Coastal acid sulfate soil processes in Barker Inlet, South Australia

Doctor of Philosophy

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September 2010

Chapter Twelve

12. Regional significance and implications for acid sulfate soil management

The mapping techniques that were developed during this thesis (e.g. relating surface cover features to acid sulfate soil characteristics) were used to construct and improve regional scale coastal acid sulfate soil hazard maps for the Gulf St Vincent and South Australia. This work also provided the information to characterise Barker Inlet as a priority region for the Atlas of Australian Acid Sulfate Soils website, which is linked to the Australian Soil Resources Information System – ASRIS (Fitzpatrick *et al.* 2008e).

An important outcome from the early stages of the project was the production of a legislated strategy document for implementing Coastal Protection Board policies on coastal acid sulfate soils in South Australia (Coastal Protection Board 2003); Appendix H), related to the management and planning during new coastal developments.

The research was also used to define descriptive map units that underpin risk-based acid sulfate soil management guidelines for coastal developments in South Australia and that were specifically integrated into master development plans for the Gillman area (Thomas and Fitzpatrick 2006a); Appendix H).

Broader project findings were disseminated to stakeholders and the public through numerous client reports, (e.g. (Thomas *et al.* 2004a) and educational pamphlets (e.g. (Thomas 2001); Appendix H).

12.1. Regional scale mapping

For the purpose of producing a regional scale acid sulfate soil map, the twelve map units described for the St Kilda and Gillman study areas (Chapter 7) were simplified and condensed into seven broader map units (Figure 12-2). The seven map units are consistent with the national classification and terminology used for the national Atlas of Australian Acid Sulfate Soils (Fitzpatrick *et al.* 2008e). The Atlas was assembled by collating across Australia all published acid sulfate soils, land systems, marine habitat, elevation (DEM), tidal, estuarine, climate, vegetation and remotely sensed data using GIS. The Atlas map units shown in Figure 12-2 and Table 2-1 describe the acid sulfate soils in the wide range of physiographical environments in the Gulf St Vincent, and are summarised here:

Disturbed acid sulfate soil types:

(i) Sulfuric material in disturbed tidal zones (drained tidal, intertidal or supratidal mangrove or samphire marshes, particularly near Gillman).

(ii) Sulfidic material in disturbed tidal zones (drained tidal, intertidal or supratidal mangrove or samphire marshes, particularly in disturbed salt evaporation ponds).

(iii) Monosulfidic material in shallow, stagnant water bodies (e.g. poorly flushed or blocked estuaries, rivers, river tributaries, or salt evaporation ponds).

(iv) Sulfidic or Sulfuric materials buried below fill materials (Figure 12-1; Left).

Other potential acid sulfate soils types:

(v) Subaqueous materials below the low tidal mark.

(vi) Sulfidic material in contemporary tidal zones (e.g. mangrove, and samphire and salt bush marshes).

(vii) Sulfidic material in sand dune ridges (e.g. as buried layers, Figure 12-1; Right).

Figure 12-1 (Left image) Soil pit (Profile BG 2) at Gillman, Port Adelaide showing about 110 cm of calcareous clayey dredge spoil, used to raise the land surface, overlying 40 cm of sapric hypersulfidic material (derived from a former mangrove swamp) and underlain at 150 cm by coarse shelly material (chenier). This is a proposed new subgroup; Sulfic* Xerarents (Soil Survey Staff 2010). (Right image) Deep excavation at Barcoo Outlet, Adelaide (connecting the Patawolonga with the sea), and construction site through a sand ridge showing a relic hypersulfidic material buried under beach dunes (from a former mangrove swamp).

The Atlas of Australian Acid Sulfate Soils maps have been published as a web-served GIS at the Australian Soil Resource Information System (ASRIS) site (www.asris.csiro.au). The ASRIS map of the Barker Inlet area that was developed in this study is also available on-line from the ASRIS web site (refer to inset map in Figure 12-2).

In addition, Table 12-1 summarises the wide range of acid sulfate soil types identified in the Gulf St Vincent according to:

(i) Australian Soil Classification (Isbell 2002), with recent modifications to proposed new suborders based on (a) the acid sulfate materials proposed by Sullivan *et al.* (2010) and (b) the Subaqueous and Anthroposol concepts.

(ii) Soil Taxonomy (Soil Survey Staff 2010).

(iii) World Reference Base (IUSS Working Group WRB 2006).

NOTE:
This figure is included on page 363
of the print copy of the thesis held in
the University of Adelaide Library.

Figure 12-2 Map showing distribution of coastal acid sulfate soils in Gulf St Vincent and the Gillman-Barker Inlet area (inset map), modified from (Fitzpatrick *et al.* 2008d).

