

CHAPTER 3. ACID SULFATE SOILS

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INTRODUCTION

The diversity of acid sulfate soil (ASS) types in the Riverland and Murraylands of South Australia (RMS) is attributable to the wide variety of soil forming factors and landscape types in the region. These varied soil forming factors are expressed over a wide range of: (i) natural environments (geology, climate, vegetation, fresh and saline water conditions), (ii) anthropogenic modified environments (modifications from barrages, locks, blocking banks, weirs and abandoned pyrite mines) and (iii) changing climatic environments that exist now (drought triggered and winter rainfall events).

Sulfide minerals, predominantly pyrite (FeS₂), form soil sulfidic materials, and accumulate in ASS: (i) in marine environments, (ii) under fresh water conditions naturally, and where permanent ponding of wetlands, lakes and disposal ponds has occurred following construction of barrages and locks and (iii) in areas where contemporary clearing of native vegetation has caused the rising of the water table and discharge of saline groundwater. Changes to the hydrology in regulated sections of the Murray-Darling Basin (MDB) system (due to higher weir pool levels) has allowed significant accumulation of sulfidic material in subaqueous and marginal soils. If left undisturbed and covered with water, sulfidic materials pose little or no risk of acidification. However, when exposed to the air, the sulfides present react with oxygen to form sulfuric acid and often form sulfuric materials (i.e. soil materials with pH < 4 caused by sulfide oxidation). When these sulfuric materials are subsequently covered with water, significant amounts of acidity can be released into the water.

Record low inflows and river levels over recent years (since 2006) have led to the drying of many wetlands, rivers and lakes in the MDB, resulting in the exposure of sulfidic material and consequent soil acidification. The extent of the threat posed by ASS has required urgent assessment by CSIRO and others from June 2007 to the present. Despite decades of scientific investigation of the ecological (e.g. Living Murray Icon Site Environmental Management Plan: MDBC, 2006a,b), hydrological (salinity), water quality and geological features of wetlands in the MDB, we have only recently begun to appreciate the wide spectrum of inland ASS subtypes and processes that are operating in these contemporary environmental settings, especially from rising saline groundwater in discharge areas (e.g. Fitzpatrick 1991; Fitzpatrick et al. 1993, 1996) and lowering of water levels (e.g. Lamontagne et al. 2004, 2006; Hall et al. 2006; Baldwin et al. 2007; Fitzpatrick et al. 2008a,b,e,f,g,h, 2009; Fitzpatrick & Shand 2008; Shand et al. 2008b,c; Simpson et al. 2008).

The purpose of this chapter is to summarise available information on the diversity of ASS in the RMS. Across much of the RMS region, there have been wide-ranging and fundamental shifts in the "environmental equilibrium" brought about by the impact of European settlement. These changes include large scale clearing of native vegetation, building of locks and barrages to contain water flow, and over-allocation of irrigation water. These changes have been exacerbated by extreme drought conditions since 2006, which have lowered water levels in rivers, lakes and wetlands. The effects of these changes have provided the unique opportunity to study the various transformations of materials in inland ASS that arise from this disequilibrium (e.g. Fitzpatrick & Shand 2008). It is only over the past few years or so that the existence, extent and significance of inland ASS has been fully realised. The nature, type and distribution of inland ASS, the environments in which they occur (e.g. upland saline seepages, wetlands, rivers/ stream channels and lakes), and the potential impacts on surrounding ecosystems make them more complex than their coastal equivalents. A wide range of case studies is summarised in this chapter to illustrate the distribution, processes, environmental hazards and remediation options of coastal and inland ASS environments in this region, which includes: river channels (Murray and Finnis), creeks (Currency), lakes (Alexandrina, Albert and Bonney), wetlands, evaporation basins, billabongs, seepages overlying mineralized zones and ground water systems. Simplified coloured cross-sectional diagrams and photographs are used to illustrate the major soil-regolith-water processes involved and how specific types of ASS susceptible to land

degradation may be recognised. These diagrams have also been used to help community groups to understand complicated scientific processes and terminology, and how this information can be used to underpin best management practices for ASS.

NATURE AND PROPERTIES OF ACID SULFATE SOILS

Acid sulfate soils (ASS) is the name given to all those soils containing soil materials with sulfide minerals or affected by transformations of iron sulfide minerals. These soils may either contain sulfuric acid or have the potential to form sulfuric acid in amounts that have an effect on the main soil characteristics (Pons 1973; Dent 1986; Dent & Pons 1995). Other potential hazards include deoxygenation of soil or surface waters or the release of contaminants when the sulfide minerals are exposed to oxygen. In general, the following three broad genetic soil materials in ASS are recognized (e.g. Fanning 2002):

- Sulfuric material (pH < 4) containing sulfuric acid (may also contain iron sulfide minerals) at shallow depths (Fig. 1; see glossary for definition). These materials were previously referred to as actual, active or raw ASS materials.
- Sulfidic, hypersulfidic (Fig. 1) or hyposulfidic materials containing mainly iron sulfide minerals (FeS_2) (see glossary for definitions), previously called potential or unripe ASS materials.
- Monosulfidic materials (Fig. 2), which contain dominantly monosulfide minerals (FeS) that are still waterlogged (see glossary for definitions). A previous term used was monosulfide black ooze (MBO).

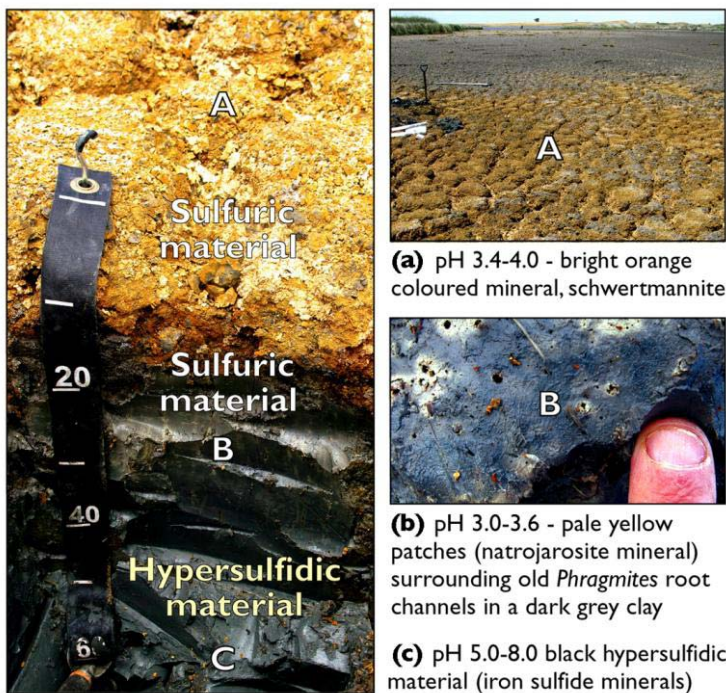


Figure 1. Photograph of a typical acid sulfate soil in an exposed dry river bed of the Finnis River, showing: (a) sulfuric material on the surface with the orange-yellowish precipitate schwertmannite [$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$]; (b) sulfuric material in the subsurface soil where pale yellow patches or mottles occur with the mineral natrojarosite [$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$]; and (c) black hypersulfidic material in the subsoil (From Fitzpatrick et al. 2009).

Iron sulfide minerals are one of the end products that form as part of the process of sulfate reduction (i.e. the use of SO_4^{2-} during microbial respiration, Fig 3). Sulfate reduction is a natural process that occurs in virtually all lakes, rivers, wetlands and oceans.

However, the quantities of sulfide minerals that will accumulate in a given environment are a function of many factors. The requirements for high rates of sulfate reduction and sulfide accumulation are:

- High concentrations of dissolved sulfate.
- Saturation of soils and sediments for periods long enough to favour reducing conditions (i.e. subaqueous and waterlogged soils – see glossary).
- Availability of labile carbon to fuel microbial activity.
- Availability of dissolved Fe or Fe containing minerals.



Figure 2. Monosulfidic material (or monosulfidic black ooze: MBO), in acid sulfate soil exposed in a shallow back swamp/wetland (Paiwalla wetland adjacent to the Murray River; Site E4 in Fig. 5; Fitzpatrick et al. 2008f). Monosulfidic material, if mobilized in water bodies, is able to rapidly remove dissolved oxygen from that water.

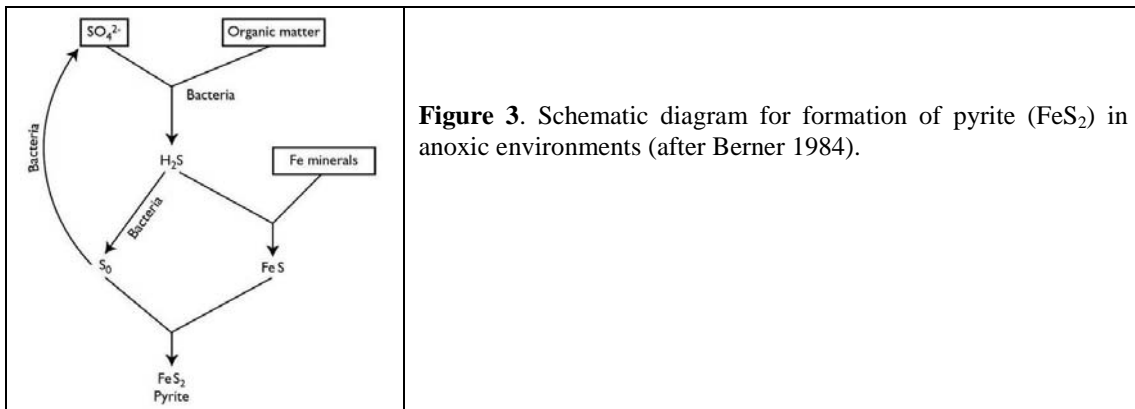


Figure 3. Schematic diagram for formation of pyrite (FeS_2) in anoxic environments (after Berner 1984).

Soil materials that contain sulfides and are capable of acidifying to sulfuric materials are called hypersulfidic materials (see glossary), which can be environmentally damaging if exposed to air by disturbance. Exposure results in the oxidation of pyrite, with each mole of pyrite yielding 4 moles of acidity (i.e. 2 moles of sulfuric acid). This process transforms hypersulfidic material to sulfuric material when, on oxidation, the material develops a pH of 4 or less (Isbell 1996); note that a sulfuric horizon has a pH of 3.5 or less according to the US definition in Soil Survey Staff (1999, 2003).

The weathering of pyrite starts with exposure of pyrite to oxygen (in air). Pyrite is usually stable if submerged in water under reducing conditions. In general, it is the exposure of fine grained pyritic framboids (from the French framboise meaning raspberry) (Fig. 4) to repeated wetting/drying cycles and the action of bacteria present near the soil surface that generates sulfuric acid. The complex details of the oxidation process and formation of sulfuric materials are described by several workers (e.g. Fanning & Fanning 1989; Nordstrom & Alpers 1999; Bigham et al. 1990, 1996, 2000, 2002; Fanning 2002). When hypersulfidic materials containing sulfides and low contents of acid neutralizing minerals (e.g. calcite) are exposed to air by drainage or excavation, they become strongly acidic sulfuric materials, and a serious acid-drainage problem may develop. Acidification occurs if the amount of acidity produced exceeds the buffering capacity of soil. In sulfuric materials, the products of the chemical reactions can: (i) remain as dissolved constituents of pore waters, (ii) form a range of secondary minerals in the form of salt efflorescences comprising sulfate-rich salts due to evaporation (e.g. epsomite and hexahydrate), (iii) undergo a series of hydrolysis reactions and precipitate new minerals such as iron oxyhydroxides and iron oxyhydroxysulfates (e.g. jarosite, natrojarosite, schwertmannite and sideronatrite) and (iv) propagate pedogenic weathering cycles. Hence, the various products or minerals may or may not be present at a given site on a given day depending on weather conditions. These minerals are important to recognize because they store acidity and metals that can subsequently generate poor water quality. Several studies have shown that dissolution of salt accumulations along stream banks during a rainstorm temporarily lowers pH and increases metal loads in streams (e.g. Bigham et al. 1996). Such water quality impacts can have damaging effects on

aquatic ecosystems e.g. causing fish kills, and can complicate efforts to remediate acid drainage. Rainfall events can also flush salts, leading to pulses of contaminated water flowing into streams.

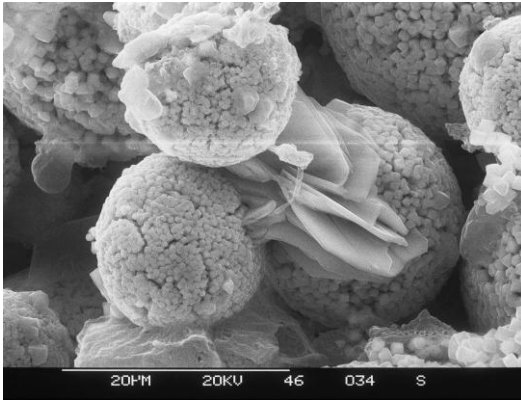


Figure 4. Scanning electron micrographs of: (i) rounded pyrite “framboids” (up to 20 µm diameter) and (ii) large platelets of sideronatrite $[\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot \text{OH} \cdot 3\text{H}_2\text{O}]$ derived from the oxidation and dissolution of pyrite crystals in an acid sulfate soil from the upper Dairy Creek catchment in the Mt. Lofty Ranges (Site G3 in Fig. 5). Imaging was performed using Secondary Electron mode. From Fitzpatrick et al. (2000).

Evidence that low pH is caused by oxidation of sulfides within a soil profile is provided by one of the following:

- Pale yellow (straw coloured) mottles and coatings of jarosite or natrojarosite [see (a) in Fig. 1]; orange-yellowish coatings of schwertmannite [see (b) in Fig. 1], bright yellowish-green coatings of sideronatrite [see (c) and (d) in Fig. 8 and Fig. 4] and the distinct golden yellowish or greenish crystals of metavoltine $[\text{K}_2\text{Na}_6\text{Fe}^{2+}\text{Fe}^{3+}_6(\text{SO}_4)_{12}\text{O}_2 \cdot 18\text{H}_2\text{O}]$ (e.g. see Fig. 30) indicating the presence of sulfuric material (pH <4). Schwertmannite was first sampled and identified in inland ASS in the Mount Lofty Ranges, South Australia in 1990 (Fitzpatrick et al. 1992; 1993; 1996; Fitzpatrick & Self 1997; see page 53 in Fitzpatrick & Shand 2008, which shows a photograph of the original field site near Mt Torrens with Professor Schwertmann after whom the mineral schwertmannite is named).
- Underlying grey to black hypersulfidic material [see (c) in Fig. 1] that during the slow drying process will react with oxygen from the air to form sulfuric material.

When ASS materials become strongly acidic, acid drainage water can be produced. This acid together with associated bioavailable toxic elements (*inter alia* heavy metals, aluminium and other contaminants e.g. gases) contribute to environmental (soil, water, air), infrastructure (corrode concrete and steel) and mining issues. These impacts can be measured in terms of:

- Poor water quality with loss of amenity, damage to estuarine environments and reduction in wetland biodiversity.
- The need for rehabilitation of disturbed areas to improve water quality and minimise impacts.
- Loss of fisheries and agricultural production.
- Additional maintenance of community infrastructure affected by acidic corrosion.

In summary, ASS materials may occur in subaqueous, waterlogged and drained conditions in coastal, inland, mine spoil and wetland environments (see glossary). In Australia, ASS occupy an estimated 215,000 km² of which 58,000 km² is coastal ASS and 157,000 km² is inland ASS (Fitzpatrick et al. 2008a). In the coastal zone, 41,000 km² are exposed at some point during the tidal cycle, with the remaining 17,000 km² being permanently subaqueous. More than 126 km² of coastal ASS with sulfuric material have been mapped. The financial costs to infrastructure development and primary industries around Australia, due to ASS impacts and management are significant (\$10 billion in 2000: National Working Party on Acid Sulfate Soils, 2000). In the current agency structure in Australia, these issues often fall between jurisdictions (e.g. agriculture, environment, fisheries/oceans, water, atmosphere, mineral exploration and mining; see Fitzpatrick et al. 1998). However, public recognition of this serious problem has been reflected in government legislation in South Australia (Fitzpatrick et al. 2008), NSW, Qld and. In addition, there is much support from local government and industries to develop statutory requirements for rehabilitation.

Geographical Areas of Acid Sulfate Soils in the Riverland and Murraylands Region

Most of the Riverland and Murraylands region in SA (RMS) is underlain by limestone and stranded coastal dunes, which are also often calcareous (see Chapters 1 and 2 above). Nevertheless, a wide

distribution of ASS with sulfuric materials ($\text{pH} < 4$) has been identified in several areas throughout the RMS due to the oxidation of exposed sulfides in drying wetlands, rivers and lake systems caused by either drought conditions (2006 to 2009; e.g. Fitzpatrick & Shand 2008) and rising saline sulfate-rich groundwaters.

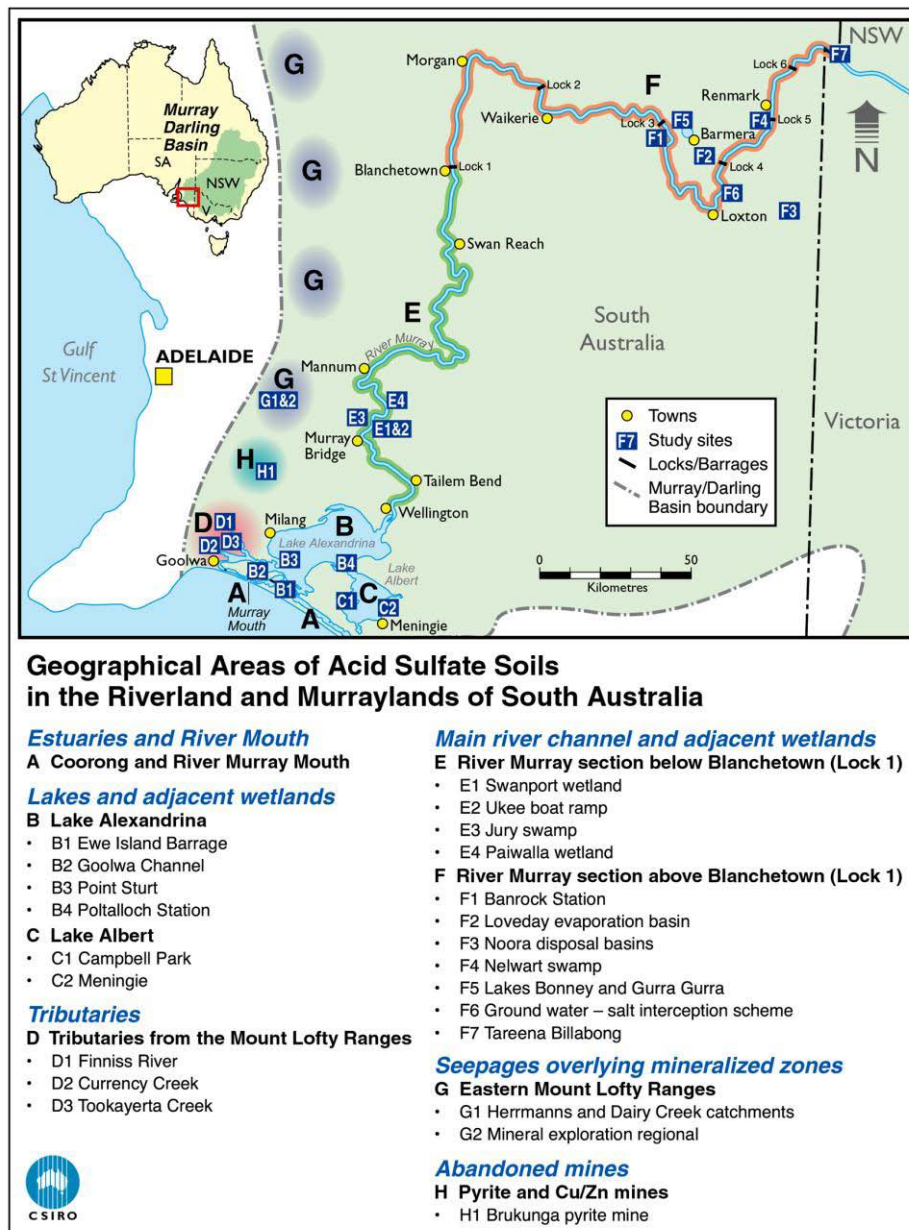


Figure 5. Map showing Geographical Areas and selected case study sites of Acid Sulfate Soils in the Riverland and Murraylands of South Australia (RMS).

The RMS region contains a remarkably wide range of types of ASS in different landscape settings or geographical areas (Fig. 5), which occur because of the diversity of geology and geomorphology, together with changing hydrological and biogeochemical conditions. As shown in Figure 5, the RMS has been subdivided into the following Geographical Areas of ASS, each with unique biogeochemical environments such as parent material, geomorphology, hydrology and soil materials (e.g. sands, clays and peats): (i) Estuaries and River Mouth comprising Coorong and Murray Mouth (Area A in Fig. 5) with dominant marine influence; (ii) Lakes and adjacent wetlands comprising Lake Alexandrina (B) and Lake Albert (C); (iii) Tributaries including those from the Mount Lofty Ranges (D); (iv) Main river channels and adjacent wetlands comprising the Murray River section below Blanchetown (E) and the Murray River section above Blanchetown (F) – with numerous billabongs, swamps, disposal evaporation basins, drains and lakes (e.g. Lake Bonney); (v)

Seepages overlying mineralized zones comprising the Eastern Mount Lofty Ranges (G); and (vi) Abandoned mines comprising waste rock stockpiles and tailing impoundments from pyrite, copper and zinc mines (H).

