Acid Sulfate Soils Centre

A FIELD GUIDE TO ESTUARINE SOIL-LANDSCAPES IN BARKER INLET, SOUTH AUSTRALIA

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Cover Photograph:

View of dead mangroves and contaminated water at Gillman, South Australia
Photographer: Brett Thomas (© 2008 CSIRO)

EXECUTIVE SUMMARY

In nature, some things are best left alone, buried well beneath the surface! But housing, marina and infrastructure developments frequently disturb coastal soil-landscape environments comprising acid sulfate soils and sediments – sometimes with disastrous consequences.

This field guide booklet summarises the soil-landscapes in Barker Inlet associated with formation of pyrite and sulfuric acid in Acid Sulfate Soils (ASS). Two case study areas in Barker Inlet have been selected to illustrate the diverse properties and impacts of coastal acid sulfate soils. A wide range of ASS types containing sulfidic materials ($pH > 4$ with pyrites), sulfuric materials ($pH < 4$ with oxyhydroxysulfates of Fe and Al) and monosulfidic black ooze ($pH > 4$ with monosulfides) are currently developing in different physical settings, which occur mostly because of changing hydrological and biogeochemical conditions in Barker Inlet.

The loss of tidal inundation has caused a lowering of the watertable in the Gillman area, enabling oxygen to diffuse into sulfidic materials, which caused pyrite oxidation and the formation of sulfuric materials. Impacts include land and water degradation; noxious odours and greenhouse gas emissions.

Colour photographs of key soil features, mechanistic cross-section diagrams and maps are presented to illustrate the major geomorphic stages in acid sulfate soil-landscape evolution. This booklet also details the chemical and physical changes that occur when tidal influences are altered or excluded in these environments. Various sources of organic matter fractions (i.e. sapric and hemic materials), minerals (e.g. pyrite, jarosite/natrojarosite, sideronatrite, tamarugite and gypsum), and micro-scale weathering pathways and mechanisms occur under drained (e.g. tidal exclusion through levee bank construction) and undrained (e.g. ranging from natural tidal to intertidal, to supratidal zones) conditions.

Maps showing the distribution of the various types of Acid Sulfate Soils and their extent in hectares for Gulf St Vincent and Barker Inlet and “risk classes” are also provided.

Management and remediation options for acid sulfate soils are presented.

The South Australian government has responded to the challenge of managing coastal Acid Sulfate Soils environments by introducing planning and development controls for coastal Acid Sulfate Soils through the Coast Protection Board (CPB).

SUMMARY OF FIELD SITES

This field guide booklet summarises factors associated with formation of pyrite and sulfuric acid in the wide range of Acid Sulfate Soil (ASS) types and the key impacts this has on coastal, estuarine and mangrove swamp environments in Barker Inlet shown in **Fig. 1**. This field guide sets out to provide, interpret and view in the field the following critical environmental and geological information on formation of the wide range of coastal acid sulfate soils:

- Quaternary coastal marine facies and mangrove transgression since 1935 (**Figs. 1 & 3**).
- Current tidal inundation with occurrence of mangroves and samphire marsh (**Figs. 1, 4 & 13).**
- Loss of tidal inundation with mangrove deaths caused by construction of levee banks between 1890s and 1950s' (**Figs. 1 & 2).**

The following localities at St Kilda (along the Mangrove Trail) and near Port Adelaide (Gillman area) are used to display the main features:

Locality 1. St Kilda Mangrove Trail at Fooks Terrace, St Kilda to view the critical role, which intertidal mangrove woodlands and samphire salt marsh play in maintaining marine environments. The Mangrove Trail comprises a 2km boardwalk that meanders through the mysterious mangrove forest and samphire areas of the Barker Inlet Aquatic Reserve, which provides excellent examples of:

- Occurrences of a wide range of organic rich acid sulfate soils (**Fig. 4**) with high concentrations of pyrite (**Fig. 5**) and shell fragments (**Fig. 6)**.
- The bund wall (levee banks) built in the 1890s from St Kilda to the south along the landward extent of mangrove woodlands is shown in **Fig. 6** (including occurrences of a Chenier ridge, seagrass and tidal mud flats and salt evaporation ponds).
- Tidal creeks filled with rotting organic matter (sapric material) formed from sea-grass and ulva causing extreme anoxic or reducing conditions (**Fig. 7)**.
- Examples of mangrove deaths / knocked down mangroves caused by soil conditions "toxic" to the mangrove pneumatophores, which have to retreat to "higher ground" (**Fig. 7)**.

Locality 2: Garden Island (**Fig. 1**) to view almost pristine tidal, intertidal or supratidal mangrove and samphire marshes and how they function. It provides good examples of occurrences of organic rich acid sulfate soils with high concentrations of pyrite.

Locality 3: Grand Trunkway at Gillman to view along the bund wall (**Figs. 1, 2 & 8**):

- Almost pristine tidal, intertidal or supratidal mangrove marshes (North Arm River).
- Construction of bund walls/ levee banks in 1890, 1935 and 1950 to reclaim intertidal mangrove woodlands and samphire salt marsh for agriculture and industry.
- Dead mangroves, highly polluted waters and soils (previously proposed MFP site).
- Recent establishment of huge industrial sites on reclaimed land, dredge spoil.

Locality 4. Range Wetland area at Gillman (near Wingfield Dump) via a guided tour with on-site explanations and field demonstrations, provides excellent examples of:

- Drainage waters with extremely high concentrations of sulfuric acid and metals, especially Al, Mg (**Figs. 9 and 10**).
- Organic rich acid sulfate soils with bright yellow jarosite mottles, exposed in excavated drains (**Fig. 11**): demonstrate sampling, chip-tray incubation (**Appendix 2**)
- Several rehabilitation experiments [see Coast Protection Board (2003)). Dredge spoil overlying relict ASS materials (**Fig. 12C**)
- Monosulfidic material in drains and wetlands (**Fig. 13**). Index of Squishiness Test (**Appendix 4**).
- Walk up to the Wingfield Dump lookout, which provides an excellent overview of entire area to illustrate the wide range of soil-landscape map units (**Fig. 14, Table 1; Fig. 15 & 16, Table 2**), bund wall constructed over 50 years ago, dead mangroves and polluted stream waters.

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1. NATURE AND PROPERTIES OF ACID SULFATE SOIL LANDSCAPES

The following summary and interpretation of the fascinating and critically important Acid Sulfate Soils (ASS) in Barker Inlet is largely derived from information described by: Fitzpatrick et al. (2008a,b) and supplemented by observations and studies performed by Fitzpatrick 1991; Fitzpatrick et al. (1993; 2008b,c), Fitzpatrick & Self (1997), Merry et al. (2003), Poch et al. (2009); Thomas et al. (2003a, b; 2004) and Thomas (2010).

Acid Sulfate Soils (ASS) are all those soils in which sulfuric acid may be produced, is being produced, or has been produced in amounts that have a lasting effect on main soil characteristics (Pons 1973). This general definition includes: (i) potential, (ii) actual (or active), and (iii) post-active ASS, three broad genetic soil types that continue to be recognised (e.g. Fanning 2002).

Acid Sulfate Soils form in the coastal, estuarine and mangrove swamp environments of Barker Inlet and the Gulf St Vincent (GSV), because these waterlogged or highly reducing environments are ideal for the formation of sulfide minerals, predominantly iron pyrite (FeS_2). Soil horizons that contain sulfides are called sulfidic material (Isbell 1996; Soil Survey Staff 2003) or hypersulfidic material (Sullivan et al. 2010), and can be environmentally damaging if exposed to air by disturbance. Exposure results in the oxidation of pyrite, with each mole of pyrite yielding 4 moles of acidity (i.e. 2 moles of sulfuric acid). This process transforms sulfidic or 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 Soil Survey Staff (2003). When ASS become strongly acidic (e.g. pH <3.5) acid drainage water is produced. This acid together with toxic elements that are leached from sediments can kill fish, and contaminate oysters and groundwater, and can corrode concrete and steel in homes, underground pipes and buildings. These impacts can be measured in terms of:

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

Infrastructure development and primary industries around Australia are facing a $10 billion legacy of acid sulfate soils (National Working Party on Acid Sulfate Soils, 2000). Public recognition of this serious problem has been reflected in government legislation in NSW, Qld and SA. In addition, there is much support from local government and industries to develop statutory requirements for rehabilitation.

Of the 215,000 km^2 of ASS in Australia, 58,000 km^2 is coastal ASS and 157,000 km^2 is inland ASS (Fitzpatrick *et al.* 2008a, 2010). In the coastal zone of Australia, 41,000 km^2 are exposed at some point during the tidal cycle, with the remaining 17,000 km^2 being permanently subaqueous. More than 126 km^2 of coastal ASS with sulfuric material have been mapped, however this is a significant underestimate, which will be modified with ongoing field investigations and acquisition of more detailed local spatial data sets. The coastal ASS underlie coastal estuaries and tidal flats close to major population centres in Australia.

1.1. Gulf St Vincent and Barker Inlet

To investigate the distribution, processes, environmental hazards and remediation options of Mediterranean-type coastal ASS in GSV, several case studies have been conducted in Barker Inlet, which is 20 km north of Adelaide and covers an area of about 25 km^2 (Fig. 1). These investigations were concentrated mainly at: (i) St Kilda, which consists of a transect through tidal and intertidal mangrove woodland and salt marshes, and (ii) Gillman, which is a highly degraded wetland adjacent to the city of Port Adelaide (Figs 1, 2). Over 50 years ago, ~1 000 ha of coastal wetland were drained for urban and industrial development by the construction of a levee bank, a network of drains and tidal floodgates. Construction of the levee bank subdivided the intertidal environment and initially conditions were similar on both sides of the levee bank. Subsequently, within the bunded area, drainage and acidification degraded about 325 ha (e.g. Harbison 1986; Fitzpatrick 1991; Fitzpatrick et al. 1992; Thomas et al. 2003a), while outside the levee bank the undrained soils are approximately in their original condition, and now provide a baseline for the assessment of environmental change. Consequently, these changes to Barker Inlet, (Fig. 1), have allowed several investigations of drainage-induced changes in ASS from a series of drained and undrained sites at Gillman and St Kilda (Fitzpatrick 1991; Fitzpatrick & Self 1997; Poch et al. 2009; Thomas et al. 2004; Thomas 2010).

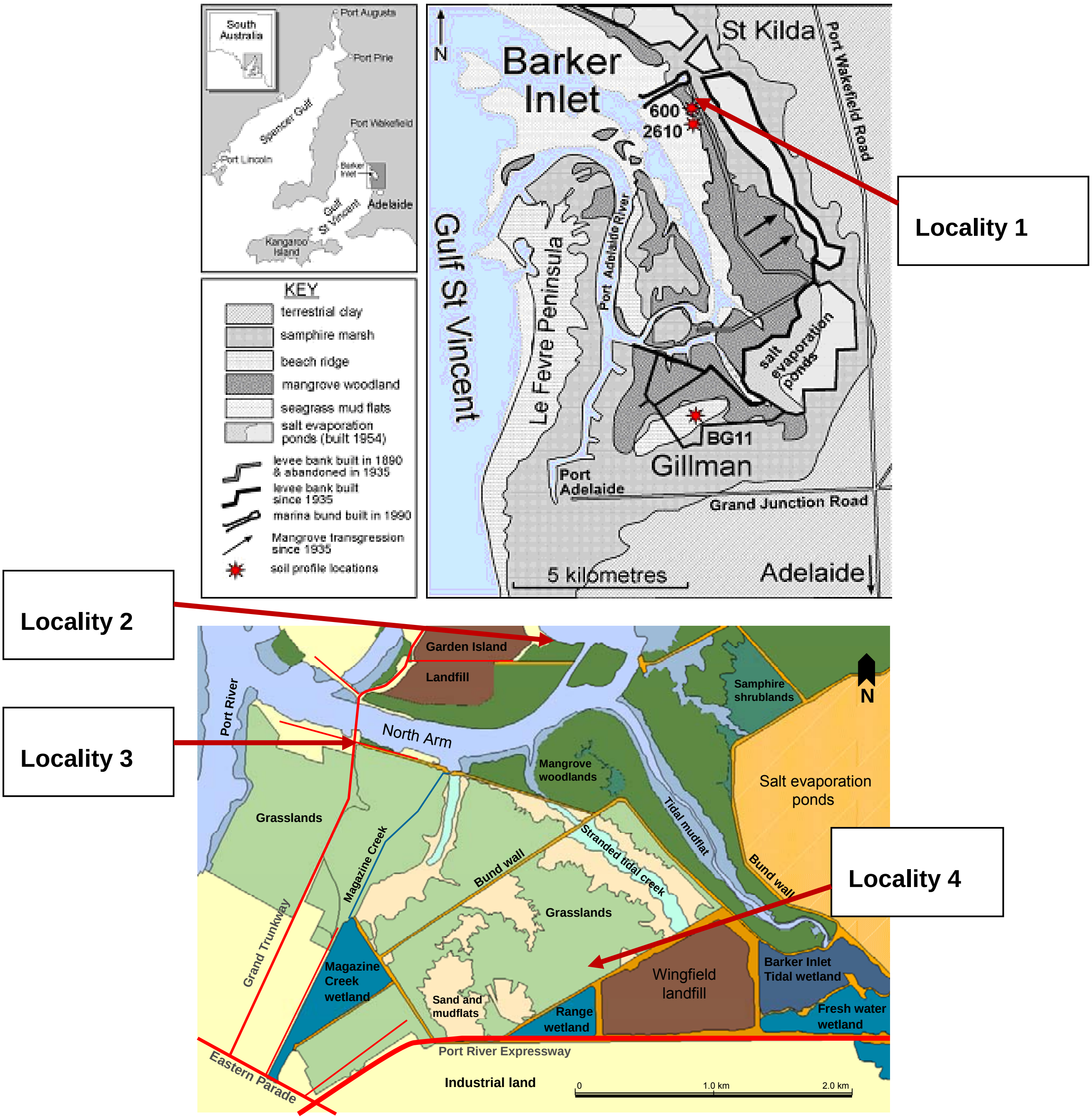


Figure 1 Barker Inlet tidal estuary (above) showing the major original vegetation types, physiographic settings and two study areas located at St Kilda ("natural" mangrove woodlands with acid sulfate soil profiles 600 and 2610 located in this area) and Gillman (below). The Gillman site is predominately vacant, consisting open grasslands, samphire shrublands and salt and sand flats. It is bordered by urban and industrial development to the south and abuts tidal mangrove woodland along North Arm. The Gilman area has been progressively reclaimed from the intertidal and supratidal environments of Barker Inlet since the 1930s by construction of a series of bund walls that prevent tidal inundation for agriculture and industry. The land at Gillman was soon abandoned due to severe acidification, salinity and stormwater ponding. The acid sulfate soil profile BG11 is located in this "reclaimed" area. (From Fitzpatrick et al. 2008b,c; Thomas 2010).

Figure 2 View of the landward (drained) side of the artificial bund wall at Gillman, which was constructed in the 1950s to prevent tidal inundation showing: dead mangrove tree stumps (background) and contaminated water in a stranded tidal creek with water containing orange iron oxyhydroxide surrounded by white salt deposits and dead mangrove. This site has low aesthetic characteristics Refer also to locality map (Fig. 1) and schematic soil-landscape cross sections (Figs 8 and 9).

The recent geological evolution of Barker Inlet has largely been controlled by global sea level fluctuations (Edmonds 1995). Two million years ago sea level was 45 m lower than at present and Gulf St Vincent was dry land. Alluvial fans formed as rivers and streams drained from the higher land inland, depositing sands, gravels and particularly the thick Hindmarsh Clay (Fig. 3) that underlies Barker Inlet and Adelaide.

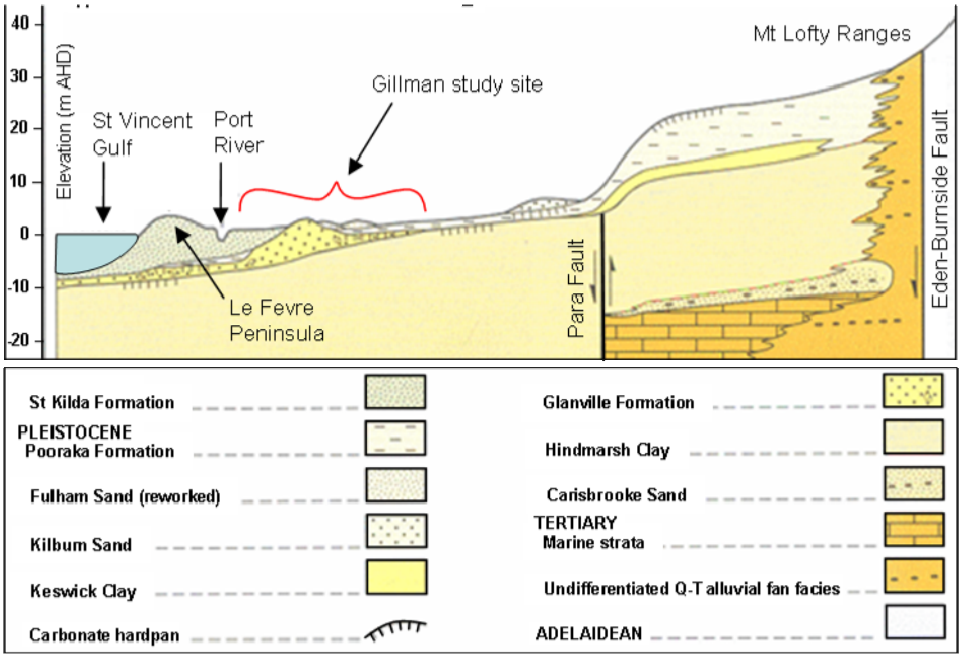


Figure 3 Schematic cross-section from Le Fevre Peninsula to the Mount Lofty Ranges, showing relationships between Quaternary coastal marine and continental facies of the St Vincent Basin. The St Kilda Formation (Holocene sands and clays) overlay the Glanville Formation (Pleistocene clays), and they together on-lap the thick alluvial Hindmarsh Clay Formation (after Belperio & Rice 1989; Belperio 1995; and Thomas 2010).

About 9000 years ago sea level rose. The Le Fevre peninsula (Figs. 1 and 3) was built between 6000 years ago and the present, by sand building up as a result of wave and wind action. The reworking of coastal sediments since sea level stabilisation about 7,500 BP resulted mostly in the northerly extension of sand ridges on Le Fevre Peninsula and the Port River outlet (Figs. 1 and 3).

The establishment of extensive sea-grass meadows led to the rapid accumulation of marine and estuarine sediments resulting in coastal progradation throughout the late Holocene (Edmonds 1995). Progradation led to the simultaneous back-barrier development of marshes and mangrove swamps parallel to the shoreline. The Barker Inlet embayment is now mostly in-filled except for the Port River estuary.