Table 12-1 Acid sulfate soil types, map symbol[1], Australian Soil Classification[2], Soil Taxonomy[3], World Reference Base[4], Risk Class, Treatment categories[5] and aerial extent for Gulf St Vincent. Modified from (Fitzpatrick *et al.* 2008d)

Acid sulfate soil type	**Map Symbol[1]**	**Australian Soil Classification[2]**	**Soil Taxonomy[3]**	**World Reference Base[4]**	**Risk Class**	**Treatment category[5]**	**Area (Ha)**
Sulfidic material in contemporary tidal zones	Ab (p2)o	Sulfidic Intertidal Hydrosols; Sulfidic *Subaqueous Hydrosols; Epicalcareous, Intertidal Hydrosols	Terric Sulfisaprists; Terric Sulfihemists; Sulfic Haplowassists; Sapric Sulfiwassists; Typic Sulfiwassists; Haplic Sulfiwassents; Typic Sulfiwassents; Haplic Sulfaquents; Sulfic Hydrowassents; Typic Hydrowassents; Typic Endoaquents	Sapric or Hemic Histosols (Protothionic, Tidalic)	High	H - XH	8,936
Sulfuric material in disturbed (drained) tidal zones	Ax (a1)o Ax (a1)h Ax (a1)	Sulfuric Sapric Organosol; Sulfuric Hypersalic Hydrosols; Sulfuric, Salic Hydrosol	Terric Sulfosaprists; Terric Sulfohemists; Hydraquentic Sulfaquepts; Salidic Sulfaquepts; Sulfic Fluvaquents; Typic Sulfaquepts; Sulfaqueptic* Sulfiwassents	Sapric or Hemic Histosols (Hyperthionic, Drainic) Subaquic or Salic Fluvisols (Hyperthionic, Drainic)	Very High	VH - XH	135 87 188
Sulfidic material in disturbed (drained) tidal zones	Bx (p3)	Sulfidic Hypersalic Rudosols; Epicalcareous, Hypersalic Hydrosol; Haplic, Hypersalic Hydrosol	Haplic Sulfaquents; Salidic Sulfaquents; Typic Haloquepts; Aeric Haloquepts	Haplic Gleysols (Protothionic, Arenic)	Moderate	M- H	5,273
Sulfidic material in disturbed (drained) tidal zones (mainly monosulfidic material)	Ax (m1) Ax (m3 Bx (m3))	Sulfidic Hypersalic Rudosols; Sodosolic, Salic Hydrosol Sulfuric, Hypersalic Hydrosol*	Haplic Sulfaquents; Typic Hydrowassents; Salidic Sulfaquepts	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 extra tidal flats	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 sand plains and dunes	Ai(p2)	Sulfidic Arenic Rudosols	Sulfic Fluvaquents; Sulfaquents	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 Fluvaquents; Sulfic* Xerarents; Haplic Xerarents	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 Sulfaqueptic* Xerarents	Spolic or Urbic Technosols (Orthothionic)	Very High	VH - XH	17
Subaqueous materials below the low tidal mark	Aa(p3)	Sulfidic *Subaqueous Hydrosols	Sulfic Haplowassists; Sapric Sulfiwassists; Typic Sulfiwassists; Haplic Sulfiwassents; Typic Sulfiwassents; Haplic Sulfaquents	Histic Gleysols (Protothionic, Arenic)	Moderate	M- H	15,964
						TOTAL	57,222

[1] Map Symbols from Figure 12-2: Atlas of Australian Acid Sulfate Soils (Fitzpatrick *et al.* 2006)/ Australian Soil Resource Information System (ASRIS) site (**www.asris.csiro.au**);

[2] Australian Soil Classification (Isbell 2002). [3] Soil Taxonomy (Soil Survey Staff 2010), *Proposed new subgroup; [4] IUSS Working Group (IUSS Working Group WRB 2006);

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

12.2. Regional acid sulfate soil hazard associations

The regional map and database information was used to determine the risk to development (infrastructure and environment) should the sulfuric and sulfidic materials in the soil profiles be disturbed (i.e. acid sulfate soil Risk Classes in Table 12-1). Risk classes are associated with treatment categories (Table 12-1) that were based on management guidelines developed in Queensland (Dear *et al.* 2002). The ranking of regions and localities by importance of acid sulfate soil ‘hotspots’ (resulting from site disturbance) in relation to environmental, economic and social effect is implicit in the legend of the risk maps (Table 12-1; Figure 12-2). The highest risk areas are those associated with sulfidic materials in sandy soils in tidal and intertidal zones.

Soils with sulfuric material from former sandy tidal zones inside bund wall areas [i.e. disturbed acid sulfate soil indicated in map unit code Ax(a1)] have a spatial extent of 1.88 km^2 in the Gillman area (Figure 12-2) and have been assigned treatment categories Very High to Extra High (Table 12-1). Sulfidic materials in supratidal [Ac(p2)] and extratidal [Ad(p2)h] areas in Gulf St Vincent almost universally contain finely divided or shelly carbonate materials with excess potential to neutralise acid that may be formed (i.e. hyposulfidic materials). Consequently, these areas fall into the treatment categories Moderate to Low (Table 12-1), depending on whether additional mixing of materials is required for neutralisation to occur. Intertidal areas in South Australia often have sufficient carbonate materials or seawater flushing to neutralise any acidity formed during periods of low tide when oxygen may enter exposed soil. However, the consumption of seawater bicarbonate deprives downstream ecosystems of this resource.

12.3. Management options for coastal acid sulfate soil 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 acid sulfate soil around Gulf St Vincent. Where acid sulfate soil is disturbed, there is a risk to human health, local infrastructure and the local environment. However, appropriate management of acid sulfate soil during development can improve discharge water quality, increase agricultural productivity and protect infrastructure and the environment (Thomas *et al.* 2004a). Such improvements can generally be achieved by applying low-cost land management strategies based on the identification and avoidance of acid sulfate soil materials, slowing or stopping the rate and extent of pyrite oxidation, and by retaining existing acidity within the acid sulfate soil landscape (Thomas and Fitzpatrick 2006c). 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 (Thomas and Fitzpatrick 2006a).