HISTORICAL BACKGROUND OF ACID SULFATE SOILS

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

Aboriginal peoples

Aboriginal peoples of Australia record creation stories (see Chapter 6 below) about the remarkable changes that occurred both when the sea level began rising 18,000 years ago and when the current sea level stabilised about 5,000 years ago. The creation stories and oral traditions of indigenous people have been passed down from generation to generation, especially about the detailed knowledge of the nurseries (i.e. wetlands – reed beds were much more extensive in the past), many of which contain inland Acid Sulfate Soils. For example, the Ngarrindjeri people believe the land and water is a living body and that they are a part of its existence (Ngarrindjeri Tendi et al. 2007). In the Ngarrindjeri Nation *Yarluwar-Ruwe* plan (Ngarrindjeri Tendi et al. 2007) it is stated: “*The land and waters must be healthy for the Ngarrindjeri people to be healthy. We say that if wetlands/nurseries die, our Ngartji [totem or special friend] die, then Ngarrindjeri will surely die.*”

Early explorers

The first European explorers to sight and even settle in Australia possessed great skills of observation. It is important to realise that the early explorers were usually not trained scientists and that their primary concerns were to delineate the major terrain features of the interior and to survive. Moreover, many of the early explorers originated or worked in environments quite different from Australia. Early explorers' observations and reports on soils had mainly to do with pastoral or agricultural production rather than with the natural history of wetlands or back swamps. Nevertheless, the following observations remain of interest with regard to past and current known occurrences of inland Acid Sulfate Soils:

Captain Charles Sturt was one of the earliest recorders of soil information in South Australia. Following his previous experience along the Murrumbidgee, Murray and Darling rivers from 1828 to 1829, Sturt explored from Cawndilla near the Menindee Lakes westward into the north-east deserts of South Australia in 1844-46. His journals (Sturt 1849) reveal him to be an observant and inquisitive explorer. The following quotations from his published journals reveal a few of his perceptions about the possible natural occurrences of inland Acid Sulfate Soils in wetlands: Sturt was the first known European to have travelled down the Murray River to its mouth in 1830 when he noted the following in his journal that “*the shores of the lakes were densely covered with fresh water reeds in one continuous belt as far as the eye could see*” (suitable conditions for the formation of hypersulfidic material because of the considerable build-up of organic matter in the dense reeds in waterlogged soils). As he passed across the region of the South Australian border he records “... we travelled over firm and open plains of clay and sand, similar to the soil of the plains of the Murray”. *Sunday, August 17th 1845 (Page 156)*: “For the last six miles the country has fallen off greatly, the flats are broader and of a white clay with but little grass upon them. The sand hills are very high and the sand as red as brick, and from their summits the view to the NW is as dreary as can be imagined.... Surface water is becoming very scarce, and what we are obliged to use is *as thick as a puddle and looks like a mixture of Magnesia and Rhubarb. The pools in truth are not more than two inches deep, and as it blows more or less violently every day the mud gets so mixed that it will not settle.* I may say that we have not had a drop of wholesome water since November.....”. *Sunday September 7th 1845 (Page 180)*: “Its channel was white as the driven snow and it was flanked by sand banks on which the marks of flood were 12 feet high. *There was no water in the bed where we struck it, but the bed was too soft for us to cross with the horses* so that we turned up it northerly, passing a long sheet of water on which the *salt was coated like ice.* Tracing it upwards at a mile we crossed a high sand ridge, and beneath us saw the dry basin of this creek surrounded by samphire. Crossing it we took up our old course, and traversed flats of salt formation between sandy ridges dark with samphire bushes excepting where there were white patches thinly coated with salt, the shallow receptacles for water.

The bottoms of these were spongy and soft. “The mineral salts in the waterholes such as this cause the clay sediments to settle, and also **produce foul-smelling mud** under the white crust”.

Edward John Eye, the explorer, “**The Founder of the First Irrigation Settlement**” in South Australia (1841) and Government Official at Moorundie near Blanchetown, noted the possibilities of “**rich alluvial soils**” in wetlands adjacent to the Murray River during his overland journey of 1838 when he passed through Moorundie (Mack 1958-2003). Many of these soils were subsequently inundated with water with the installation of locks and weirs in 1930s – 1940s (Fig. 7), which enabled considerable build-up of sulfidic and monosulfide material in these soils.

Ernestine Hill (1969; first published 1937) from “*Water Into Gold*” noted (page 12) “In the late 1830s Lake Bonney was described as a fine lake of fresh water about 30 miles in diameter (e.g. Fig. 6). Thousands of ducks were on the water” and (page 15): “In marked contrast, in 1841 **a sulphurous silence lay over Lake Bonney. The bed of the lake was as dry as a bone**”.



Figure 6. Changes in water level at Lake Bonney caused by isolating it from the Murray River using a temporary embankment to generate water savings in order to help mitigate drought-related problems in the MDB. Clockwise from above: July 2007 (showing mobilising of black monosulfides with water disturbance) to drying in April 2008, which shows white salt efflorescences comprising thenardite (Na_2SO_4) and minor amounts of eugsterite (Na-Ca-sulfate mineral) along the beach at Barmera (Site F5 in Fig. 5). (from Fitzpatrick et al. 2008g)

The early scientists

Field survey investigations of Australian soils were first commenced by Taylor and England (1929) in the Renmark Irrigation District on the Murray River (Wells & Prescott 1983). By 1940, all then existing irrigation areas in SA had been investigated and/or mapped, including the irrigated, drained Phragmites swamps on the lower Murray River (Taylor and Poole 1931a) between Murray Bridge and Wellington (Fig. 5). Significantly, these soil survey investigations also included the lake bed of Lake Albert, which was being considered for drainage and development as an irrigated pasture/cropping area similar to the swamps (Taylor and Poole 1931b). An occurrence of inland Acid Sulfate Soil was recognised as a potential problem as early as 1929 by Taylor and Poole (1931b) in Lake Albert. This soil survey required subaqueous soil inspections and novel sampling techniques. At that time, they noted the presence of what we now call Inland Acid Sulfate Soil, one soil having a pH of 3.9, and they successfully argued that the lake should not be drained for agriculture. Their original soil samples were retrieved from the CSIRO Land and Water soil archive in Canberra, and analysed for pH before and after peroxide treatment for comparison with the original measurements made 78 years previously. In this case, the original, 1930s results can be taken as the original pH values (pH 8.5) and the low 2007 pH values (pH 2 to 4) used as a long-term incubation experiment, which confirmed the acidifying effects of exposure of the soils to the atmosphere (Fitzpatrick et al. 2008e).

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

ACCUMMULATION OF SULFIDES IN INLAND ACID SULFATE SOILS

The Murray River system is a good example of an inland system, which is not only highly stressed at present but has been highly managed for the last 70 to 80 years (Fig. 7). The introduction of locks, weirs and barrages (Fig. 7) in the early part of the 20th century to contain water flow has allowed extensive agricultural development (e.g. Mack 1958-2003; see also Chapter 4 below). However, the prolonged inundation of the river, wetland and lake systems has had a significant impact on the formation of various types of ASS in these ecosystems due to loss of natural wetting-drying cycles, so critical for maintaining biodiversity and wetland functioning. This change has promoted the build-up of sulfide minerals (mostly iron pyrite) and sulfidic materials in newly formed subaqueous soils and greatly slowed the removal of these acid-forming materials from the system (ultimately to the sea).

The concentration of pyrite in the subaqueous soils (i.e. lakebeds) in the Lower Lakes (Lake Alexandrina and Lake Albert) varies at different inundation ranges. Prior to construction of the barrages, which separate the freshwater in the Lower Lakes from the seawater of the Southern Ocean (Fig. 7), the water level within the Lower Lakes did not fall below sea level (0 m AHD). The subaqueous soils below sea level had not been exposed to oxygen for thousands of years, therefore, the concentration of sulfides in the sediment was significantly greater than those above the marine or fresh water inundation range. Following installation of the barrages in 1940, the water level in the Lower Lakes has, until very recently, been maintained around a pool level of +0.75 m AHD. Hence, during periods of low flow or high evaporation, the lake level in Lake Alexandrina has remained relatively constant in that it has only dropped to around +0.5 m AHD and very rarely lower than +0.4 m AHD (as indicated by the graph in Fig. 8, which shows water levels from 1974 to approximately June 2009).

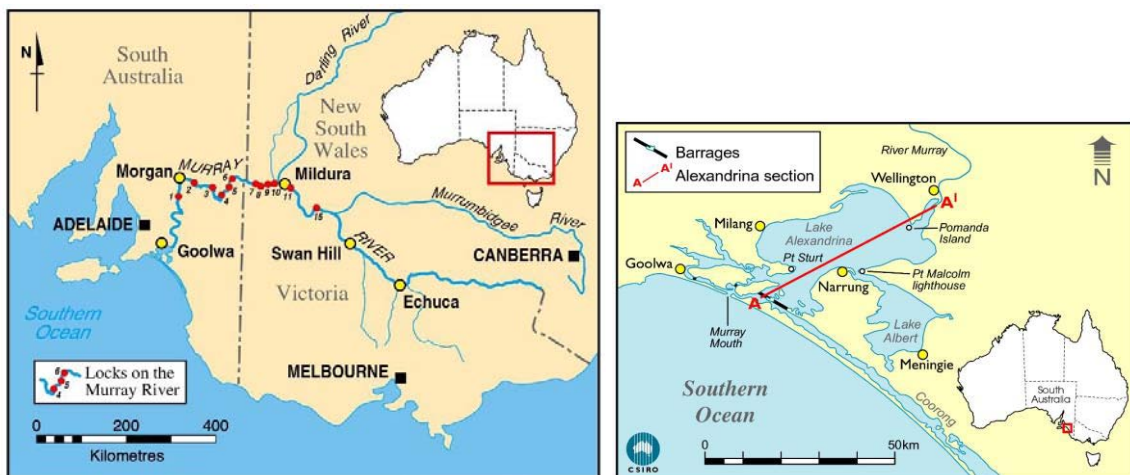


Figure 7. Locality maps showing: (i) part of the Murray and Darling River systems in the Murray Darling Basin (MDB) along with locks on the Murray River (left map) and (ii) barrages (constructed to keep sea water out of the Lower Lakes) and the cross section (A–A') across Lake Alexandrina used to construct the predictive soil-regolith models in Figures 22 to 27 (right map).

DRAINAGE AND DISTURBANCE OF ACID SULFATE SOILS

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

- *Removal of native vegetation* e.g. increasing recharge, rising of saline water tables (e.g. Coram et al. 2001).
- *Agriculture* e.g. tillage, pugging by cattle, creating densipans or introducing oxygen to sulfidic discharge areas (e.g. Fitzpatrick 2008).
- *Improved farming systems using vegetation* e.g. reducing recharge, lowering of water tables by using deep-rooted plants (e.g. Barrett-Lennard et al. 2003).
- *Erosion* e.g. local lowering of the water table by gully formation and deepening; removal of surface soil layers by wind or sheet erosion forming scalds and expose hardpans.
- *Engineering works* e.g. construction of weirs, blocking banks, levee banks and drains; surface and groundwater pumping.
- *Drought conditions* causing the lowering of water levels in lakes (Fig. 8), rivers and wetlands.

As water levels declined in Lake Alexandrina, Lake Albert and the Murray River system, especially in the section below Blanchetown (Lock 1), due to the extreme drought conditions that commenced in about 2006 (e.g. see example for Lake Alexandrina in Fig. 8), the anaerobic sulfidic materials that were once covered by water became exposed to oxygen at the river and lake margins (see example in Fig. 8), and in adjacent wetlands. With continued lowering of water levels, the hypersulfidic material became progressively oxidised to greater depths in the soil profile (Fig. 8). With drainage, hypersulfidic material in the anaerobic soils have become oxidised and transform to sulfuric material (pH <4), with consequent water quality, ecological and public health issues from metal/metalloid mobilization (e.g. accumulations of surface crusts of salt efflorescences comprising sulfate-rich evaporite minerals shown in Fig. 8), de-oxygenation, wind erosion and noxious gas release (e.g. Hicks & Fitzpatrick 2008). These effects have been particularly severe in the Lower Murray and Lower Lakes region (Fig. 8) where research has progressed beyond studying the occurrence and distribution of ASS to understanding the impacts on adjacent environments through the mobilisation and transport of acidity and solutes (e.g. Fitzpatrick et al. 2008a,b,c,d,e,f; Simpson et al. 2008). Such questions have involved harnessing skills in aqueous geochemistry, hydrodynamic modelling and ecological risk assessment (Stauber et al. 2008). These investigations have also stimulated investigations into the occurrence and impacts of inland ASS across the entire MDB (Fitzpatrick & Shand 2008).

In summary, acid sulfate soil materials are much more abundant in these estuarine, riverine and lacustrine environments (i.e. Geographical Areas A to F in Fig. 5) than previously recognised (e.g. Fitzpatrick et al. 2008a,g,h).

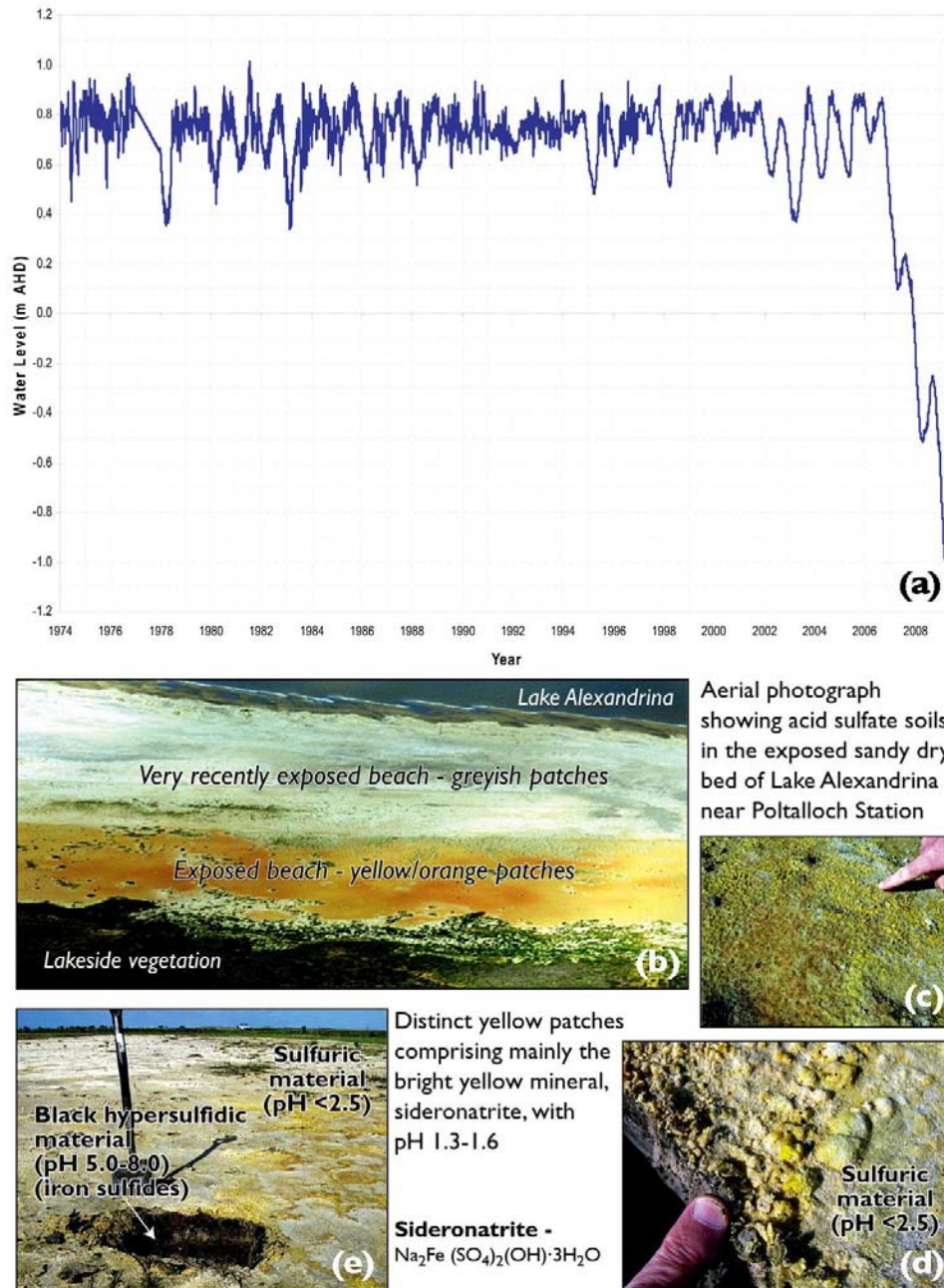


Figure 8. (a) Graph showing Lake Alexandrina water levels from 1974 to approximately June 2009 (DWLBC 2009) (in July 2009 the water levels were approaching -1.0 m AHD, which is more than 1 m below the historically lowest water levels). (b) Aerial photograph showing of the exposed sandy dry lake-bed of Lake Alexandrina (near Pottaloch Station, Narrung area; B4 in Fig. 5) with surface crusts comprising the following coloured salt efflorescences: (i) bright yellowish colour on slightly elevated surfaces as seen in the close-up photographic views [(c) and (d)] and (ii) orange patches occurring on the edges of lightly elevated surfaces [(c)]. (e) Soil pit with black hypersulfidic material (iron sulfides) at depth overlain by sulfuric material with distinct yellow patches of the bright yellow mineral, sideronatrite, with a pH ranging between 1.3 to 1.6 (Fitzpatrick et al. 2008e,h).

ACID SULFATE SOIL MANAGEMENT OPTIONS

Summary of principles

While increased disturbance of hypersulfidic material (promoting oxidation of sulfides) is the principal cause of the formation of sulfuric materials, one would expect that the principal management option would be to reverse the situation (i.e. keep anoxic or under anaerobic conditions to slow or stop the rate and extent of pyrite oxidation). This can be achieved either by keeping sulfidic material

anaerobic under saturated conditions or by rapid drying of sulfidic material to slow the biological process, which are responsible for the formation of acid. However, the selection of appropriate management options to prevent oxidation of sulfides will depend on the nature and location of the ASS materials, and their position in the landscape (e.g. availability of sufficient amounts of water to either maintain or generate anoxic or waterlogged conditions). Reversing the process by rewetting, once oxidation has occurred, is not straightforward, because it is at this time that the risks from acid and metal mobilisation are highest. This is why reliable ASS risk or hazard maps, at appropriate scales, and characterizing ASS landscapes are so important. Understanding, the soil properties and processes as well the water table hydrology is fundamental to selecting the best options for drainage and the most appropriate management of the soils when they are drained. Appropriate management of ASS during development can improve discharge water quality, and protect infrastructure and the environment. Such improvements can generally be achieved by applying low-cost land management strategies (e.g. Dear et al. 2002). Ranked in order of priority ASS management follows the following general of principles (Fitzpatrick et al. 2008i):

Minimise disturbance or drainage of ASS materials

Select an alternative non-ASS site, rather than undertake remediation. If an alternative site is not feasible, design works to minimise the need for excavation or disturbance of ASS materials, by undertaking shallow excavations for drainage measures or foundations, and avoid lowering groundwater depth that may result in exposure of soils. If ASS materials are close to the surface, cover with clean soil to lessen the chance of disturbance and insulate from oxygen.

Prevent oxidation of sulfidic material

This may include staging the development project to prevent oxidation of sulfidic material by covering it with an impermeable barrier (e.g. clay), or placing any excavated sulfidic material quickly back into an anaerobic environment, usually below the water table.

Minimise oxidation rate and isolate higher risk materials from exposure

This may include covering ASS materials with soil or water to reduce oxygen availability and control the movement of water, or by controlling bacteria or by applying other limiting factors (e.g. alkalinity) through either physical or chemical means to reduce oxidation rate. The amount of ASS requiring excavation and/or dewatering can be minimized through reconsideration of the design for the proposed development. This consideration will relate to an understanding of where exactly, in terms of lateral and depth occurrences, ASS is positioned on the site. Dewatering impacts can more easily be minimized through installation of hydraulic impediments to dewatering such as engineered ‘curtains (e.g. shoring), re-injection wells and galleries, infiltration basins, and wet excavations.

Contain and treat acid drainage to minimise risk of significant offsite impacts

Acidity and oxidation products that cannot be retained on-site may be managed by other techniques such as acidity barriers or wetlands that intercept and treat contaminated water before it is finally discharged into rivers or estuaries. Typically, this would involve installing a leachate collection and treatment system (e.g. using limestone), a permeable reactive barrier (e.g. lime slot) to intercept and neutralize acidic water as it moves through the soil, or installing an impermeable barrier to locally confine acidic groundwater.

Provide an agent to neutralise acid as it is produced

This would involve mixing the ASS material with an excess of limestone (CaCO_3), or other neutralising agent to buffer the pH in the soil. The amount of lime required depends on acidity already produced and potential for further production of acid. One of the issues with this option is the large amount of lime that is sometimes required and the effects it could have on biota. Liming, as a substitute for reflooding, and application to dry soils, also poses a problem as the lime would need to be mixed in with the soils. This would mean churning up wetland beds and further disturbance of the soils. However, surface application could effectively neutralise acid soil formed at the surface, which is most prone to erosion or to which animals and humans may be directly exposed.

Applying mulched organic matter on top of a wetland bed so that as it breaks down the organic matter acts as a buffer to the acid in sulfuric materials.

Where feasible, controlled reflooding with seawater can be used to neutralise acidity in sulfuric materials and dilute acidity, dissolved metals, metalloids and non-metals (e.g. from sulfate-rich salt efflorescences). Seawater contains alkalinity of about 140 mg/L as bicarbonate equivalent. However, the acids and any metals that would initially dissolve in the seawater should not be permitted to flush out to the ocean until removed by natural processes. If flushing is not possible, salinity and sulfides are likely to progressively accumulate in such areas (e.g. lower lakes) over time. Note that flooding with sea water also helps the process of exclusion of oxygen, as mentioned above.

Separate sulfidic materials

This may include the use of mechanical separation, such as sluicing or hydrocyclone to separate sulfide minerals (e.g. pyrite crystals) from the sulfidic material, followed by treatment (e.g. liming) or disposal of the sulfide minerals in an anaerobic environment.

Hasten oxidation and collection and treatment of acidic leachate

This involves spreading the ASS materials in a thin layer on an impervious area to activate rapid oxidation. Rainfall or irrigation leaches the acid and this leachate is collected and treated (e.g. by liming).

Management of stockpiled ASS materials

This includes minimising the quantity and duration of storage, minimising the surface area that can be oxidised, covering the soil to minimise rainfall infiltration, stormwater control measures, controlling erosion and collection, and treatment of runoff (leachate).

Planning and development controls

There are numerous planning and development controls for coastal ASS, which already exist in South Australia through the Coast Protection Board (Fitzpatrick et al. 2008i).

