite (FeS), (G) regulation of pore-water Fe^{II} via precipitation-dissolution of siderite ($FeCO_3$), (H) and formation of pyrite (FeS_2; kinetically retarded due to high pore-water Fe^{II} concentrations) (source: Burton *et al.* 2006d).

CSIRO Land and Water developed a conceptual model to explain four sequential drying phases and the development of different acid sulfate soil (ASS) subtypes that occur: deep water sulfidic ASS; subaqueous ASS; waterlogged and saturated ASS, and; drained and unsaturated ASS (Figure A-17).

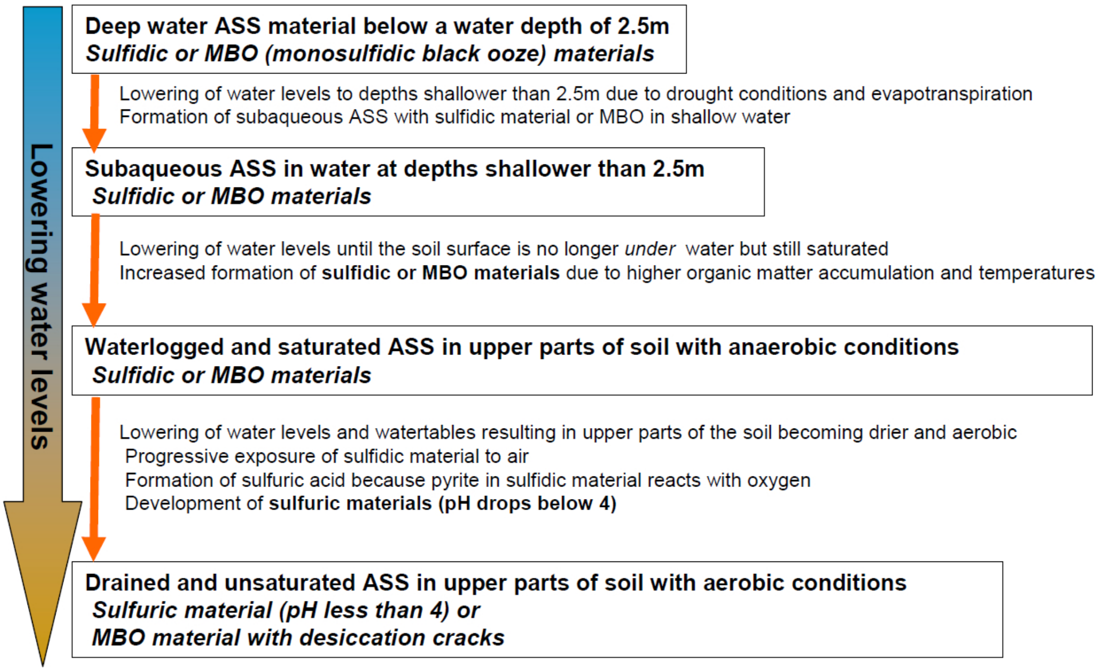


Figure A-17. Generalised conceptual model showing the sequential transformation of four Classes of ASS due to lowering of water levels (source: Fitzpatrick *et al.* 2008a. Copyright CSIRO).