At Gillman and other areas in St Vincent Gulf, the selection of management options will depend on the properties and location of the acid sulfate soil materials and their position in the landscape. This is why reliable acid sulfate soil risk maps, at appropriate scales, that characterise acid sulfate soil landscapes are so important. Suitable amelioration techniques that were identified for different areas in this study are linked to map units in Table 12-2.

Acid sulfate soil management generally requires the principles:

(i) Educate;

Information enables acid sulfate soils to be avoided or managed appropriately.

(ii) Minimise disturbance or drainage of acid sulfate soil materials;

Select an alternative non-acid sulfate soil site, rather than undertake remediation. If an alternative site is not feasible, design works to minimise the need for excavation or disturbance of acid sulfate soil materials, by undertaking shallow excavations for drainage measures or foundations, and avoiding lowering groundwater depth that may result in exposure of soils. If acid sulfate soil materials are close (e.g. < 0.3 m) to the surface, cover with clean soil to lessen the chance of disturbance and to insulate from oxygen ingress.

(iii) Prevent oxidation of sulfidic material

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

(iv) Minimise oxidation rate and isolate high risk materials from exposure

This may include covering acid sulfate soil materials with soil or water to decrease oxygen availability and control the movement of water, or by controlling bacterial activity or by applying other limiting factors (e.g. alkalinity) through either physical or chemical means to decrease oxidation rate.

(v) Contain and treat acid drainage to minimise risk of 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.

(vi) Provide an agent to neutralise acid as it is produced

This would involve mixing the acid sulfate soil material with an excess of lime, or other neutralising agent.

(vii) Separate sulfidic materials

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

(viii) Hasten oxidation and collection and treatment of acidic leachate

This involves spreading the acid sulfate soil 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).

(ix) Management of stockpiled acid sulfate soil 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).

Table 12-2 Summary of acid sulfate soil mitigation methods suited for the map units.

Map unit no.	Remediation Options	Principles	Remediation/management strategy Scenario
1	Re-flooding or burial	Improve discharging water quality through constructed **Wetlands (Bio-remediation)** and **Neutralise** acidic groundwater or surface seepage from filled areas.	Soils suited to **re-flooding** using either **seawater** and/-or **storm-water** to construct a permanent wetland system as the soils contain only sulfidic material that is currently below **permanent** saline or brackish water. These areas fringe the Gillman site and will intercept and neutralise any acidic groundwater before being released to Barker inlet. These areas will act as a sink for metal contaminants.
2			Soils suited to **re-flooding** using either **seawater** and or **storm-water** to construct a permanent wetland system as the soils contain sulfidic material that is currently below **seasonal** (semi-permanent) saline or brackish water. These areas fringe the Gillman site and will intercept and neutralise any acidic groundwater before being released to Barker inlet. These areas will act as a sink for metal contaminants.
3	Re-flooding or Burial	**Stop oxidation** of sulfidic material, **Contain** and **Neutralise** acidic groundwater to improve discharging water quality through **Bio-remediation.**	These areas are suited to **re-flooding** using either **seawater** and or **storm-water** as the current water table is close to the surface and soil acidification is minor. Where these soils are to be **Buried,** they should compress, reducing their porosity and pushing them below the water table. Lime should be added to the surface prior to burying where sulfuric material is present.
4	Burial, Chemical neutralisation and Containment using Watertable Management or Re-flooding		**Burial** and loading soils (both sulfidic and sulfuric materials) should compress soil reducing their porosity and pushing them below the water table. This process should **stop further oxidation of sulfidic material** and **neutralise existing acidity** by allowing carbonate rich groundwater to contact the sulfuric horizon. **Lime** should be added to the surface prior to burying where sulfuric material is present. **Watertable management** should ensure the compressed soil materials remain saturated at all times. Fill material should be geotechnically and chemically suited to its intended purpose, have acid buffering capacity. Incorporate layers of coarse material to break the capillary rise of saline and or acidic groundwater.
5	Burial, Chemical neutralisation and Containment of acidic groundwater using Watertable Management	**Stop oxidation** of sulfidic material and **Contain** acidic groundwater by raising and stabilizing the watertable **(Watertable Management).**	The **burial** of soils in this area should **stop the further oxidation of sulfidic material** by raising and stabilising the watertable height. **Watertable management** should aim to maintaining a watertable height just above sulfidic material (e.g. just above the 4Bjg3 horizon in soil profile BG 11) but low enough to limit the movement of groundwater from below the filled area. **Lime** should be added to the surface prior to burying to assist in the neutralisation of sulfuric materials and acidic groundwater. Fill material should be geotechnically and chemically suited to its intended purpose, have acid buffering capacity. Incorporate layers of coarse material to break the capillary rise of saline and or acidic groundwater.
6			
7			
8	Avoid disturbing sulfidic material	**Avoidance**	**Avoidance**
9			**Neutralisation**
10			
11			
12	Mix soil profile layers	**Neutralisation**	Self neutralising and alkalinity resource
C.			

12.4. Planning and development controls

Planning and development controls for coastal acid sulfate soil were developed and legislated as policy in South Australia through the Coastal Protection Board (Coastal Protection Board 2003). A summary of the strategy used to implement this policy is presented in Appendix H and at: http://www.environment.sa.gov.au/coasts/pdfs/no33.pdf. Based on the studies in this thesis, controls and guidelines for coastal development at Gillman, along with some examples of trialled remediation techniques (e.g. experimental drains, see Figure 10-3a, and loading experiments, see Figure 6-14, Figure 6-15 and Section 9.4) have been developed. These controls, guidelines and trials are described in Thomas *et al.* (2004a), Thomas (2004), Thomas and Fitzpatrick (2006a) and Thomas and Fitzpatrick (2006c).