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

DESCRIPTIVE, EXPLANATORY AND PREDICTIVE TOPOSEQUENCE MODELS

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

- Descriptive soil-regolith models.
- Explanatory soil-regolith models.
- Predictive soil-regolith models (generalised and specific).

The descriptive soil-regolith process model shown in Figure 9 characterises past geomorphological processes in the development of deep weathering and erosion, and current saline, alkaline, sodic, sulfidic or sulfuric soil forming processes. Such models help to develop practical frameworks and solutions for managing soils. The descriptive soil-regolith model is used as the precursor or framework for developing the explanatory soil-regolith model (3D), also shown in Figure 9, which represents current and past water levels. These are in turn used to develop predictive soil-regolith models (4D) for a particular region (generalised models) or area (specific models). For example, the generalised predictive model shown in Figure 10 is for the Lower Lakes and Murray River region (i.e. areas B, C, D, E and F in Fig. 5) and illustrates the evolutionary cycles during the sequential changes in soil properties due to decreasing water levels caused by extreme drought conditions and winter rainfall rewetting. Specific predictive soil-regolith models have been constructed to illustrate a particular area (e.g. area D1 in Figs. 13 to 14). Consequently, the predictive soil-regolith models (4D) consist of a collage of figures, which illustrates several evolutionary cycles of soil-regolith events.

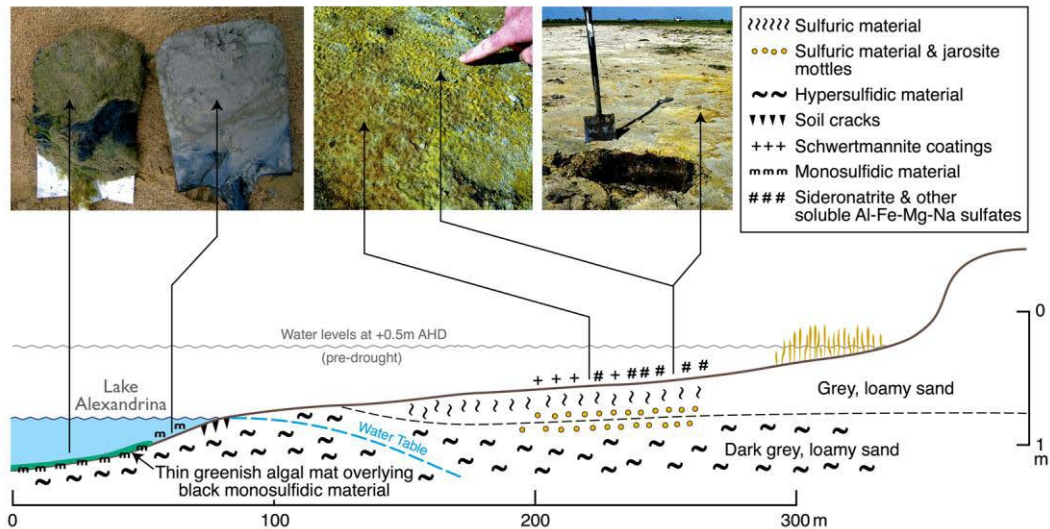


Figure 9. Descriptive and Explanatory soil-regolith model constructed from field and laboratory data that characterises the spatial variation of ASS materials. This soil-regolith or hydro-toposequence model describes the cross-section from subaqueous soils in Lake Alexandrina to elevated land near Poltalloch Station (Site B4 in Fig. 5). Note: The water table level pattern is exaggerated because of the inflated vertical scale necessary to display all the soil features.

Descriptive and Explanatory soil-regolith models

To understand the lateral linkages and relationships between soil and landscape indicators (soil profile features), a systematic structural approach has been used to characterise soil-regolith features at different points along toposequences (Fritsch & Fitzpatrick 1994; Fitzpatrick et al. 2009). Colour photographs of typical profiles along the toposequence are used (e.g. Fig. 9), along with relevant field soil properties including texture, structure, matrix colour and mottling. Soil chemical and mineralogical properties were determined in the laboratory. Each cross-section mapping unit or layer delineated is called a soil feature. A soil feature thus represents a limited range of one or more soil-regolith properties.

Fitzpatrick et al. (2009) used these descriptive soil-regolith toposequence models to construct explanatory soil-landscape process models to explain contemporary geochemical hypersulfidic to sulfuric transformation processes present in the lower parts of the hydro-toposequence (Fig. 9). This model explains the formation of sulfuric materials by illustrating the pedological, geological, biogeochemical, mineralogical and hydrological processes occurring along the soil-water interface.

These explanatory soil toposequence models can describe the vertical and horizontal changes in ASS materials across a wide range of landscapes (e.g. Fig. 9). The combination of soil morphological features allows similar soil layers to be matched between different sites along the toposequence (Fig. 9). A number of sites were placed in an approximate transect stretching from the water to the higher landscape position as indicated in Figure 9.

The example shown in Figure 9 describes in detail the spatial variation of the following soil features caused by receding water levels due to current extreme drought conditions: (i) monosulfidic material in the subaqueous soils, (ii) the prominent bright yellow mineral, sideronatrinite, with a pH ranging between 1.3 to 1.6 on the soil surface, which overlies black hypersulfidic material in the soil pit (see close-up views in Fig. 8) and (iii) brownish-orange coatings of the mineral schwertmannite, which forms from sideronatrinite (dissolves in rainwater and re-precipitates as schwertmannite). The minerals schwertmannite and sideronatrinite are good mineral indicators of the presence of sulfuric material (pH <4).

The oxidation of sulfidic materials often leads to the formation of secondary sulfate minerals, the most commonly recognised in coastal systems being jarosite, which acts as a store of acidity. In inland systems, the combination of sulfide oxidation with high rates of evaporation has led to the formation of an extremely wide range of surface mineral efflorescences or evaporites (Fitzpatrick et al. 2008e,f,g,h, 2009). Many of these were thought to be extremely rare, until the recent lowering of

water levels, but have now been documented over wide areas. A number of mineral combinations have been identified in different local pH environments across the Murray Darling Basin:

- sideronatrite, metavoltine, alunogen, tamarugite, copiapite, epsomite, hexahydrite, botryogen, pickeringite, redingtonite, halotrichite, tschermigite and gypsum in often sandy or organic-rich sulfuric materials with pH < 2.5,
- natrojarosite, jarosite and plumbojarosite in clay-rich sulfuric materials with pH 3.5-4.0,
- schwertmannite (orange-yellowish; pH 4), white, poorly-crystalline Al oxyhydroxide precipitates (pH 5 to 6) and lepidocrocite (orange pH 6),
- ferrihydrite (reddish-brown; pH >6), akaganéite (reddish-orange; 6-7).

The formation of these complex suites of sulfate and oxyhydroxysulfate salts (of Fe, Al, Na, Pb, Ca, As, Zn) and Fe oxides are indicative of extreme and often rapidly changing local environments and variations in Eh (redox), pH and availability of Fe, S and other elements (e.g. Bigham et al. 2002; Fitzpatrick & Self 1997; Skwarnecki & Fitzpatrick 2003). If the affected site is not managed properly, the minerals may become a problem when dissolved during re-flooding, or have potential to be windblown when dry. Farm stock should be prevented from ingesting these salts (similar to Epsom salts) because this is likely to lead to scouring. Magnesium sulfate, also present, may become toxic when ingested.

In summary, the layer distribution of soil materials detailed in these explanatory soil-regolith toposequence models provides an improved understanding of the spatial extent of various ASS materials (Fig. 9). For example, they show that sulfuric material occurs down to 50 cm depth and deeper in dry soils, and that this acidified material is more common in cracked clayey soils (e.g. Fig. 1). Hypersulfidic material occurs either below the sulfuric layer typically below the water table in the soil. The hypersulfidic layer ranges in thickness up to and in some areas more than one metre, often in black, soft clay. In the river channel near Pomanda Island, there are layers of hypersulfidic materials tens of metres thick (Fitzpatrick et al. 2008e). These explanatory soil-regolith toposequence models also provide an understanding of the soil distribution that have then allowed predictive maps to be constructed and updated with more confidence (e.g. Fitzpatrick et al. 2008a,h, 2009).

Predictive conceptual models

The generalised predictive conceptual model shown in Figure 10 illustrates the Lower Lakes and Murray River region that has dried due to drought lowering of water levels and winter rainfall rewetting (Fitzpatrick et al. 2008e,f,h; 2009). It outlines sequential transformation progressively through **five** sediment/soil types due to lowering of water levels and rewetting from:

1. Alkaline deep water sediments →
2. Alkaline subaqueous soils →
3. Neutral waterlogged soils containing “benign” hypersulfidic material →
4. Acidic drained soils containing “nasty” sulfuric material (pH<4) →
5. Rewetted acidic subaqueous soils and water.

The generalised predictive conceptual model (Fig. 10) was constructed using all readily accessible information, which included data from archival/historical and published soil data (e.g. Taylor and Poole 1931a,b; de Mooy 1959; Fitzpatrick et al. 2008a,e,f,g,h, 2009), vegetation, DEM data and geological information for the region together with photographs from a typical area to help illustrate the conceptual model (e.g. in this case from the Finnis River at Wally's Landing see Figs. 5, 11 & 12).

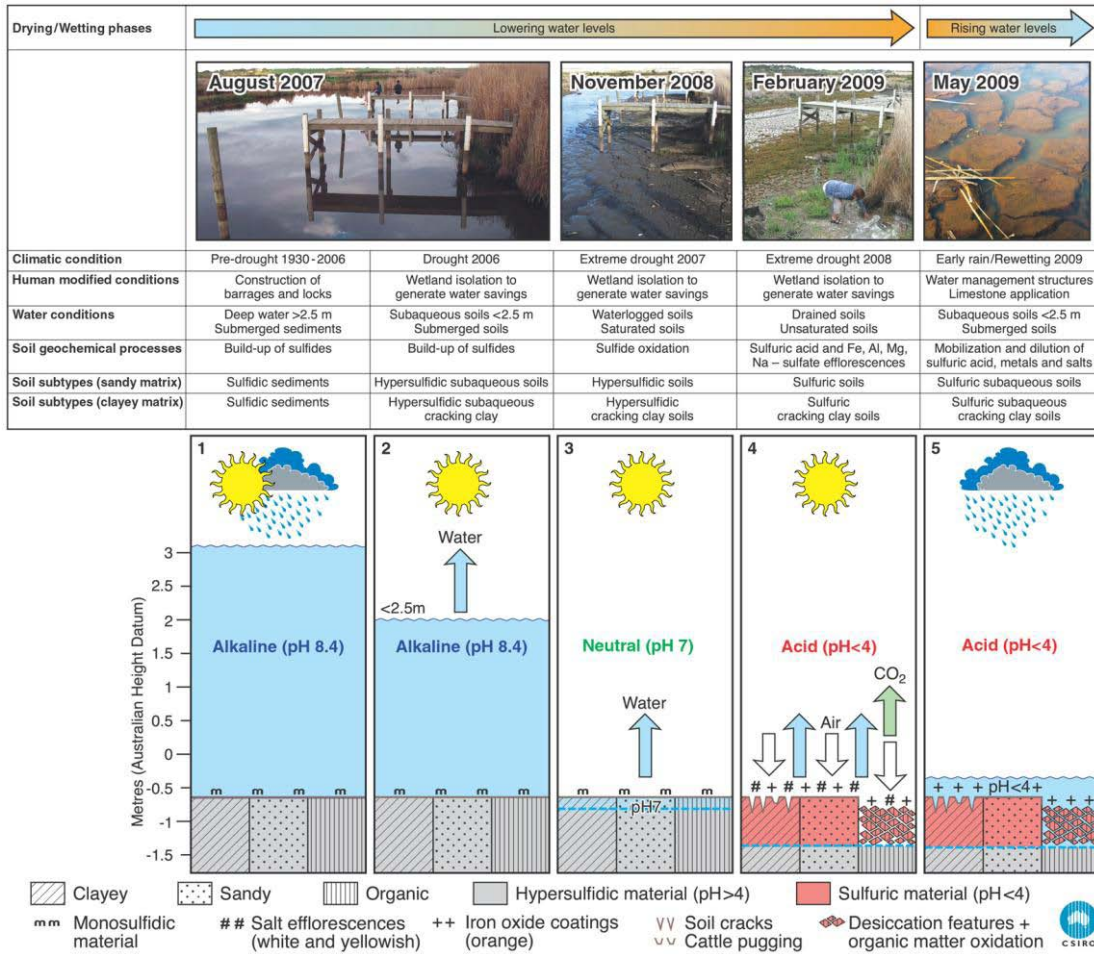


Figure 10. Generalised predictive model illustrating how climate variation (drought triggered and early winter rains), environmental conditions imposed by humans (e.g. modifications from barrages, isolating wetlands and weirs) and water conditions (subaqueous, waterlogged, dried and rewetted) play a vital role in the alteration of soil geochemical processes and sequential transformation of ASS subtypes (modified from Fitzpatrick et al. 2008a,e,f,h). Photographs from the Finnis River at Wally's Landing (Site D1 in Fig. 5; Figs 11) illustrate the sequential changes in soil properties due to: (i) decreasing water levels for August 2007, November 2008 and February 2009 caused by extreme drought conditions, and (ii) winter rainfall rewetting resulting in rising water levels in May 2009.

CASE STUDIES - TRIBUTARIES

Background information

These case studies summarise the wide range of properties and the areal extent of the various subtypes of ASS and ASS management options being applied in the tributaries in the lower reaches of Finnis River, Currency Creek, Black Swamp and Goolwa Channel region (see area D in Fig. 5; Fitzpatrick et al. 2009). In summary, more than 91% of the representative sites assessed in November 2008 had a high, very high, or extra high ASS hazard classification. It was found that 37 of the 39 sites (94%) investigated had sufficient net acidity that, if disturbed, would be a major area of concern (Fitzpatrick et al. 2009).

Changes in water level in the Finnis River at Wally's Landing (Fig. 11) are shown in Figure 12. The August 2007 photograph shows the river with hypersulfidic subaqueous clayey soil under 80 cm of water at the end of the jetty. Hypersulfidic organic clayey soil was sampled in the *Phragmites* reeds four metres from the bank/waters edge. The November 2008 photograph shows substantial lowering of water levels to produce mainly waterlogged or saturated acid sulfate soil (hypersulfidic cracking clay soil – end of jetty). The February 2009 photograph shows further lowering of water levels to expose a clayey dry river-bed with cracks and salt efflorescences (sulfuric cracking clay soil). The red square shown in the February 2009 photograph in Figure 12 indicates the location of the

acidic white fluffy salt efflorescences adjacent to *Phragmites* reeds, which is shown in close-up on the lower right hand side photograph.

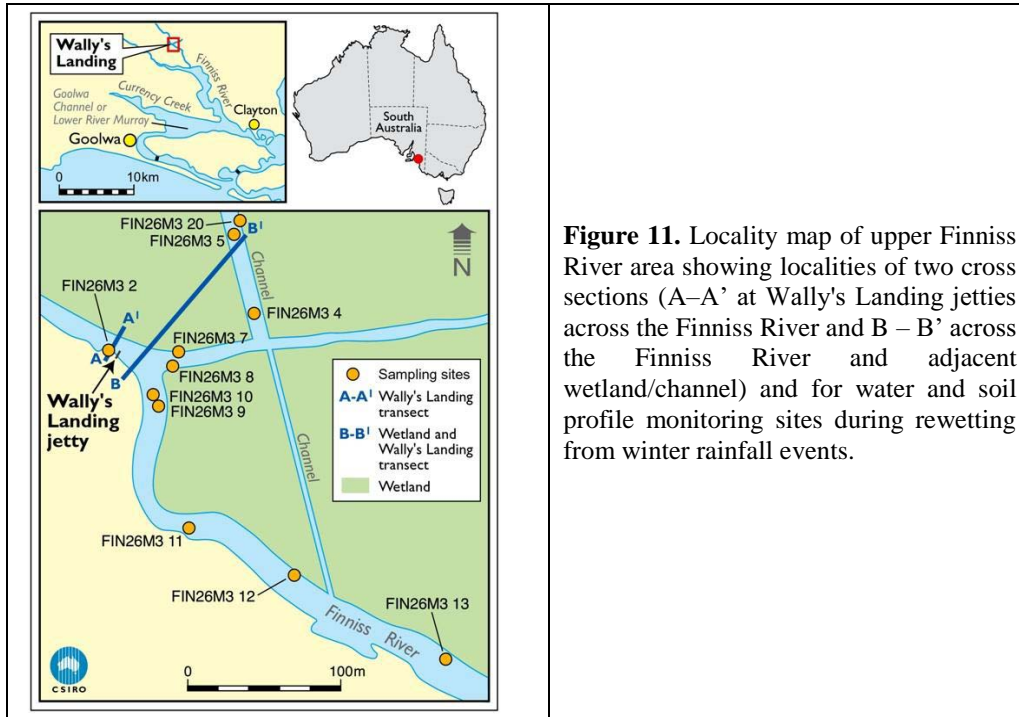


Figure 11. Locality map of upper Finnis River area showing localities of two cross sections (A–A' at Wally's Landing jetties across the Finnis River and B – B' across the Finnis River and adjacent wetland/channel) and for water and soil profile monitoring sites during rewetting from winter rainfall events.

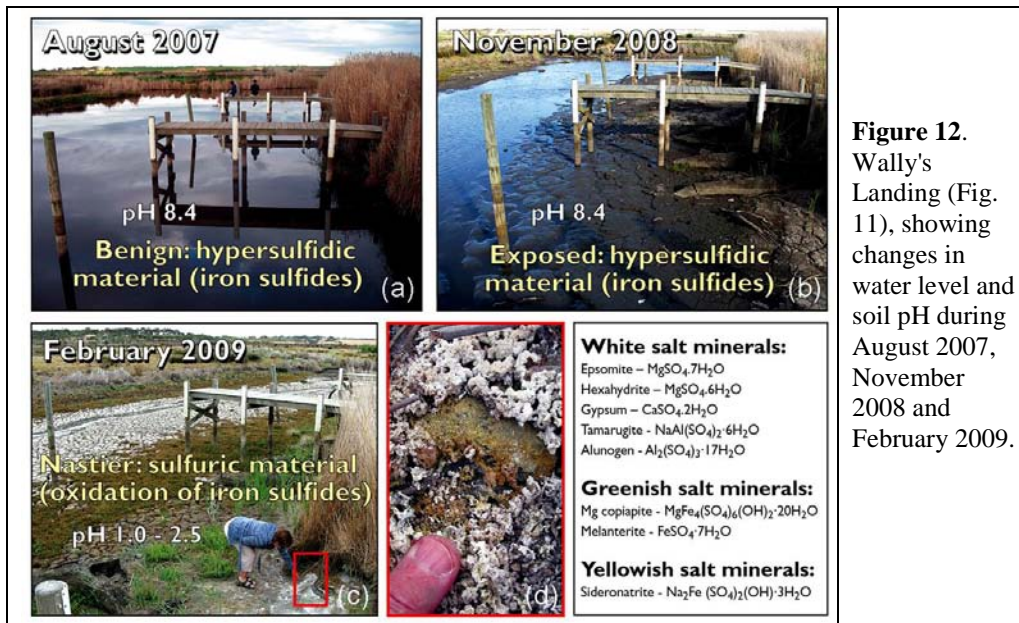


Figure 12. Wally's Landing (Fig. 11), showing changes in water level and soil pH during August 2007, November 2008 and February 2009.

Acid Generating Potential

The combined standard methodologies of: (i) soil morphology, (ii) field pH testing, (iii) pH peroxide testing, (iv) acid-base accounting (Ahern et al. 2004), (v) soil incubation (ageing), and (vi) mineralogical analyses has confirmed that these soils either contain sulfuric acid (sulfuric material, $pH \leq 4$), or have the potential to oxidise and form sulfuric acid when exposed to air (oxygen) because of high concentrations of sulfide minerals (hypersulfidic material). This potential is being realised in many areas along the Murray and Lower Lakes. However, the risk of soil acidification would be significantly lower if water levels were kept at a level high enough to maintain anaerobic conditions.

Metals and Mobilisation

Metal mobilisation is likely to be significant in sulfide-containing soils that have undergone oxidation (Fitzpatrick et al. 2009). Sulfide minerals scavenge trace metals, which may be released during

oxidation. During 24 hour laboratory mobilisation tests on ASS, the water pH generally became similar to that measured for the soils (Simpson et al. 2008). Metal release was rapid in sulfuric materials producing high dissolved concentrations of Al, Cd, Co, Cu, Cr, Mn, Ni, V and Zn. Greater concentrations of metals were released from the more clay-rich Finnis River soils than from the sandy soils in Currency Creek. In general, the concentrations of metals released increased greatly at pH < 5. Tests demonstrated that the rewetting of dried acid sulfate soils has the potential to release significant quantities of environmentally degrading substances. The release of nitrate and phosphate from the dried soils was low. The attenuation of dissolved metal concentrations through co-precipitation and adsorption to aluminium and iron oxyhydroxide phases is likely to occur as acidic, metal-rich waters mix with more neutral or alkaline water.

Mineralogy

At several sites, abundant occurrences of minerals in salt efflorescences and sub-surface horizons were recorded by Fitzpatrick et al. (2009). In the bright yellowish green and orange surface efflorescences (e.g. Figs 12-15), and pale yellow mottles in subsoils (Figs 13-15), X-ray diffraction analyses identified sideronatriite, schwertmannite and jarosite/natrojarosite minerals, respectively. The pH values of the bright yellowish green surface efflorescences was very acidic (pH < 2) and the orange and pale yellow minerals were acidic (pH < 3 to 4). The presence of all of these minerals indicates high contents of iron sulfides (principally pyrite) in the original materials. It is predicted that large quantities of sulfuric acid will be produced in the hypersulfidic, subaqueous soils if the river levels continue to drop significantly and the adjacent wet soils are allowed to dry. Where winter rainfall has rewet previously identified sandy sulfuric soils with pH values of 1.6 to 2.5, tamarugite [NaAl(SO₄)₂.6H₂O], with traces of sideronatriite were subsequently identified with pH values ranging from 0.5 to 0.8 during slight rewetting of the mineral surfaces.