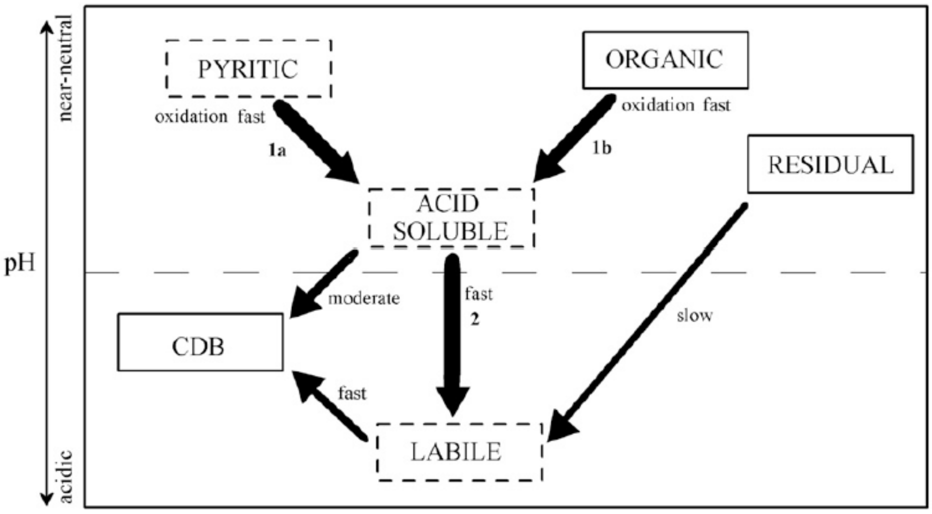


Figure A-18. Conceptual diagram showing metal mobilisation pathways and indicative dynamics between sequential extraction pools in sulfidic sediments. (Labile fraction - soluble species and exchangeable metal ions; CBD – crystalline oxide fraction) (source: Claff *et al.* 2011).

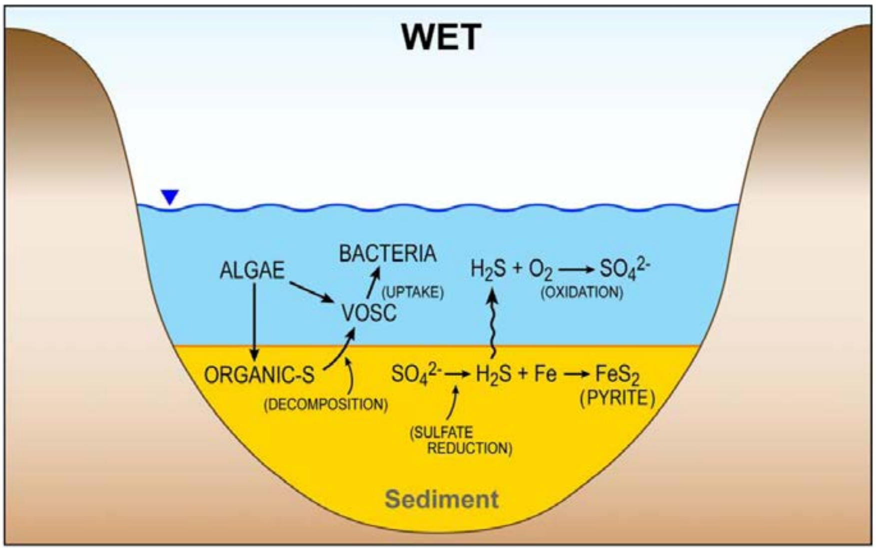


Figure A-19. Sulfur cycling in wetlands under wet conditions showing the major pathways for sulfur transformations (source: Hicks and Lamontagne 2006. Copyright CSIRO).