12.5. Summary

This chapter presented information that has been put into practice and used by State and local authorities to increase awareness of acid sulfate soil problems and their management in the region. These approaches were achieved by:

(i) Producing detailed maps incorporating Atlas map units to show the regional distribution of coastal acid sulfate soils

(ii) Hazard identification (based on information from this thesis, namely Chapters 7, 9 and 10) and hazard management, and

(iii) Relating mapped soil types to management approaches / options.

Chapter Thirteen

13. Conclusions and future work

13.1. Introduction

The Barker Inlet is one of many coastal landscapes with acid sulfate soils around Australia and the world where past inappropriate practices were undertaken through ignorance. This resulted in increased formation of sulfuric material, metal mobilisation and pyrite oxidation products, which present ongoing hazards to the environment and infrastructure.

The aims of this research were focussed initially on identifying, describing and comparing complex pedological, redox, geochemical, hydrochemical and mineralogical processes for the following two contrasting coastal landscapes in Barker Inlet:

(i) a ‘near pristine’ landscape at St Kilda, and
(ii) a degraded landscape at Gillman.

This thesis has developed a series of descriptive, explanatory and predictive soil-regolith process models to describe the pedological and geochemical interactions, at a variety of scales, from the:

(i) *wetland scale* by conducting detailed site survey investigations and collating historical data for two study sites in the Barker Inlet,
(ii) *landscape feature scale* by conducting detailed investigations in focus areas and constructing idealised toposequence models,
(iii) *soil profile scale* by intensely studying representative ‘type’ soil profiles,
(iv) *microscopic-scale* by using light microscopy, scanning electron microscopy and X-ray methods to describe structural and temporal relationships of soil redoximorphic and mineralogical features from an array of acid sulfate soil materials.

These investigations enabled production of acid sulfate soil maps at local landscape scales, which were then used to extrapolate to regional scales in areas that share similar coastal physiography to the study areas. The local and regional scale maps produced in this thesis were published in the Atlas of Australian Acid Sulfate Soils, which is viewable via the ASRIS website (www.asris.csiro.au).

The models and soil maps presented in this thesis have been used to educate land managers about the nature and distribution of acid sulfate soils in Barker Inlet, and provide options for acid sulfate soil management. In relation to the Barker Inlet and similar areas further afield around the South Australian coastline, this thesis will continue to assist land managers to:

(i) better manage and ameliorate acid sulfate soils sites, and
(ii) better implement development policy in the coastal protection zone.

Conclusions from each of the relevant research chapters in this thesis are presented in the sections below. Finally, recommendations for future work are presented at the end of this chapter.

13.2. Conclusions

13.2.1. Soil morphology, classification and descriptive soil-regolith models

This work provided detailed morphological information of the wide range of acid sulfate soil types and materials that occur in the Barker Inlet within both: **(i)** natural intertidal areas, and **(ii)** non-tidal, disturbed areas.

This is the first attempted application of the following new definitions and terminologies to more precisely classify the coastal acid sulfate soil materials and profiles in South Australia using:

(i) hypersulfidic material, hyposulfidic material and monosulfidic material terminology (Sullivan *et al.* 2010), and
(ii) subaqueous soils, described as ‘Wassists’ and ‘Wassents’, by Soil Taxonomy (Soil Survey Staff 2010).

The most recent Keys to Soil Taxonomy (Soil Survey Staff 2010) offers improved characterisation and classification of acid sulfate soil landscapes over past editions because it now accounts for subaqueous soils.

Classification of acid sulfate soil materials using sulfuric, hypersulfidic, hyposulfidic and monosulfidic materials (Sullivan *et al.* 2010) has provided a much improved practical link to describe hazard assessment. This is mainly because their respective definition requires measurement of soil pH, $pH_{Incubation}$ and reduced inorganic sulfur (i.e. for discriminating between hypersulfidic and hyposulfidic materials) and Acid Volatile Sulfur (i.e. AVS for identifying monosulfidic material).

Both the Australian Soil Classification (Isbell 2002) and Keys to Soil Taxonomy (Soil Survey Staff 2010) are less developed in defining acid sulfate soil *hazards* that do not relate to acidity because they tend to miss key hazard indicators such a AVS when classifying soils. For example:

- The Australian Soil Classification (Isbell 2002) and Keys to Soil Taxonomy (Soil Survey Staff 2010) do not describe hyposulfidic material and monosulfidic materials (Sullivan *et al.* 2010) as acid sulfate soil materials.

These materials are required to contain at least 0.01% reduced inorganic sulfur and hence have the ability to release metals upon oxidation. Monosulfides also have potential to deoxygenate large surface water bodies.

- Sulfuric material that occurs below a permanently saturated layer of water is not accounted for in the Australian Soil Classification (Isbell 2002) and Keys to Soil Taxonomy (Soil Survey Staff 2010). These soil conditions were identified in areas where acidic groundwater permanently occurred above the surface of acidic soil profiles (e.g. as in the open drains located at Gillman focus area A, adjacent to profile BG 15, which have continually contained surface water of < pH 3 since 2002).

Consequently, these soil profiles should be described as being subaqueous and containing a sulfuric horizon (Soil Survey Staff 2010) or sulfuric material (Isbell 2002).