Hydrogeochemistry

Some of the waters in soil pits of the dry river-beds and wetlands of Currency Creek (with deep cracks) and Finnis River (sands) had acidic pH values ranging from 3.4 to 3.9. Some river waters sampled in Currency Creek and Black Swamp in November 2008 contained moderate to low concentrations of alkalinity (<117 mg/L and 31 mg/L respectively as HCO₃⁻).

The alkalinity of Lake Alexandrina has helped to maintain the alkalinity of the remnant Currency Creek and Finnis River waters whilst these are still connected, along with local contributions from ground waters and evaporation. Acid sulfate soil impacts are most likely to have an effect where net acidities are high and surface water alkalinities are low, such as in Currency Creek, where alkalinities are lower than in Lake Alexandrina (currently 200 to 250 mg/L).

Data from Wally's Landing in May 2009 showed that the pH in the flowing river was circumneutral following rewetting from recent winter rainfall. However, water in cattle pugs close to the river was found to be very acidic (pH 3.2). In a major anabranch of the Finnis River, the flowing stream water was found to produce acidic pulses (pH 3.3 to 4.0) with relatively high specific electrical conductance (SEC) of 13300 μS cm⁻¹.

Finnis River explanatory soil-regolith model for clays (Site D1 in Fig. 5)

The explanatory soil-regolith model shown in Figure 13 has been constructed to show the generalised relationship between the various clayey soil profiles sampled and described and how the underlying layers and ASS materials vary across the landscape (Fitzpatrick et al. 2009). The model highlights large cracks in the underlying subsoil that formed columns during drying. The top surface of the columns were extremely hard and coated on the upper and side surfaces with various minerals including jarosite (FIN 20), schwertmannite (FIN 23), sideronatriite (FIN 23) and other soluble Al-Fe-Mg-Na sulfates. These clay columns overlay a black soft organic rich clay layer that varied in thickness and proximity to the surface. Underlying this was a black, very soft clay. The upper columnar layer was classified as sulfuric material and the underlying soft clay as hypersulfidic material. When these ASS materials were sampled in November 2008, the sulfuric material in the cracking clay (FIN 20) had thick soft layers (pale yellow mottles/ precipitates) of jarosite in the cracks (pH 3.3) and the water in the large cracks had a pH of 3.5 (Fitzpatrick et al. 2009).

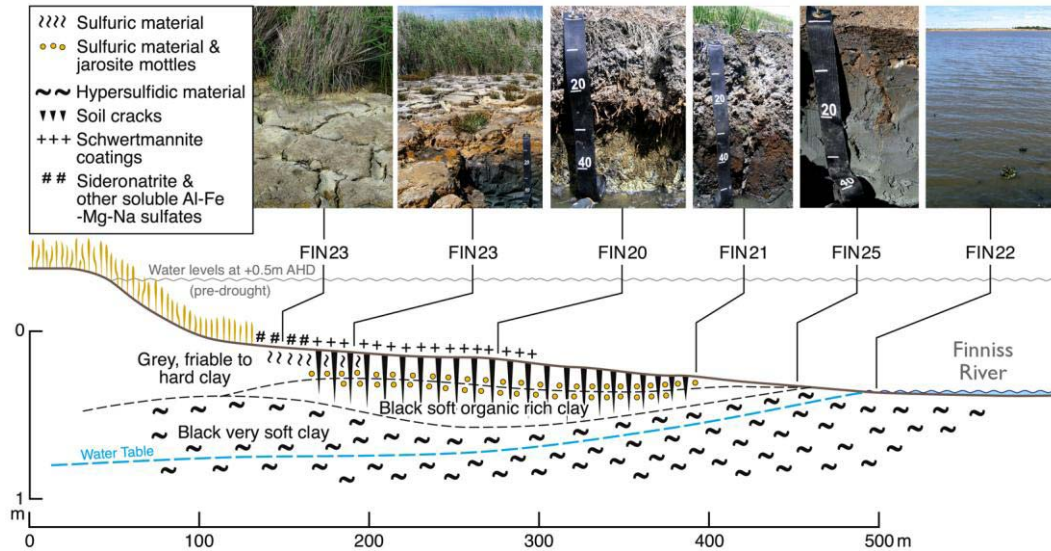


Figure 13. Explanatory soil-regolith toposequence model for profiles FIN20 to 25, located on the west side of Finniss River (site D1 in Fig. 5) (from Fitzpatrick et al. 2009).

Currency Creek explanatory soil-regolith model for sands (Site D2 in Fig. 5)

The explanatory soil-regolith model shown in Figure 14 (profiles CUR27 to CUR28) is characterised by sandy surface materials to a depth of 50 cm.

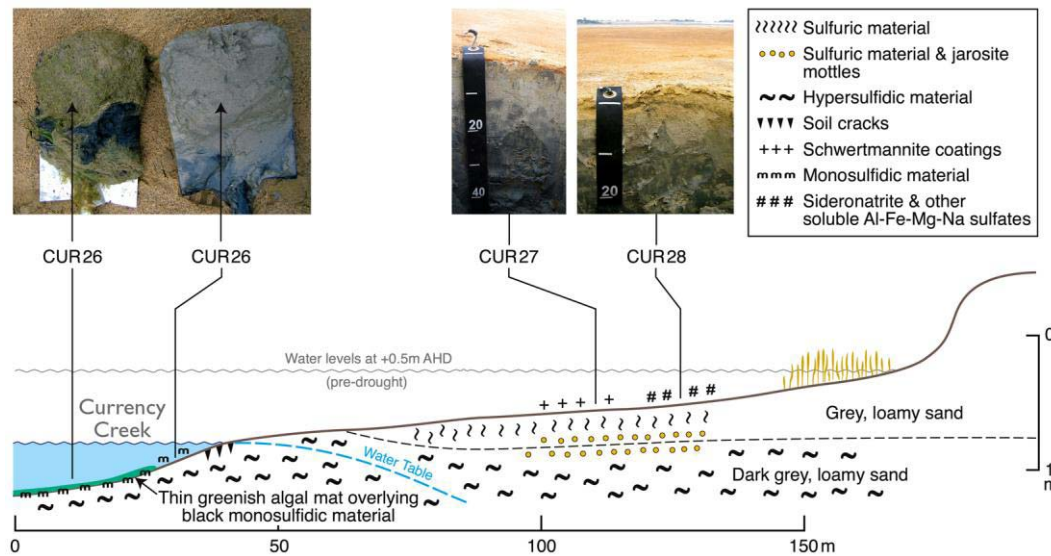


Figure 14. Explanatory soil-regolith toposequence model for profiles CUR27 to 28, located on the north-eastern side of Currency Creek (site D2 in Fig. 5) (from Fitzpatrick et al. 2009).

The widespread occurrence of bright yellowish, 2 to 5 mm thick, sandy friable crusts can be observed in CUR28. These layers contain mainly precipitates of the mineral sideronatrite, which occur as rosettes and platelets on the soil surface in sulfuric material (< pH 2.5). Sideronatrite is formed from the oxidation and dissolution of pyrite framboids, which occur mainly in the form of spheroidal aggregates of pyrite crystals (Fig. 4). Sideronatrite in the yellowish crusts dissolves and re-precipitates as orange coloured schwertmannite (CUR27) in immediately adjacent zones where the pH is slightly more alkaline, to display distinct orange patches or areas on the soil surface, and orange mottles to a depth of 2 to 10 cm (CUR27). This mineral forming process occurs during cyclic wetting and drying events with rainfall, which causes water to dissolve sideronatrite and transport ferrous Fe and sulfate ions to adjacent “micro-ponds” where schwertmannite rapidly crystallises (Fitzpatrick & Shand 2008). The formation of these minerals is indicative of local geochemical environments that are rapidly changing due to variations in pH and rates of Fe, S and Na mineralisation. Thick layers (0 to

30 cm) of monosulfidic material also occur below thin algal mats in the subaqueous acid sulfate soil soils in Currency Creek (e.g. profile CUR26).

Goolwa Channel explanatory soil-regolith model for sands (Site B2 in Fig. 5)

The explanatory soil-regolith model shown in Figure 15 for profiles CUR15 to CUR19 is characterised by a firm brownish grey sandy surface that has some areas forming pockets of black fibrous organic material (e.g. CUR17). Underlying this was sandy clay which in turn overlay yellowish clay containing some calcrete (e.g. CUR18). The sandy dry surface near the landward end had prominent thin layers of sideronatrinite on the surface. Mid-way along the toposequence transect, sulfuric material with prominent mottles and streaks of natrojarosite in the upper soil layers (e.g. CUR18) was present. The lower dark grey layers all contained hypersulfidic materials.

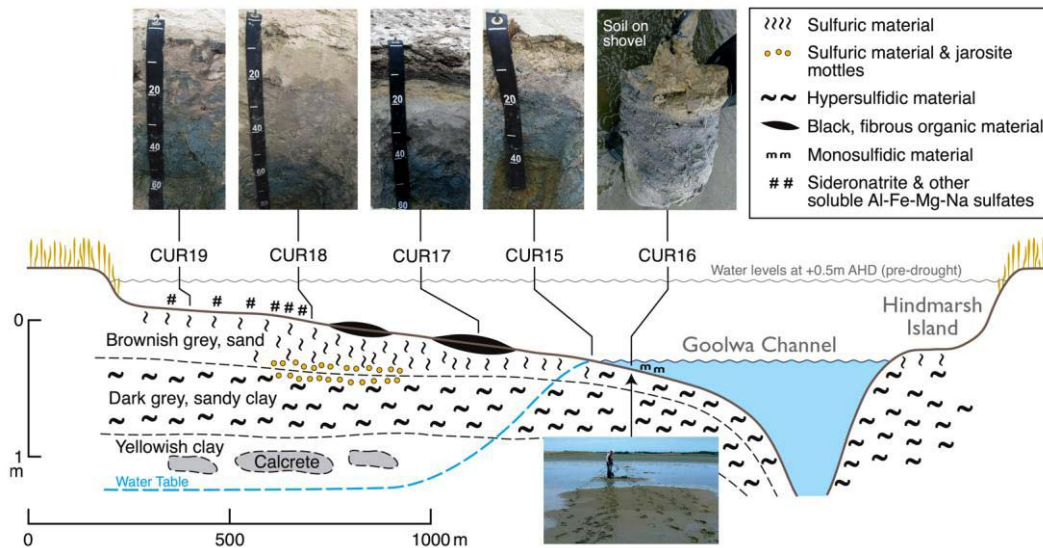


Figure 15. Explanatory soil-regolith toposequence model for profiles CUR15 to 19, located on the north-eastern side of Goolwa Channel (site B2 in Fig. 5) (from Fitzpatrick et al. 2009).

Finniss River predictive soil-regolith models (Site D1 in Fig. 5)

Predictive soil-regolith models illustrating the formation and transformation of sulfidic materials have been constructed for the Finniss River and adjacent wetlands in the area near Wally’s Landing (Figs. 11 & 12). These models provide an understanding of how the soil materials change with time and in relation to causative events. Based on field investigations and historical/palaeo-pedological knowledge of the Finniss River, a series of eleven conceptual models have been constructed (Fitzpatrick et al. 2009) to illustrate how various ASS materials in subaqueous, waterlogged (saturated) and dried conditions have sequentially changed, and the consequences of rewetting from recent winter rainfall events (Figs. 16 - 18).

To illustrate sequential changes in ASS materials at different water levels caused by drying (drought triggered) and rewetting (recent winter rains), we have constructed a series of conceptual models consisting of eleven cross-sections across the Finniss River (see A – A’ transect in Fig 11) and adjacent wetland (see B – B’ transect in Fig 11) at Wally’s Landing.

(i) Before the 1880s (5,500 BC to 1880s). The lower Finniss River cycled between natural wetting and flushing, and partial drying conditions in response to seasonal and climatic cycles occurring in the upper Murray-Darling Basin and its own catchment. During wetter periods, the river accumulated sulfidic materials from sulfate contained in surface waters and groundwaters (Fig. 16). However, during periods when river flows were lower (Fig. 16 - lower panel), the river and adjacent wetlands partially dried causing oxidation of sulfidic materials, especially on the dry margins with the potential formation of sulfuric materials. In wetter times and during floods, the acidic material was submerged causing dilution or neutralisation of acidity, entrainment of soluble materials in the river waters or the reformation of sulfidic material. The build-up of sulfidic materials in the Finniss River was thus regularly kept in check by oxidation and removal during scouring floods.

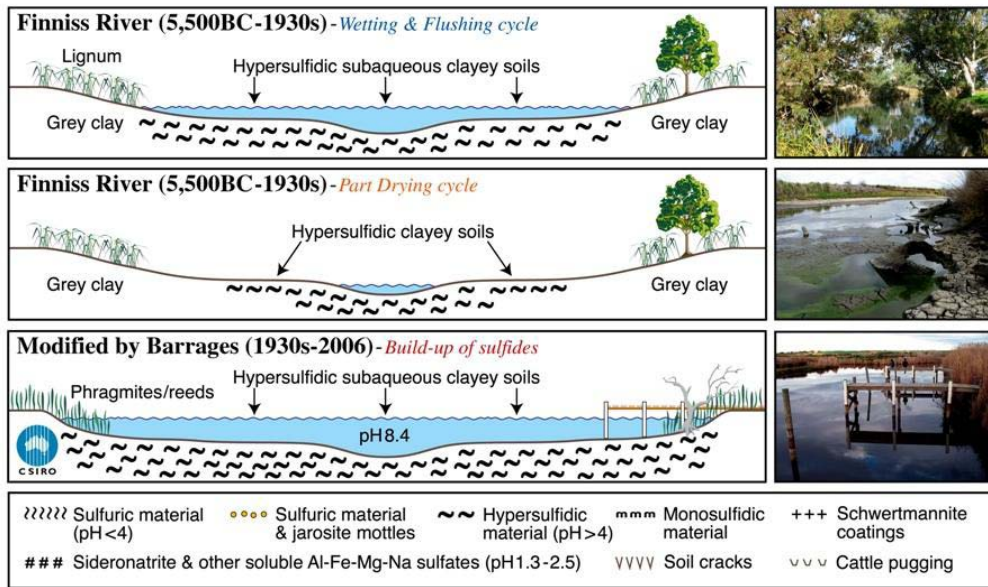


Figure 16. Predictive soil-regolith models for Finniss River (A – A’ transect in Fig. 11; Fig. 12) illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycles during the time prior to major pre-European development (5,000 BC to 1880s). The first picture taken upstream of Wally’s Landing to represent its possible original condition.

(ii) From the 1930s to 2006. Water levels in Lake Alexandrina and Finniss River were first managed using locks and barrages (Figs 16-18) in the 1930s and continues to the present, with the exclusion of seawater being their main function. The installation of locks and barrages allowed considerable build-up of sulfidic, hypersulfidic and monosulfidic material in the lower lakes and tributaries due to: (i) the evaporative concentration of sulfate from river nutrient/salt loads during periods of stable pool levels and from groundwater sources, and (ii) the lack of scouring and seasonal flooding. This has led to the formation of subaqueous ASS (hypersulfidic subaqueous clayey soils) with ultra-fine monosulfidic material accumulating in low-flow backwaters and along the vegetated edges of the wetlands.

(iii) From 2006 to November 2008. During this drought period, partial drying of the river and adjacent wetlands took place (Figs 17 & 18), and the river and lake levels continued to decrease (Fig. 8). The subaqueous ASS (hypersulfidic subaqueous clayey soils) transformed to waterlogged ASS (Hypersulfidic clayey soils).

(iv) From November 2008 to February 2009. During the November 2008 to February 2009 period, extreme drying of Lake Alexandrina and adjacent wetlands took place (Figs 17 & 18) because of the extended drought conditions and lower lake levels (Lake Alexandrina had almost lowered to -1.0 m AHD; see Fig. 8). Most wetlands adjacent to Lake Alexandrina effectively became hydraulically disconnected from the lake. These conditions also permitted oxidation of sulfides due to increased soil aeration from deepening of desiccation cracks (> 50 cm), especially in areas that are organic-rich (>10 % organic carbon) and clayey (>35% clay). This resulted in the formation of sulfuric material to depths up to 50 cm (sulfuric clayey soils). Under these low pH conditions, acid dissolution of the layer silicate soil minerals caused the release of Fe, Al, Mg, Si (and other elements) (Figs 17 & 18). The continued drying of the Finniss River and the adjacent wetlands caused further desiccation, and the precipitation of sulfate-rich salt efflorescences in desiccation cracks and on the sandy edges on the river (Figs 17 & 18). Areas with monosulfidic materials continued to dry out, also causing desiccation cracks to develop in the fine textured material.

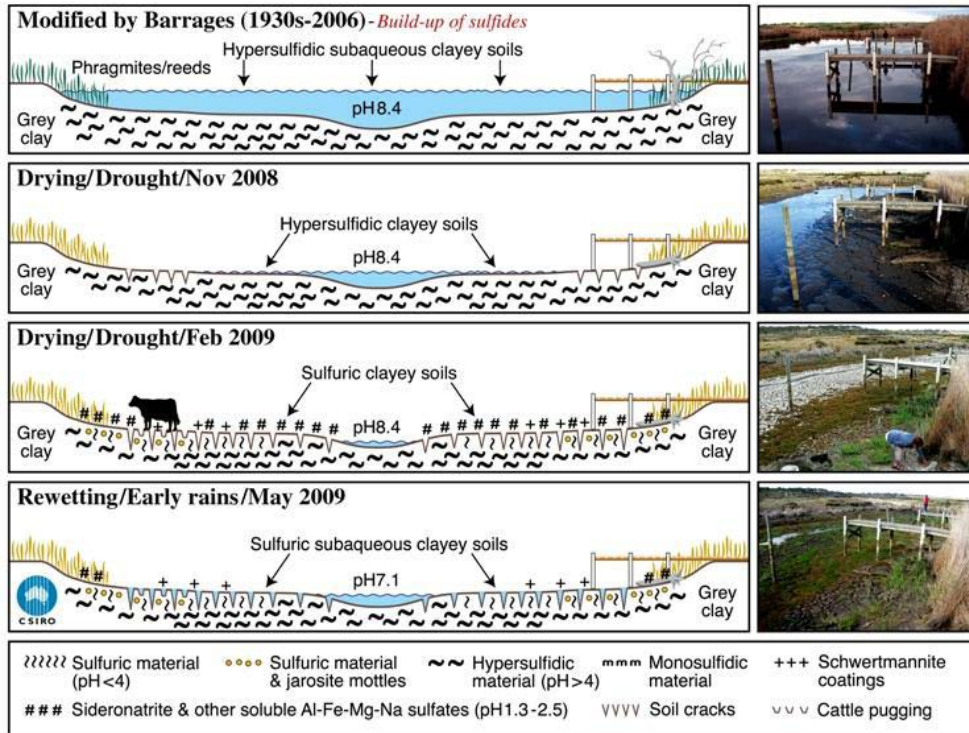


Figure 17: Predictive soil-regolith models for the Finnis River at Wally's Landing (A – A' transect in Fig. 11) illustrating modification of water flows by barrage installations causing the build up of sulfides under continuous subaqueous ASS conditions from 1930s to 2006 followed by progressive drying (middle two panels), and finally a rewetting phase in May 2009 (lower panel) resulting in acidic waters in the cracks and cattle pugs, and in running waters in adjacent wetlands.

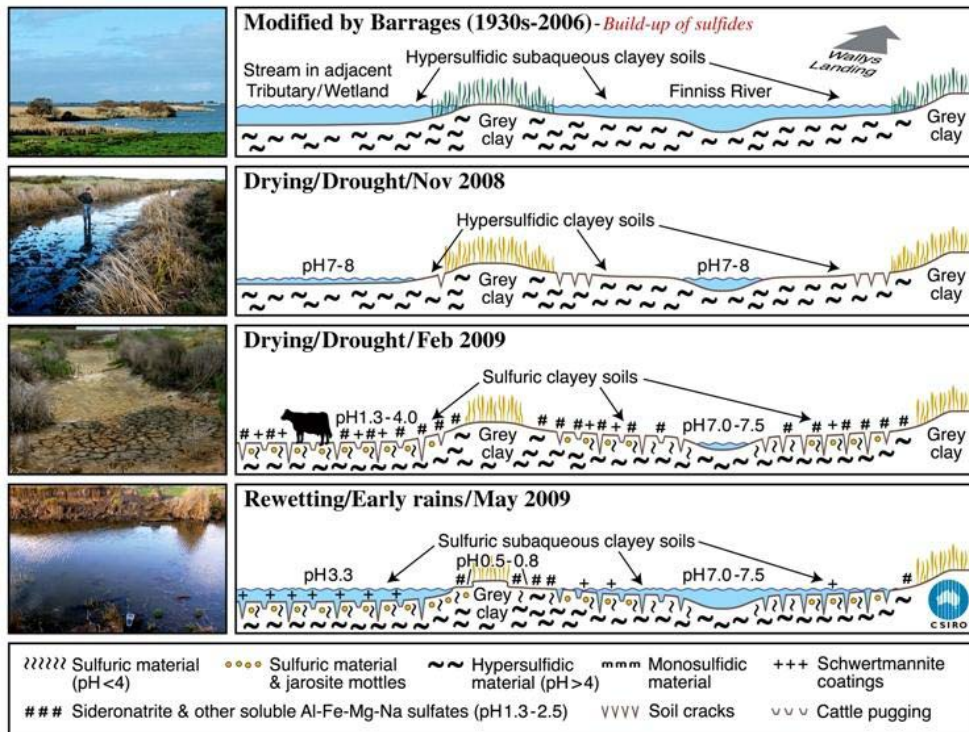


Figure 18: Predictive soil-regolith models across the Finnis River and adjacent wetland (B – B' transect in Fig. 11) illustrating modification of water flows and progressive drying (middle upper panels), and finally a rewetting phase in May 2009 (lower panel) resulting in acidic pools and running water (pH 3.3 to 4) in the cracks and cattle pugs (pH 0.5 to 0.8).

(v) **May 2009** (Figs 17 & 18 – lower panels). During May 2009, rewetting of the river and adjacent wetlands (cracks and areas pugged by cattle filled with water) caused sulfate-rich salt efflorescences to dissolve and wash into cracks and cattle pugs (pH 1.3 to 2.5) and rewetting soil surfaces with extremely low pH values (pH 0.5 to 0.8). The lower reaches of the river have a pH of 7.1 (Fig. 17). The higher river pH values on the southern side were likely partly maintained by the discharge of alkaline ground water. However, at the same time strongly flowing extremely acidic (pH 3.3) water was observed in the adjacent anabranches and wetlands draining the lower alluvial plain (Fig. 18).