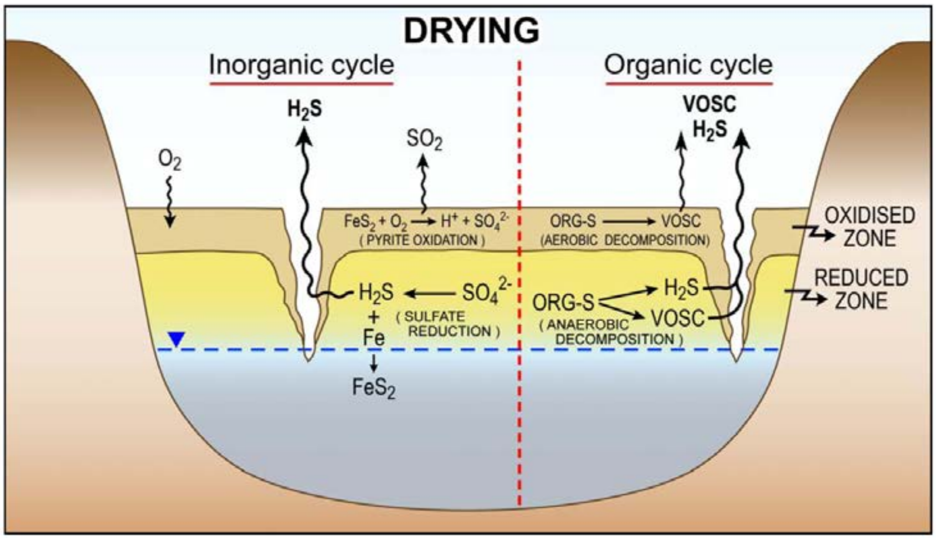


Figure A-20. Sulfur cycling in wetlands under drying conditions showing the major pathways for sulfur transformations (source: Hicks and Lamontagne 2006. Copyright CSIRO).