Seagrass banks developed in shallow water, but this gradually became enclosed and estuarine mangroves took over in the intertidal zones. Then the early settlers arrived and the area became severely modified by human activities. The Gilman area has been progressively reclaimed from the intertidal and supratidal environments of Barker Inlet by construction of a series of bund walls that prevent tidal inundation for agriculture and industry (Figs 1 and 2).

Subsidence rates of 1 mm per year have been documented in the Barker Inlet area (Belperio 1993), and are attributed to movement along the Para Fault, ground water extraction and consolidation of inter-tidal soils after drying due to construction of levee banks (Figs. 1 and 2). The presence of “sulfide-rich sediments” in the Gillman area was identified firstly by Harbison (1986), and observed in later investigations (Belperio & Rice 1989, Belperio & Harbison 1992, Belperio 1993).

In 1991, CSIRO was contracted to conduct an urgent investigation of the Gillman area for the proposed construction of a multi-function-polis (MFP; Appendix 1; Fitzpatrick, 1991). The MFP was a concept for a high technology community comprising housing, education and leisure facilities, and high-tech industries to provide employment. Fitzpatrick (1991) alerted the promoters to the problem of acid sulfate soils, and for this and other reasons the project was eventually abandoned.

Prior to 1991, no specific soil investigations had been conducted to identify and characterise types of Acid Sulfuric Soils and their extent in the Barker Inlet area. However, based on several later investigations (e.g. Fitzpatrick 1991, Fitzpatrick et al. 1992, 1993, 1996; 2008b,c; Fitzpatrick & Self 1997, Thomas et al. 2004, Poch et al. 2009; Thomas 2010), the properties, formation and distribution of the following 6 major types of ASS materials that commonly occur as layers in soil profiles in the wide range of physiographical environments in Barker Inlet, are summarised in discussions below:

- Contemporary tidal zones with hypersulfidic material (mangrove and samphire marshes).
- Disturbed tidal zones with sulfuric material (drained tidal, intertidal or supratidal mangrove or samphire marshes, particularly near Gillman).
- Disturbed tidal zones with hypersulfidic material (drained tidal, intertidal or supratidal mangrove or samphire marshes, particularly in disturbed salt evaporation ponds).
- Sandplains and dunes overlying relict buried layers of hypersulfidic material.
- Anthropogenic fill materials overlying buried hypersulfidic and sulfuric materials.
- Subaqueous soils below the low tidal mark with hypersulfidic and monosulfidic materials beneath shallow, stagnant water bodies (e.g. poorly flushed or blocked estuaries, rivers, river tributaries, salt evaporation seeps and seagrass mud flats associated with Barker Inlet Estuary and Port Adelaide River).

1.2. Contemporary tidal zones with sulfidic materials

Localities 1 and 2. St Kilda Mangrove walk and Garden Island Boat Ramp (Fig. 1).

These two localities provide good examples of modern tidal floodplains with mangrove and samphire marsh environments comprising a range of organic rich acid sulfate soils with hypersulfidic, hyposulfidic and monosulfidic materials.

Coastal acid sulfate soils with hypersulfidic material occur in modern tidal floodplains, which are <5 m above sea level where sulfate, iron and other salts are available from seawater and estuarine sediments. These soils form due to permanently waterlogged or saturated conditions from the interaction of seawater with abundant organic material. Where these organic-rich soils accumulate more than 18 % organic carbon, they classify as Histosols and Hydrosols (see Table 1 for correlation between the three soil classification systems in common usage). In Barker Inlet organic-rich soils contain two different forms of organic soil materials, as defined by the amount of rubbed fibre content: namely: (i) sapric (forms <17% by volume rubbed fibre), and (ii) hemic (forms >40% rubbed fibre) (Soil Survey Staff 2003). Hence horizons that contain predominantly sapric material contain a high proportion of decomposed organic matter whereas hemic materials contain a moderate proportion of decomposed organic matter. These organic rich soils contain either sulfidic material (Isbell 1996; Soil Survey Staff 2003) or Hypersulfidic (Sullivan et al. 2010) because when incubated as a layer 1 cm thick under moist conditions and while maintaining contact with the air at room temperature, they show a reduction in pH to 4 or less within 8 weeks.

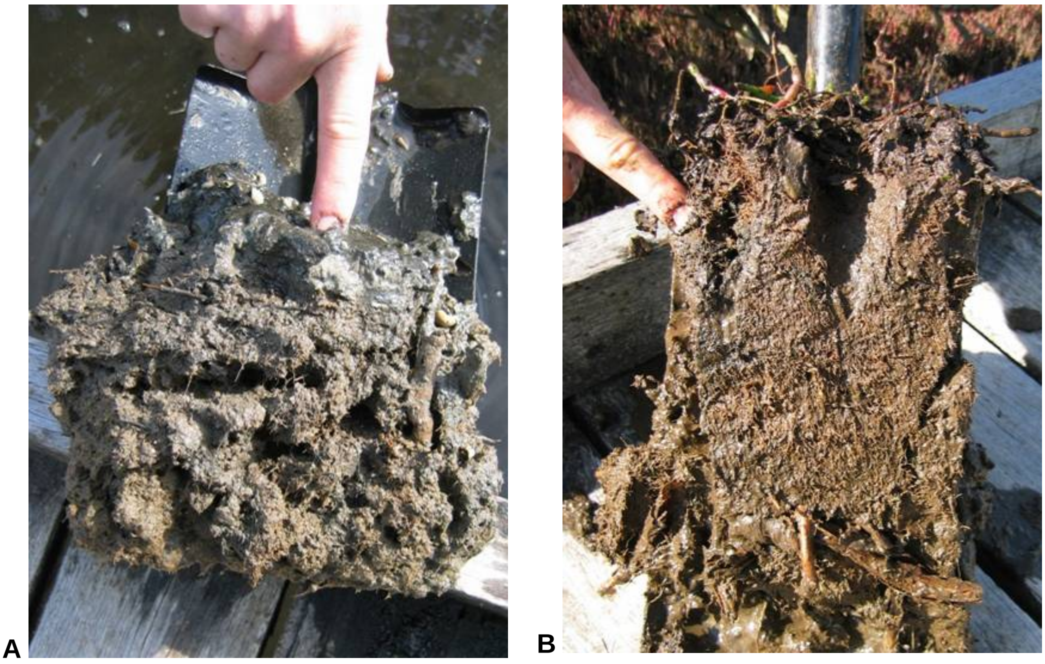


Figure 4 Photographs of hypersulfidic material in permanently saturated contemporary tidal zones featuring layers with dominant: **A** (left) sapric material (Terric Sulfisaprist), highly decomposed roots from mangrove trees and samphire vegetation, and **B** (right) hemic material (Terric Sulfihemist), moderately decomposed mangrove roots and pneumatophores from mangrove trees (width of each photograph is ~ 20 cm). (from Fitzpatrick et al. 2008b,c)

Acid sulfate soils in Barker Inlet commonly have thin layers of hemic materials at the near surface with dominant sapric materials at depth (Fig. 4A). The sapric material identified in these soils is more finely divided and reactive than the coarser, “fibric” materials commonly observed in tropical areas, where organic carbon decomposition rates are much faster. The sapric materials in temperate climate soils form from the detritus of seagrass (*Posidonia* sp.), sea lettuce (*Ulva* sp.) and mangroves in GSV. The dominant sapric material contributes strongly to the intense reducing conditions (i.e. low redox potential, or Eh values to -600 mV SHE), especially where mangrove dieback is present in the St Kilda area (see discussion below). A dominant hemic-rich soil is shown in Figure 4A.

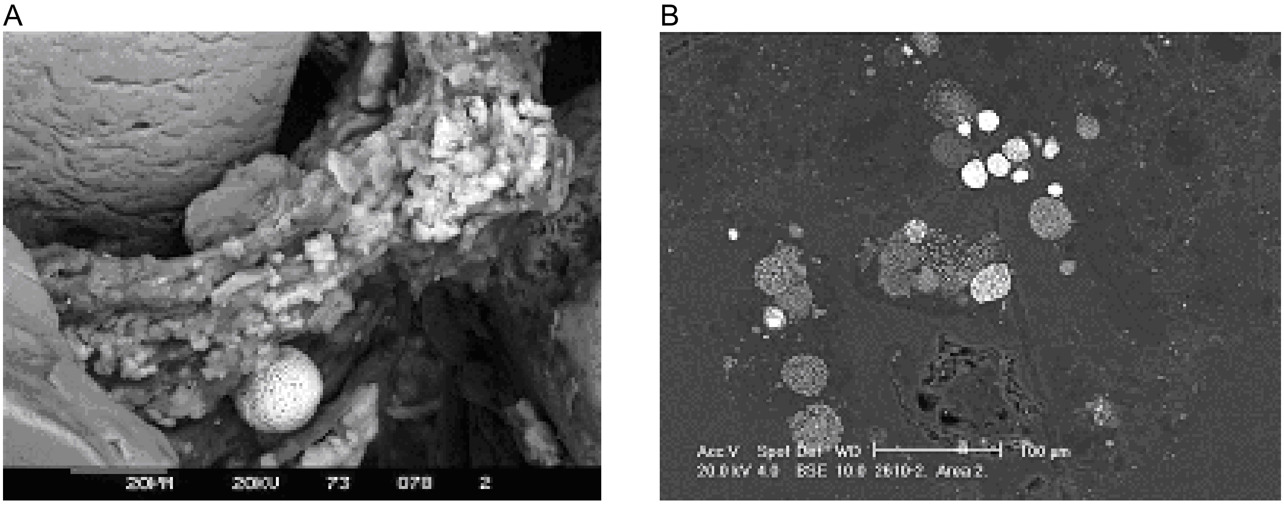


Figure 5 Scanning electron micrographs using back scattered electron (BSE) mode of hypersulfidic material: **A** (left) featuring large, spherical pyrite framboid in a void adjacent to roots, salts and quartz particles found in sandy soil from Gillman, and **B** (right) polished resin-impregnated block from the Oa2 horizon (8-30cm) showing clusters of loosely and tightly packed pyrite framboids within the groundmass adjacent to porous sapric material from mangrove forest soil at St Kilda. Fitzpatrick et al. 2008b,c).

The fragmentation of pyrite framboids in sapric material, observed in Figure 5B, is possibly due to wave and tidal action (Fitzpatrick et al. 1993), and bioturbation. Mangroves are dying in localised parts of the intertidal swamp areas at St Kilda (i.e. Fig. 6 near profile 2610 - refer to Fig. 7) due to erosion of soil around the base of large mangrove trees. This has occurred where eutrophication of the soil has adversely affected the health of mangrove roots and pneumatophores, causing them to retreat from areas where the soil has very low redox (Eh) conditions (Thomas 2010).

These degrading processes are exacerbated by regional subsidence and sea level rise (Thomas et al. 2004). Eutrophic conditions have developed in the subsoils as the nutrient content of metropolitan seawater has increased, resulting in the loss of seagrass (*Posidonia* sp.) and increased growth of sea lettuce (*Ulva* sp.). Fine, sapric, organic material is accumulating in the mangrove forest where it is forming unstable sediments that develop extremely low redox (Eh) conditions as decomposition occurs (Thomas et al. 2004; Thomas 2010). Sapric material is filtered or trapped from the seawater by mangrove trees along the seaward edge of the forest, protecting the trees further inland from the same degrading conditions.

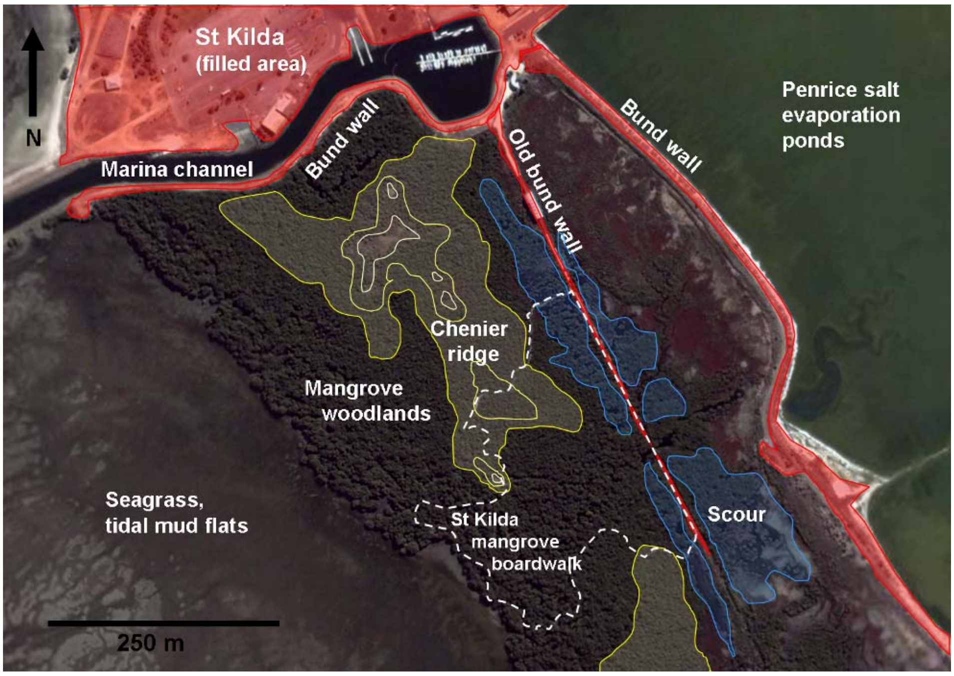


Figure 6 Aerial photograph of the St Kilda study site with major topographic features highlighted. The topography of the site is very much related to vegetation type, corresponding to tidal influence. Seagrass and mudflats occur in the lowest lying areas to the west of the site and are generally between -1.0 and 0.0 m AHD, mangrove trees cover the majority of the site where elevation ranges between 0.0 and 1.0 m AHD, while samphire vegetation occurs along shell-grit mounds that have less tidal influence, ranging 1.0 to 1.5 m AHD. Levee banks form the highest land features at the study site, being between 2 and 3 m AHD. (From Thomas, 2010).

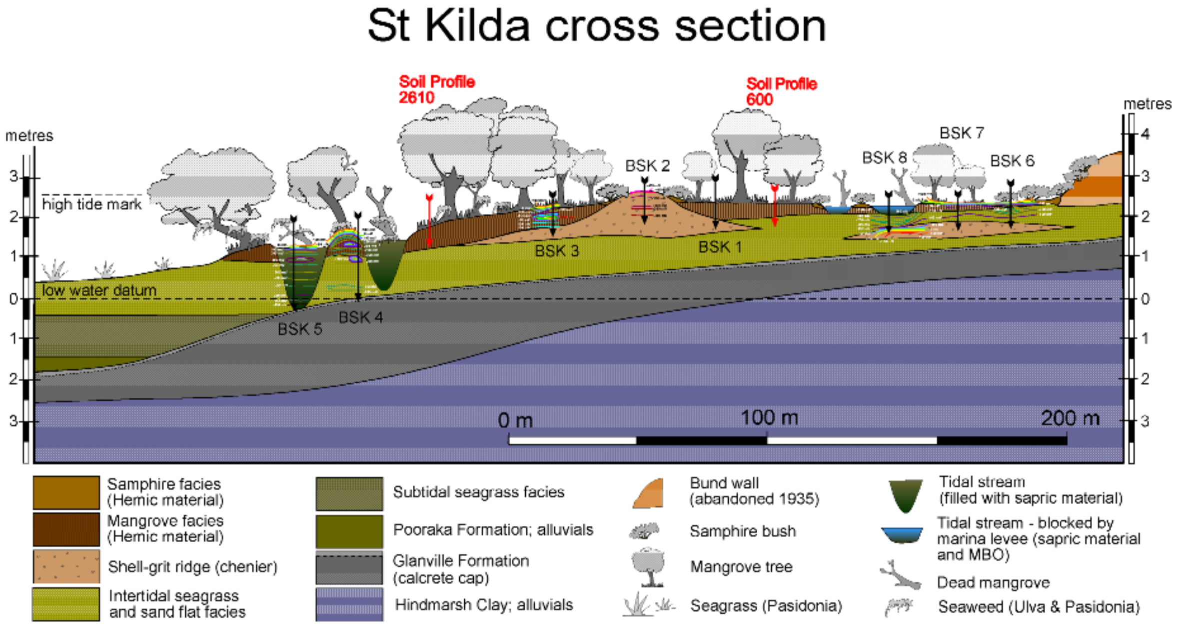


Figure 7 In the 1890s a levee bank was built from St Kilda to the south along the landward extent of mangrove vegetation (Figure 1). The bund wall was breached and abandoned in 1935 and there is now little evidence of soil acidification in the re-flooded area, but there is evidence of soil consolidation from drying and loss of organic matter. In some areas healthy mangrove soil is slowly being eroded away by outward flowing water through the tidal creeks. The creeks are filled with rotting organic matter such as sea-grass and ulva (sapric material) and causing extremely reducing conditions (Eh values down to –410mV). These soil conditions are “toxic” to the mangrove pneumatophores, which have to retreat to “higher ground” (less reducing soils). This leaves the creek banks very susceptible to erosion, further restricting the area in which pneumatophores can survive. When these areas become too small, the trees are unstable and easily knocked down during storms, killing them (From Fitzpatrick et al. 2008b and Thomas, 2010).

1.3. Disturbed tidal zones with dead mangroves and sulfuric materials

In several parts of Barker Inlet, bund walls were constructed across tidal zones (e.g. mangrove and samphire swamps) nearly 50 years ago to cut off tidal flushing, which effectively disturbed (drained) these areas causing mangrove trees and samphire vegetation to die (Figs 1, 2, 8, 9, 10 11).

Locality 3. Grand Trunkway at Gillman on bund wall /levee banks that were constructed in 1890, 1935 and 1950 to reclaim intertidal mangrove woodlands and samphire salt marsh for agriculture and industry. This site provides good examples of:
(1) Almost pristine tidal, intertidal or supratidal mangrove marshes (North Arm),
(2) Dead mangroves; highly polluted waters and soils (previously proposed MFP site)
(3) Recent establishment of huge industrial sites on reclaimed land, dredge spoil.

Excluding seawater from the original hypersulfidic material caused the surface to dry and oxidise sulfide to produce sulfuric acid (pH commonly between 2.5-3.5) and bright yellow mottles of jarosite [$KFe_3(SO_4)_2(OH)_6$] (Figs. 8, 9, 10 11). This process transforms hypersulfidic material to sulfuric material. Sulfuric material in the GSV can be composed of either organic (i.e. Histosols) or mineral material (15 cm or more thick), and has both pH less than 4 and bright yellow jarosite mottles (Figs 8 to 11). See Table 1 for correlation between the three soil classification systems in common usage.

Locality 4: Range Wetlands in the Gillman area (Figs 1 – BG11, 8 to 11).