Spatial distribution of Acid Sulfate Soils

The ASS maps of the Finnis River, Currency Creek and Goolwa Channel areas (area D in Fig. 5) shown in Figure 19 indicate the projected areal extent of sulfuric and sulfidic soil materials with: (a) water levels at -0.5 m AHD (February, 2008) when these soils were originally mapped using limited available data (Fitzpatrick et al. 2008a), (b) previously predicted occurrence at -1.0 m AHD, and (c) predicted occurrence for a future scenario of -1.5 m AHD (Fitzpatrick et al. 2008a). The predicted distribution at -1.0 m AHD (Figure 16b) closely approximates the extent of all ASS materials identified in late November 2008 (Fitzpatrick et al. 2009) when the water level was -0.7 m AHD and closely relates to the data displayed in the explanatory and predictive soil-regolith toposequence models (e.g. Figs 10-18).

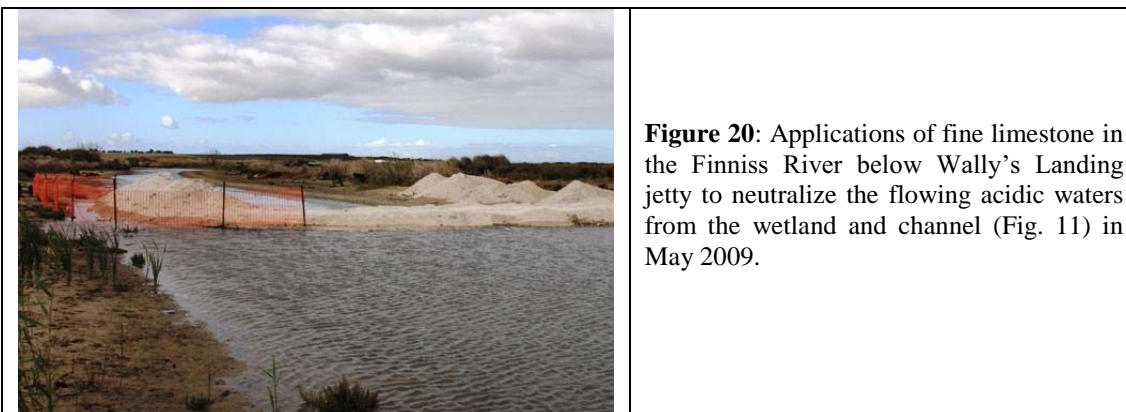
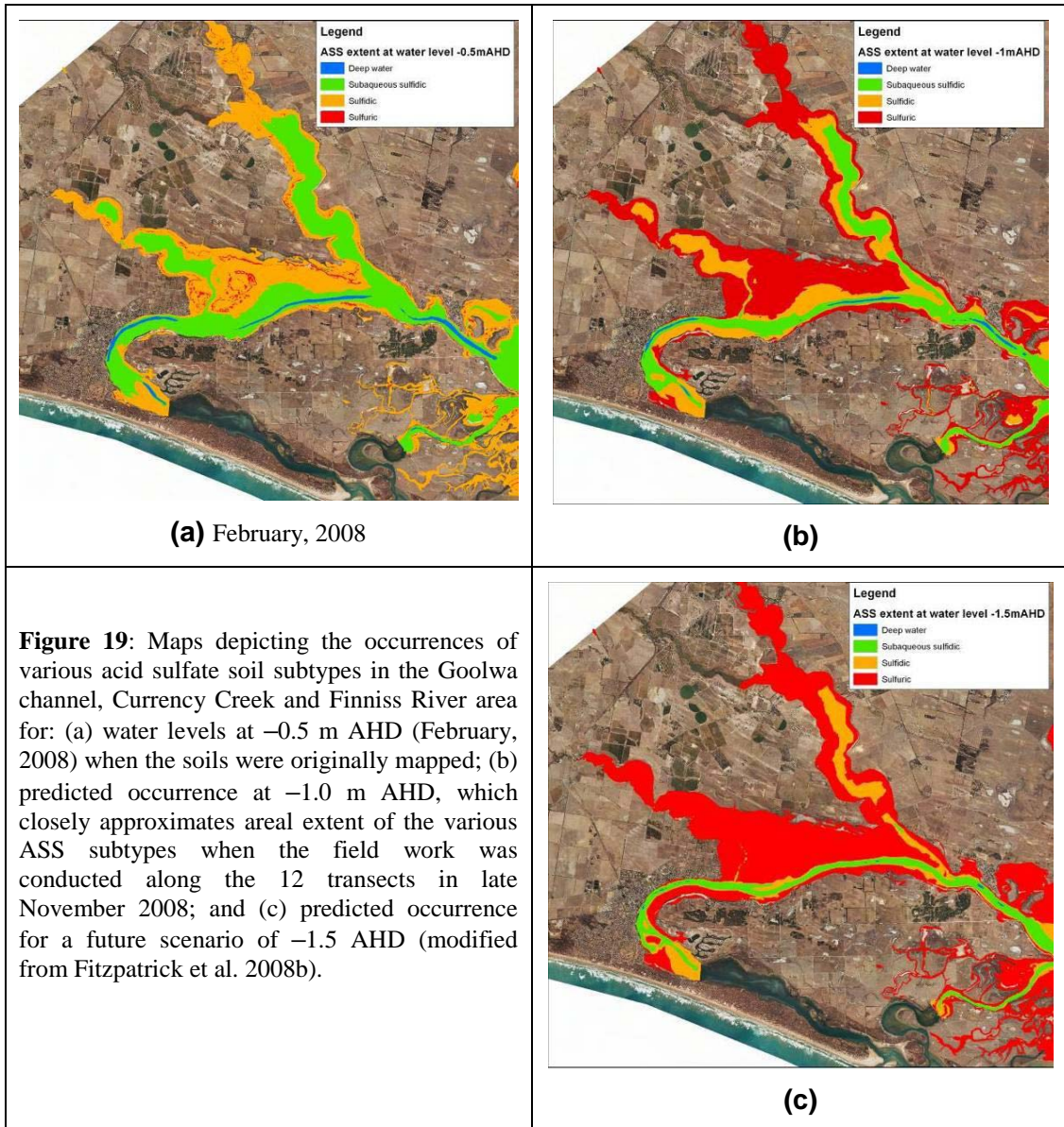
Management of acidity

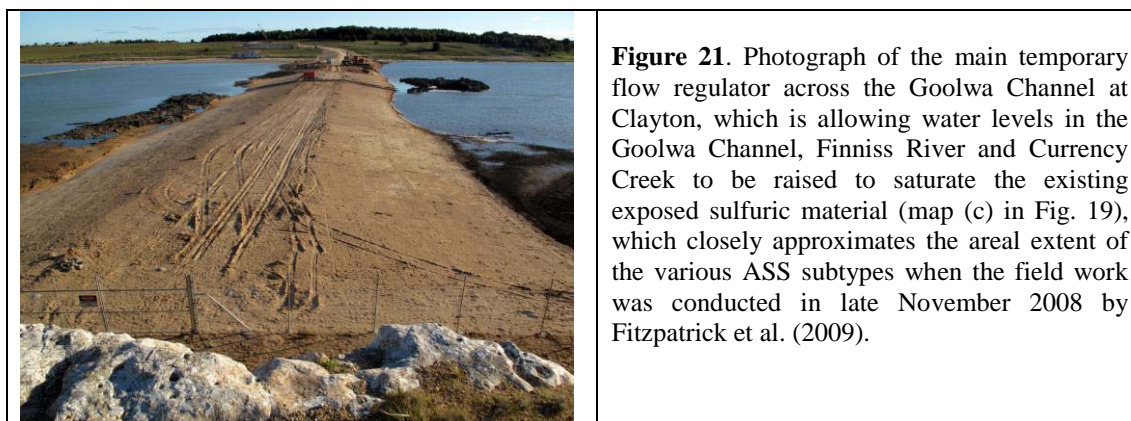
Monitoring of ASS and river waters was undertaken as an essential component of ASS assessment in this region, especially during the winter rewetting phases when acidity, metal mobilisation and widespread occurrences of salt efflorescences occurred (Figs 17 & 18 – lower panels; Fitzpatrick et al. 2009). The acidic conditions triggered the application of fine limestone to the lower Finnis River (and Currency creek) during the winter rainfall rewetting period to neutralize the flowing acidic waters from the wetland and channel to maintain pH above the critical level of 4.5 (Fig. 20).

Management of water levels to maintain future saturation of Acid Sulfate Soils

As a consequence of the widespread occurrence of sulfuric materials (Fig. 19) and acidic waters in the Goolwa Channel, Finnis River and Currency Creek areas, the Federal government, in accordance with a referral under the EPBC Act, approved a set of emergency actions to undertake management measures to mitigate Acid Sulfate Soils (DEWHA 2009).

A temporary flow regulator across the Goolwa Channel at Clayton was constructed (Fig. 21) to allow water levels in the Goolwa Channel, Finnis River and Currency Creek to be raised in order to saturate the recently exposed sulfuric and hypersulfidic materials (Fig. 19). The constructed height of the regulator is approximately $+2.5$ m AHD (to allow sufficient freeboard), but the water level will be managed to a maximum level of $+0.7$ m AHD by one-off pumping. The pool level was initially raised to $+0.7$ m AHD by pumping water from Lake Alexandrina. This action required approximately 20 GL. In addition, a low-level regulator (0 m AHD) has been constructed across the mouth of Currency Creek to permit continued saturation of sulfidic, hypersulfidic and sulfuric materials to minimise sulfide oxidation and to allow the early season flows, which will mobilise acid and heavy metals, to be held back allowing in-situ bioremediation to proceed.





ESTUARIES AND RIVER MOUTH

Sulfidic material in contemporary tidal zones

Acid sulfate soils are also present in the Murray River Mouth and Coorong (Area A in Fig. 5), the saline to hypersaline estuary and lagoon between the Lower Lakes and the Southern Ocean (Fitzpatrick et al. 2008h). The sulfidic, hypersulfidic and monosulfidic materials in these ASS have formed in the shallow permanently waterlogged subaqueous soils in the Coorong from the interaction of seawater with abundant organic material. Although sulfidic materials are formed in the Coorong, the high carbonate mineral content of this sub-coastal environment means that there is excess neutralising capacity available to counter-act potential acid formation. Notwithstanding this, it is possible that under some conditions localised acidification may occur where there is either not enough ANC, or the carbonate (shells) is coarse grained and therefore not acting to neutralise the acidity effectively.

Malodours developed on exposure of monosulfidic materials have been observed in the Coorong region for a long period of time and are regarded as a natural occurrence. These foul smelling gases are formed when monosulfidic material is present and are a recognised risk factor in ASS environments (Hicks & Fitzpatrick 2008). The presence of thick accumulations of subaqueous monosulfidic material can be readily dispersed through wind and wave action, and may result in rapid de-oxygenation of the water column.

Provided the mouth of the Murray River remains open to sea water entry, the Coorong would not be expected to deteriorate significantly as ASS conditions with sulfuric material are unlikely to develop in any significant way.

LAKES AND ADJACENT WETLANDS

Lakes Alexandrina and Albert (Areas B & C in Fig. 5) are large freshwater lakes that receive water principally from Murray River flows but also from the Eastern Mount Lofty Ranges via the Finniss River and Currency Creek. These interconnected freshwater lakes have been physically segregated from the estuarine environments of the Coorong and Murray Mouth by a series of five barrages, which were completed in the 1940's and are constructed to a height of approximately +0.83 m AHD (Fig. 7). According to Phillips & Muller (2006) they have a target maximum fill level of +0.75 m AHD. Prior to European settlement, the Lower Lakes may have experienced brief periods of seawater intrusion during severe drought periods, but generally the lakes would have remained fresh, or at worst, brackish. Based on soil investigations (Fitzpatrick et al. 2008e,h) and historical/palaeopedological knowledge, a series of 8 conceptual models have been constructed that illustrate how various ASS materials in subaqueous, waterlogged (saturated) and dried conditions have sequentially changed, and will change over time in the Coorong and Lower Lakes. To illustrate these sequential changes, a predictive soil-regolith model was constructed for Lake Alexandrina using cross-sections (Lake Alexandrina cross section A-A' is shown in Fig. 7) covering the periods:

- (i) before the 1880s (approximately 5,500 BC to 1880s period), when Lake Alexandrina cycled between natural wetting and flushing, and partial drying conditions,
- (ii) during the 1880s to 1930s when the river and lake systems were modified for irrigation purposes,
- (iii) during the 1930s to 2006, when Lake Alexandrina was first managed using locks and barrages,

- (iv) during 2006 to 2007 when partial drying of wetlands and beaches surrounding Lake Alexandrina took place during 2007 to 2008 when complete (unprecedented since installation of the barrages) drying of beaches surrounding Lake Alexandrina and adjacent whole wetlands took place,
- (v) during 2008 to 2009 if no pumping from Lake Alexandrina occurs and extreme drought conditions continue, and
- (vi) during the 2008, when pumping water from Lake Alexandrina to Lake Albert took place to maintain water levels to prevent further oxidation of sulfidic material and rewetting of sulfuric materials.

Lake Alexandrina predictive soil-regolith model (Area B in Fig. 5)

(i) Before the 1880s (5,500 BC to 1880s). Lake Alexandrina cycled between natural wetting and flushing (Fig. 22 - upper panel) as described above for the tributaries area (Fig. 16). It underwent partial drying conditions in response to seasonal (i.e. winter/summer) and climatic (e.g. drought/wet) cycles occurring in the upper MDB. During wetter periods, Lake Alexandrina underwent regular wetting and flushing cycles. Lake Alexandrina accumulated sulfidic materials from sulfate contained in surface waters and groundwaters, with occasional partial intrusion of sea water. However, during dry periods such as droughts (Fig. 22) when river flows were lower, Lake Alexandrina and adjacent wetlands dried, causing oxidation of sulfidic materials, especially on the drier margins. Pyrite in the sulfidic material was oxidised with the likely formation of sulfuric acid and potentially the formation of sulfuric materials. In wetter times and during floods, the acidic material was submerged in the water column, with dilution/neutralisation of acidity, entrainment of oxidation products in the water and the reformation of sulfidic material. The build-up of sulfidic materials in Lake Alexandrina was regularly kept in check by oxidation and removal through episodic scouring by floods.

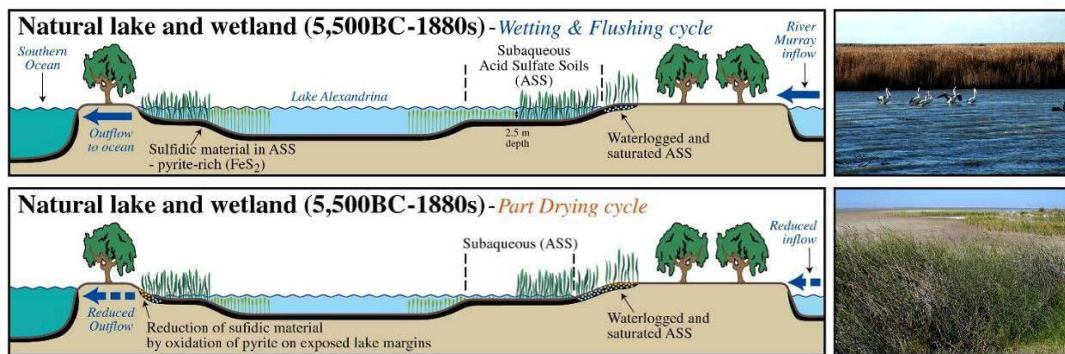


Figure 22. Predictive soil-regolith models (A-A’; Fig. 7) for Lake Alexandrina; illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycle conditions during pre-colonial times (5,000 BC–1880s).

(ii) The 1880s to 1930s period. European colonists moderated the flows of the Murray River and Lower Lakes by extraction upstream for irrigation and by the construction of locks from the 1920s to ensure reliable navigation and irrigation (Fig. 23). During this period Lake Alexandrina was “managed for flood irrigation” (e.g. mainly dairy farming).

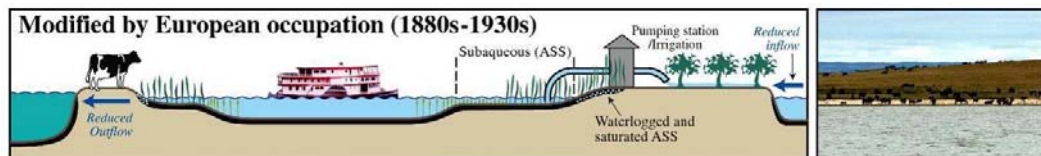


Figure 23. Predictive soil-regolith model (A-A Fig. 7) for Lake Alexandrina; illustrating modification of water flows by European occupation (1880s–1930s).

(iii) from 1930s to 2006. Lake Alexandrina was managed using locks and barrages (Fig. 24). The installation of locks and barrages allowed considerable build-up of sulfidic and monosulfidic material in the Lower Lakes (subaqueous sulfidic materials) due to: (i) the evaporative concentration of sulfate-containing nutrient/salt loads under stable pool levels and from groundwater sources, (ii) the

lack of scouring and seasonal flooding. Ultra-fine monosulfidic material also accumulated in low-flow backwaters and along the vegetated edges of the wetland.

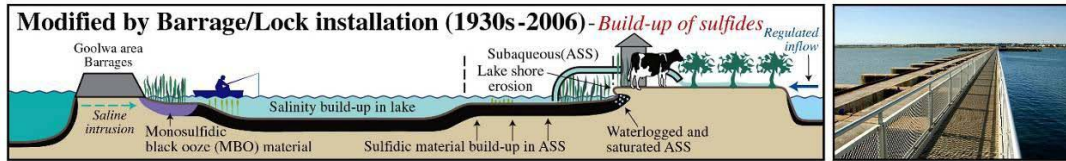


Figure 24. Predictive soil-regolith model (A-A' Fig. 7) for Lake Alexandrina; illustrating modification of water flows by barrage (and lock) installations causing the build up of sulfides under subaqueous ASS conditions from 1930s–2006.

(iv) **From 2006 to 2007.** Partial drying of wetlands and beaches surrounding Lake Alexandrina took place (Fig. 25) due to the drought conditions from 2006 to 2007 when river and lake levels continued to lower. During this period, subaqueous ASS transformed to waterlogged ASS (i.e. ASS that are wet or saturated long enough to produce periodically anaerobic conditions).

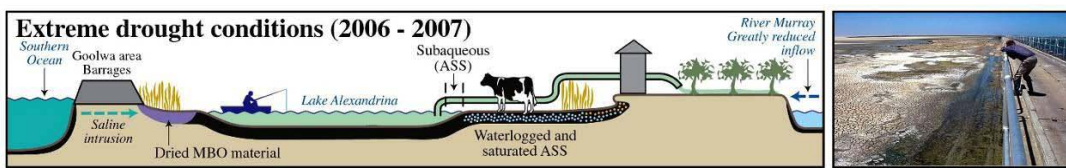


Figure 25. Predictive soil-regolith model (A-A' Fig. 7) for Lake Alexandrina, illustrating extreme drought conditions in 2006– 2007 where subaqueous ASS transform to waterlogged ASS (i.e. ASS that are wet or saturated long enough to produce periodically anaerobic conditions, thereby influencing the growth of plants: e.g. hydric soils with sulfidic material).

(v) **From 2007 to 2008.** Drying of extended beaches surrounding Lake Alexandrina and adjacent wetlands took place (Fig. 26). Most wetlands adjacent to Lake Alexandrina effectively became hydraulically disconnected from the lake. This resulted in the formation of sulfuric material with depths up to 75 cm. These conditions have also permitted deepening of desiccation cracks (>50 cm), especially in areas that are organic-rich (>10% organic carbon) and clayey (>35% clay). The continued drying of Lake Alexandrina and the adjacent wetlands caused further desiccation, and the precipitation of a wide range of sulfate-rich salt efflorescences in desiccation cracks and on the sandy beaches surrounding the lake. Areas with monosulfidic material continued to dry out, also causing desiccation cracks to develop in the fine textured material (Fig. 26).

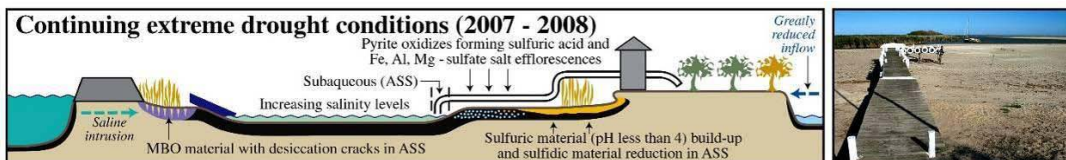


Figure 26. Predictive soil-regolith model (A-A'; Fig. 7) for Lake Alexandrina; illustrating the formation of: (i) sulfuric material (pH <4) by oxidation of sulfides in sulfidic material, (ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued lowering of water levels under persistent extreme drought conditions during 2007–2009.

(v) **Rewetting scenario post 2008** (Fig. 27) illustrating the various rewetting scenarios of initial acidification, metal and salt mobilisation during low water flows, followed by metal dilution, immobilisation and flocculation during sustained increased water flows and ponding (Fig. 27). In September 2009, CSIRO identified an area of more than 200 ha of acidic surface water (pH 2.74 to 3.05) in Loveday Bay, a rewetted part of Lake Alexandrina containing sulfuric materials.

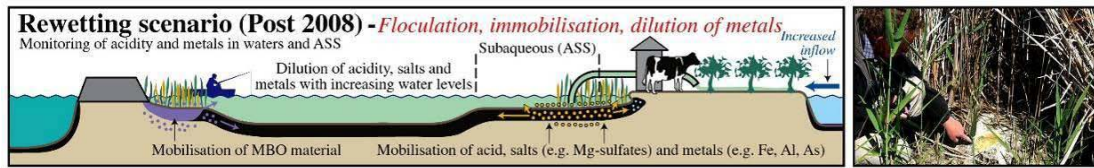


Figure 27. Generalised schematic cross section (A-A'; Fig. 7) model for Lake Alexandrina; illustrating the various rewetting scenarios of initial metal and salt mobilisation during low water flows followed by metal dilution, immobilisation and flocculation during sustained increased water flows and ponding.