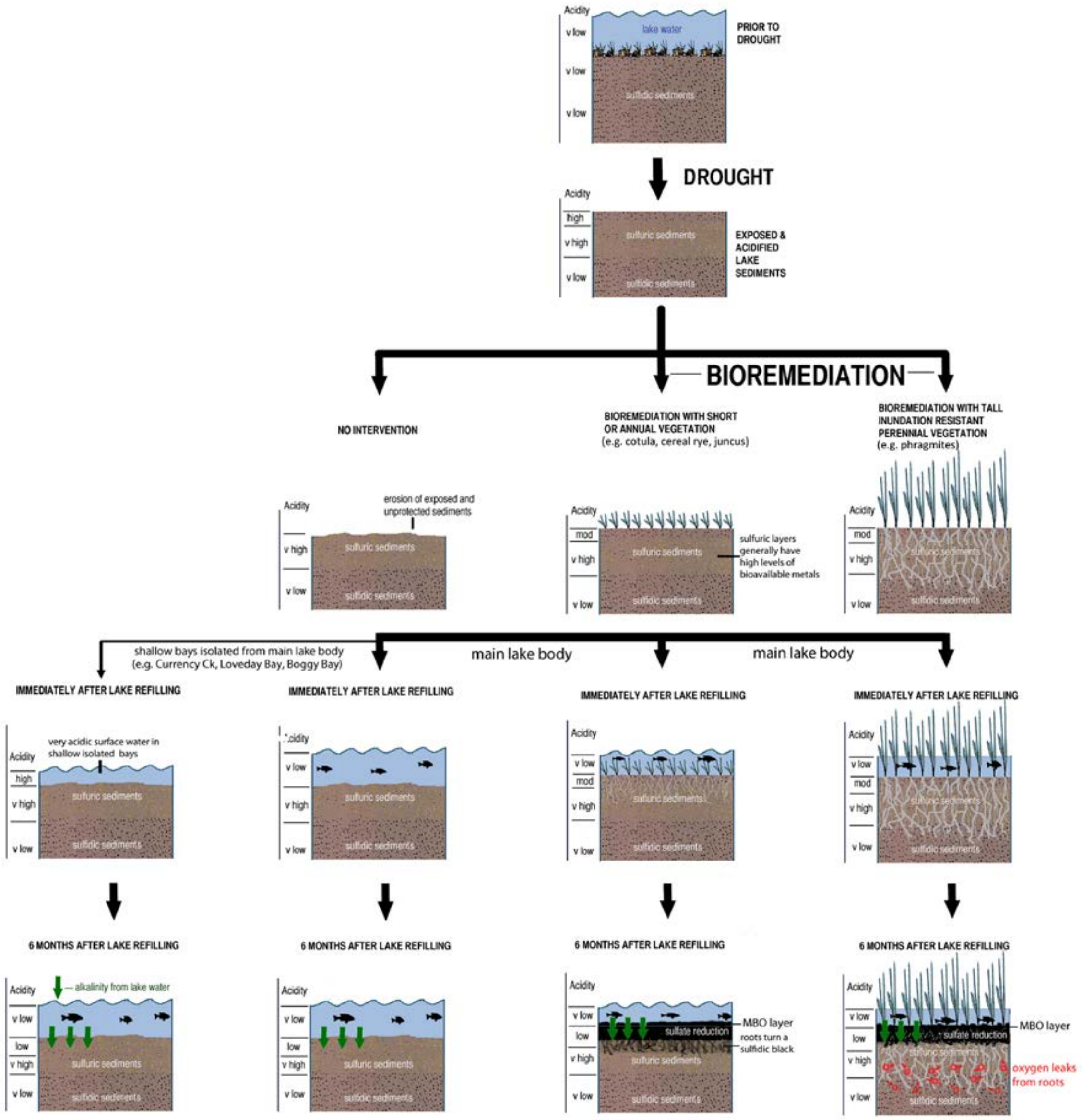


Figure A-21. Conceptual diagram of sulfur cycling and acidity as affected by bioremediation (source: Sullivan *et al.* 2011).

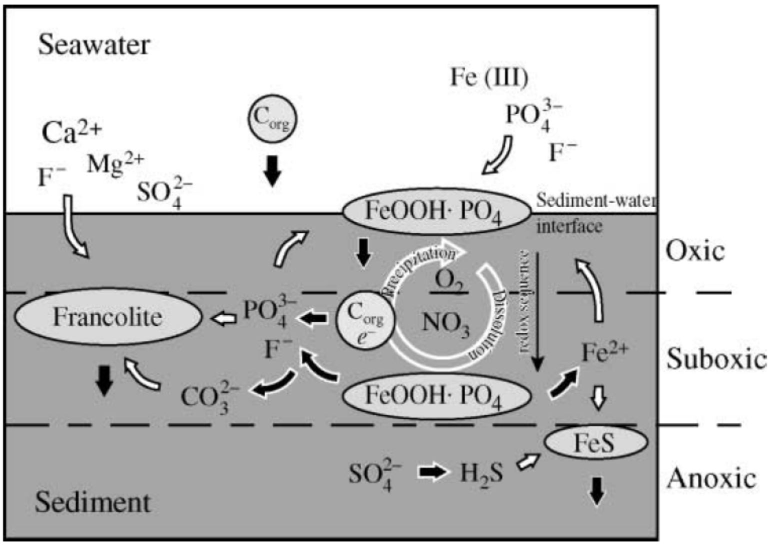


Figure A-22. Conceptual diagram of the coupled iron and phosphate cycles during early diagenesis in marine sediments. Light grey ovals and circles represent solid phases, black arrow are solid-phase fluxes. White-outlined black arrows indicate reactions, white arrows are diffusion pathways (source: Ruttenberg *et al*. 2003).