The Wingfield Dump lookout provides an excellent overview of the entire Gillman area where the various soil-landscape map units displayed in Figure 15 can easily be observed. The bund wall constructed over 50 years ago, dead mangroves and polluted stream waters (Figs. 1 and 2) can also be seen.

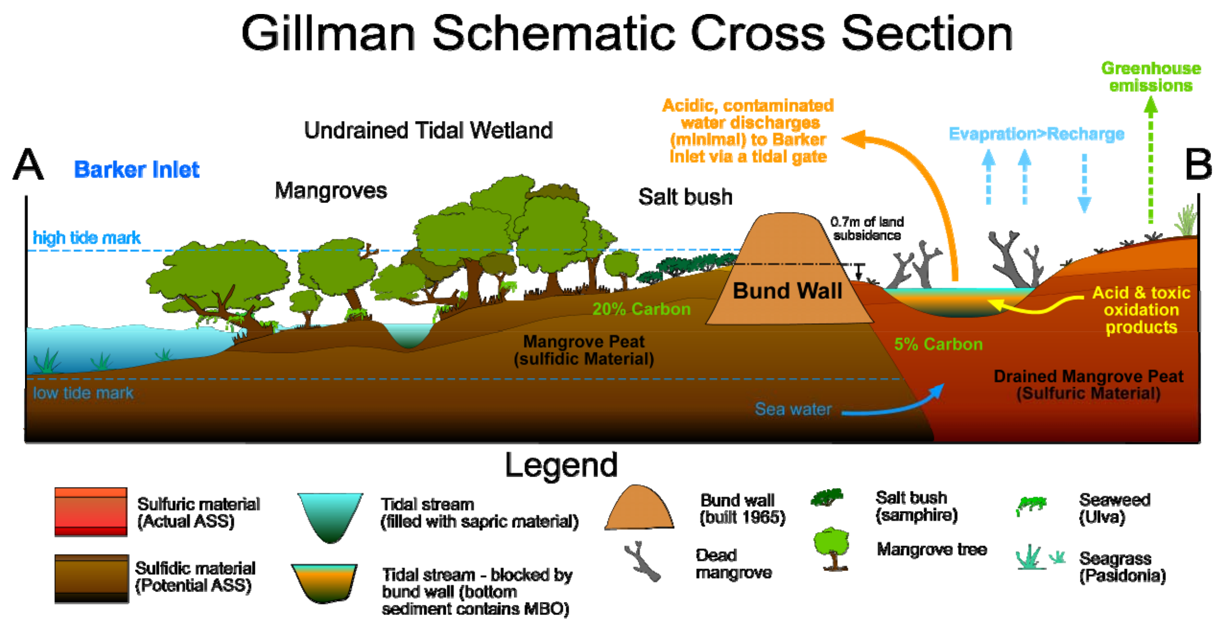
The site provides good examples of acid sulfate soils with sulfuric material, which are exposed in excavated drains (Figs. 8 to 11). Examples of rehabilitation experiments such as lime treatment, bioremediation and drainage systems to treat ASS with sulfuric materials can also be inspected.

The schematic cross-sections in Figures 8 and 9 illustrate how the former back barrier sand ridge at Gillman has developed a 2 m thick soil profile with sulfuric material because pyrite framboids in and surrounding decomposed mangrove pneumatophores have oxidised to form yellow jarosite mottles (4Bj horizons) and acidity where neutralising by alkaline materials is limited. Coatings of jarosite and iron oxides form rapidly along large root channels during periods of drying. Some small, unoxidised pyrite framboids still occur in the underlying sandy, sulfuric horizons (horizons 4Bj3, 4Bj4). In the upper horizons (0-58 cm), the oxidation of pyrite in organic residues caused precipitation of iron oxides and lenticular gypsum crystals, which are now being leached out of the profile (Figs. 10 and 11).

At Gillman, it has been estimated that about 85 % of sulfides above the oxidation front of these ASS have oxidised over the past 50 years, with an estimated 520 000 t of H_2SO_4 being produced (Thomas et al. 2004). The back barrier sands have limited acid neutralising capacity and the pH of soil solution is generally less than 2.5. Long term, *in situ* redox monitoring (Thomas 2010) indicated that the large seasonal variation in watertable height (>1 m) contributes to the reformation of pyrite and consumption of acidity near the base of the profile during the wetter months, where soil organic matter content is still adequate for reducing conditions to return. This pyrite oxidises during successive dryer months.

According to Belperio & Harbison (1992), at Gillman, 0.7 m of ground subsidence (shown in Fig.8), coincides with an area of about 400 ha of exposed mangrove peat that has been subjected to meteoric infiltration and aeration since the bund wall was constructed in the 1950s. The sulfuric acid produced from pyrite oxidation has resulted in acidic interstitial waters. The highly acid waters with pH values < 3.5 at Gillman have released large amounts of ferric iron that continue to oxidise pyrite and decalcify surrounding sediments to a depth of >2 m (Harbison 1986, Belperio & Harbison 1992, Beplerio 1993, Thomas et al. 2004). Decalcification is greatest in the earliest reclaimed areas, and gypsum is locally present along the sharp redox front between decalcified and the unaltered marine sediments (Belperio & Harbison 1992).

Most of the sulfuric acid that has been produced is still contained within the soil profile due to the low hydraulic gradient of the area. However, when a drain is excavated (see Figs. 9 and 10) and the soils are further drained, salt efflorescences precipitate rapidly on the soil surface along the drain walls (Fig. 8). These soluble salts dissolve during subsequent rain events and contribute to acidity and metal content in the drainage waters.



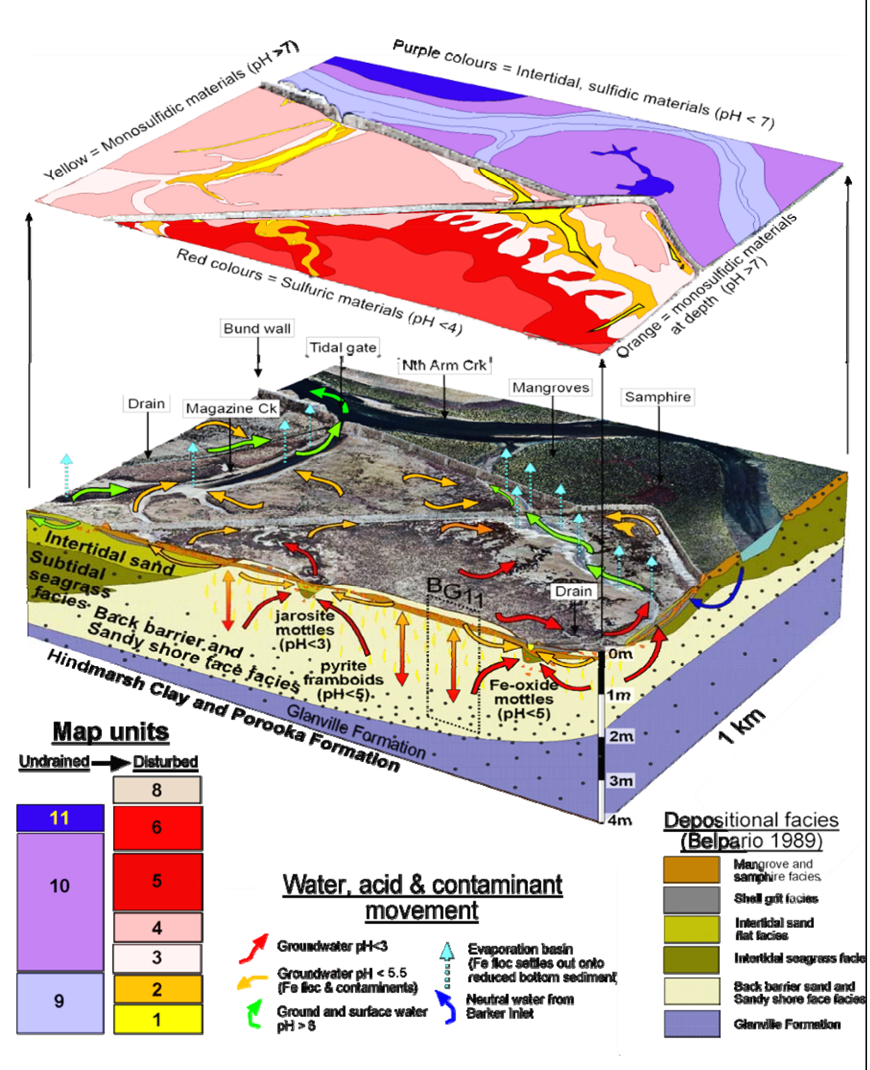


Figure 8 Schematic soil-landscape cross sections at Gillman in Barker Inlet. Normal tidal dynamics are interrupted by a bund wall (levee bank) causing oxidation of hypersulfidic and monosulfidic materials to occur, which contributes to degraded acidic saline land, denuded vegetation, reduction of wetland biodiversity, poor estuarine and stream water quality, ground subsidence, increase in greenhouse emissions and loss of amenity.

The 3D-soil-regolith explanatory model also shows the following contrasts between tidal and drained coastal landscapes:
(i) the top layer sulfuric (Red), sulfidic materials (purple) and monosulfidic (yellow) materials are displayed and (ii) in bottom layer the depositional facies, location of pyrite oxidation and movement of acidic groundwater and contaminants within the site; and arrows indicate surface and groundwater water flow paths (Fitzpatrick et al. 2008b; Thomas 2010).

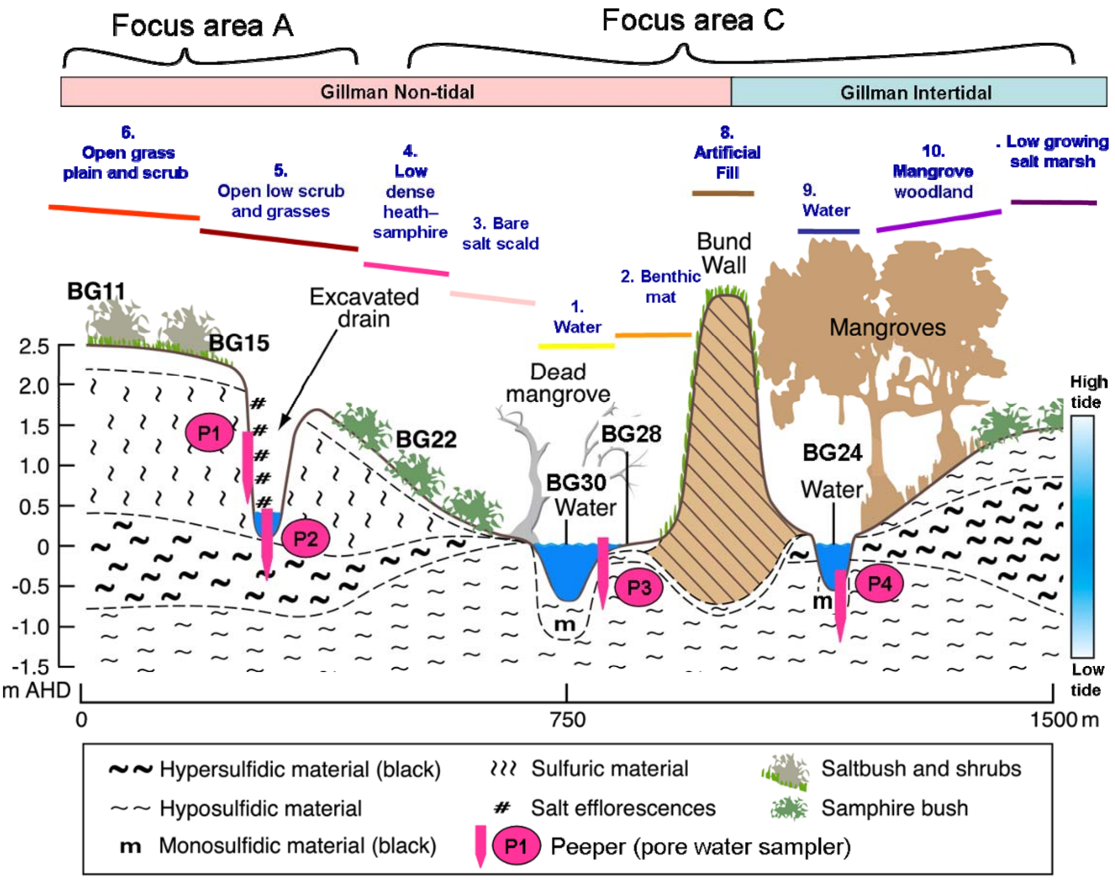


Figure 9 Detailed schematic soil-landscape cross section at Gillman in Barker Inlet illustrating the distribution of the various acid sulfate soil materials (from Thomas 2010).

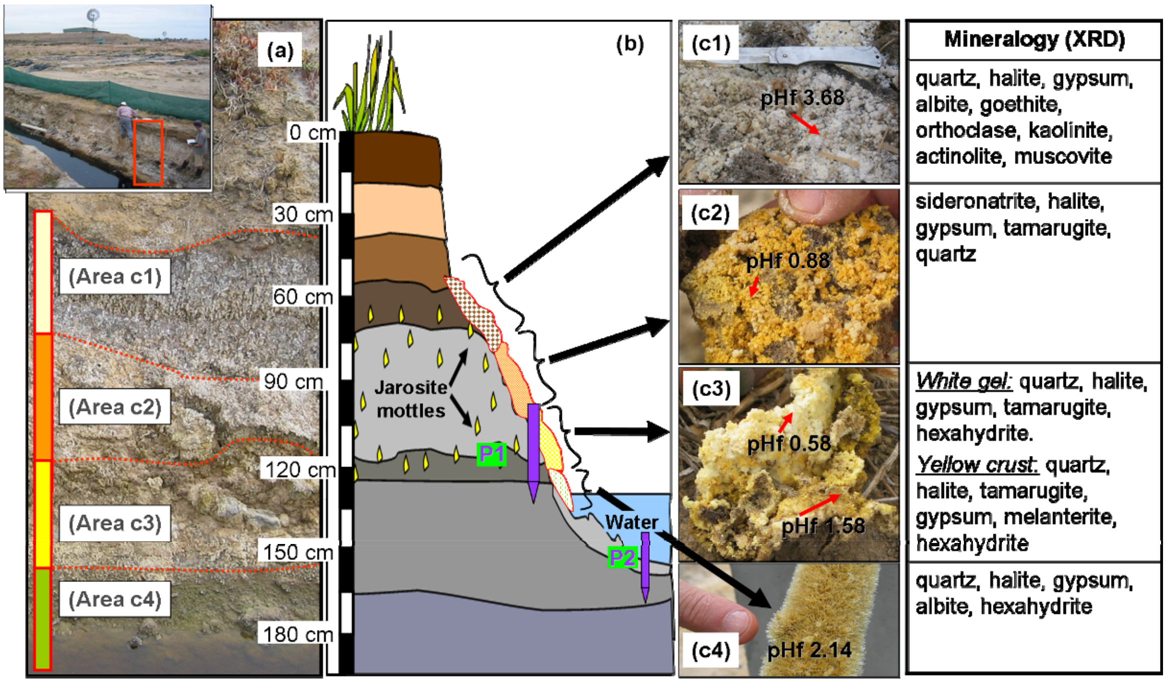
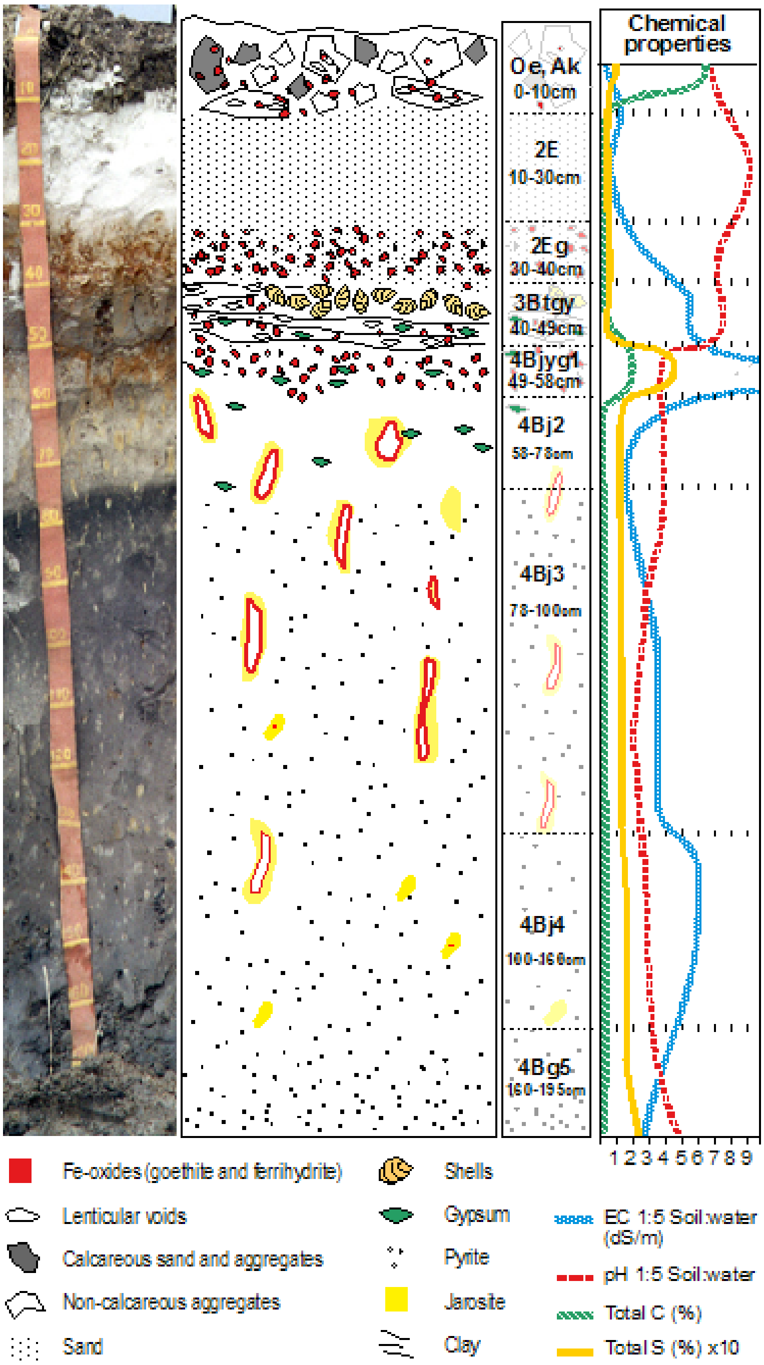


Figure 10 (a) Salt efflorescences precipitated on the exposed wall of soil profile BG 15 in a drain at Gillman, near Adelaide. (b) Schematic cross section of the drain showing position of peeper P1 within the drain wall and peeper P2 in the bottom of the drain. (c) Mineralogy of salt efflorescences from each of the areas (c1-c4). (From: Thomas *et al.* 2010).