Spatial Distribution of ASS in Lake Alexandrina

Combined bathymetry, soil and vegetation mapping in a GIS was used to construct ASS maps to help predict the distribution of the various subtypes of ASS according to three scenario maps (Fitzpatrick et al. 2008a,d,e,h), which depict sequential changes in ASS materials at different water levels in Lake Alexandrina of +0.5 m AHD (pre-drought), -0.5 m (approximate level during early 2008), and for -1.5 m AHD (an extreme case, should lower lake inflows persist). These are presented schematically for Lake Alexandrina in a series of simplified maps in Figure 28 (more detailed maps are available in reports by Fitzpatrick et al. (2008a,e,h). The maps show the distribution of different subtypes of ASS (deeper than 2 m; subaqueous sulfidic; sulfidic and sulfuric) as lake water levels drop, and soils de-water.

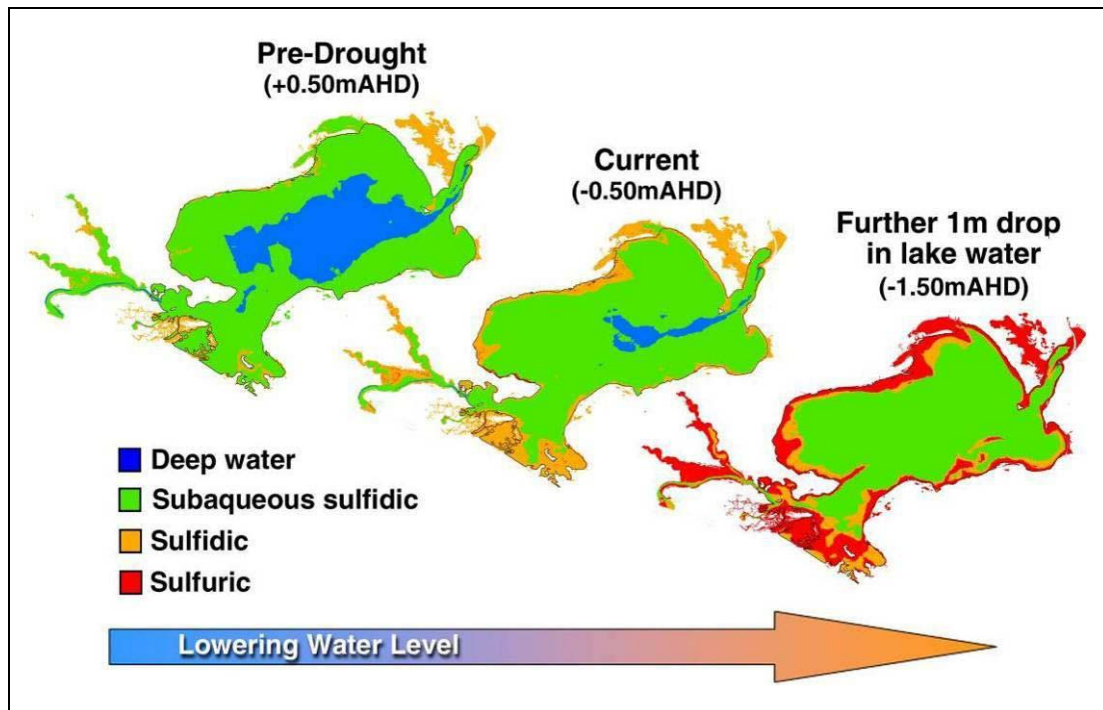


Figure 28 Predictive scenario maps depicting changes in acid sulfate soil materials at different water levels in Lake Alexandrina (+0.5 m AHD, -0.5 m AHD and -1.5 m AHD) from Fitzpatrick et al. (2008b). Finnis River, Currency Creek and Goolwa Channel are the three extensions occurring on the left side of Lake Alexandrina.

Management of ASS in the Lower Lake systems

The management option for preventing more sulfidic material in Lake Albert oxidising to form sulfuric material was implemented by pumping water from Lake Alexandrina to Lake Albert to maintain water levels (Fig. 29). This option was based on: (i) identification of abundant sulfuric and sulfidic materials in Lake Albert when water levels were -0.3 m AHD, (ii) predicted formation of abundant sulfuric materials when water levels drop further if the extreme drought conditions in the Lower Lakes continued (see ASS maps, Fig. 28) and (iii) the absence of satisfactory environmental flows resulting in restoration of water levels in the lower lakes. The South Australian and Australian Federal governments have continued to maintain water levels in Lake Albert at approximately -0.3 m

AHD by pumping water at a rate of 400 ML/day from Lake Alexandrina to Albert to prevent the water level in Lake Albert dropping below -0.6 m AHD (Fig. 29), to minimise the risk of soil and water acidification. Lake Albert was disconnected from Lake Alexandrina after the construction of an earthen bank (see photograph in Fig. 29) before pumping commenced in early 2008. During most of 2008, pumping water from Lake Alexandrina to Lake Albert took place to successfully maintain water levels (Fig. 29).

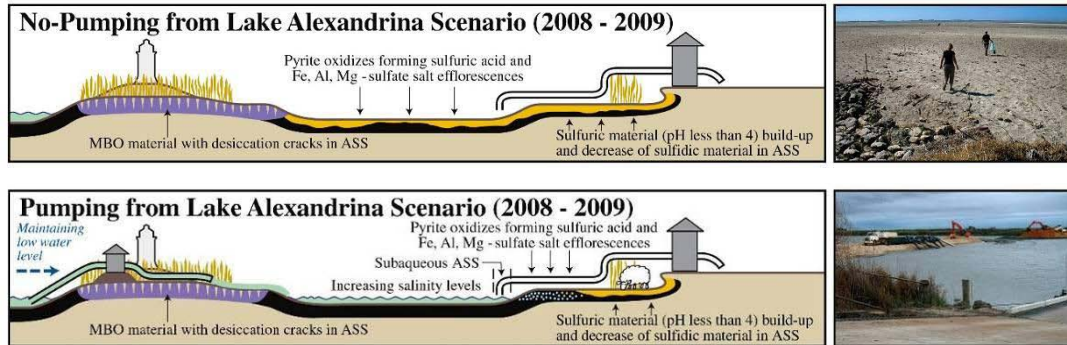


Figure 29. Generic conceptual models for Lake Albert showing: (a) the formation of sulfuric materials on the edges of the lake – “no management or no pumping scenario” (upper panel) illustrating the widespread formation of: (i) sulfuric material (pH <4) by oxidation of sulfides in sulfidic material, (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, and (b) management by protecting sulfidic materials from oxidation using partial water inundation – “pumping of water from Lake Alexandrina scenario” (lower panel) where an earthen bank between Lake Albert and Lake Alexandrina was constructed in early 2008, which disconnected Lake Albert from Lake Alexandrina.

MURRAY RIVER SECTION BELOW BLANCHETOWN (LOCK 1): MAIN RIVER CHANNEL AND ADJACENT WETLANDS

Swanport wetland explanatory soil-regolith model (Site E1 in Fig. 5)

The biggest impact on drying wetlands has been in the stretch of the Murray River below Lock 1 (Area E in Fig.5), where most wetlands dried completely during 2007-08. The impacts of ASS in these wetlands have been very variable depending on the amount of sulfide minerals present and the buffering capacity of the previously sub-aqueous soils (Fitzpatrick et al. 2008f). A number of distinctive bright yellow oxyhydroxysulfate minerals have been identified in these wetlands as a consequence of sulfide oxidation. In these wetlands, the presence of such key “indicator minerals” has proved particularly useful in the field identification of sulfuric materials (Fig. 30). In fact, it was these prominent features, which originally led CSIRO to first discover the presence of sulfuric materials in the Swanport wetland near Murray Bridge in June 2007 (Fitzpatrick et al. 2008f).

The salt efflorescences sampled from sulfuric materials at Swanport and Ukee wetlands proved to be an assemblage of sulfate-containing minerals (Fitzpatrick et al. 2008f). Movement and accumulation of such soluble salts is typical of drained soils under extremely acidic conditions (pH <3.5). In surface soil samples at the Swanport and Ukee wetlands these salt efflorescences comprised salts with a yellowish (natrojarosite) or golden mineral determined to be the rare mineral metavoltine ($\text{Na}_6\text{K}_2\text{FeFe}_6(\text{SO}_4)_{12}\text{O}_2 \cdot 18\text{H}_2\text{O}$), which formed botryoidal encrustations on the edges of cracks (Fig. 30) as an alteration product of weathered pyrite. This discovery documents the first occurrence of metavoltine in Australia and possibly the first ever occurrence associated with acid sulfate soils. White crystals of alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) were also identified, having formed as a result of acidic (pH < 2.5), sulfate-bearing solutions that reacted with layer silicates in the soils. These localised solutions were rich in ferrous and ferric iron and also contained dissolved potassium and sodium. Metavoltine and alunogen are presumed to be the last minerals to form in areas of intense evaporation. The sulfuric material, which also contained hexahydrate and gypsum, developed after drainage of the soils as watertable levels dropped below 40 cm in June 2007 to below 90 cm in November 2007 (Fig. 30).

Management of ASS by retaining acidity and monosulfidic material within wetlands

The management scenario presented here is based on the availability of sufficient water for ASS management. In order to address the fate of identified sulfuric material in adjacent wetlands on the river system between Lock 1 and Wellington, the management option shown in the lower panel of Figure 31 involved the construction of a sluice gate at the river inflow of the managed Paiwalla wetland (Site E4 in Fig. 5). Hence, the successful management of ASS in the Paiwalla wetland has involved careful maintenance of water levels by controlling in- and out-flows.

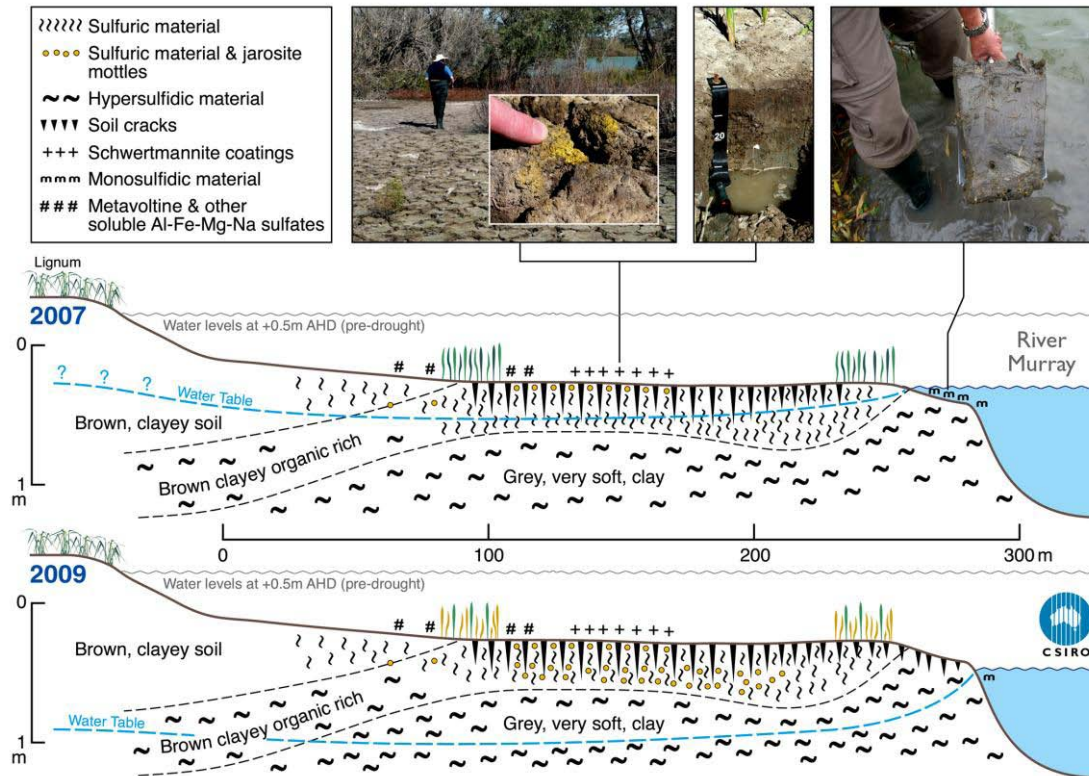


Figure 30. Schematic cross section models for Swanport wetland (site E1 in Fig. 5) showing: Acid Sulfate Soil with sulfuric material in drained wetlands adjacent to the Murray River (left), which shows extensive cracking and accumulation of scale-like, bright golden yellow crystals of metavoltine ($K_2Na_6Fe^{2+}Fe^{3+}_6(SO_4)_{12}O_2 \cdot 18H_2O$) and white crystals of alunogen (From Fitzpatrick et al. 2008f).

Under this management scenario, sulfuric materials and metal salts have been contained in the wetland, thus allowing targeted and controlled management to occur to reinstate and maintain wetland quality. This management option enables the sulfate-rich salt efflorescences to dissolve and become diluted and once appropriate wetland/redox conditions resume, sulfidic materials reform, while metals bioaccumulate, or accumulate in the subaqueous soils. It also reduces the risk of saline, nutrient-laden and acidic-metal-rich water draining back into the river as river levels fall and/or rise. In contrast, under an unmanaged wetland scenario (upper panel, Fig. 31) or river bank there is little control of the mobilisation of sulfuric materials and eventual fate of sulfate, monosulfidic materials and salts, the fates of which are controlled by natural – but moderated – river water flows and floods (although the volume of water in the river channel would provide considerable dilution to such materials).

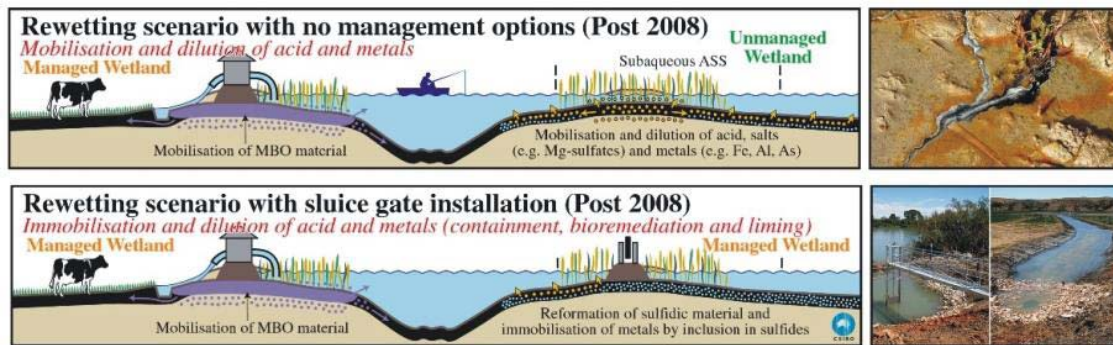


Figure 31. Generic conceptual model for lower-Murray River banks and wetlands between Blanchetown and Wellington (Site E1 in Fig. 5); re-wetting management post-2008: no management scenario (upper panel) and management by sluice gate scenario (lower panel).

RIVER SECTION ABOVE BLANCHETOWN (LOCK 1)

Banrock Station (Site F1 in Fig. 5)

Banrock Station wetland is located in the lower Murray River system, about 15 km west of Barmera in South Australia (Site F1 in Fig. 5). This Ramsar wetland effectively by-passes Lock 3 (Fig. 7) and consists of a single, elongate lagoon covering some 120 hectares at pool level (+8.6 m AHD). A second, eastern lagoon (130 ha) is connected to the main Banrock lagoon but is usually dry at pool level, becoming flooded when water levels are above 9.2 m AHD. The wetland is connected to the River by one meandering inlet creek, and one outlet creek (with flow control structures on each creek installed in 1993) and is situated in a river red gum floodplain that covers an area of about 520 ha.



Figure 32. Photographs of areas in the Banrock Ramsar wetland (Site F1 in Fig. 5) near the inlet creek in May 2008 showing: (1a) sampling a sandy, sulfuric soil profile (RBA1) at the medium to high water mark in *Typha* and *Phragmites* reeds, and (1b) dry, cracked, sulfidic clays in the near surface soils in the bed of Banrock wetland.

Banrock wetland predictive soil-regolith model (Site F1 in Fig. 5)

The main Banrock lagoon was permanently flooded from 1925, when Lock 3 was constructed (Figs. 5 & 7), to 1993 when partial drying phases were introduced as a wetland management tool. From 1993 to June 2006 the wetland has been partially dried each winter (to introduce semi-natural wetting-drying cycles). The wetland almost completely dried from 2007 to June 2008 (18 months; Fig. 32). The wetland was re-flooded in June 2008 and a drying cycle introduced in October 2008. To illustrate these sequential changes as well as the historical/geological changes, we have constructed the following series of predictive soil-regolith models across the Banrock wetland:

- (i) Before 1880s (approximately 5,500 BC to 1880s period).
- (ii) During the 1880s to 1930s period when the river and wetland systems were first used for navigation and irrigation.
- (iii) During the 1925 to 1993 period when the river and wetland systems were first managed using locks.

- (iv) During the 1993 to 2006 period when partial drying cycles and substantial rewetting cycles occurred because of the installation of sluice gates.
- (v) During the January 2007 to June 2008 period (18 months) when unprecedented drying took place.
- (vi) During June 2007 to October 2008 period (5 months) when complete rewetting took place.

(i) **Before the 1880s (5,500 BC to 1880s).** The Banrock wetland cycled between natural wetting and flushing, and partial drying conditions in response to seasonal and climatic cycles occurring in the upper MDB (Fig. 33).

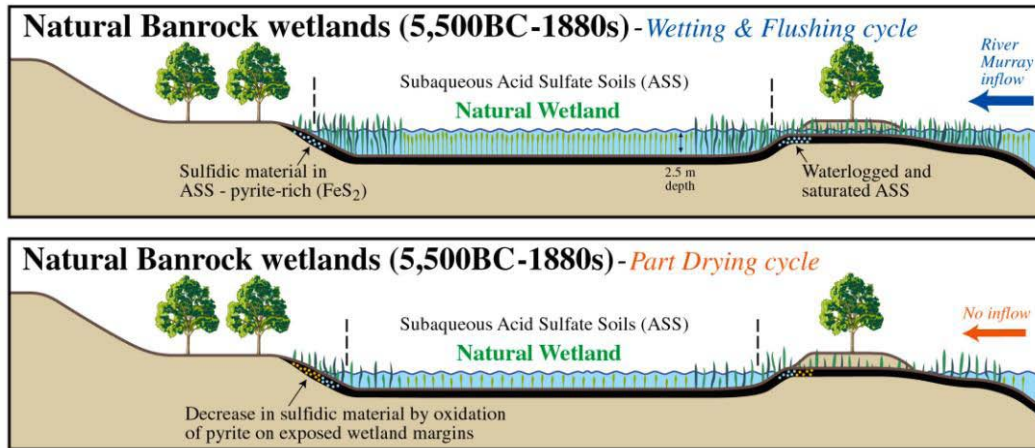


Figure 33. Predictive soil-regolith models for Banrock wetland illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycle conditions during pre-colonial times (5,000 BC-1880s).

Waters received by the wetlands were transferred via channels, overland flow, and by infiltration. The wetlands accumulated sulfidic materials from sulfate contained in surface flows and groundwaters. However, during dry periods such as droughts (Fig. 33 – lower panel) when river flows were lower, the wetland dried, causing oxidation of sulfidic materials, especially on the dry margins. Pyrite in the sulfidic material was oxidised with likely formation of sulfuric acid and possibly formation of sulfuric materials. During wetter times and in flood periods, the acidic material was submerged, with dilution/neutralisation of acidity and the reformation of sulfidic material. The build-up of sulfidic materials in the Banrock wetland was regularly kept in check by oxidation and removal by scouring floods.

(ii) **The 1880s to 1930s period.** European settlers moderated the flows of the Murray River by the installation of various irrigation network systems (Fig. 34). During this period the wetland was “managed for flood irrigation” (e.g. citrus and dairy).

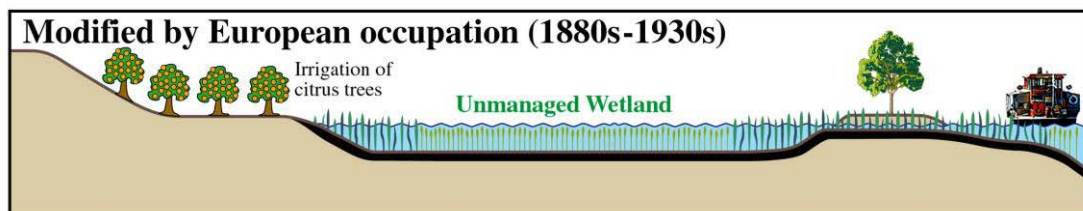


Figure 34. Predictive soil-regolith model for the Banrock wetlands; illustrating modification of water flows by European occupation (1880s- 1930s).

(iii) **The 1925 to 1993 period.** The river and wetland systems were managed using locks (Fig. 7). The installation of locks enabled considerable build-up of sulfidic and monosulfide material in the wetland (Fig. 35).

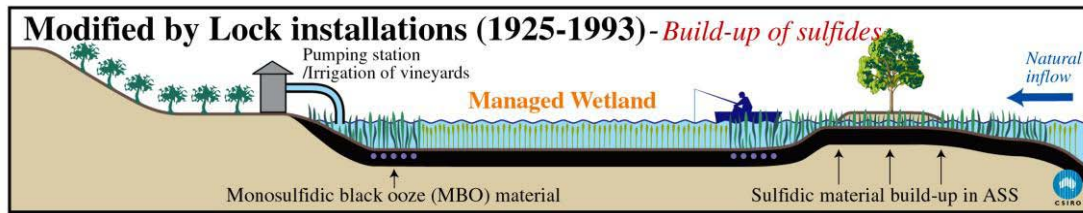


Figure 35. Predictive soil-regolith model for the Banrock wetland illustrating modification of water flows by lock installations causing the build up of sulfides under continued subaqueous ASS conditions from 1925-1993.

(iv) **The 1993 to 2006 period.** Partial drying cycles and substantial rewetting cycles occurred due to the installation of flow control structures (sluice gates) (Fig. 36). During dry periods (Fig. 36 – top panel) the wetland partly dried in places, causing likely oxidation of sulfidic materials, especially on the margins of the wetland.