Sulfuric material has also been identified under neutral and/or alkaline surface waters in wetlands and lakes within the Murray Darling Basin (e.g. Fitzpatrick *et al.* 2010b).

- Keys to Soil Taxonomy (Soil Survey Staff 2010) does not adequately classify soils with sulfidic materials (i.e. Hypersulfidic material) occurring below 1 m of the soil surface (where the upper portion of the profile contains non-acid sulfate soil material (or hyposulfidic material).

For the purpose of describing acid sulfate soil hazards it is important to identify the deep (below 1 m) occurrence of hypersulfidic or sulfuric materials. This is because, during land development many excavations go beyond 1 m, such as for marinas or drains. It is also important to identify where these acid sulfate soil materials have been buried. This condition was identified at the St Kilda study site in profile BSK 4. In addition, recently (during 2010) a large area at Gillman containing sulfuric material has been covered with 3-4 m of waste derived fill (i.e. a mixture of waste soil, recycled aggregate and mineral based industrial residue) in order to raise the low lying site for industrial development. The fill platforms can be seen on the most recent aerial photograph (June 2010) of the site (Appendix A).

- Unlike Soil Taxonomy (Salidic Sulfaquepts), The Australian Soil Classification (Isbell 2002) does not describe sulfuric material occurring below a salic horizon.

Soils with this condition (i.e. Salidic Sulfaquepts), were identified at the Gillman study site in a former tidal creek depression that traversed sulfuric materials (e.g. profile BG 4 at focus area B) and classified as a Hypersalic Hydrosol. To account for the acidity hazard associated with profile BG 4 it was classified as a Sulfuric, Hypersalic Hydrosol throughout this thesis.

13.2.2. Mapping

The correlations that were established between landscape features and soil characteristics in this thesis were used to produce soil maps. Previous groundwater conditions and geomorphology, together with soil and contamination information, provided a valuable data-set to obtain an improved understanding of the temporal and spatial variability of the physiography, which enabled map unit boundaries to be refined.

Soil-landscape maps were used to portray the spatial variability of soils in the landscapes. The map and legends locate and describe where potential hazards, such as: acidity, potential acidity, salinity, deoxygenation and metal mobilisation occur or might occur in the landscape.

Surface cover types in conjunction with micro-topography and geomorphology provided surrogates for mapping acid sulfate materials. The use of geophysical techniques and historic aerial photography improved demarcation of map unit boundaries and therefore improved hazard assessment.

The spatial distribution and concentration of acidity (i.e. the components of net acidity) within the Barker Inlet was linked to:

- *geomorphological features* such as sulfuric material, which is closely linked to sandy shoreface and back barrier sand units at Gillman),
- *past sea level fluctuations* where it is proposed that the formation of sulfuric material at Gillman commenced >1500y B.P., as a result of local sea level regression following the mid-Holocene high stand, and
- *recent artificial drainage and stormwater management*.

The maps and soil-regolith cross-sections showed that existing acidity is largely stored as retained acidity in the sandy shoreface facies and is unlikely to move off site unless the hydraulic or drainage regime of the area is altered. Export of pyrite oxidation products to Barker Inlet over the past 85 years since the bund wall was constructed has likely been low due to:

- containment of oxidation products within the Gillman site by the bund walls,
- low hydraulic gradients, which limit movement of acidity,
- carbonate-rich soil horizons that fringe the main acid store, and
- thick monosulfides occur within the ponding and evaporation basins, which are down hydraulic gradient from the major area of acidified soils, provide a sink for acidity and metals.

However, un-managed development at Barker Inlet that disturbs the soils or changes the local hydrology could cause severe environmental damage by increasing the oxidation of pyrite and off-site transportation of acidity and other metal contaminants.

The acid sulfate soil maps identify areas that are suited to the application of various remediation techniques or areas where disturbance should be avoided. This allows for remediation options to be matched to proposed development plans, to achieve desired environmental outcomes.

13.2.3. Redox monitoring

Long-term redox monitoring equipment was developed as part of this project. It was deployed in the field at the St Kilda and Gillman sites and the data collected were used to gauge the influence of: **(i)** tidal flooding, **(ii)** diurnal and seasonal temperature change, **(iii)** rainfall events, and **(iv)** hydromorphic zones on the soil redox potential within demarcated mapping units. Descriptive soil-regolith toposequence models were developed to illustrate the variations in redox conditions within tidally influenced areas, non-tidal areas and recently disturbed sites. The redox data were also used to validate geochemical results and mineralogical observations.

Tidal influences on redox conditions:

- Temporal variability in Eh was generally in phase with tidal cycles.
- Redox potentials responded rapidly and significantly to tidal drainage and flooding cycles that altered oxygen supply to the surface and subsoils, and therefore controlled the type and rate of soil biological processes.
- Strength (flow rate) of tidal flushing influenced the amplitude of fluctuations in Eh measurements. Redox potentials were lowest in areas with the most stable hydraulic conditions (least amount of tidal flushing).
- Diurnal fluctuations of lower amplitude that were out of phase with tides were likely to be related to changes in temperature and solar radiation, and variation in the productivity of soil microbes and vegetation.
- Monitoring intervals of less than once hourly are required to interpret responses of Eh measurements to physico-chemical variables in dynamic environments (field-based studies).

- Mobilisation of trace elements in these environments can vary diurnally in response to the measured diurnal fluctuations in Eh. This has implications for modelling trace element mobility and sulfide oxidation rates in these environments through Fe cycling.