Oe, Ak: Crumb structure, calcareous, siliceous, lenticular voids, sand-size iron nodules, not related to pores. Ferrihydrite-goethite nodules are pseudomorphs after pyrite framboids.

2E: Sand, little organic residue. Very fine clay coatings on sands.

2Eg: Sand, goethite pseudomorphs after pyrite associated with blackened organic matter. Shell lenses with gypsum on surfaces.

3Btgy: Layered clay, lenticular voids with gypsum crystal infillings. Few jarosite coatings.

4Bjyg1: Sulfuric material, sand, jarosite and gypsum coatings around roots, iron coatings on jarosite. Infillings of lenticular gypsum, decreasing with depth. Horizontal intercalations of blackened organic matter and black pseudomorphs of pyrite. Coarse lenticular pores (mangrove pneumatophores).

4Bj2, 4Bj3 and **4Bj4:** Sulfuric material and pyrite. Jarosite coatings around large root channels. Fe-oxide coatings on jarosite. Few scattered pyrite framboids in groundmass.

4Bg5, 4Bg6: Hypersulfidic material (pyrite framboids).

Figure 11 Main macro- and micromorphological features and chemical properties of an ASS soil with sulfuric material in disturbed tidal zones (Table 1 - Hydraquentic Sulfaquept) from Gillman showing horizons with five lithological discontinuities, which includes sulfuric material (58 to 160 cm) and hypersulfidic material (160 to >195 cm). Groundwater height fluctuates seasonally between 140 cm and 180 cm. (modified from Poch et al. 2009).

Extremely acidic environments that occur in open drains (Fig. 9) where soluble Fe and sulfate-salt efflorescences precipitate provides a vector for the movement of trace metals to pore water and surface water. The efflorescences are also a store of acidity, Na, Ca, Mg, Cl, Sr and SO_4 and metals (e.g., Al, Fe, Zn, Ni) to precipitate in oxic-acidic conditions and may present an environmental hazard to connected water bodies following rainfall. The salts (containing Fe and S) also contribute to the formation of monosulfidic material in water bodies lower in the landscape where soil conditions were reducing with neutral pH.

Metal concentrations (Cu, Ni, Pb and Zn) were elevated in topsoil of profile BG 15 (Fig 10; Thomas et al. 2010). The source of metals was likely anthropogenic. Potential sulfidic acidity was highest between 95 cm and 120 cm, with chromium reducible sulfur (SCR) concentrations up to 6.88%, contributing to a positive net acidity of 5700 mol H+/t (Thomas et al. 2010). Sulfuric materials occurring between 60 cm and 120 cm depth contained significant acidity, in the form of titratable actual acidity (TAA) and retained acidity, at the level where the dominant salt efflorescence mineral was sideronatrite [$Na_2Fe(SO_4)_2(OH).3H_2O$] (Fig 7). Metals (Zn, Ni, Fe, and Al) were enriched in soil pore water collected in the top 5 cm of peeper P1, located in the oxic-acidic drain wall (Fig. 10). Salt crusts in Areas c2 and c3 had a field pH < 1 (Fig. 10), indicating ASS weathering. Trace element concentrations in soil layers were similar to concentrations in juxtaposed salt crusts.

In summary, acidic drain waters contained elevated Al, Fe and other major cations and anions, but did not contain detectible concentrations of trace elements. Nearby circum-neutral stream waters only contained elevated concentrations of Fe, where hyposulfidic and monosulfidic materials occurred, with an Acid Volatile Sulfur content of 1.15 % (AVS).

1.4. Disturbed tidal zones with hypersulfidic material

In several parts of Barker Inlet, bund walls were also constructed across tidal zones nearly 50 years ago to cut off tidal flushing for construction of numerous salt evaporation ponds for commercial salt extraction (Fig. 1). In most of these contemporary and abandoned evaporation ponds (Fig. 12A), mixtures of hypersulfidic materials and MBO occur to produce a wide range of soil types (Table 1).

Figure 12 **A** (left) Soil pit in an abandoned commercial salt evaporation pond showing about 25 cm of black hypersulfidic and mainly MBO materials overlying >50 cm of gleyed clay, **B** (centre) Deep excavation at Barcoo Outlet (connecting the Patawolonga with the sea) and construction site through a sand ridge showing a relict hypersulfidic material buried under beach dunes (from a former mangrove swamp). **C** (right) Soil pit near Gillman, Port Adelaide showing about 70 cm of calcareous clayey dredge spoil, used to raise the land surface, overlying 80 cm of relict sapric hypersulfidic material (derived from a former mangrove swamp) and underlain at 140 cm by coarse shelly material. (from Fitzpatrick et al. 2008b,c).

1.5. Sandplains and dunes overlying hypersulfidic material

There is evidence of relict, buried, hypersulfidic material formed in mangrove soils below sand dunes in the Adelaide (e.g. Cotton 1950) and Port Adelaide areas, but these layers are likely to be maintained below the water table, as was the case of Barcoo Outlet excavation (Fig. 12B). Excavation through sand dunes is expected to be uncommon. It is common to see iron oxide materials staining beaches. We have observed oxidation of iron sulfides leaving iron oxide staining on beaches; however neutralising capacity is provided through tidal flushing and carbonate minerals within the sand. Consequently, these deep, sandy, relict ASS types fall into the treatment category “Low” (Table 1).

Relict, buried hypersulfidic material formed in mangrove soils has also been found below calcareous clays (probably with significant terrestrial input) at Price on upper GSV (Merry et al. 2003). The peaty hypersulfidic material usually has both high organic carbon and total sulfur contents, with a strong H_2S smell. Although the overlying clay (upper 40 cm) is often significantly calcareous, the relict hypersulfidic material contains insufficient buffering to neutralise the acid potentially produced, should the material be exposed to the air. The presence of these peaty hypersulfidic layers being about 80-100 cm thick also presents a high risk of de-watering under load with consequent consolidation. Indicator shells (Anadara) confirm that at least some of the buried mangrove sediments observed in GSV are older than 120 000 years.

1.6. Anthropogenic fill materials overlying buried hypersulfidic and sulfuric materials

Much of the land surrounding Barker Inlet has been progressively filled since the early 1900s to raise the land surface above the high tide mark. The fill material has been sourced from all over the Adelaide region and includes a mixture of clays, sands, building rubble and industrial by-products such as slag. Dredged sediments from the Port River were commonly disposed of on land (Fig. 12C) to produce a range of hypersulfidic and sulfuric Anthroposols (Table 1). Here and elsewhere, these buried materials lie below road fill and constructions in coastal areas.

It is likely that some of this fill material was hypersulfidic when it was dredged, and has since oxidised. In most cases sufficient carbonate would have been present in the sediment to neutralise the acid generated as the pyrite oxidised, but this may not always be the case. Disposing of hypersulfidic sediments on land always presents some risk to the environment.

1.7. Subaqueous soils below the low tidal mark with hypersulfidic materials

Hypersulfidic and monosulfidic materials occur in subaqueous soils (and sediments) beneath shallow water bodies such as in estuaries (Barker Inlet Estuary), rivers (Port Adelaide River), river tributaries and streams (Fig. 13A), salt evaporation ponds (Fig. 12A) or seeps (Fig. 13B), natural salt pans (Fig. 13C) and seagrass mud flats (Fig. 1).

Monosulfidic material is a subaqueous or waterlogged mineral or organic material that contains mainly oxidisable monosulfides rather than pyritic sulfides. They usually have a field pH of 4 or more but may become acid (pH <4) when disturbed due to hydrolysis of ferrous iron. In most cases, the presence of carbonates of calcium, magnesium and sodium in MBO materials will neutralise the acidity as it forms. In several parts of the bunded Gillman area, thick accumulations of MBOs have formed in drains, tidal creek depressions and low-lying, permanently waterlogged areas (Fig. 13B), and act as a sink for metal contaminants, protecting the Barker Inlet environment (Harbison 1986; Thomas et al. 2003a). The levee banks also prevent acid, salt and nutrients being discharged into Barker Inlet at any significant rate because the bunded area acts as an evaporation basin (Figs 1, 2, 8).

The recognition of the occurrence and importance of monosulfides in soil materials led in 2005 to the inclusion of monosulfidic materials as a distinguishing property within mapping units of the Australian National Atlas of Acid Sulfate Soils (Fitzpatrick et al. 2008a; 2010; Table 1). High nutrient environments together with the activity of algae and micro-organisms generates reduced redoximorphic conditions, which results in the formation of black smelly, iron monosulfides. When sub-aqueous materials rich in monosulfides are resuspended (e.g. black plume observed in Fig. 13A), they will rapidly oxidise, potentially removing most of the oxygen from the water column (Sullivan *et al.* 2002). This can lead to fish kills, especially in enclosed areas such as marinas or estuaries. In eastern Australia, the re-suspension of subaqueous hypersulfidic soils or sediments containing MBO during the flushing of drains by high runoff events has been linked to deoxygenation by Sullivan et al. (2002). Hence, MBO is reactive if exposed to oxygen, but left undisturbed these materials are harmless. Monosulfidic soil materials have the ability to affect local environments favourably by scavenging and immobilizing metal pollutants (e.g. Harbison 1986; Simpson et al. 1998). However, when a drain is excavated within this bunded area, alumino-sulfo salts (e.g. tamarugite), iron oxyhydroxysulfate salts (e.g. sideronatrite) and salt efflorescences (e.g. starkeyite) precipitate on the soil surface along the drain edges (Figs. 9 and 10). These soluble salts dissolve during rain events and contribute to MBO formation, acidity and metal content in drainage waters. Some of these processes are summarised in the schematic models shown in Figs 8 to 10.

Figure 13 **A** (left) Black monosulfidic black ooze (MBO) material on shovel excavated from the shallow stream adjacent to mangroves at St Kilda. Note black plume of the resuspended MBO in water able to remove most of the oxygen from the water, **B** (centre) Accumulation of black MBO, which underlies a reddish-brown iron oxide gel in a saline low lying, permanently waterlogged area at Gillman, **C** (right)) Typical soil profile in a section of salt pan showing a salty clay crust and underlying layer of black MBO, which in turn overlies a brownish carbonate-rich clay (Light Beach, GSV). (from Fitzpatrick et al. 2008b,c)

1.8. Noxious odours

Foul, offensive odour problems have been encountered near areas rich in hypersulfidic materials. For example, St Kilda, north of Adelaide is sometimes plagued with noxious smells during the warmer months, when hypersulfidic materials partially dry during low tide. These offensive smells occur when sediments extremely enriched in sulfides are exposed to the atmosphere. Hydrogen sulfide production (H_2S—the rotten egg smell) by drying hypersulfidic materials is thought to be a significant cause of the noxious smells. Drying hypersulfidic materials also produces sulfur dioxide (SO_2). Aside from the foul odour problem, H_2S and SO_2 are also of concern for human health at high concentrations, e.g. in confined spaces such as excavations. A number of malodorous organic-S gases (such as dimethyl oligosulfides) can also be produced under the conditions favourable to H_2S production (Franzmann et al. 2001).

1.9. Climate change and greenhouse gas emission

The aspects of the projected climate change that are most likely to affect ASS in GSV are rising sea levels and increased storm surges. The Intergovernmental Panel on Climate Change has estimated sea level rises of between 9 and 88 cm from 1990 to 2100 (Church et al. 2001). Sea levels are thought to have risen between 10 and 20 cm over the past century. In the Port Adelaide area, land subsidence has also been observed (Belperio 1993). Since the coastal areas north of Adelaide are low-lying, intertidal land supporting mangroves and salt marsh is likely to extend inland, expanding ASS with thickening hypersulfidic layers where progradation also occurs, though the expansion inland may be restricted by existing levees and road construction. A net expansion in area of reduced, hypersulfidic environments is likely to result in increased production of methane, a potent greenhouse gas.

Draining and exposure of what were formerly peaty mangrove soils in the Gillman area has resulted in decomposition of the peats over a few decades and contributed to CO_2 production (Fitzpatrick and Wright 1994; Fitzpatrick and Merry 1999; Hicks and Fitzpatrick 2008). The schematic cross-section of the Gillman area by Fitzpatrick and Merry (1999) illustrates how carbonates in soils with calcite horizons (i.e. calcrete and calcite-containing sands e.g. Petrocalcic Xerochrepts) are currently being dissolved by the development of immediately adjacent acid sulfate soils with sulfuric materials (Sulfaquepts). The Ca remaining after dissolution of the carbonates, which includes shells is retained in the system as gypsum crystals (Poch et al., 2009; Fig. 11). Although the production of acid on oxidation of hypersulfidic materials usually results in the decomposition of carbonate minerals, there is thought to be no net CO_2 production as the carbonate minerals are likely to re-form in marine environments.

2. DISTRIBUTION OF ACID SULFATE SOILS

2.1. Mapping of coastal acid sulfate soils

Maps of ASS covering the entire SA coastline were initially developed by Merry *et al.* (2003) from the following data sets:

(i) Vegetation mapping of coastal habitats (Fotheringham & Coleman (2007).

(ii) Geology and geomorphology mapping.

(iii) Field inspection and laboratory analyses for 70 sites.

(iv) Detailed ASS investigations in Barker Inlet based on 1:40,000 scale aerial photography.

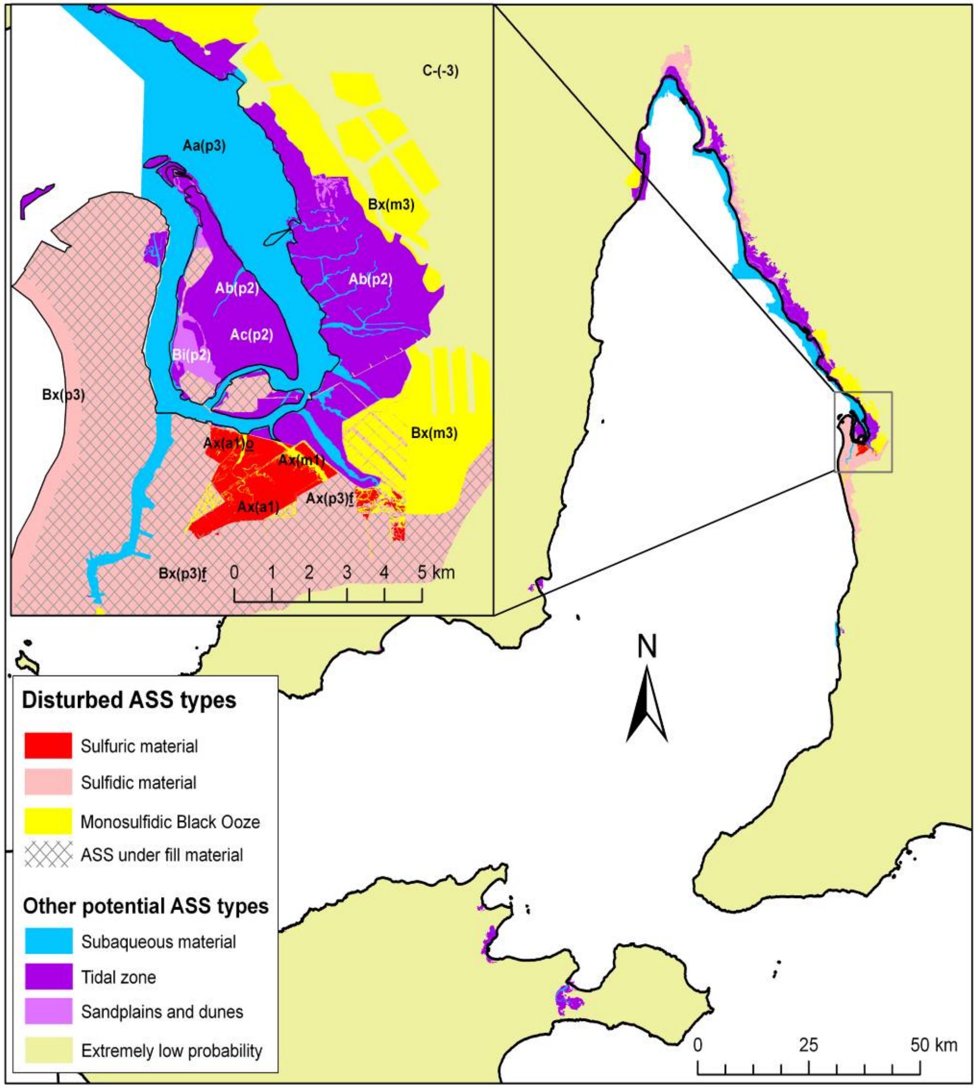
The following, methodology was used to classify and map ASS in GSV, as part of the national mapping program to develop a unified Atlas of Australian Acid Sulfate Soils with a detailed legend containing consistent national classification and terminology (Fig. 14; Fitzpatrick et al. 2008; 2010), and based on collation and assembling of all published ASS, land systems, marine habitat, elevation (DEM), tidal, estuarine, climate, vegetation and remotely sensed data using GIS.

This map base is viewable as part of the Atlas of Australian Acid Sulfate Soils and published as a web-served GIS (Fig. 14) at the Australian Soil Resource Information System (ASRIS) site (http://www.asris.csiro.au/index_ie.html).

A detailed ASS map of the Gillman area, based on 1:10,000 scale mapping (Thomas et al. 2004), is also available on-line from the ASRIS web site (inset map in Fig. 14). The detailed ASS map shown in Fig. 15 was recently completed by Thomas (2010).

The ASS map and database information were used to determine the risk of development of sulfuric material should the soil profiles be disturbed (i.e. ASS Risk Class in Table 1). The risk classes associated with treatment categories (Table 1) were based on management guidelines developed in Queensland (Dear et al. 2002). The ranking of regions and localities by importance of ASS 'hotspots' (resulting from site disturbance) in relation to environmental, economic and social effect is implicit in the legend of the risk maps (Table 1; Figs. 14, 15 and 16). Each map unit has an associated risk indicated that is based on soil properties. The highest risk areas are those associated with sulfidic (Isbell 1996) or hypersulfidic (Sullivan et al. 2010) materials in sandy soils in tidal and intertidal zones supporting mangroves. These soils usually have insufficient neutralising capacity (e.g. carbonate, exchangeable basic cations or clay minerals), so that the introduction of oxygen during excavation or exposure would potentially result in net sulfuric acid generation (see Table 3 showing net acidity values for selected profiles).