The accumulated pyrite in the thick sulfidic material is likely to have partly oxidised with formation of sulfuric acid and possibly formation of sulfuric materials, similar to the natural system described in Figure 32. During the rewetting cycles, the acidic material was submerged in the water column, with dilution/neutralisation of acidity and the reformation of sulfidic material. Hence, the build-up of sulfidic material in the wetland was controlled by regular periods of oxidation. In 2006, the pump used for irrigation purposes was removed because of the Ramsar status of the wetland (in Fig. 37 the old irrigation pump has been removed and a new pump installed for pumping river water into the wetland).

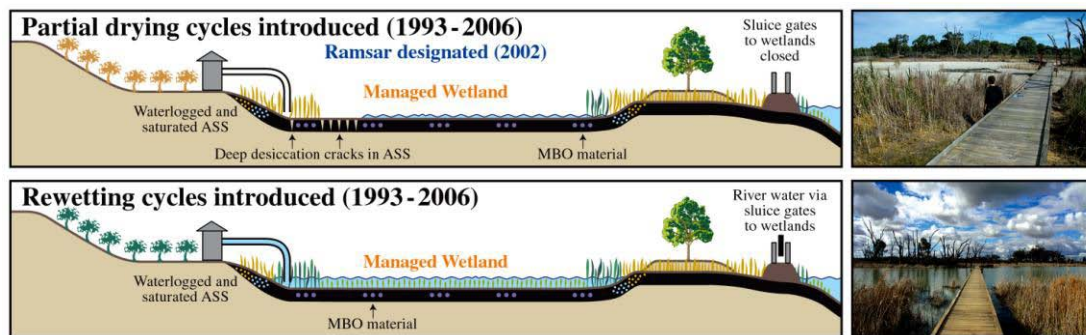


Figure 36. Predictive soil-regolith models for the Banrock wetland illustrating the installation of sluice gates to manage the partial drying cycle (upper panel) and the rewetting/ flushing cycle (lower panel) during 1993 to 2006). The Banrock wetland was designated a Ramsar site in 2002.

(v) **The 2007 to June 2008 period** (18 months). When drying of the upper soil in whole wetland took place (Fig. 37), the wetland effectively became hydraulically disconnected from the river channel. During this period, subaqueous ASS transformed to waterlogged ASS and eventually to dried ASS. This resulted in the formation of sulfuric material to depths up to 50 cm and deepening of desiccation cracks (> 50 cm), especially in areas that are organic-rich (>10 % organic carbon) and clayey (>35 % clay). Under such low pH conditions, acid dissolution of the layer silicate soil minerals is likely to have caused the release of Fe, Al, Mg, Si (and other elements) and the formation of sulfate-rich salt efflorescences in and near soil surfaces (Fig. 37). The continued drying of the wetlands has caused further desiccation, and the precipitation of sulfate-rich salt efflorescences in desiccation cracks and on the sandy edges of the wetland. Areas with monosulfides continued to dry out, causing desiccation cracks to develop, especially in the fine textured material.

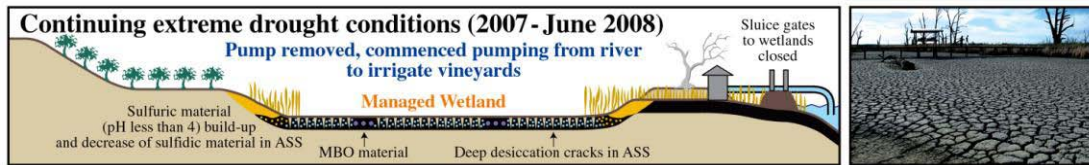


Figure 37. Predictive soil-regolith conceptual model for the Banrock wetland illustrating the formation of: (i) sulfuric material (pH <4) by oxidation of sulfides in sulfidic material on the edges of the wetland, (ii) sulfate-rich salt efflorescences, and (iii) deep desiccation cracks; due to continued lowering of water levels under persistent extreme drought conditions during 2007 – 2008.

(vi) **From June 2007 to October 2008 period (5 months).** When complete rewetting took place by pumping water into the wetland (Fig. 38), sulfuric, sulfidic and monosulfide materials, including sulfate-rich salt efflorescences become diluted and mobilised. Once appropriate wetland/redox conditions resume, sulfidic materials are likely to reform, while metal salts bioaccumulate, or accumulate in sediments. Under this management scenario, there is control of the distribution and eventual fate of sulfates, monosulfides and salts.

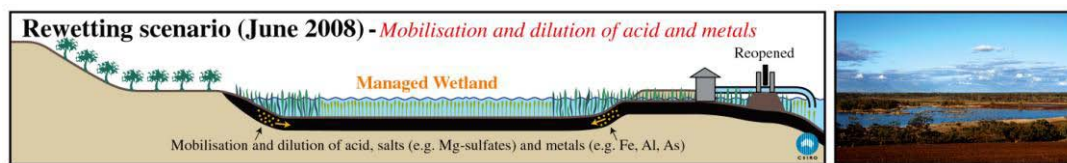


Figure 38. Predictive soil-regolith conceptual model for the Banrock wetland showing the complete re-wetting of the whole wetland in June 2008 with inundation of sulfuric materials, which occur on the edges of the wetland.

Continued management of this managed Ramsar wetland will involve the careful maintenance of water levels by controlling in-flows and out-flows. Under this management scenario, sulfuric materials and metal salts will be contained in the wetland and flushed at appropriate times, thus allowing targeted and controlled management to occur to re-instantiate and maintain wetland quality.

Loveday Disposal Evaporation Basin (Site F2 in Fig. 5)

The presence of sulfidic soils in a number of wetlands historically used as evaporation basins was studied by Lamontagne et al. (2004 & 2006), who concluded that a large number have sufficient alkalinity to neutralise acid generated by the oxidation of pyrite (Fig. 39). Many of these saline disposal basins contained monosulfidic materials, and although acid generation from sulfuric materials may not be a major issue, other problems such as deoxygenation of surface waters, metal mobilisation and foul smelling odours remain an issue (Hicks & Fitzpatrick 2008).



Figure 39. Loveday hypersaline disposal basin, adjacent to the Murray River (Site F2 in Fig. 5), showing large irreversible trans-horizon polygonal cracks with very coarse columnar ped structures; the result of desiccation and dewatering of clayey subaqueous soils during wetting and drying cycles. It was originally a natural wetland prior being used as a salt disposal basin. The surface of the peds is coated with thin salt incrustations and efflorescences dominated by microcrystalline gypsum, halite, Mg-calcite and Sr-rich aragonite. Pyrite framboids were still present within peds despite being exposed to the atmosphere for several months.

Detailed studies by Wallace et al. (2008a) of the Loveday Disposal Basin, previously used for irrigation discharge, have shown that sulfidic soils are mainly developed in the top 40 cm, principally associated with organic-rich sulfidic wetland clays (Fig. 39). They showed that wetting and drying cycles may lead to areas where the acid generation potential was greater than stored alkalinity due to the transport of alkalinity in the soils during evaporation and concentration of carbonate at the soil

surface. Although alkalinity was generally sufficient to mitigate acidification risks at the scale of the wetland, local areas were found where net acidity was generated and jarosite was present.

Noora Disposal Basin (Site F3 in Fig. 5)

The Noora Disposal Basin, east of Loxton, is used as a disposal site for saline waters from salt interception schemes designed to minimise salinity impacts on the Murray River (Site F3 in Fig. 5). Monosulfides containing up to 0.6 % S_{CR} are present in some parts of the basin (Fig. 40) and were inundated with saline water (similar SEC or EC to seawater). However, the acid neutralising capacity (ANC) in the monosulfides was very high (up to 50% ANC as $CaCO_3$), more than sufficient to neutralise potential stored acidity (Shand et al. 2008c).



Figure 40. Noora disposal basin showing black monosulfides (monosulfidic material) beneath a very thin oxidised layer.

Nelwart Lagoon (Site F4 in Fig. 5)

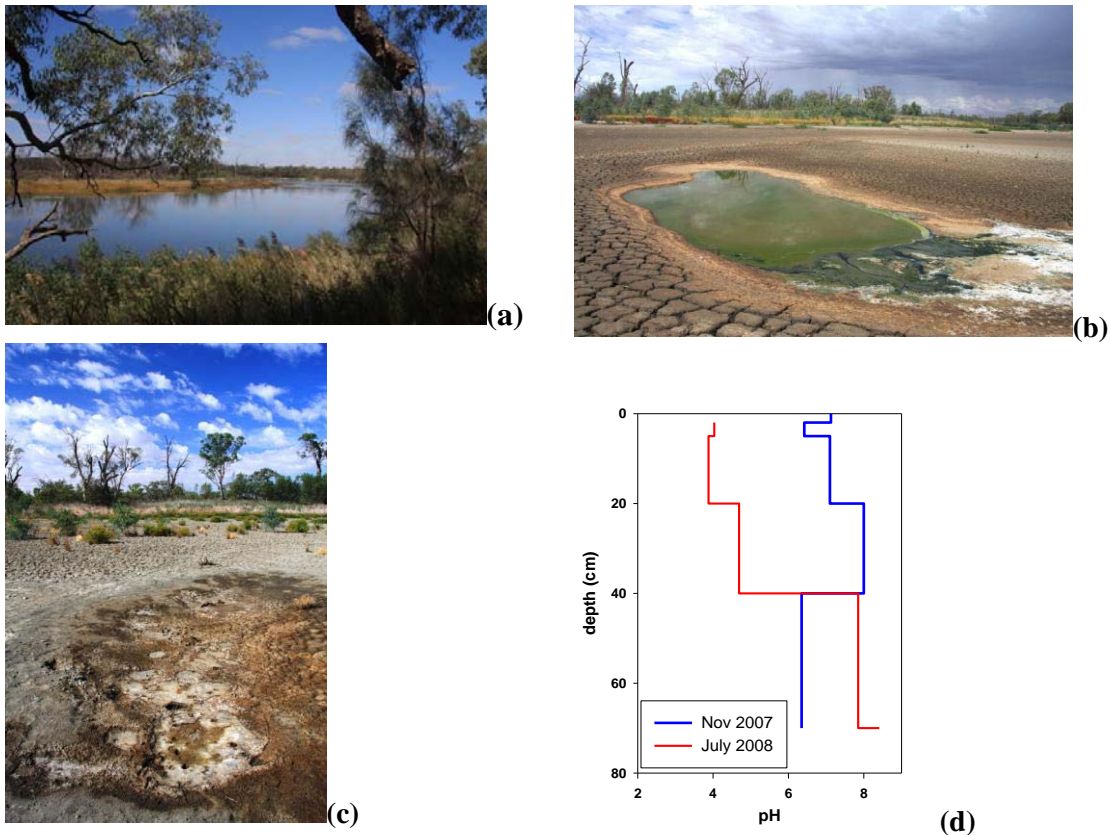


Figure 41. Nelwart Lagoon (Site F4 in Fig. 5): (a) containing surface water; (b) dried wetland showing remnant water, cracked clay soils and surface efflorescences; (c) groundwater discharge area showing salt efflorescences; (d) plot showing decrease of pH is surface soil layers during drying of the wetland.

Nelwart Lagoon, near Renmark is typical of a number of wetlands adjacent the Murray River (Site F4 in Fig. 5). This oxbow lake was temporarily cut off from the Murray River in 2007 to help maximise water savings during this period of reduced inflows to the river (Fig. 41). The wetland soils initially comprised hypersulfidic clay-rich soils with hypersulfidic subaqueous sandy soils around the margins. A number of groundwater springs were identified at the edges and within the wetland during the drying process. These springs provide sulfur as well as alkalinity to the wetland system, and monosulfidic material were a typical characteristic at the discharge points.

As the wetland dried, sulfuric materials gradually became dominant over most of the wetland, with a number of sulfate-rich efflorescences forming on surface layers. These included natrojarosite, sideronatrite and tamarugite. A number of Mg and Na sulfate minerals were also noted, particularly where groundwater discharges were present. Where the buffering capacity of the soils was low, the soil pH generally showed a decrease in surface layers as drying progressed (Fig. 41).

Ground water salt interception scheme (Site F6 in Fig. 5)

The clogging of bore pumps and screens by an amorphous Al-hydroxysulfate in a salt interception scheme near Bookpurnong was attributed to the oxidation of pyrite present in the Lower Loxton Sands aquifer of Pliocene age (Shand et al. 2006, 2008a). The Loxton Sands is composed of a sequence of lower and upper shoreface, beach, estuarine, dune and back-barrier lagoonal sediments. The clogging occurred some time after pumping and the groundwater pH values were slightly acidic to neutral, where Al solubility is theoretically very low.

The presence of large amounts of pyrite was confirmed using SEM. Figure 42 illustrates that both framboidal and octahedral pyrite were present. The textures of the sediment and pyrite morphology are very similar to present day coastal ASS, and Shand et al. (2006, 2008a) postulated that the pyrite, which was present in fine-grained facies may have formed as part of an ancient coastal ASS.

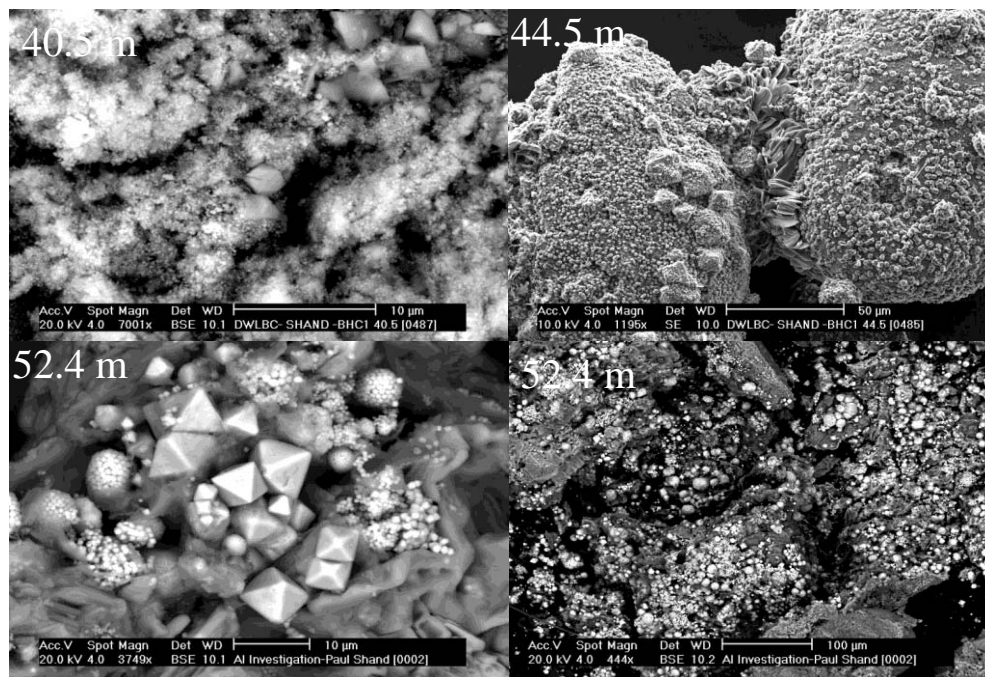


Figure 42. SEM images of samples from Loxton Sands (samples depths shown in metres). 40.5 m: Fe oxyhydroxide coating of sand grain with euohedral to subhedral crystals of alunite-jarosite; 44.5 m: two sand grains coated with abundant euohedral (cuboid and octahedra) pyrite and bridging laths of hydroxysulfate mineral (natrojarosite); 52.4 m (left image) framboidal and octahedral pyrite on a base of natrojarosite-natroalunite; (right image) abundant coatings of framboidal pyrite (bright areas).

In addition to pyrite, secondary sulfate minerals of natrojarosite-natroalunite were abundant (Fig. 42), indicating acidic conditions. The sediments were recovered from cores which had been stored and the hydroxysulfate minerals are likely to have formed by pyrite oxidation and dissolution of aluminosilicate minerals (clays and feldspar) during slow drying of the core material. Their

presence indicates that there was insufficient buffering to neutralise the acidity generated during oxidation of the pyrite.

A conceptual model (Fig. 43) was developed whereby cavitation and lowering of the water table towards the redox boundary introduced oxygen and induced acid production and Al mobilisation at the redox boundary. The mixing of this locally-derived acidic groundwater with circumneutral pH water from above and below the boundary induces rapid Al precipitation on borehole screens, and in particular at the pump inlet. This model explains the delay in clogging as well as the conflicting hydrogeochemistry (high Al concentrations at circumneutral pH).

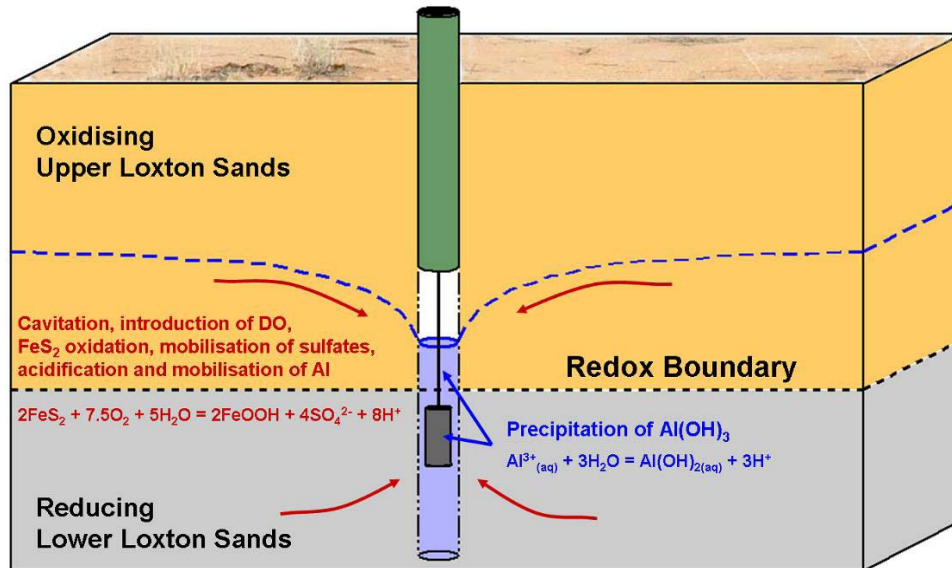


Figure 43. Conceptual diagram showing the development of a cone of depression during extended pumping. Oxygenated water is introduced below the redox boundary allowing pyrite oxidation, the production of acidity and dissolution of aluminosilicate minerals (e.g. clays). Mixing of this water in the high pH environment of the bore column causes rapid precipitation of Al-oxyhydroxide on screens and in the pump.

SEEPAGES OVERLYING MINERALISED ZONES IN MT. LOFTY RANGES

The Acid Sulfate Soils overlying mineralised zones in the Mount Lofty Ranges (Area G in Fig. 5) differs from the ASS in the Murray River flood plains system (Areas B to F in Fig. 5) because the source of sulfur is from sulfatic-rich ground waters derived from sulfide mineralization (ore bodies) of the Kanmantoo rocks of the eastern Mt Lofty Ranges.

Herrmanns catchment explanatory soil-regolith model (Site G1 in Fig. 5)

Fitzpatrick et al. (1996) constructed descriptive and explanatory soil-regolith process models to describe: (i) water flow paths in saline seepages (Cox et al. 1996; Salama et al. 1999), (ii) development of sulfidic and sulfuric materials in ASS, and (iii) contemporary geochemical dispersion and erosion processes present in the lower parts of a toposequence in the Herrmann catchment in the Mount Lofty Ranges (Figs 44 & 45). Sulfidic material containing pyrite framboids was formed in these seepages by a combination of: (i) saline groundwaters with high sulfate concentrations (with other elements sourced from mineralised zones e.g. Pb and Zn) seeping up through soils, (ii) anaerobic conditions, and (iii) organic carbon in saturated soils, generated sulfidic material containing pyrite framboids formed by anaerobic bacterial reduction of sulfate. When these sulfidic materials are exposed to air, pyrite is oxidised producing sulfuric acid, which dissolves soil minerals and leads to precipitation of a number of secondary mineral combinations such as: (i) sideronatrite, tamarugite, copiapite, halite and gypsum in sandy sulfuric materials with pH < 2.5, (ii) natrojarosite, jarosite and plumbojarosite in clay-rich sulfuric materials with pH 3.5-4, and (iii) schwertmannite (pH 4), ferrihydrite (pH >6), akaganéite and white, poorly-crystalline Al oxyhydroxide precipitates.

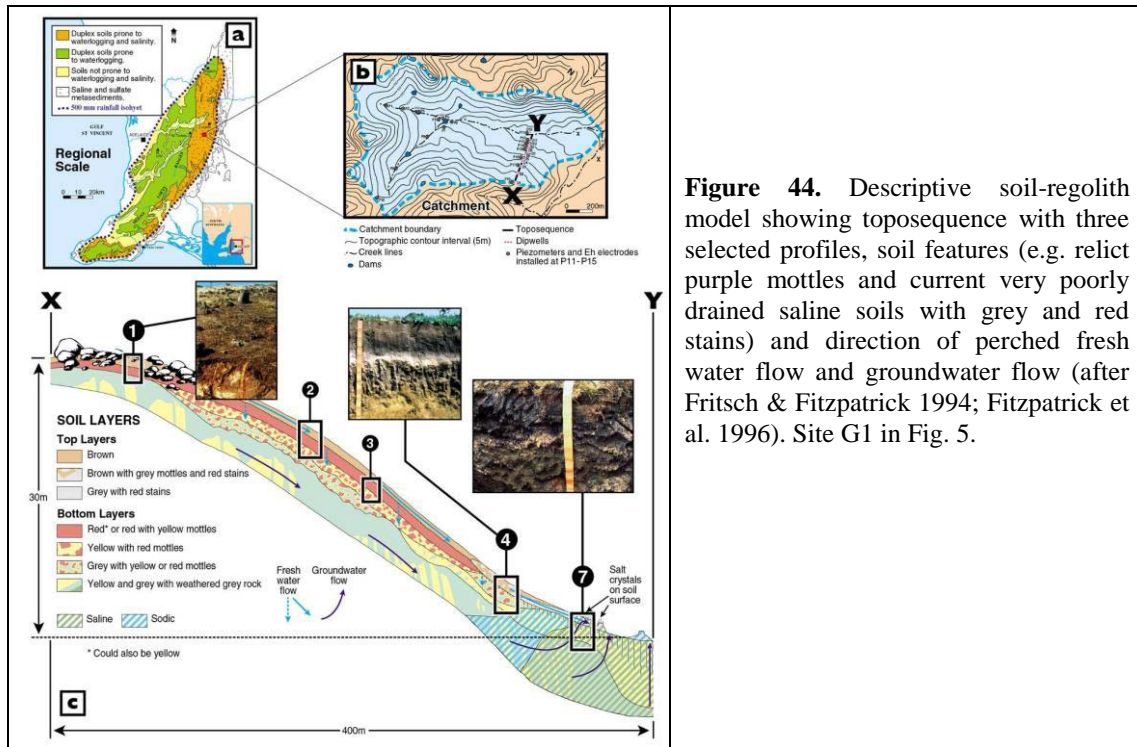


Figure 44. Descriptive soil-regolith model showing toposequence with three selected profiles, soil features (e.g. relict purple mottles and current very poorly drained saline soils with grey and red stains) and direction of perched fresh water flow and groundwater flow (after Fritsch & Fitzpatrick 1994; Fitzpatrick et al. 1996). Site G1 in Fig. 5.