Redox conditions in non-tidal areas:

- Eh measurements in non-tidal, sub-aerial environments were characterised by relatively minor diurnal fluctuations.
- Non-tidal, subaqueous soils did, however, experience significant diurnal redox fluctuations, similar to intertidal environments. The diurnal redox fluctuations observed for these subaqueous soils was attributed to a combination of solar radiation, microbial activity, wind-induced wave action and temperature.
- Redox conditions within the water column became more reducing when monosulfidic materials in subaqueous soils were disturbed during rainfall / storm events.
- Rainfall events caused the upper portion of sub-aerial profiles to become more reducing.
- Redox conditions within sulfuric materials were generally oxidising. However, acidic, strongly reduced redox conditions were measured within sandy sulfuric materials for profile BG 11 during wet winter months. Reducing conditions recorded in sulfuric material was likely due to seasonal rising of groundwater heights and heterogeneity of soil redoximorphic conditions (micro-scale features) within the soil profile.
- Seasonal variation in ground water table height may have contributed to the reformation of pyrite and the consumption of acidity within re-wetted sulfuric material in areas where soil organic matter content was adequate for microbial activity.
- Redox variability across meso- and micro-scale redoximorphic features (e.g. jarosite mottles) could be better quantified by installation of multiple Pt electrodes into and adjacent to redoximorphic features, and by careful subsequent excavation of the Pt electrodes so the micro-environment surrounding the tip of Pt electrodes could be described.

- As expected, excavation of a drain within the sulfuric materials caused soil redox conditions to become significantly more oxidising, with ensuing hazards.

Recommendations for data collection with redox monitoring equipment:

- Synchronous monitoring of soil pH values with Eh would benefit characterisation of soil geochemical conditions and geochemical modelling. This is because soil pH may fluctuate over a tidal cycle, drop substantially if sulfuric materials are re-flooded, and surface waters may acidify if monosulfidic material is suspended in an oxygen rich environment.
- Replacing reference electrodes regularly (every 4-6 months).
- Allowing platinum electrodes to equilibrate for 2 to 7 days within either reduced or oxidised soil environments.
- Long-term redox monitoring over many flooding and drying cycles partially overcomes the problems of spatial heterogeneity, however excavating each Eh electrode at the end of monitoring to observe the micro-environment around tip of the Pt electrode provides valuable additional information for interpreting soil redox data.
- Installing replicate Pt electrodes (up to 4 is recommended per soil layer) to characterise redox conditions within dynamic environments such as in Barker Inlet, e.g. **(i)** in tidal areas, **(ii)** at the sediment/water interface of subaqueous soils, **(iii)** within the water column, and **(iv)** in oxidising environments.
- Interpretations of Eh data obtained during long-term monitoring using data loggers are improved by short recording intervals (sub-hourly) and regular site visits to observe the general operation of the monitoring system and dynamics of the environment, particularly within tidal settings.
- Including (additional) multiple channels to monitor soil and water pH, EC, temperature, water levels and weather data, and web connectivity (via mobile or satellite phone) for downloading data and streaming live web-cam footage of tidal, weather or physical variables that may influence soil and water redox measurements. Consideration of site security issues would be imperative prior to installation of field equipment.

13.2.4. Geochemistry and hydrochemistry

The soil geochemical and hydrochemical data collected in this study provided evidence of the temporal behaviour of trace elements in acid sulfate soil materials at Gillman and St Kilda. Defining trace element characteristics along toposequences allowed a soil-regolith explanatory model to be developed that depicts the spatial distribution and movement of elements and acidity within these landscapes.

Geochemical investigations showed:

- Metals and metalloids (As, Pb, and Zn) were elevated in topsoils of both intertidal and non-tidal (drained) soil profiles at Gillman, and are likely contaminants due to incoming windblown material from industrial sources. In non-tidal areas Cu and V, and to a lesser extent Ni, were also elevated in topsoils.
- In non-tidal areas As, Cr, Pb, V and Zn were relatively stable in topsoils (post active acid sulfate soils) due to their high pH, and high Mn and Fe contents.
- Seasonal variations in redox and pH conditions promoted the down profile migration of trace elements, which became concentrated at the redox front.
- Zinc, Cu, Pb, V and other trace metals have accumulated in subaqueous soils (of the drains and creeks that fringe the areas containing sulfuric material) that contain high concentrations of pyrite and monosulfide. This contrasts with intertidal areas where subaqueous, sulfidic soils occurring in permanently flooded tidal creeks have not accumulated contaminants from more elevated positions in the intertidal landscape.

Hydrochemical investigations showed:

- Trace elements concentrations, such as Cu, Cr, Ni, Pb and Zn exceeded ANZECC guidelines in extremely acidic ($pH < 3.2$) surface waters or soil pore waters of soil pits or drains where salt efflorescences occurred. These conditions are only likely to occur in areas mapped as units 5 and 6, and only in areas where the subsoils are (currently) or become exposed.
- Trace elements Cd, Cu, Cr, P, Ni, Pb and Zn are not significantly concentrated in pore waters or surface waters draining sulfuric material at Gillman.
- Dissolution of aluminosilicate minerals in sulfuric materials resulted in Al being one of the most elevated elements in acidic pore waters and surface waters at

Gillman, and was several orders of magnitude higher than the ANZECC guidelines.