Soils with sulfuric material from former sandy tidal zones inside bund wall areas [i.e. disturbed ASS indicated in map unit codes Ax(a1)o or h] with associated environmental problems have been specifically identified in the Gillman area (1.6 km^2) and fall into the treatment categories High to Extra High (Table 1). Hypersulfidic materials in supratidal [Ac(p2)] and extratidal [Ad(p2)h] areas present moderate risk in GSV because of the almost universal presence of finely divided or shelly carbonate materials with excess potential to neutralise acid that may be formed. Consequently, these areas fall into the treatment categories Moderate to Low (Table 1), depending on whether additional mixing of materials is required. Intertidal areas have sufficient carbonate materials or sea water flushing to neutralise any acidity formed during periods of low tide when oxygen may enter exposed soil.



LEGEND[1]

Map codes in figure: **A**,**B** or **C**; **x**, **a**, **b**, **c**, **i** (**a, p, m 1,2 or 3**) **o**, **f**, **or h**

Probability of Occurrence of Acid Sulfate Soils:

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

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

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

Codes:

x - Disturbed ASS materials such in former tidal zones inside bund wall areas (e.g. Gillman); former or contemporary salt evaporation ponds.

a - Subaqueous materials below low tide mark (Light blue colour)

b - Sulfidic material within upper 1 m in intertidal flats (e.g. mangroves) – Dark purple colour

c - Sulfidic material within upper 1 m in supratidal flats (e.g. samphire) – Dark purple colour

d - Sulfidic material within upper 1 m in extratidal flats (salt marshes)

i - Sulfidic material below 1m from surface in sandplains and dunes 2- >10 m AHD (e.g. relict buried sulfidic material in Figure 7b). AHD = Australian Height Datum, which approximates mean sea level; (Light purple colour)

Subscripts to codes:

(a-) - Sulfuric material - (Red colour)

(m-) - Monosulfidic Black Ooze (MBO) material. (Yellow colour)

(p-) - Sulfidic material – (Dark and light purple and blue colours)

Confidence levels (Isbell 1996) Map polygon contains ASS, and:

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

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

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

Descriptors:

o - Organic material (sapric and hemic material)

f - Fill material (dredge fill or housing) (Black cross hatching)

h –Hypersaline or gypseous horizons generally within 10 cm of surface.

[1] Atlas of Australia Acid Sulfate Soils (Fitzpatrick *et al.* 2006)/ Australian Soil Resource Information System (ASRIS) site (www.asris.gov.au).

Figure 14 Map showing distribution of coastal ASS in Gulf St Vincent and Gillman-Barker Inlet (inset map). (From Fitzpatrick et al. 2008b,c)

Table 1 ASS types, map symbol[1], Australian Soil Classification[2], Soil Taxonomy[3], World Reference Base[3], Risk Class, Treatment categories[4] and aerial extent for Gulf St Vincent (from Fitzpatrick et al. 2008b,c).

ASS type	**Map Code**[1]	**Australian Soil Classification**[2]	**Soil Taxonomy**[3]	**World Reference Base**[3]	**Risk Class**	**Treatment category**[4]	**Area (Ha)**
Sulfidic material in contemporary tidal zones	Ab (p2)o	Histic-Sulfidic Intertidal Hydrosols	Terric Sulfisaprists Terric Sulfihemists	Sapric or Hemic Histosols (Protothionic, Tidalic)	High	H - XH	8 936
Sulfuric material in disturbed tidal zones	Ax (a1)o Ax (a1)h Ax (a1)	Sulfuric Sapric Organosol Sulfuric Hypersalic Hydrosols	Terric Sulfosaprists Terric Sulfohemists Hydraquentic Sulfaquepts, Salidic Sulfaquepts Sulfic Fluvaquents	Sapric or Hemic Histosols (Hyperthionic, Drainic) Subaquic or Salic Fluvisols (Hyperthionic, Drainic)	Very High	VH - XH	135 87 188
Sulfidic material in disturbed tidal zones	Bx (p3)	Sulfidic Hypersalic Rudosols	Haplic Sulfaquent	Haplic Gleysols (Protothionic, Arenic)	Moderate	M- H	5 273
Sulfidic material in disturbed tidal zones (mainly MBO)	Ax (m1) Ax (m3 Bx (m3))	Sulfidic Hypersalic Rudosols	Haplic Sulfaquent	Anthraquic Gleysols (Protothionic, Drainic)	Moderate	M- H	5 973
Sulfidic material in upper 1 m in supratidal flats often with samphires	Ac(p2)	Histic-Sulfidic Supratidal Hydrosols	Terric Sulfisaprists Terric Sulfihemists	Sapric or Hemic Histosols (Protothionic, Tidalic)	High to moderate	M-H	4 244
Sulfidic material in upper 1 m in extratidal flats (saltbush)	Ad(p2)h	Histic-Sulfidic Extratidal Hydrosols	Terric Sulfisaprists Terric Sulfihemists	Histic Gleysols (Protothionic, Tidalic)	High to moderate	M-H	7 139
Sulfidic material in sandplains and dunes	Ai(p2)	Sulfidic Arenic Rudosols	Sulfic Fluvaquent Sulfaquent	Subaquic or Tidalic Fluvisols (Protothionic, Arenic)	Moderate to Low	L - M	2 751
Sulfidic material buried below fill materials	Ax (p3)f Bx (m3)f	Dregic or Urbic Sulfidic Anthroposols	Thapto-Histic Sulfaquents	Spolic or Urbic Technosols (Protothionic)	Moderate to Low	L - M	6 602
Sulfuric material buried below fill materials	Ax (a1)f	Sulfuric Hypersalic Hydrosols	Hydraquentic Sulfaquepts	Spolic or Urbic Technosols (Orthothionic)	Very High	VH - XH	17
Subaqueous materials below the low tidal mark	Aa(p3)	Sulfidic [5]Subaqueous Hydrosols	Terric Sulfisaprists Terric Sulfihemists	Histic Gleysols (Protothionic, Arenic)	Moderate	M- H	15 964
TOTAL							57 222

[1] Map Codes from Figure 14: Atlas of Australian Acid Sulfate Soils (Fitzpatrick et al. 2008a, 2010)/ Australian Soil Resource Information System (ASRIS) site (www.asris.gov.au).

[2] Australian Soil Classification (Isbell 1996).

[3] Soil Taxonomy (Soil Survey Staff 2003)

[3] IUSS Working Group WRB (2006)

[4] Treatment category: L=Low level treatment; M = Medium level treatment, H = High level treatment, VH = Very high level treatment, XH = Extra High level treatment (from Dear et al. 2002)

[5] Proposed new suborder

Table 2 Map units located within Gillman Focus areas A, B, C and D combined with soil profiles classified according to Soil Taxonomy (Soil Survey Staff 2010), the Australian Soil Classification (Isbell 2002) and acid sulfate soil material terminology from Sullivan et al. (2010) (From Thomas 2010)

Map unit no. (unit colour)	Soil profile no.	Australian Soil Classification (Isbell 2002)	Soil Taxonomy (Soil Survey Staff 2010)	Acid Sulfate Soil materials
Disturbed former intertidal to supratidal areas (Gillman study site)				
1. Water	**BG 30** **BG P 5**	Sodosolic Salic Hydrosol Sodosolic Salic Hydrosol	Typic Hydrowassents	Hyposulfidic, monosulfidic
2. Benthic mat, bare salt scald, mud flats	**BG 4, 28, 31**	Sulfuric, Hypersalic Hydrosol Epicalcareous, Hypersalic Hydrosol Haplic, Hypersalic Hydrosol	Salidic Sulfaquepts Typic Haloquepts Aeric Haloquepts	Hypersulfidic, hyposulfidic, monosulfidic
3. Bare salt scalded mud flats	**BG 17, 32**	Sulfuric, Salic Hydrosol Haplic, Hypersalic Hydrosol	Salidic Sulfaquepts Aeric Haloquepts	Sulfuric, hypersulfidic, hyposulfidic, monosulfidic
4. Dense low heath -samphire shrublands	**BG 22, GGT 5**	Haplic, Hypersalic Hydrosol Sulfuric, Salic Hydrosol	Aeric Haloquepts Typic Sulfaquepts	Sulfuric, hyposulfidic
5. Open low scrub - grasses	**BG 15**	Sulfuric, Salic Hydrosol	Typic Sulfaquepts	Sulfuric, hypersulfidic
6. Open grass plain and scrub	**BG 11, 5**	Sulfuric, Salic Hydrosol	Typic Sulfaquepts	Sulfuric, hypersulfidic, hyposulfidic
7. Bare, scalped, salt scalds, sand flat	**MFP 14**	Sulfuric, Salic Hydrosol	Typic Sulfaquepts	Sulfuric, hypersulfidic, hyposulfidic
8. Artificially filled areas and embankments	**GGT 2**	Sulfidic, Dredgic Anthroposol	Haplic Xerarents	Hypersulfidic, hyposulfidic, monosulfidic
9. Water	**BG 24**	Hemic, Epicalcareous, Intertidal Hydrosol	Typic Hydrowassents	Hyposulfidic, monosulfidic
10. Mangrove woodlands	**BG 21**	Hemic, Sulfidic, Intertidal Hydrosol	Sulfic Hydrowassents	Hypersulfidic, hyposulfidic, monosulfidic
11. Low growing salt marsh plants	**BG 20**	Hemic, Sulfidic, Intertidal Hydrosol	Sulfic Hydrowassents	Hypersulfidic, hyposulfidic, monosulfidic

Table 3 Map units in Gillman area combined with soil profiles classified and net acidity (Thomas 2010)

Soil profile number	Map unit	Aust. Soil Classification (Isbell 2002)	Soil Taxonomy (Soil Survey Staff 2010)	Acid Sulfate Soil materials present	Significant net acidity occurrence
BG 11	**6.** Open grass plain and scrub	Sulfuric Salic Hydrosol	Typic Sulfaquepts	Sulfuric, hypersulfidic hyposulfidic	190 cm @ 203 mole H^+/t from 50 cm depth
BG 15	**5.** Open low scrub and grasses	Sulfuric Salic Hydrosol	Typic Sulfaquepts	Sulfuric, hypersulfidic	105 cm @ 1903 mole H^+/t from 65 cm depth
BG 17	**3.** Bare salt scalded mud flats	Sulfuric Salic Hydrosol	Salidic Sulfaquepts	Sulfuric, hypersulfidic	95 cm @ 1491 mole H^+/t from 25 cm depth, including an AVS content of 0.03%
BG P 5	**1.** Water	Sodosolic Salic Hydrosol	Typic Hydrowassents	Hyposulfidic, monosulfidic	5 cm @ 456 mole H^+/t from 0 cm depth, including an AVS content of 1.1%

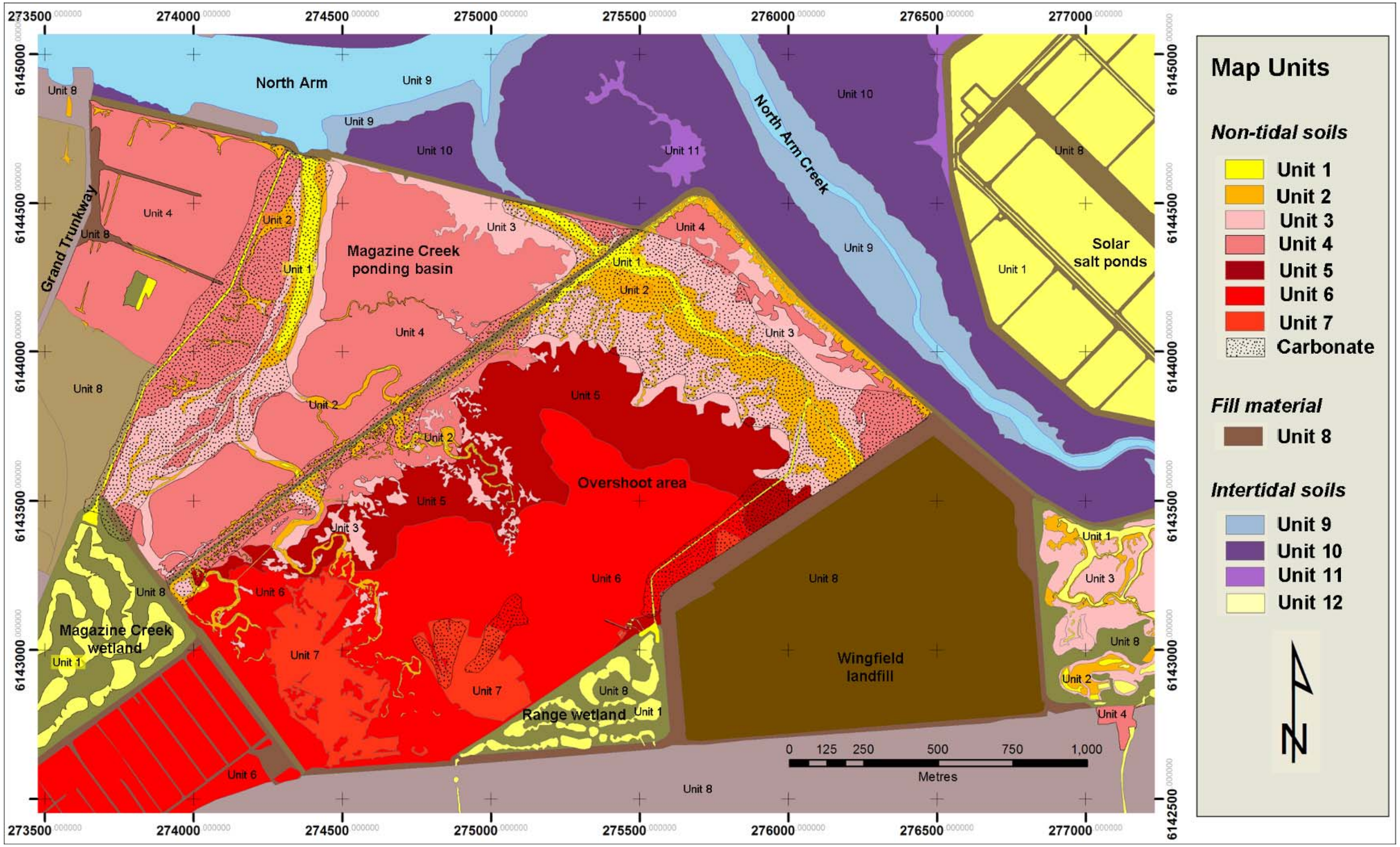


Figure 15 Soil-landscape map for the Gillman study site. Refer to Table 2 for a detailed map legend and descriptions of Map units. The Dean Rifle Range was located at coordinates E 73500, N 6142500 (at the bottom left corner of the map). From Thomas (2010).

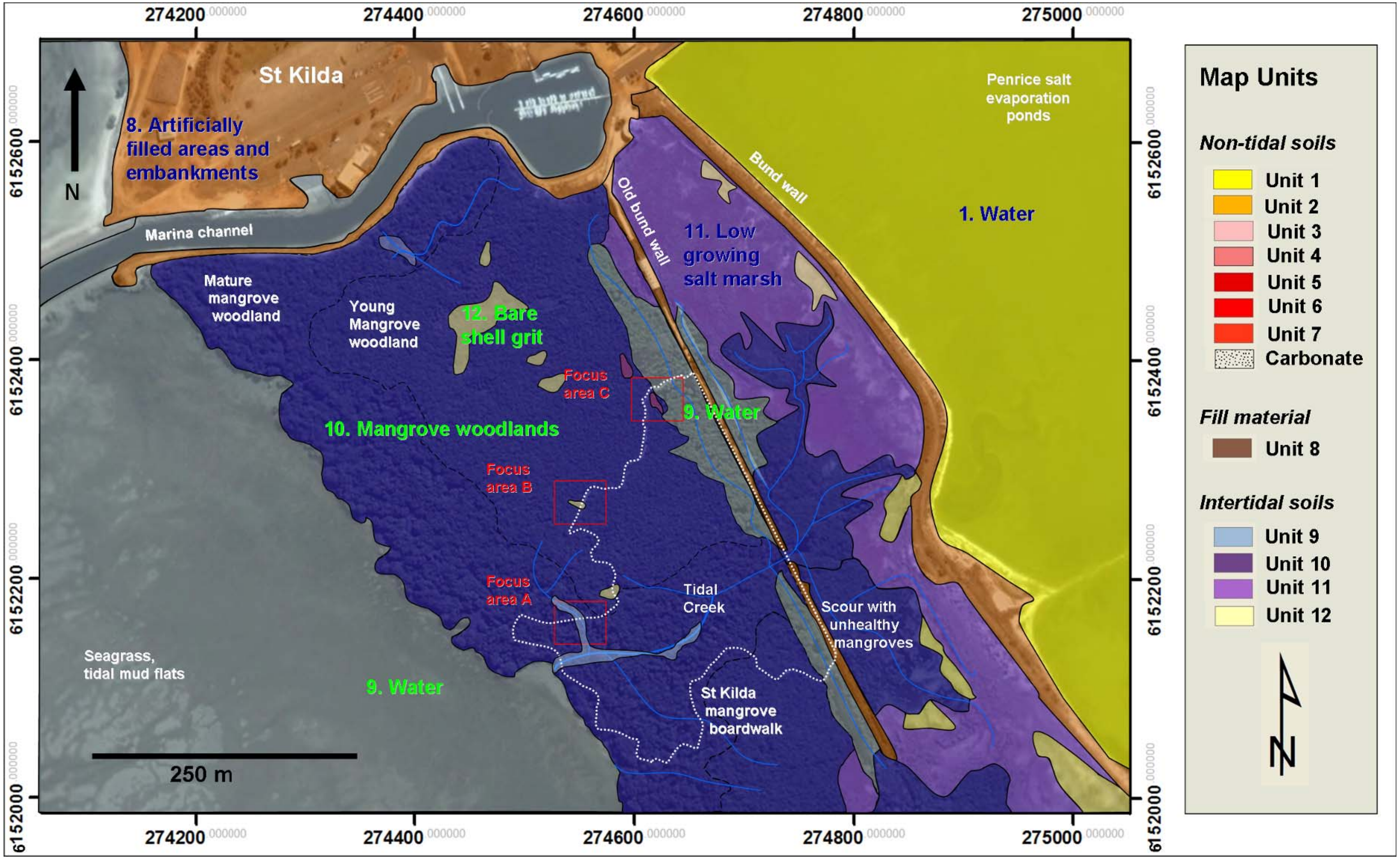


Figure 16 Soil-landscape map for the St Kilda study site. Refer to Table 2 for a detailed map legend and descriptions of Map units (From Thomas, 2010).

2.2. Management of Acid Sulfate Soils in Gulf St Vincent

Coastal development projects such as land reclamation, digging ponds for aquaculture, sand and gravel extraction or dredging for ports and marinas are likely to disturb ASS around GSV. Where ASS is disturbed, there is a risk to human heath, local infrastructure and the local environment. However, appropriate management of ASS during development can improve discharge water quality, increase agricultural productivity and protect infrastructure and the environment (Thomas et al. 2003b). Such improvements can generally be achieved by applying low-cost land management strategies based on the identification and avoidance of ASS materials, slowing or stopping the rate and extent of pyrite oxidation, and by retaining existing acidity within the ASS landscape. Acidity and oxidation products that cannot be retained on-site may be managed by other techniques such as acidity barriers or wetlands that intercept and treat contaminated water before it is finally discharged into rivers or estuaries. Selection of management options will depend on the nature and location of the ASS materials, and their position in the landscape. This is why reliable ASS risk maps, at appropriate scales, and characterizing ASS landscapes are so important.