The exposure of sulfidic material in eroded stream banks may result in the rapid weathering of pyrite present in previously buried swamp deposits (e.g. shown in Fig. 45). The chemical and microbial reactions that form sulfuric acid can dissolve a variety of layer silicate minerals, mobilising aluminium and trace metals. In addition to pyrite, the underlying rocks in this region contain sphalerite and traces of galena and other minerals that contain zinc, lead and arsenic. These elements are often concentrated in white and reddish seeps and pools at the base of the eroded streamline and greatly exceed criteria for protection of fresh-water aquatic organisms. In addition, the seeps and soil leachate contain elevated concentrations of dissolved iron, aluminium, and sulfate. Soluble sulfate minerals (sideronatriite and tamarugite) were found to crystallise on the bank face immobilizing the metals when these waters evaporate. However, during rainfall events, these minerals readily dissolve releasing the stored acidity and metals to runoff and infiltrating stream water. The cycle of salt formation and dissolution contributes to acid-drainage from the site as long as moist sulfidic material remains exposed to air.

These descriptive process models have been used to help characterise catchment-scale variability of relict (past geomorphological processes in development of deep weathering and erosion) and current (saline, sodic and acid sulfate soils) soil forming processes to develop practical solutions for ameliorating soils at farm scale (Fitzpatrick et al. 2003a,b), and for use in mineral exploration (Skwarnecki et al. 2002; Skwarnecki & Fitzpatrick 2003, 2008; Fitzpatrick & Skwarnecki 2005).

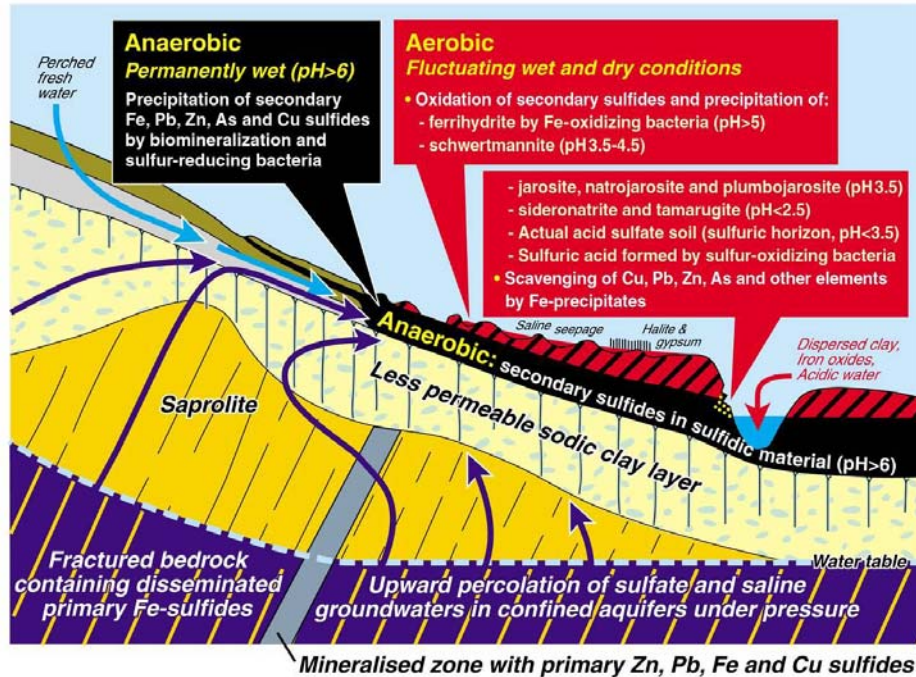


Figure 45. Explanatory soil-regolith model showing geochemical dispersion and erosion processes in saline seepages and formation of secondary sulfides in sulfidic material in a perched wetland and sulfuric materials along eroded drainage lines (after Fitzpatrick et al. 1996).

Mount Lofty Ranges predictive soil-regolith model (Area G in Fig. 5)

Fitzpatrick et al. (2000a) used the information contained in Figures 44 & 45 to construct a generalised predictive soil-regolith model showing the sequential hydrogeochemical processes that transform sulfidic material in a perched wetland to sulfuric material (Fig. 46).

Stage 1: Saline groundwater enriched in sulfate (SO_4^{2-}) seeps up through the soil, along with other solutes such as Na^+ , Ca^{2+} , Mg^{2+} , AsO_4^{2-} , I^- and Cl^- , and concentrates by evaporation to form various mineral precipitates within and on top of the soil surface (Fig. 46a). The combination of: (i) rising sulfate-containing groundwater, (ii) anaerobic conditions associated with saturated soils, (iii) agricultural activity, and (iv) fractured rocks relatively enriched in Fe, S, Pb, Zn, etc. led to the formation of sulfidic material and precipitation of anomalous concentrations of Pb and Zn. If the soil is wet and contains sufficient organic carbon, anaerobic bacteria use the oxygen associated with the sulfate (SO_4^{2-}) during the assimilation of carbon from organic matter. This process produces pyrite and forms sulfidic materials (Fig. 46a) (Fitzpatrick & Skwarnecki 2003).

Stage 2: Sulfuric materials result when pugging from animals, drainage works or other disruptions expose pyrite in previously saturated soils to oxygen in the air. Thus, pyrite is oxidised to sulfuric acid and various Fe sulfate-rich minerals, and sulfuric material forms (Fig. 46b). When sulfuric acid forms, the soil pH can drop from ca. neutral pH to below pH 4; locally, pH may decrease to as low as pH 2.5. The sulfuric acid dissolves clay particles in soil, causing base cations and associated anions (e.g. Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , SiO_4^{4-}), trace elements, and metals such as Fe^{3+} and Al^{3+} to be released into the soil and transported to stream waters. As the regolith structure degrades due to the accompanying sodicity, soils become clogged with dispersed clay and Fe precipitates and they lose their permeability and groundcover. This prevents groundwater below from discharging and forces it to move transversely through the soil (Fig. 46b). Soil around the clogged area eventually erodes, causing movement of acid, dissolved metals and salts into waterways and dams. If cattle or other activities continue to disturb the soil around the newly created sulfidic material, the area affected continues to expand (Fig. 46b) (Fitzpatrick & Skwarnecki 2005).

Stage 3: If these processes become expressed on the surface of the soil, bare eroded saline scalds surrounding a core of lower permeability, highly saline, eroded sulfuric material may result (Fig. 46c). These saline landscapes are characterised by slimy red or white ooze and scalds with impermeable Fe-rich crusts. As shown in Figure 46, when the sulfidic materials undergo change, different salt and Fe minerals form because of differences in pH, increases in salinity and differences in relative

concentrations of salts. In the final stage of formation, a hard soil layer remains, with only few salts (Fig. 46c). Schwertmannite was first sampled and identified in inland ASS in the Mount Lofty Ranges, South Australia in 1990 (Fitzpatrick et al. 1992, 1993, 1996; Fitzpatrick & Self 1997).

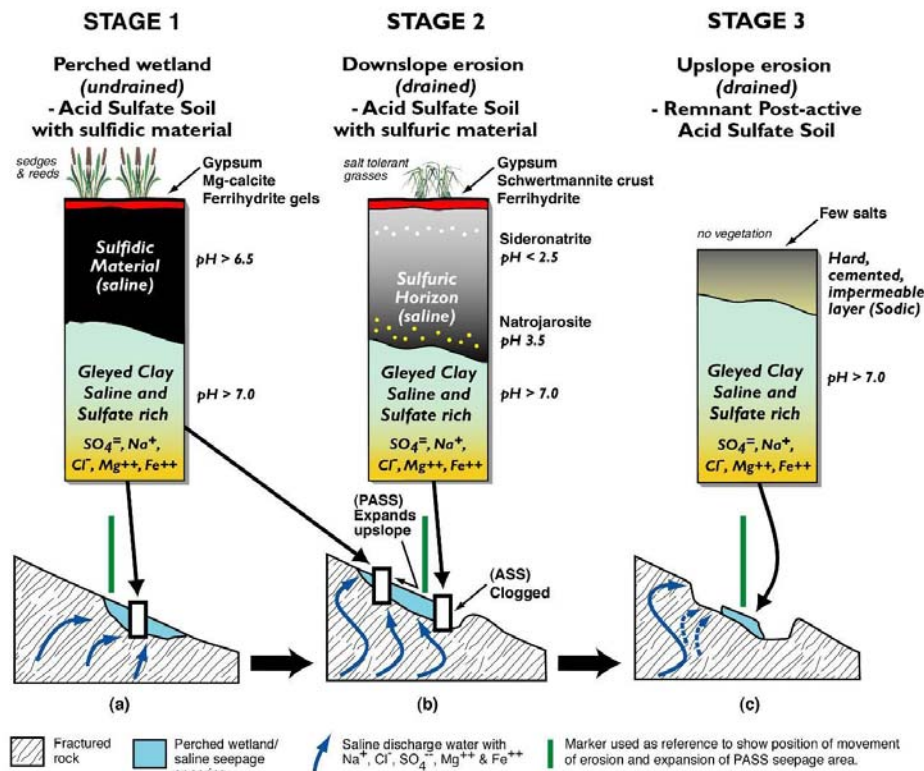
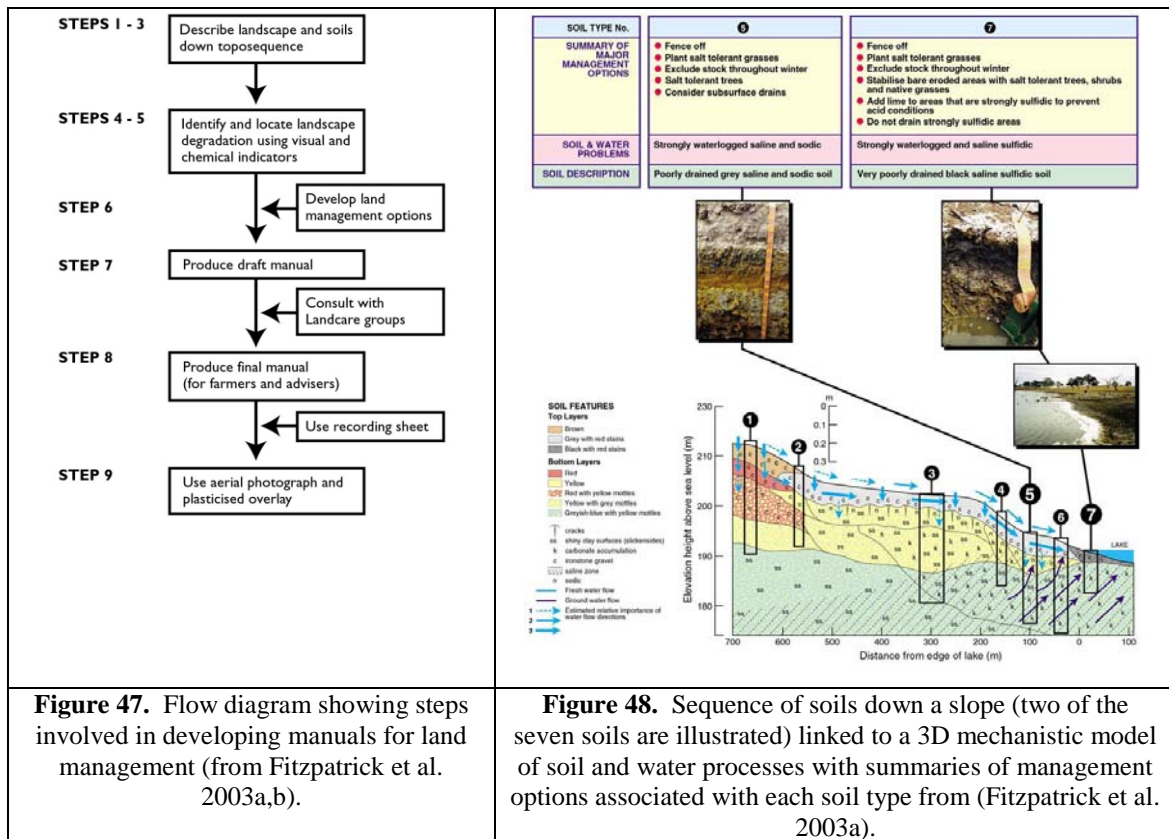


Figure 46. Predictive soil-regolith model showing the hydrogeochemical processes, which transform sulfidic material in a perched wetland to highly saline sulfuric material (after Fitzpatrick et al. 2003b).

Degraded agricultural areas in this region are conspicuous by the presence of ephemeral to semi-permanent saline seepages with surface accumulations of Fe oxyhydroxides and salts that overlie strongly reduced subsoil horizons containing pyrite formed by bacterial sulfate reduction. During wet winters, surface reddish-brown precipitates of ferrihydrite, containing high levels of scavenged cations (e.g. As and Si) is the dominant Fe oxyhydroxide formed. In summer, the seasonal changes in soil redox conditions strongly modify the geochemistry of the soil solution causing ferrihydrite to transform to goethite and schwertmannite in the presence of excess sulfate and chloride, usually in the form of cemented crusts (Fig. 46c). Schwertmannite is indicative of a weathering environment with soil solutions having a pH in the range 3 to 4 and sulfate concentrations between 1000 and 3000 mg/L (Schwertmann & Fitzpatrick 1992; Fitzpatrick et al. 1996).

Pictorial manuals for land management planning in the Mt Lofty Ranges

Approaches for managing ASS in the upland saline seepages in the Mt Lofty Ranges (Area G in Fig. 5) is briefly covered in this section. The sequence of steps used to develop an easy-to-follow pictorial manual for identifying soil indicators, land use options and best management practices for this area are shown in Figure 47 (Fitzpatrick et al. 2003a). Steps 1-5 describe soil layers and construct them in toposequences (descriptive, explanatory or predictive models), which are used to help map soil types in areas with variable geochemistry (Fitzpatrick et al. 2003a,b).



Steps 6-9 involve local communities in developing the manual by integration and adoption, where knowledge of the hydrological and soil-regolith processes models (bottom half of Fig. 48) and production systems are bought together in recommendations for appropriate best management practices (top half of Fig. 48). For example, in the Mount Lofty Ranges (Fitzpatrick et al. 1997; 2003a,b) and Woorndoo region in Victoria (Fig. 48; Fitzpatrick et al. 1997; 2003a,b) fencing and protecting saline-sulfidic wetlands from physical disturbance (e.g. cattle) has:

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

ABANDONED MINES (Area H in Fig. 5)

A wide range of minespoil Acid Sulfate Soils have been identified and characterised in waste rock stockpiles, tailing impoundments and mine retention ponds at several minespoil environments in the Mount Lofty Ranges (Area H in Fig. 5). These soils are essentially the same as those in seepages overlying mineralized zones, except the pyritic rocks have been deposited on the landscape surface, often filling-up whole valleys. A wide variety of ASS soils developed from rocks in various stages of physical and chemical breakdown have been described and sampled along hydro toposequences (i.e. from the drier upper to wetter lower surfaces) of minespoils at the Brukunga pyrite mine (Site H1 in Fig. 5). Fitzpatrick & Self (1997) identified schwertmannite, jarosite, goethite and gypsum in orange and yellow precipitates in acid drainage water seeping through the rehabilitated pyrite-rich tailings dam and waste-rock dumps at the abandoned Brukunga pyrite mine.

UPPER SOUTH EAST OCCURRENCES

In Acid Sulfate Soils in the swales authigenic pyrite, marine-derived sulfates, as well as other stored salts have been identified at Cooke Plains in the upper south east (Hollingsworth et al. 1996; Fitzpatrick & Merry 1999). These soils have acquired saline sulfide characteristics in recent times because of rising, saline ground water (Barnett 1992) and seasonal waterlogging caused by land clearing since European settlement (circa 120 years ago) (Hollingsworth et al. 1996; Fitzpatrick &

Self 1997). Sufficient organic matter is present for microorganisms to transform sulfate to sulfide so that, in the presence of reduced iron (derived from the weathering of ilmenite grains in these sandy dune soils), iron sulfide forms. During the dry summer months, these sulfides oxidise and react with dissolved calcium to form hydrated calcium sulfate (gypsum). Excess sodium in the chloride saturated solution precipitates as halite.

Finally, the drain constructed through Tilley Swamp (Fitzpatrick et al. 2008c) has provided an opportunity to observe the pedological, geochemical and mineralogical properties of ASS materials within the drain, both recent (active acid sulfate soil weathering features) and relict (post-active acid sulfate soil weathering features, Fanning & Fanning 1989; Fanning 2002). Important materials that develop in the drains during periods of low flow are thin layers of sulfidic material, monosulfidic material, salt efflorescences and iron oxyhydroxide minerals on drain walls. A 3D explanatory soil-regolith model of water processes has been constructed by Fitzpatrick et al. (2008c) that explain and predict processes giving rise to the production, export and fate of leachate and minerals in the open drains.

CONCLUSION

This chapter has highlighted the extremely wide diversity of inland and coastal acid sulfate soil types in the Riverland and Murraylands of South Australia, from small seepages in the Mt Lofty Ranges to billabongs and wetlands along and adjacent to the Murray River channel to the Lower Lakes and Coorong near the Murray River Mouth. The current drought in South-eastern Australia has had a major impact on water resources and availability in the Murray Darling Basin. Nowhere can this be more clearly seen than in the lower reaches of the Murray River below Lock 1 (Blanchetown) where water levels are at an unprecedented low (in many areas below sea level). The low water levels have caused a number of impacts related to acid sulfate soils to be realised for the first time, particularly soil acidification, and more locally water acidification and metal mobilisation. Scientific studies have only begun to address the real impacts of these soils under future management and climate change scenarios, and much work still needs to be completed before future risks can be fully assessed.

GLOSSARY

Acid Sulfate Soil environments

- **Coastal environments** or modern-day coastal zones - those areas landwards of the coastal waters influenced by processes or activities that affect the coast and its values - as defined by NRMMC (2006) comprising "coastal ASS" in estuarine systems such as the Murray River Mouth estuary and Coorong.
- **Inland environments** - those areas, which occur inland of modern-day coastal zones (as defined by NRMMC (2006) comprising "inland ASS" in upland systems such as the Mount Lofty Ranges.
- **Minespoil environments** - those areas, which occur in: (i) waste rock stockpiles and tailing impoundments (e.g. Fitzpatrick et al. 1998) and (ii) mine retention ponds (Fitzpatrick & Self 1997; Nordstrom & Alpers, 1999) - comprising "minespoil ASS" and "acid-rock drainage".

Acid Sulfate Soil materials (modified from Sullivan et al. 2009)

- **Sulfuric material** - pH less than 4 (Isbell 1996).
- **Sulfidic material*** - soil materials containing detectable sulfide minerals (containing greater than or equal to 0.01% sulfidic S). The intent of this term is to be used in a descriptive context (e.g. sulfidic soil material) and to align with general definitions applied by other scientific disciplines such as geology and ecology (e.g. sulfidic sediment). **This term differs from previously published definitions in various soil classifications (e.g. Isbell 1996).*
- **Hypersulfidic material** - Hypersulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by having a field pH of 4 or more and by experiencing a drop in pH by at least 0.5 unit to 4 or less when incubated aerobically at field capacity. The duration of the incubation is either: (i) until the soil pH changes by at least 0.5 pH unit to below 4, or (ii) until a stable pH is reached after at least 8 weeks of incubation.
- **Hyposulfidic material** - Hyposulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by having a field pH of 4 or more and by not experiencing a drop in pH by at least 0.5 unit to 4 or less when incubated aerobically at field capacity. The duration of the incubation is until a stable pH is reached after at least 8 weeks of incubation.
- **Monosulfidic material** - soil materials with an acid volatile sulfur content of 0.01%S or more. Monosulfidic materials are subaqueous or waterlogged organic-rich materials that contain appreciable concentrations of monosulfides (e.g. Sullivan et al. 2002; Bush et al. 2004; Burton et al. 2006a, 2006b). Monosulfidic black oozes are specific materials characterised by their gel-like consistence. Monosulfidic

materials have a field pH of 4 or more, commonly > pH 7-8, but may not become extremely acidic (pH <4) when drained. Recognition of the occurrence and importance of monosulfides in soil materials led to inclusion of monosulfidic materials as a distinguishing property in the legend of the Australian Atlas of Acid Sulfate Soils (Fitzpatrick et al. 2008a).

Atlas of Australian Acid Sulfate Soils - web-based hazard assessment tool with a nationally consistent legend, which provides information about the distribution and properties of both coastal and inland ASS across Australia (Fitzpatrick et al. 2008a). This tool is available on ASRIS (Australian Soil Resource Information System: www.asris.gov.au)

Drained Soils – soils in environments where the soil was previously saturated with water and the water level has lowered allowing air instead of water to fill the soil pore spaces.

Subaqueous Soils – soils in shallow permanently flooded environments covered by less than 2.5 m water, which is not too deep for the growth of rooted plants (Stolt 2006);

Waterlogged Soils – soils in environments where there is sufficient water to fill the soil pore space but not pond above the soil surface for any length of time.

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Natural History of the Riverland and Murraylands



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Cover: River red gums (*Eucalyptus camaldulensis*) on the Murray River near Qualco, South Australia.
Photograph by John Jennings.

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15	Mammals – Sue Carthew & Terry Reardon	397-416