- Hydrolysis of aluminium salts increased acidification, which further promoted the release of cations and anions (e.g. Na, Mg, Ca, Ba, Cl, SO_4^{2-}, SiO_4^{4-}, etc.) and trace elements to pore waters and surface waters.
- The lateral mobility of contaminants was predominantly by erosion of topsoils, which also promoted the movement Fe and Al oxyhydroxides into drains and creeks.
- Oxidation products were reduced and metal contaminants sequestered by sulfides at the lowest positions in the landscape at Gillman.

This work has shown that localised vertical and lateral mobility of contaminants at Gillman has been greatly enhanced by loss of tidal flooding, and consequent acidification of soils. Metals and trace elements in acidic waters were often greater than the ANZECC water quality guidelines.

13.2.5. Mineralogy – nature and properties of salt efflorescences

Salt accumulations on soil-surfaces in this coastal region resulted from a combination of the following characteristics: **(i)** Mediterranean type climate, **(ii)** hydrogeology, **(iii)** saline seepages, and **(iv)** salt crusting formed in drains above sandy sulfuric and hypersulfidic materials.

This thesis provided the first documented occurrence of sideronatrite [$Na_2Fe(SO_4)_2(OH).3H_2O$], tamarugite [$NaAl(SO_4)_2.6H_2O$] and alunogen [$Al_2(SO_4)_3.18H_2O$] distributed in coastal acid sulfate soils in Australia.

Although salt efflorescences have the ability to remove potentially toxic trace elements form soil pore waters and stream waters they are potentially mobile through physical movement (detachment) and remain water soluble. They are also a store of the sequestered trace elements and acidity. The mineralogy, pH, Eh and geochemical composition of the soils and salt efflorescences helped to explain the mobility distribution and concentration of trace elements in these complex acid sulfate soil environments. The results obtained during this study indicated that:

- Salt efflorescences that dissolved during wet periods and re-precipitated during summer played an important role in the transient storage of acidity and of components (Fe, Al, Na, Ca, Mg, Cl, Sr and SO_4). These components probably contributed to the increased formation of pyrite and iron monosulfides in wetter soils such as stranded tidal creeks at Gillman.
- Salt efflorescences containing blödite, tamarugite, pentahydrite, jarosite, gypsum and halite that formed on salt flats or spoil piles have potential for aerial entrainment and offsite transport of trace elements and contaminants.
- Scavenging of trace elements (As, Br, Ce, La, Mo and Sr) by sulfate salts was observed, but only slightly elevated concentrations of B, Ni and Zn were observed in drain or soil pit waters, even though most of the salts were dissolved from the drain or pit walls during winter months.
- Gypsum, halite, jarosite, goethite and possibly hexahydrite did persist as solid phases during wet winter months and may account for the sequestration of As, Mo, U and V by goethite and Br, Ce, La and Sr by gypsum, halite and / or hexahydrite.
- Scavenging of metals by carbonate minerals may have occurred in alkaline micro-environments.
- Seasonal formation of metal sulfides may provide a sink for trace elements, such as Mo, which appeared to have accumulated near the base of drains in hypersulfidic material that was subaqueous during winter months.
- Limiting the precipitation of salt efflorescences along drain walls is unlikely to reduce the total amount of trace elements moving to drain waters, however it would allow for a more uniform flow of trace elements to drain waters. This would reduce the occurrence of large, episodic fluxes of metals entering the drains, which are undesirable for the preservation of down stream aquatic organisms.
- Limiting the accumulation of salt efflorescences may reduce the risk of sulfide oxidation by ferric iron in down stream subaqueous soils, where water pH is higher than in the drain near the source of the salts.

These processes were collectively summarised in an evolutionary and predictive soil-regolith model. The precipitation of salt efflorescences could be minimised by covering drain walls to slow evaporation at the surface and maintain humidity (e.g. by placing mulch or geo-textiles on drain walls or by using pipes instead of open drains). Ultimately the best way to limit the issues associated with sulfuric, saline salt efflorescences is to locate drains away from sulfuric and hypersulfidic materials. This could be done quite accurately in the Barker Inlet by using the detailed soil maps of acid sulfate soil landscapes developed in this study. These processes are also likely to occur in inland acid sulfate soil systems.

13.2.6. Micromorphology

Soil micromorphological investigations, which included scanning electron microscopy were used to describe and characterise biological, physical, chemical and mineralogical processes within two intertidal soils and one drained supratidal soil profile. These techniques were used to:

- Define the various types of organic matter fractions (e.g. sapric, hemic, fibric materials) in the soil profiles.
- Describe the occurrence of sulfide minerals (e.g. pyrite, monosulfides and chalcopyrite) in the soil profiles.
- Develop and describe micro-scale weathering pathways and mechanisms under changing hydrological, physical and biogeochemical conditions in acid sulfate soils.

Micromorphology of intertidal (undrained) acid sulfate soils indicated that:

- Sapric material was more decomposed and less porous than hemic material, and allowed the formation of larger pyrite framboids.
- Partial oxidation of pyrite along coarse pores formed lenticular gypsum crystals because of the dissolution of carbonate in a low pH environment.
- The morphology and form of pyrite and gypsum crystals within the soil profile indicated that conditions of their formation are on a micro-scale.

Micromorphology of drained coastal acid sulfate soils indicated that:

- Sulfide oxidation was extensive and was confirmed by the presence of iron oxyhydroxide pseudomorphs (goethite crystallites and framboids) after pyrite, jarosite and gypsum crystals.