Ranked in order of priority, ASS management follows the list of principles:

Minimise disturbance or drainage of sulfidic 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 avoiding 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 hypersulfidic material

This may include staging the development project to prevent oxidation of hypersulfidic material by covering it with an impermeable barrier (e.g. clay), or placing any excavated hypersulfidic 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.

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

Typically, this would involve installing a leachate collection and treatment system (e.g. using lime), a permeable reactive barrier (e.g. lime slot) to intercept and neutralise acidic groundwater as it moves thought 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 lime, or other neutralising agent.

Separate hypersulfidic materials

This may include the use of mechanical separation, such as sluicing or hydrocyclone to separate sulfide minerals (e.g. pyrite crystals) from the hypersulfidic 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 sulfidic and sulfuric 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 SA through the Coast Protection Board (CPB). These controls and guidelines, along with some examples of remediation techniques trialled at Gillman, can be found in the Guidelines and Risk Assessment Criteria of Coast Protection Board (2003) and the cited web link.

3. CONCLUSIONS

The loss of tidal inundation has caused a lowering of the watertable in the Gillman area in Barker Inlet, enabling oxygen to diffuse into the hypersulfidic soils, which caused pyrite oxidation and soil acidification. The descriptive and mechanistic models presented illustrate the major geomorphic stages in soil-landscape evolution and detail the chemical and physical changes that occur when tidal influences are altered or excluded in these environments. Oxidation of hypersulfidic materials and monosulfidic black ooze following the lowering of water tables or soil disturbance is contributing to degraded saline seepages and poor stream water quality.

The ASS map legend produced as part of the Atlas of Australian Acid Sulfate Soils and treatment categories based on Dear et al. (2002) was used to produce “ASS risk classes” for the Gulf St Vincent.

The South Australian government has responded to the challenge of managing coastal ASS environments in South Australia by introducing planning and development controls for coastal ASS through the Coast Protection Board (CPB). These controls and guidelines, along with some examples of remediation techniques trialled at Gillman, can be found in the Guidelines and Risk Assessment Criteria of Coast Protection Board (2003) and cited web link. The Atlas of Australian Acid Sulfate Soils will assist in refining and updating ASS maps in the GSV to enable informed risk management, both in terms of the maintenance of existing development, and the assessment of future development proposals.

4. ACKNOWLEDGMENTS

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6. GLOSSARY - Classification of Acid Sulfate Soil materials

The Acid Sulfate Soils Working Group of the International Union of Soil Sciences agreed to adopt in principle the following five descriptive terminology and classification definitions of acid sulfate soil materials proposed by Sullivan *et al.* (2010) at the 6th International Acid Sulfate Soil and Acid Rock Drainage Conference in September 2008 in Guangzhou, China. This new classification system for acid sulfate soil materials has also been adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project (Murray–Darling Basin Authority, 2010) for use in the detailed assessment of acid sulfate soils in the Murray-Darling Basin.

The criteria to define the soil materials are as follows:

Acid Sulfate Soil Materials

1. **Sulfuric materials** - soil materials currently defined as sulfuric by the Australian Soil Classification (Isbell 1996). Essentially, these are soil materials with a $pH_w < 4$ as a result of sulfide oxidation.
2. **Sulfidic materials*** – soil materials containing detectable sulfide minerals (defined as containing greater than or equal to 0.01% sulfidic S). The intent is for this term to be used in a descriptive context (e.g. sulfidic soil material or sulfidic sediment) and to align with general definitions applied by other scientific disciplines such as geology and ecology (e.g. sulfidic sediment). The method with the lowest detection limit is the Cr-reducible sulfide method, which currently has a detection limit of 0.01%; other methods (e.g. X-ray diffraction, visual identification, Raman spectroscopy or infra red spectroscopy) can also be used to identify sulfidic materials.

   **This term differs from previously published definitions in various soil classifications (e.g. Isbell, 1996).*
3. **Hypersulfidic material** - Hypersulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by experiencing a drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2-10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is either:
   a. until the soil pH changes by at least 0.5 pH unit to below 4, or
   b. until a stable pH is reached after at least 8 weeks of incubation.
4. **Hyposulfidic material** - Hyposulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by not experiencing a drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2-10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is until a stable pH is reached after at least eight weeks of incubation.
5. **Monosulfidic materials** - soil materials with an acid volatile sulfur content of 0.01%S or more.

Non-Acid Sulfate Soil materials

In addition the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project agreed to identify the other acidic soil materials arising from the detailed assessment of wetland soils in the Murray-Darling Basin even though these materials may not be the result of acid sulfate soil processes (e.g. the acidity developed during ageing or incubation may be the result of Fe^{2+} hydrolysis, which may or may not be associated with acid sulfate soil processes). Also the acidity present in field soils may be due to the accumulation of acidic organic matter and/or the leaching of bases. Of course, these acidic soil materials may also pose a risk to the environment and would be identified during the course of the Phase 1 detailed assessment (Murray–Darling Basin Authority 2010). The definition of these *other acidic soil materials* for the detailed assessment of acid sulfate soils in the Murray-Darling Basin is as follows:

1. **Other acidic soil materials** – Either:
   a. non-sulfidic soil materials that acidify by at least a 0.5 pH_w unit to a pH_w of <5.5 during moist aerobic incubation, or
   b. soil materials with a $pH_w \geq 4$ but < 5.5 in the field.

2. **Other soil materials** – soils that do not have acid sulfate soil characteristics.

7. APPENDIX 1 – Proposed MFP site

The Gillman site was destined to become the location for the **futuristic Multi-Function Polis (MFP).** The MFP was intended to be a high quality mixed use urban development where people could generally live, work and recreate within their local area, whilst serving as a centre for research and education, and a focus for international business investment in new and emerging technologies. Extensive investigation and planning work was undertaken in proving up the MFP. A consolidated list of approximately 150 reports exists.

The following CSIRO Division of Soils Technical Report, published in December 1991 (Fitzpatrick, 1991), entitled: “Preliminary assessment of the properties and development of saline acid sulphate soils at the Gillman MFP Australia Site” and accompanying letter to “PPK Consultants” provides the first positive identification and occurrence of sulfidic (hypersulfidic) and sulfuric materials in Acid Sulfate Soils at the MFP site and in South Australia.

The Manager,
Mr. Doug Kneebone,
PPK Consultants,
100 North Terrace
Adelaide, S.A. 5000.

15/12/91

Attention: Mr. Doug Wallace

Dear Sir,

Re PRELIMINARY ASSESSMENT OF THE PROPERTIES AND DEVELOPMENT OF SALINE ACID SULPHATE SOILS AT THE GILLMAN MFP AUSTRALIA SITE

I have pleasure in forwarding my report on the properties of saline acid sulphate soils in part of the "Mangrove facies" at the proposed MFP - Australia site at Gillman as they relate to problems associated with earthworks (quality of materials) and water quality.

The information provided here is based on a very limited number of observations made during a 2 hour field inspection of the site. Described in detail are two soil profiles from which samples were taken for some laboratory analysis. Owing to the small amount of work currently undertaken, it is important not to extrapolate these results across the whole site until further soil correlation work is done. However, the prospects for easy land reclamation is clearly conditioned by the presence of very reactive reduced sulfidic saline materials/horizons in saline 'acid sulphate soils' and 'potential acid sulphate soils'. Clearly more specific soil surveys followed by related chemical and physical investigations (bearing in mind that special sampling procedures are required to analyse these types soils) need to be conducted in order to understand how to treat these kinds of complex materials before they are excavated or compacted *in situ*.

These soils are certainly complex in both their chemical and physical properties. In collaboration with Dr. W. D. Hudnall (Louisiana State University, USA) we have recently undertaken detailed studies of similar acid sulphate soils at St. Kilda. We will be presenting some of this work at the International Symposium on Acid Sulphate Soils in Vietnam in March 1992). It is now becoming recognized that acid sulphate soils are difficult soils to manage and I am confident that much will be gained in knowledge by my attending the International Symposium. We at CSIRO Division of Soils have all the resources necessary for undertaking appropriate work on these soils.

Please do not hesitate to contact me for further discussion or clarification of any points raised in this report.

Dr. R.W. Fitzpatrick.
Principal Research Scientist.
Date: 15/12/91

CSIRO Division of Soils **TECHNICAL report 11/1991**

NOT FOR PUBLICATION
The material contained herein has not
been refereed. It may be quoted as a
personal communication following
written consent of the authors.

REPORT TO PPK CONSULTANTS

PRELIMINARY ASSESSMENT OF THE PROPERTIES AND DEVELOPMENT OF SALINE ACID SULPHATE SOILS AT THE GILLMAN MFP AUSTRALIA SITE

by R.W. Fitzpatrick. CSIRO Division of Soils, Adelaide

Introduction

This Report provides a preliminary assessment of the pedological properties of saline acid sulphate soils in part of the "Mangrove facies" (Belperio and Rice, 1989; Belperio and Harbison, 1992) at the proposed MFP - Australia site at Gillman as they relate to problems associated with earthworks (quality of materials) and water quality.

This report was commissioned by Mr. Doug Kneebone of PPK Consultants on Wednesday 11th December, 1991. PPK Consultants requested more detailed information on the properties of those soils that were likely to cause problems with earthworks (quality of materials) and water quality.

Background

Assessment of the following two previous reports: "MFP-Adelaide Site Assessment Study, Preliminary Geotechnical, Groundwater and Agronomic Investigations" by Coffey Partners International (CPI) Report No. A2151/1-AS dated 20th December 1990 and "Design Concept Development and Core Site Assessment" by Kinhill Delfin have indicated that insufficient specific detailed soil investigations were made on the upper two metres of material in the "Mangrove facies". These reports contain geological and geotechnical descriptions of materials to depths up to several metres but are lacking in detailed pedological descriptions and interpretations of the surface horizons regarding the reactivity of sulphidic materials.

The recognition of acid sulphate soils in Australia and research into their behaviour has been limited. This is possibly a reflection of the small area these soils occupy in relation to the total area of the continent. Hence, none of the published major Australian soil classification systems have specifically provided for such soils. However, an International Soil Classification System known as Soil Taxonomy (Soil Survey Staff, 1990) does provide a framework for classifying and interpreting the management problems associated with such complex soils.

A 2 hour field inspection of some soils in the "Mangrove Facies" at the MFP Australia Site near Gillman, South Australia was conducted on 10th December, 1991 by Dr. R. W. Fitzpatrick and Ian Hollingsworth (CSIRO Division of Soils, Adelaide) and Dr. W. D. Hudnall from Louisiana State University, USA who is a specialist in Soil Taxonomy and Classification of acid sulphate soils. The objectives of this brief investigation were to:

(i) provide two detailed soil profile descriptions of soils in the "Mangrove Facies";

(ii) sample and classify these soils according to Soil Taxonomy (Soil Survey Staff, 1990) and

(iii) provide a brief outline of the properties and possible development of these soils (i.e. changes) in the context of landuse.

Results

The main site described and sampled was near the CSIRO Division of Water Resources piezometer site opposite North Arm (Fig. 1 in Pavelic and Dillon, 1993): Two detailed profile descriptions including some laboratory data are given in appendix 1.

Summary of findings.

1. Field observations together with limited laboratory measurements confirm the occurrence of a range of saline 'acid sulphate soils' as well as 'potential acid sulphate soils' . This is based on the identification of the following soil horizons/materials using Soil Survey Staff (1990) from which soil types were identified:

(i) sulfuric materials/horizons (i.e. actual acid sulphate soils);

(ii) sulfidic materials/horizons (i.e. potential acid sulphate soils);

(iii) sapric materials/horizons (humified peat or organic-rich soils);

(iv) based on the positive identification of the above materials/horizons the soils within the "Mangrove Facies" are classified as "Histosols" at the order level using the International Soil Taxonomy classification system (Soil Survey Staff, 1990). At the more detailed level of classification (family level) they classify as either: Terric Sulfohemists, loamy skeletal, carbonatic, euic, thermic or Terric Sulfihemists, loamy skeletal, carbonatic, euic, thermic .

2. If the acid sulphate soils containing sulfidic materials are drained, or if the sulfidic materials are otherwise exposed to aerobic conditions (e.g. by earthwork excavations) the sulphides oxidise to form sulphuric acid. The pH which is near neutrality before drainage or exposure will drop below 2. In other words, the sulfidic materials at the Gillman site transform rapidly to sulfuric materials/horizons.

3. The sulfuric materials/horizons are quite high in their content of relatively soluble salts containing iron and heavy metals which will tend to be flushed out during rainstorms.

4. It seems apparent that for better land use planning of areas with acid sulphate soils, such as the "Mangrove Facies and the Supratidal Marsh Facies" better definition and characterisation is required. This could be achieved by conducting:

(i) more specific field soil investigations (pedological),

(ii) more detailed soil profile descriptions,

(iii) specific soil surveys to identify detailed soil boundaries or sub-facies within the "Mangrove Facies and the Supratidal Marsh Facies" so as to avoid these materials in the planning of the lakes and villages.

The following specific chemical and physical investigations (bearing in mind that special sampling procedures are required to analyse these types soils) should be conducted in order to understand how to treat the materials:

(i) monitor in situ the Eh and pH seasonally,

(ii) determine **n-values (**Pons and Zonneveld, 1965),

(iii) bulk density,

(iv) conduct leaching experiments after exposing the sulfidic materials to air,

(v) fractionate the various forms of sulphur and iron.

Detailed Soil Processes possibly occurring in the "Mangrove Facies" at the Gillman Site.

Soil development can take place very rapidly on the sulfidic materials, which now occurs below the permanent water table at the proposed Gillman MFP Site. This process is especially rapid because of its locality in a Mediterranean climate (i.e. the extreme wetting and drying). For the development of a sulphuric horizon, it is necessary that the water table be below the surface at least during part of the year or that the sulfidic material be excavated and placed above the water table to dry. The formation of the sulphuric materials (horizons) does not appear to take place in these materials when permanently beneath the water table. If the sulphidic materials were to be compacted with earth moving equipment at an early stage, it is expected that the chemical ripening process to form sulphuric materials would be slowed down because of less movement of air and water into and/or through the soil.

Below the permanent water table are black sapric unripe sulfidic materials like the Oa2 horizon given in the profile description (App 1). These materials are potential acid sulphate soil materials with high water content and associated high n-values (Soil Survey Staff 1990). These materials also have very low bulk density (less than 0.40 Mg m-3) because of high water content and organic matter. These materials have near neutral to alkaline pH (7 -8.5) measured in a minimum of water when sampled moist. They also emanate hydrogen sulphide gas and particularly so when exposed to drops of hydrochloric acid indicating the presence of monosulphides. These materials are highly anaerobic especially in the soil horizon at a depth of 65 to 75 cm (*Appendix 1*).

When the sulfidic material is exposed to air in zones above the water table and desiccation occurs, the dark organic matter materials change irreversibly to very dark grey and lose their ability to evolve hydrogen sulphide when exposed to HCl. As they dry a granular structure is formed as shown in the (App1). This is when a sulphuric horizon is found to form by sulfuricization. Salts, predominantly ferrous sulphate are formed upon the oxidation of the iron sulphides. Bright yellow and red iron oxide salts together with halite from salts in the ground water accumulate at or near the surface of the soil by wicking and desiccation during dry periods of the year. Fresh rain of storm water causes the salts to dissolve and may temporarily raise the pH. Under these conditions the dissolved ferrous iron is oxidized and hydrolyzed to form the reddish mineral ferrihydrite or the bright yellow mineral jarosite and these processes form additional acidity.

Under these oxidising and leaching conditions above the water table the sulphur and heavy metals are eluviated form the sulphuric horizons/ materials (apparently in these kinds of soils, the heavy metals may be present in the sulfidic material as metal sulphides or co-precipitated with the iron sulphides). Upon oxidation, metal sulphates form and are eluviated. This eluviation could even be enhanced by the high salt content known to be present in these soils by displacing the metal cations from cation exchange sites on the clay and organic matter.

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Appendix 1

SOIL PROFILE DESCRIPTIONS AT GILLMAN MFP AUSTRALIA SITE

The following two soil profile descriptions were described, classified and sampled by Dr. R. W. Fitzpatrick and Mr. I. D. Hollingsworth (CSIRO Division of Soils, Adelaide) and Dr. W. H. Hudnall (Louisiana State University. USA) near the CSIRO Division of Water Resources piezometer site opposite North Arm (see Fig. 1 in Pavelic and Dillon, 1993).

Profile locality: 20 m From Edge of Canal

Date: 9/12/91

Described by: R.W. Fitzpatrick, I. D. Hollingsworth and W. H. Hudnall

Water table: 36 cm

Soil Classification:

According to Soil Taxonomy; Soil Survey Staff, 1990):

Terric Sulfihemist, loamy skeletal, carbonatic, euic, thermic.

According to Soil Taxonomy; Soil Survey Staff, 1992:

Terric Sulfisaprist, loamy skeletal, carbonatic, euic, thermic .

Slope: 2%

Oa1(P21) - 0 to 8 cm dark reddish brown (5YR 3/2) with common (10 to 20 %), medium (5 to 15 mm), distinct reddish brown (5YR 4/4) mottles; granular peat (less than 5 % clay); field pH on unexposed material pH 6.5; field pH on exposed material after 3 days pH less than 3.5; water repellent; clear wavy boundary.

Oa2(P21) - 8 to 36 cm, very dark grey (5YR 3/1) sandy sapric peat (humified); field pH on unexposed material pH 7.0; field pH on exposed material after 3 days pH less than 3.5; sharp smooth boundary.

C1 - 36 to 64 cm, brown (7.5YR 5/2) silty sand with 10 to 20 % medium sized shells; field pH on unexposed material pH 9.5; field pH on exposed material after 3 days pH less than 3.5; sharp smooth boundary.

C2 - 64 to 480 cm, dark grey (2.5Y 4/0) silty clay loam; common (10 to 20 %) very fine humified sea grass roots with to <2 % medium sized shells;; field pH on unexposed material pH 9.5; field pH on exposed material after 3 days pH less than 3.5;

C3 - 480 cm+ Calcrete

Profile locality: 50 m From Edge of Canal

Date: 9/12/91

Described by: R.W. Fitzpatrick, I D. Hollingsworth and W. H. Hudnall

Water table: 85 cm

Soil Classification:

According to Soil Taxonomy; Soil Survey Staff, 1990:

Terric Sulfohemist, loamy skeletal, carbonatic, euic, thermic

According to Soil Taxonomy; Soil Survey Staff, 1992.