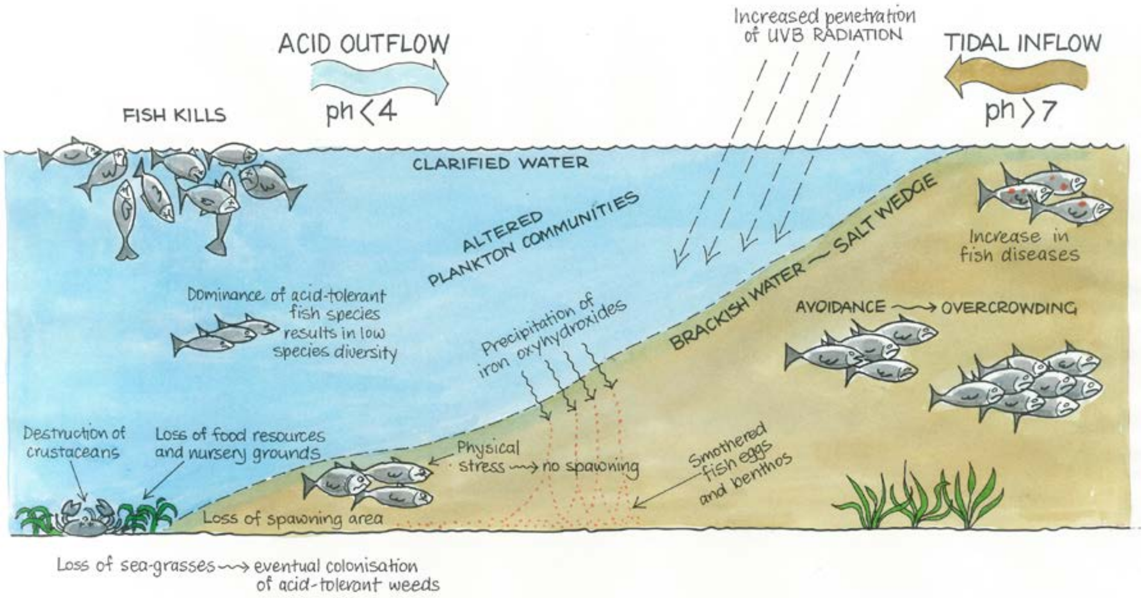


Figure A-23. Illustration summarising potential acid sulfate soil impacts on fish and aquatic life (source: Sammut 2000. Art work by Jenni Binns).

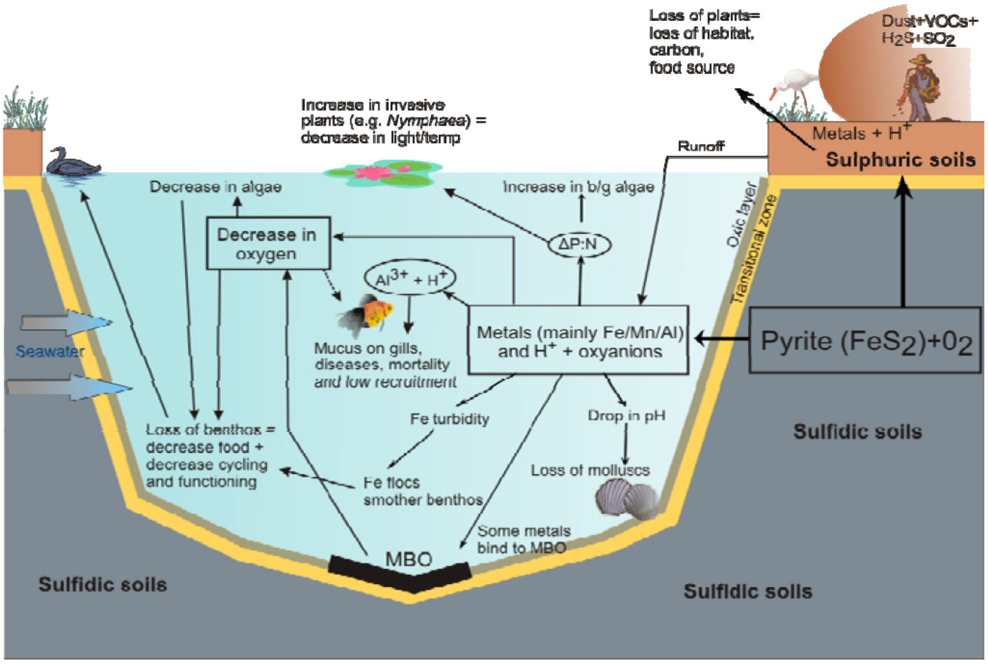


Figure A-24. Conceptual model of potential acid sulfate soil impacts in the Lower Lakes (source: Stauber *et al.* 2008. Copyright CSIRO).


Southern Cross
GeoScience