Terric Sulfosaprist, loamy skeletal, carbonatic, euic, thermic .

Slope: 2%

Oa1(P21) - 0 to 3.5 cm, dark grey (5YR 4/1 dry) very dark grey (5YR 3/1), granular peat (2-5mm granular peds and < 5 % clay); very few (<2%), medium (5 to 15 mm), distinct reddish brown (5YR 4/4) mottles; field pH on exposed material ranged from dominantly 6.0 to less than 4.5 in places; Laboratory pH is 5.9 (1:5 water). After treatment with hydrogen peroxide the pH is 3.5. and the colour turns dark reddish brown (5YR3/3) ;water repellent; clear wavy boundary.

Oa2(P22) -3.5 to 6.5 cm, reddish yellow (7.5YR 6/6 dry) strong brown (7.5YR 3/2) granular peat (2-5mm granular peds and < 5 % clay); strong brown (7.5YR 3/2) common (10 to 20 %), ferruginous nodules, medium (2-6mm), weak; yellowish red (5YR 4/6), reddish yellow (5YR 7/6d) common (10 to 20 %), soft ferruginous powdery mottles, medium (2-6mm), weak; field pH on exposed material ranged from dominantly 6.0 to less than 4.5 in places; water repellent; sharp smooth boundary. Laboratory pH is 4.6. After treatment with hydrogen peroxide the pH is 2.9 and the colour turns dark reddish brown (5YR3/3).

Oa3(P23) - 6.5 to 15 cm, black N2; sandy sapric peat (humified) with very few distinct mottles of strong brown (7.5YR 3/2); field pH on unexposed material pH 6.5; ; sharp smooth boundary.

Oa4(P24) - 15 to 65 cm, very dark grey (10YR 3/1) sandy matrix with dark brown sapric material (7.5YR 3/4); sandy sapric peat (humified); field pH on unexposed material pH 6.5; ; sharp smooth boundary. Moist laboratory pH is 3.4. After treatment with hydrogen peroxide the pH is 1.5. and the colour turns dark brown (7.5YR3/4).

Oa5(P25) - 65 to 75 cm, dark greyish brown (2.5Y 4/2) sandy matrix with black N2 sapric material and with very common distinct mottles of greyish brown (2.5Y 5/2); sandy sapric peat (humified); field pH on unexposed material pH 6.5; sharp smooth boundary. Moist laboratory pH is 6.9. After treatment with hydrogen peroxide the pH is 1.39, and the colour turns dark brown (10YR4/3).

C1 - 75 to 86 cm, dark greyish brown (2.5Y 4/2) sandy matrix with; brown (7.5YR 5/2) silty sand with 10 to 20 % medium sized shells; sandy sapric peat (humified); field pH on unexposed material pH 9.5; field pH on exposed material after 3 days pH less than 3.5.

8. APPENDIX 2 – Incubation Testing

Field Morphology, Sampling and Incubation Testing (must commence in the field)

By Rob Fitzpatrick

The approach during a first sampling visit is to select sites to form a transect, with sites chosen to cover the range of soils from: (i) the lowest point in the wetland if dry, or at a safe depth to sample if water was present to (ii) more elevated locations to the erstwhile high water mark. As such, the transect should comprise a “hydrosequence” along the landscape, reflecting various hydrologic conditions, and drying and wetting ages. In the final account, the number and location of sample sites is determined by the experience of the field soil surveyor.

Sample site location coordinates is obtained using a global positioning system (GPS), using the WGS 84 Datum: Zone 54 South. At dry sites soil samples should be taken from soil pits dug to approximately 0.6 m deep. Where soils are below water (i.e. subaqueous soils), samples should be obtained by wading and using a shovel to obtain the upper 0.4 m and augers for deeper sampling. Irrespective of soil conditions (wet or dry), soil profiles should be sampled on a layer-by-layer basis where changes (colour, morphology) in the soil material were identified. About 3 to 5 layers should be sampled per soil profile, and typically layers consisting of a surface (about 0 to 0.05 m), subsurface (0.05 – 0.2 m), and subsoil (about 0.2 – 0.6 m).

Soil colour should be determined on all samples in the moist state using Munsell Soil colour notation (Munsell Soil Color Charts, 2000). Soil colour is usually the first property recorded in a morphological description of soils (and may be the only feature of significance to a layperson). Soil colour provides an indicator of drainage or redox status in soils because soil colour relates to soil aeration and organic matter content (Fitzpatrick et al., 1999).

Incubation (ageing) testing

This method, which is often considered to represent a more realistic scenario for acid sulfate soil testing, is based on the “incubation” (or ageing) of soil samples. A number of specific techniques are employed, but all are based on keeping the sample moist for a specified period (usually a number of weeks; recent recommendations have increased the period from 8 to 19 weeks), which allows slow oxidation of sulfide minerals to occur. Although this may mimic nature more closely and does not force reactions to occur (as with the peroxide test) or rely on total ‘potential reaction’, it can be argued that the complex processes occurring in the field are not adequately reproduced during this laboratory ageing, e.g. complex processes including exchange with sub-surface waters (containing ANC) or biogeochemical reactions. These factors should also be taken into consideration wherever possible, although often require a thorough understanding of water movement (e.g. groundwater), and are often site and scenario specific.

The samples should be described in the field according to standard methodology (e.g. McDonald et al. 1990; Schoeneberger et al. 2002; MDBA 2010). For each layer, depth ranges, morphology and physical properties should be recorded and included: colour (matrix and mottles), texture, structure, consistency, and occasional other identifiable features such as stickiness, plant material, odour and concentrations.

Multiple soil samples should be taken from each layer and included:

- Bulk soil samples (typically > 500 g) should be placed in pre-labelled, thick, sealable plastic bags and mixed, for pH analysis and bulk storage.
- Two sets of sub-samples from the bag should be taken and placed in two 70 ml screw-top plastic jars, with care taken to exclude air by filling the jars to the maximum level to limit sulfur oxidation during transit and storage. One can be used for XRD (powder X-ray diffraction) and XRF (X-ray fluorescence spectrometry) analyses, and the other for chromium reducible sulfur (S_{CR}) analyses.
- Occasionally, samples of acidic yellowish and reddish-orange coloured salt efflorescences, coatings and mottles should be described and carefully collected for mineralogical analyses using XRD.

Two sub-samples from the layers should be placed in two separate chip-trays (Fitzpatrick et al 2010).

- One for display morphologically representative aggregates for each of the sampled layers (compartments filled to ¾ full with preferably undisturbed clods/samples) for later visual reference (e.g. during report writing and then placed in the CSIRO Land and Water soil archive).
- The second chip-tray for the acid sulfate soil incubation test ($pH_{incubation}$) in the laboratory (compartments filled to 1/3 full with disturbed crushed samples and moistened with distilled or deionised water).
- Each compartment is to be adjacently labelled (on the inside of the lid) with the layer sample ID, and on the outside of the chip-tray labelled with survey locations and collection date (Figure A2.1)

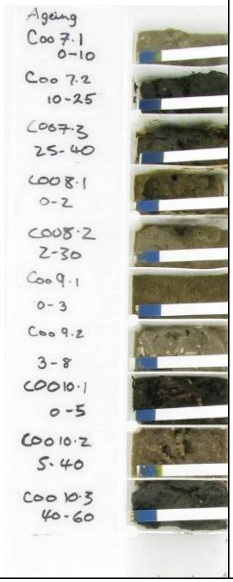
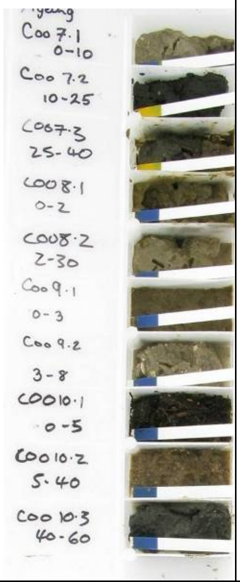
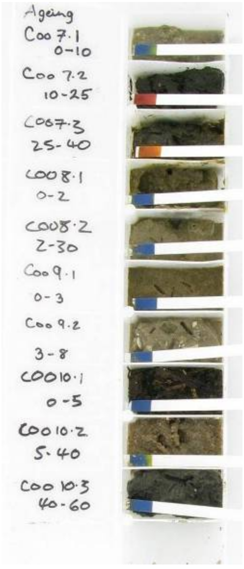
Field testing (T 0)	8 weeks (T +8)	10 weeks (T +10)
		

Figure A1.2. Time sequence (T 0, T +8, T +10) for a chip-tray of soils from the Coorong in South Australia undergoing incubation. Each photograph shows soil pH as indicated by Merck pH strip colours at: (i) T 0, at sampling in the field, (ii) at T +8, after incubation for 8 weeks and (iii) at T +10, at 10 weeks. Here pH indicator strip colours indicate that most samples remain alkaline or neutral (blue colour >pH 7) with only two becoming acid after incubation for 10 weeks (red or pink colour - pH 3.9 to 4). (Fitzpatrick et al. 2008). NOTE – the preferred method is to measure the pH of the whole soil using a calibrated pH meter (Fitzpatrick et al. 2008).

Soil $pH_{incubation}$, pH_{water} and $pH_{peroxide}$ (i.e. pH_{FOX} test) analyses. Measuring $pH_{incubation}$ is the standard method used in the Australian Soil Classification (Isbell 1996). The method has been described in more detail by Sullivan et al. (2009) and Fitzpatrick et al. (2010). These measures are used to help determine the various types of acid sulfate soil materials present by undertaking the following range of pH measurements:

I. $pH_{incubation}$ at time zero (T0) to estimate the field status of soil acidity based on the soil pH measurement (in a minimum of water to permit measurement) at the time of sampling in the field directly in the chip-tray to identify sulfuric materials; and hypersulfidic or hyposulfidic materials after incubation.
II. $pH_{incubation}$ after at least a time of 8 weeks (T8) after sampling and incubation change to identify:
    - hypersulfidic material: has a field pH of 4 or more (i.e. T0) and experiences a substantial* drop in pH to 4 or less when incubated. The duration of the incubation is either: a) until the soil pH changes by at least 0.5 pH unit to below 4, or b) until a stable** pH is reached after at least 8 weeks of incubation.
    - hyposulfidic material has a field pH of 4 or more (i.e. T0) and does not experience a substantial* drop in pH to 4 or less when incubated. The duration of the incubation is either: a) until the soil pH changes by at least 0.5 pH unit to below 4, or b) until a stable** pH is reached after at least 8 weeks of incubation.

*A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.

**A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase.

III. pH_{water}, pH in 1:1 by weight in water in a test tube.
IV. $pH_{peroxide}$ pH in 1:1 by weight in peroxide identifies a potential end pH after oxidisation with hydrogen peroxide in a test tube and if it declines to 2.5 or less then it can be assumed that soil acidity problems will emerge when the soil or sediment is exposed to air.

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9. APPENDIX 3 – Field pH tests

Performing and interpreting soil field pH tests

Source, modified from: WA Department of Environment and Conservation (2009) Identification and Investigation of Acid Sulfate Soil and Acidic Landscapes. Perth, WA.

It is important to note that whilst a useful exploratory tool, soil field pH tests are indicative only, are definitely not quantitative and cannot be used as a substitute for laboratory analysis to determine the presence or absence of ASS. Laboratory analysis is needed to quantify the amount of **existing, plus potential, acidity**. This Appendix provides information on how to perform field pH tests and interpret the results from them. For further information on how to conduct and interpret these tests, consult the *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998 (*Ahern *et al.,* 1998*).*

Field pH tests should be conducted using a field pH meter calibrated according to the manufacturer's instructions. All results (pH_F and pH_{FOX} values, peroxide reaction) should be tabulated and reported.

A3.1 Suggested equipment for field tests

It is important that prior to conducting the field tests, the appropriate testing equipment is obtained. For a basic set up the following items would be required:

1. pH meter and electrode – charged and calibrated
2. at least 2 buffer solutions – e.g. pH 4.0 and pH 7.0
3. test tubes or beakers – wide, unbreakable, heat resistant, and clear e.g. Falcon 50ml polypropylene (pHF test tubes are ideally shallow to facilitate cleaning e.g. cut the top off a 50ml tube at about 10ml)
4. test tube rack or jar rack marked with depths – use a separate rack for pHF tests and pHFOX tests in case they bubble over
5. skewers or stirrers – wooden, for test tubes
6. 30% hydrogen peroxide (H2O2) pH adjusted to 4.5–5.5
7. storage bottle for H_2O_2
8. sodium hydroxide (NaOH) – to raise pH of peroxide to 4.5–5.5 (pH 5.5 ideal)
9. deionised (DI) water
10. squirt bottle for DI water
11. tissues
12. gloves and safety glasses
13. protective clothing
14. bucket – to tip used soil and hydrogen peroxide into
15. bucket and brush – to rinse tubes out in ready for next site
16. recording sheets
17. excess water for rinsing
18. first aid kit – especially eye wash solutions
19. 1M hydrochloric (HCl) acid – to test for shell presence

A3.2 Conducting field tests – Some considerations

When the analytical results are reported, the field test results (when accompanied by good soil profile descriptions) will help increase the understanding of profile processes with respect to acidity.

When performing field tests, the soil samples must not be left in the open air in the test tubes or beakers for an extended period of time before conducting the tests. If sulfides are present, there is a risk that they will oxidise, and this will substantially affect the end pH result by lowering the pHF. This will give a misleading result that the soil profile is more acid than it really is. It would be preferable (and more efficient) to prepare the field pH test tubes with the soil:water pastes and the soil:peroxide mixtures and commence the soil profile descriptions while the reactions are occurring. This way, the soils are given time to react and there is no time wasted waiting for pH_{FOX} samples to cool. It is important though, to keep an eye on the reactions as some may be vigorous and overflow, and result in contamination of nearby soil samples.

When conducting the pH_{FOX} test, it is important to allow enough time for the reaction to occur, especially if low strength (i.e. <30%) hydrogen peroxide is used.

The field pH_F and pH_{FOX} tests can be made more consistent if a fixed volume of soil (using a small scoop) is used, a consistent volume of peroxide is added and left to react for at least an hour (at a secure location, the pH_{FOX} can be left overnight). The sample can then be moistened with deionised water before reading the pH_F and pH_{FOX}.

Field tests should preferably be performed on-site, however there are many areas (e.g. wetlands) where performing field tests can prove difficult (e.g. too wet, mosquito problems). In this situation, samples must be placed on dry ice and taken to a suitable location for conducting field tests. These tests should be performed ideally within 24 hours. As some samples may contain large amounts of organic matter (especially in wetland situations) and may also contain monosulfides, any delay in performing field tests could result in misleading pH_F results.

A3.3 On–site Chemical and Material Safety Precautions

A3.3.1 Hydrogen peroxide

Care needs to be taken when using hydrogen peroxide (H_2O_2) in the field. H_2O_2 (30%) is used as the primary reagent in the pH_{FOX} test. The concentration is 10 times stronger than the peroxide commonly found in household medicine cabinets. The reaction of peroxide with soil containing iron sulfides may produce sulfurous gases, as well as giving off heat in excess of 90°C.

Caution: 30% Hydrogen Peroxide is a strong oxidising agent and should be handled carefully with appropriate eye and skin protection. **This test is suitable for experienced operators only.** Even the less concentrated 6% peroxide (which some operators are using) should be used with caution.

The peroxide when first received may have a pH of 3.5 or lower. Chemical companies commonly put stabilisers in the peroxide to prevent it from decomposing and releasing oxygen by keeping the pH low. The pH required for the field pH peroxide test is pH 4.5–5.5. This may be obtained by adding sodium hydroxide (pH 14) to the peroxide. Since both of these chemicals are highly corrosive, and many of the long-term side effects are not fully known, it is recommended that the following precautions are taken when performing field tests.

Always:

1. use gloves, safety glasses, lab coat or protective clothes;
2. conduct pH peroxide test in a well ventilated area;
3. use test tubes capable of withstanding rapid heat changes and high temperatures;
4. avoid skin and eye contact with peroxide; and
5. label all peroxide bottles with safety data information.

A3.3.2 Other chemicals

Several other chemicals are used in the field when sampling for ASS. Buffering solutions and potassium chloride (KCl) solutions are used to calibrate and maintain pH meters and care should be exercised when using these substances. Follow safety directions on Material Safety Data Sheets (MSDS).

Hydrochloric acid (HCl) is used when performing tests to assess the presence of carbonates in soil material. HCl is strongly acidic and is very corrosive to skin therefore caution is required when using it. Again, follow directions on MSDS. Store HCl separate from buffer solutions as HCl gas may slowly diffuse through the plastic bottles and alter the buffer solutions.

A3.4 Field pH test (pH_F)

The pH_F test measures the existing acidity of a soil:water paste, and is therefore used to help identify if ASS are present. If the measured pH of the soil paste is $pH_F < 4$, oxidation of sulfides has probably occurred in the past, indicating the presence of AASS. Highly organic soils or heavily fertilised soils may also return a pH_F close to 4. A pH_F >4 but <5 indicates an acid soil, but the cause of the acidity will need to be further investigated by laboratory analysis. The pH_F test does not detect any unoxidised sulfides (i.e. PASS). For this reason, this test must be used in conjunction with the pH_{FOX} test.

A3.4.1 Soil: water mixtures and soil pastes

Standard field soil pH tests have been conducted using a 1:5 soil:water mixture. This is quite successful where sands are concerned (as they breakdown readily), however in a field situation it is often difficult to get all soil into solution by shaking only for a brief period of time. In particular, where wet clays are present, it becomes very difficult in the field to shake the mixture to suspend all the clay particles in solution. It is more likely that the clay will stay in a ball and while some fine particles previously attached to the edge of the clay bolus are suspended, the remainder sticks to the bottom of the test tube. This means that the soil:liquid ratio is widened substantially and the pH of the mixture will have a higher reading, so that it will not give a true and accurate measurement of the pH of the soil. In the laboratory, this sample would be dried, ground, mixed, and shaken mechanically for hours allowing substantial time for the clay to be broken down—in the field, this option is not practical. Further, it is not practical to weigh out soils in the field to obtain a perfect 1:5 soil:water mixture, and so any solutions made up are usually done on a volumetric basis assisted by graduated test tubes, flasks, or beakers.

Making a soil:water paste is more practical for field situations and is recommended for ASS field pH (pH_F) tests. This is detailed in the procedure below. It is recommended that short test tubes are used for pH_F tests as they are easy to clean. Further, the paste must be stirred using a stirring implement (e.g. skewer or strong toothpicks). Stirring the paste well will enhance the accuracy of the pH result as the electrode will get good contact with the soil.

A3.4.2 Field pH test procedure

Procedural outline – field pH_F test

1. Calibrate battery powered field pH meter.
2. Prepare the test tubes in the test tube rack. Make sure the rack is marked with the depths so there is no confusion about the top and bottom of the profile. Use of separate racks for the pH_F and pH_{FOX} tests is recommended as contamination may occur when the pH_{FOX} reactions are violent.
3. Conduct tests at intervals on the soil profile of 0.25m or at least one test per horizon whichever is lesser.
4. Remove approximately 1 teaspoon of soil from the profile. Place approximately ½ teaspoon of the soil into the pH_F test tube and place ½ teaspoon of the soil into the pH_{FOX} test tube for the corresponding depth test. It is important that these 2 sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0–0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
5. Place enough deionised water (pH 5.5) in the pH_F test tube to make a paste similar to ‘grout mix’ or ‘white sauce’, stirring with a skewer or similar to ensure all soil ‘lumps’ are removed. Do not leave the soil samples in the test tubes without water for more than 10 minutes.
6. This will reduce the risk of sulfide oxidation—the pH_F is designed to measure existing acidity, any oxidation subsequent to the soil’s removal from the ground will not reflect the true situation. In some instances, in less than 5 minutes, monosulfidic material may start to oxidise and substantially affect the pH_F results.
7. Immediately place the spear point electrode (preferred method) into the test tube, ensuring that the spear point is totally submerged in the soil: water paste. Never stir the paste with the electrode. This will damage the semi-permeable glass membrane.
8. Measure the pH_F using a pH meter with spear point electrode.
9. Wait for the reading to stabilise and record the pH measurement. All measurements and pH calibration should be recorded on a data sheet.

TABLE A3.1: Results – field pH test

pH value	Result	Comments
$pH_F \leq 4$	Actual acid sulfate soil material (AASS) indicating oxidation of sulfides (Sulfuric material).	This is generally not conclusive because highly organic soils such as peats and occasionally heavily fertilised soils may also give pHF ≤4.
$pH_F \leq 3.7$	Expected sulfuric material if jarosite exists in the sample.	This is also an AASS. Jarosite needs a pH of 3.7 or lower to form. Horizons containing some jarosite and some other mottling (iron, grey) may have a pH >3.7 if the sample contains a mixture of jarosite and higher pH soil. This depends on the level of oxidation and the ability of the soil to 'hold' the acid.
$pH_F > 7$	Expected in waterlogged, unoxidised, or poorly drained soils.	Marine muds commonly have a pH >7 and this reflects seawater (pH 8.2) influence. May be sulfidic materials after oxidation with H_2O_2.
$4 < pH_F \leq 5.5$	An acid soil.	Investigate further for possible ASS link, e.g. sulfuric material with shell presence.

A3.5 Field pH peroxide test (pH_{FOX})

The pH_{FOX} test is used to indicate the presence of iron sulfides or PASS. This test involves adding 30% hydrogen peroxide (pH adjusted to 4.5–5.5) to a sample of soil. If sulfides are present a reaction will occur. The reaction can be influenced by the amount of sulfides present in the sample, the presence of organic matter, or the presence of manganese. Once the reaction has occurred, the pH is measured.

Adding hydrogen peroxide, a strong oxidising agent, 'mimics' what would naturally occur if the soil was exposed to air. In a natural environment, if left exposed, soils may take from two hours for sands, possibly through to many decades for heavy marine clays, for some or all of the oxidation reactions to take place. Obviously it is not practical to wait for this long for a reaction to occur.

It should be noted that although the iron sulfides are oxidised and acid is produced over a shorter amount of time than would occur naturally, the total amount of acid produced is the same. It is important to assess first the likely presence (through field tests) and secondly the level of iron sulfides present (through laboratory analyses) so that management can prevent any undesirable impacts.

The pH_{FOX} test is purely qualitative. No calculations can be performed to give an accurate account of the levels of sulfides present in the sample. Rather, the test gives an indication of whether sulfides may occur (or whether there is another form of compound contributing to acidity).

This means that a pH_{FOX} test CANNOT give an accurate measurement of how much lime should be added to the soil.

The sample of soil must be taken from the same depth increment (sub-sample) for which the pH_F was measured. It is important that the pH_{FOX} is performed on a separate sub-sample, and NOT on the soil:water paste that was prepared for the pH_F test. This will ensure that the minimal degree of dilution occurs during the oxidation phase, and that the resulting pH_{FOX} measurement is as accurate as possible an indication of the potential for oxidation of that particular sub-sample of soil.

A combination of three factors is considered in arriving at a ‘positive field sulfide identification’:

- a reaction with hydrogen peroxide - the strength of the reaction with peroxide is a useful indicator but cannot be used alone. Organic matter, coffee rock and other soil constituents such as manganese oxides can also cause a reaction. Care should be exercised in interpreting a reaction on surface soils and high organic matter soils such as peats and coffee rock and some mangrove/estuarine muds and marine clays.
  This reaction should be rated, e.g. **L** = Low reaction, **M** = Medium reaction, **H** = High reaction, **X** = Extreme reaction, **V** = volcanic reaction.

- The actual value of pH_{FOX}. - If $pH_{FOX} < 3$, and a significant reaction occurred, then it strongly indicates a PASS. The more the pH_{FOX} drops below 3, the more positive the presence of inorganic sulfides.

- A much lower pH_{FOX} than field pH_F - The lower the final pH_{FOX} value and the greater the difference between the pH_{FOX} compared to the pH_F, the more indicative of the presence of PASS. This difference may not be as great if starting with an already very acid pH_F (close to 4), but if the starting pH is neutral or alkaline then a larger change in pH should be expected. Where fine shell, coral or carbonate is present the change in pH may not be as large due to buffering. The ‘fizz test’ (effervescence with 1 M HCl) should be used to test for carbonates and shell.

Of these three factors, the final pH_{FOX} value is the most conclusive indicator, and the lower the final pH_{FOX}, the more confident one can be that PASS may be present.

A3.5.1 Strength and pH of peroxide

The pH and strength of peroxide used is important. The pH of the peroxide should be pH 4.5–5.5 (ideally pH 5.5). This ensures that the result measured is a reflection of the oxidation of the soil (if any) and not of the existing pH of the peroxide. When peroxide is purchased often the stabilisers added by the chemical companies will result in a pH of approximately 3.5. This pH can be raised by adding small amounts of sodium hydroxide (NaOH)—failure to adjust the pH can lead to false field results.

Analytical grade peroxide (30%) is most suitable for field pH_{FOX} tests as an oxidation agent that is highly effective and ‘quick’ to react with any iron sulfides in a soil sample. This strength of peroxide is highly corrosive, slightly unstable, highly reactive and can cause severe skin irritation. As such, a high level of safety precautions is required. However, there is no reason why a well-trained officer cannot safely and responsibly conduct field tests with 30% hydrogen peroxide.

A3.5.2 Field pH peroxide test procedure

Procedural outline – Field pH peroxide test

1. Adjust the pH of the hydrogen peroxide to 5.0 -5.5 before going into the field. This can be done by adding a few drops of NaOH at a time, checking the pH with the electrode regularly. NaOH is highly caustic so safety precautions must be exercised. Also, NaOH will raise the pH quickly so the pH needs to be monitored. Do NOT buffer a large quantity of hydrogen peroxide at one time. Only buffer the amount to be used in the field. Hydrogen peroxide should be well labelled and only small quantities should be taken into the field at any one time. This will ensure the longevity of the peroxide. Further, over time, the pH of the peroxide that has already been buffered may change. It is important to check the pH of the peroxide in the morning before departing to the field. Having a small quantity of NaOH in the field kit is recommended so the pH of the peroxide can be adjusted if required.
2. Calibrate battery powered field pH meter.

3. Prepare the test tubes in the test tube rack as for pH_F test. Make sure the rack is marked with the depths so there is not confusion about the top and bottom of the profile. Use of separate racks for the pH_F and pH_{FOX} tests is recommended as contamination may occur when the pH_{FOX} reactions are violent.
4. Conduct pH_F tests at intervals of 0.25m down the soil profile or at least one per horizon whichever is lesser.
5. Remove approximately one teaspoon of soil from the profile. Place approximately ½ teaspoon of that soil into the pHF test tube and place ½ teaspoon of soil into the pHFOX test tube for the corresponding depth test. It is important that these two sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0-0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
6. Add a few drops of 30% H_2O_2 adjusted to pH 4.5–5.5 to the soil in a heat-resistant test tube and stir the mixture. DO NOT add the peroxide to the test tube in which the pHF test was conducted. The pH_{FOX} test tube should not have any deionised water in it. Beakers can be used however when multiple tests are being conducted it is difficult to handle the large beaker size efficiently. DO NOT add more than a few drops of H_2O_2 at a time. This will prevent overflow and wastage of peroxide. A day's supply of peroxide should be allowed to reach room temperature prior to use (cold peroxide from the fridge may be too slow to react).
7. Ideally, allow approximately 20 minutes for any reactions to occur. If substantial sulfides are present, the reaction will be vigorous and may occur almost instantly. In this case, it may not be necessary to stir the mixture. Careful watch will be needed in the early stages to ensure that there is no cross contamination of samples in the test tube rack. If the reaction is violent and the soil/peroxide mix is escaping from the test tube, a small amount of deionised water can be added to cool and calm the reaction. Usually this controls overflow. Do NOT add too much deionised water as this may dilute the mixture and affect the pH value. It is important to only use a small amount of soil otherwise violent reactions will overflow and the sample will be lost.
8. Steps 6 and 7 may be repeated until the soil/peroxide mixture reaction has slowed. This will ensure that most of the sulfides have reacted. In the lab this procedure would be repeated until no further reaction occurs, however in the field, best judgement is recommended.
9. If there is no initial reaction, individual test tubes containing the soil/peroxide mixture can be placed into a cup of hot water (especially in cooler weather) or in direct sunlight. This will encourage the initial reaction to occur. When the sample starts to 'bubble', remove the test tube immediately from the cup and replace into test tube rack.
10. Wait for the soil/peroxide mixture to cool (may take up to 10 minutes). The reactions often exceed 90^{o}C. Placing an electrode into these high temperature situations may result in physical damage and inaccurate readings as most pH meters are set to record a result for an ambient temperature of approximately 25^{o}C.
11. Use an electronic pH meter (preferred method) to measure the pH_{FOX}. Place a spear point electrode into the test tube, ensuring that the spear point is totally submerged in the soil/peroxide mixture. Ensure that the plastic soil sleeve that exposes the spear point totally is used on the end of the electrode in preference to the protective pronged sleeve that almost totally conceals the spear point. This will ensure good contact with the soil. Never stir the mixture with the electrode. This will damage the semi-permeable glass membrane.
12. Rate the reaction using a LMHXV scale (Section A5).
13. Wait for the reading to stabilise and record the pH_{FOX} measurement.
14. All measurements and pH calibration measurements should be recorded on a data sheet.

TABLE A3.2: Results – field pHFOX test.

pH value and reaction	Result	Comments
A strong reaction of soil with peroxide – X or V	A useful indicator but cannot be used alone.	Organic matter, coffee rock, and other soil constituents such as manganese oxides can also cause a reaction. Care must be exercised in interpreting a reaction on surface soils and high organic matter soils such as peats and coffee rocks, and some mangrove/estuarine muds and marine clays.
pH_{FOX} value at least one unit below field pH_F and reaction to peroxide.	May indicate sulfidic or PASS material but depends on the initial and resultant pH.	The greater the difference between the two measurements (ΔpH), the more indicative the value is of a PASS. The lower the final pH_{FOX}, the better the indication of a positive result (e.g. a 1 unit change from pH 8 to 7 would not indicate sulfidic or PASS material, however a 1 unit change from pH 3.5 to 2.5 would be indicative).
pH_{FOX} <3, strong reaction with peroxide, and large ΔpH	Strongly indicates sulfidic or PASS material (i.e. potential for the soil to produce sulfuric acid upon oxidation.	The lower the pH_{FOX} below 3, the more positive the likely presence of sulfides. A combination of all three parameters (reaction strength, unit pH change, and final pH_{FOX} result) is most confirmatory.
A pHFOX 3–4 and reaction to peroxide.	The test is less positive and is a borderline result.	Sulfides may be present however organic matter may also be responsible for the decrease in pH. Laboratory analyses are required to confirm if sulfides are present.
pH_{FOX} 4–5	The test is neither positive nor negative.	Sulfides may be present either in small quantities and be poorly reactive under quick test field conditions, or the sample may contain shell/carbonate, which neutralises some or all acid produced by oxidation. Equally the pH_{FOX} value may be due to the production of organic acids and there may be no sulfides present in this situation. In such cases, the chromium reducible sulfur method would be best to check for the presence of iron sulfides.
pH_{FOX} >5 and little or no drop in pH from pH_F but reaction to peroxide.	Little net acidifying ability is indicated.	On soils with neutral to alkaline field pH and shell or white concretions present, the fizz test with 1M HCl should be used to test for carbonates. The SPOCAS method should be used to check for any oxidisable sulfides and the presence of self-neutralising ability.

A3.6 Field test results interpretation

Field test results are dependent on many factors including accuracy of pH meters, strength of reagents, and operator skill. The reactions and results obtained from the field pH peroxide test can be further influenced by additional factors such as soil type, moisture content, ambient air temperature, presence of organic matter, or bicarbonate as shell or seawater in the soil sample. Some of these reactions are listed in Table A3.3 together with explanatory comments.

TABLE A3.3: Some common field test results

pHF	pH$_{FOX}$[#]	ΔpH	Reaction rate	Result **PASS or ***AASS)	Comments / Possible explanation
3.5	3.3	0.2	L	AASS present	Oxidation has occurred and sulfuric acid has formed in the past. This soil may not have much more potential to oxidise further as the pH_F and pH_{FOX} are similar.
3.7	1.4	2.3	X or V	AASS present; PASS – strong indication.	Oxidation has occurred in the past. This soil has the potential to oxidise further indicated by the strong reaction, appreciable pH unit difference (pH_{FOX} is significantly lower than the pH_F) and the very low final pH_{FOX}.
6.5	2.1 (1.9)*	4.4	X or V	No AASS; PASS – strong indication	This soil is not yet oxidised but has the ability to produce sulfuric acid if exposed. Little buffering capacity in the soil. Laboratory analysis using SPOCAS could confirm this.
8.5	3.0 (3.2)*	5.5	H	No AASS; PASS – likely	The initial pH may be reflecting a strong seawater influence (pH 8.2) or some form of dissolved carbonates. The large ΔpH indicates a strong likelihood of PASS even though the pHFOX is borderline. Here, the ΔpH and the reaction gives strength to the argument. Laboratory analysis using SPOCAS and reacted calcium (CaA) could confirm this (see Ahern & McElnea (1999)).
8.0	2.0 (6.0)*	?	H	No AASS; PASS – strong indication; Considerable buffering capacity.	The initial alkaline pHF indicates a seawater influence. The initial large decrease in pH indicates the soil is likely to contain sulfides. The pH measured after 20 minutes may indicate a large % of shell dissolving into solution as the acid contacts it (a small amount of HCl added to a sample of soil could confirm its presence). Laboratory analysis using SPOCAS and Ca_A could confirm this (see Ahern & McElnea (1999)
5.5	5.4 (5.3)*	0.2	X or V	No AASS; PASS unlikely	The strong reaction is probably due to the presence of manganese in the soil sample.
5.5	3.8 (3.5)*	2.0	H (slow froth)	No AASS; PASS – possible	The strength of the reaction indicates possible organic matter. There may be some sulfides present also. Laboratory analysis using the SCR could confirm this.

[#] At completion of reaction

* pHFOX after 20 minutes (or overnight)

** PASS (sulfidic or hypersulfidic materials) – Potential Acid Sulfate Soil material

*** AASS (sulfuric material) – Actual Acid Sulfate Soil material

10. APPENDIX 4 – Index of Squishiness

FIELD ESTIMATE OF MECHANICAL PROPERTIES AS RELATED TO SOIL MOISTURE OR WETNESS: n-Values

n-Value (mechanical properties related to soil moisture or wetness)

The n-value (sometimes referred to as ``index of squishiness") concept was developed by Pons and Zonneveld (1965) to define the degree of physical ripening of soft sediments (i.e. "**pelagic ooze**" materials) as they dewater. It is a measure of the physical bearing capacity of a soil material. The following definition has been modified from Fanning and Fanning (1989) and Soil Survey Staff (1992). It is mathematically defined for Soil Taxonomy for soil materials that are not thixotropic as follows:

$$n=(A-0.2R)/(L+3H)$$

A=% water in soil in field condition, (calculated on a dry-soil basis);

R=% silt + sand

L=% clay (<2 μm);

H=% organic matter (organic carbon x 1.724).

Photograph of Professor J. L Pons undertaking the "index of squishiness" or "n-value" test. The photograph was taken by Rob Fitzpatrick in the Mekong Delta, Vietnam in 1992 during the 4th International Acid Sulfate Soil Conference.

An n-value of 0.7 of more is used in Soil Taxonomy (Soil Survey, 1992) to define certain classes considered to have ***a low bearing capacity.*** Sandy materials are considered to be physically ripe regardless of their water content.

n= <0.7: Ripe material is firm, not particularly sticky, and cannot be squeezed between fingers.

n= 0.7 to 1.0: Nearly Ripe Material is fairly firm; it tends to stick to the hands, and can be kneaded but not squeezed between fingers. Its water content is between 55 and 65%. It is not churned up, it will support by weight of stock and ordinary vehicles;

n= 1.0 - 1.4: Half Ripe Mud is fairly soft; sticky; and can be squeezed between fingers. Its water content is between 65 and 75% and its mechanical strength when disturbed is low. A man will sink ankle to knee deep unless supported by vegetation.

n= 1.4 - 2.0: Practically Unripe Mud is very soft; sticks fast to everything, and can be squeezed between fingers by very gentle pressure. Its water content is between 70 and 80%. A man will sink to his thighs unless supported by vegetation.

n= > 2.0: Totally Unripe Mud is fluid; it flows between fingers. In predominantly mineral sediments the water content is >80% by mass.

Fanning, D.S. and Fanning, M.C.B. (1989). Soil: Morphology, genesis, and classification. John Wiley and Sons, New York.

Pons J.L. and Zonneveld, I.S. (1965). Soil ripening and soil classification. Initial soil formation in alluvial deposits and classification of the resulting soils. Inst. Land Reclam. and Impr. Pub. 13. Wageningen, The Netherlands. 128pp.

11. APPENDIX 5 – Summary of dominant minerals

Table A5.1. Summary of the occurrence and distribution of secondary Fe oxides, sulfides, carbonates and salts in soil environments (modified from Bigham *et al*. 2002; Fitzpatrick 2008)

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

†Occurring only in specific soil horizons or sedimentary units

*Widespread occurrences in sandy and peaty sulfuric materials in South Australia (Fitzpatrick and Shand 2008).