- The morphology and relationships of pseudomorphs after pyrite can be used as a palaeo-indicator of the soil's physico-chemical conditions prior to oxidation.
- The micromorphology of weathering features of pyrite crystals, framboids and redoximorphic features provided insight into the pH and redox conditions (within micro-environments) and weathering rates of pyrite as oxidation proceeded.
- Iron oxide pseudomorphs after jarosite spheroids within salt efflorescences were indicators of temporal redox and geochemical changes within micro-environments.
- The preservation of pyrite crystals within an oxidised environment can occur by armouring with clay coatings and by impregnation or inclusion within gypsum and halite crystals. The kind of armouring on pyrite has implications for characterisation of acid sulfate soil types by ageing as well as implications for acid sulfate soil management.

Micromorphological investigations indicated that soils at Gillman have been subjected to a complex geomorphic and drainage history, where the loss of tidal influences caused:

- Oxidation of sulfidic materials in the upper portion of the soil profile to form non-acid sulfate soil (relic or post active acid sulfate soils).
- Oxidation of hypersulfidic materials in the lower portion of the soil profile to develop sulfuric material that led to the acidification of groundwater.
- Movement of Fe and S to lower portions of the soil profile where they underwent reduction, seasonally.

Micromorphological information was included in soil-regolith models, which helped explain mineral transformations that occurred during oxidation and re-flooding scenarios in soil profiles containing sulfuric material at Gillman.

13.3. Considerations for future work:

13.3.1. Soil morphology

For the purpose of better describing acid sulfate soil hazard it is proposed that Soil Taxonomy consider the inclusion of new Subgroups to classify soils with:

- Sulfuric horizons that are buried by anthropogenic fill material of a thickness that exceeds 1 m, but to a depth of 1.5 or at least 2 m. This is relevant for areas at Gillman (e.g. map units 5, 6 and 7) that are being progressively covered by fill materials.
- Sulfidic material (hypersulfidic) that occurs below natural soil or is buried by anthropogenic fill material of a thickness that exceeds 1 m, but to a depth of 1.5 or at least 2 m. This includes sections of Map unit 8.
- Sulfuric horizons that occur below a layer of permanent water. This situation was encountered at the Gillman study site (focus area A), within experimental drains, which have become permanently saturated.

For the purpose of improving description of acid sulfate soil hazards using the Australian Soil Classification (Isbell 2002), a working group has recently been formed to incorporate changes that account for: **(i)** monosulfidic, hypersulfidic and hyposulfidic materials and **(ii)** subaqueous soil conditions (Acid Sulfate Soil Classification Committee 2010).

Using the Australian Soil Classification (Isbell 2002) profile BG 4 classified as a Hypersalic Hydrosol, however to account for soil profiles containing sulfuric material below a salic horizon, such as for profile BG 4, it has been recommended to the working group (Acid Sulfate Soil Classification Committee 2010) that a new Great Group be created (e.g. Sulfuric, Hypersalic Hydrosol). Profile BG 4 was classified as a Sulfuric, Hypersalic Hydrosol throughout this thesis.

13.3.2. Acid sulfate soil analysis

Compare acid base accounting and incubation experimental data to refine procedural trigger values for conducting retained acidity measurements, particularly for sandy sulfuric material where multiple types of salt efflorescence minerals contain stored or retained acidity. This is recommended because a number of soil layers and horizons from profiles at the Gillman study site contained retained acidity values greater than the lime treatment trigger value of 18.7 mole H^+/t (Ahern *et al.* 2004). However, according to the Acid Sulfate Soil Guidelines (Ahern *et al.* 2004) these soil samples did not require assessment of retained acidity content because they had a pH_{KCl} greater than 4.5. In addition, acid base accounting does not account for rate limiting processes such as oxide or gypseous coatings of carbonates.

13.3.3. Mapping

The maps produced for the study sites represent land characteristics for only that period of time during which this study was undertaken. Sites with acid sulfate soils frequently change due, for example, to land development and natural processes (e.g. sea level rise). The maps should therefore be updated periodically (e.g. annually at Gillman and once every ten years at St Kilda). Changes are rapid for the Gillman area due to encroaching industrial development. Updating the soil-landscape maps could be achieved primarily by reviewing most recent aerial photography to manipulate map unit boundaries. Site investigations and continued monitoring of soil conditions would be a crucial for evaluating environmental change. Some suggested parameters for monitoring are presented below.

13.3.4. Redox condition

Improve redox monitoring systems by incorporation of pH electrodes to measure and record real time changes in pH within the soil layers being monitored for Eh. This would allow for improved geochemical modelling and data interpretation.

Add video capabilities and telemetry to data loggers so that data can be downloaded over the web and live images of the study site can be viewed. This would allow obvious environmental (or other) changes at the site to be correlated to data plots (e.g. tidal influences or vandalism).

13.3.5. Geochemistry and hydrochemistry

This work has implications for assessing contaminant movement in other coastal landscapes, particularly in areas where contaminant issues are known to occur along the South Australian coastline, such as at Port Pirie and Port Augusta (where there is a history of smelting and / or heavy industries located on or adjacent to reclaimed coastal land). The bioavailability of these metals has not been investigated in this study, however it is assumed that metals such as Cu, Ni, Pb and Zn within strongly reduced soils are associated with metal sulfides and are unlikely to be bioavailable in environments with neutral to alkaline pH.

Geochemical modelling using a software program (e.g. The Geochemist's Workbench®) that takes into account high ionic strengths could improve understanding of the geochemical behaviour of contaminants within the Barker Inlet acid sulfate soil landscapes. Consideration of the free energy concent would help explain the movement, or otherwise, of the various ions through the soil to surface waters.

Linking contaminant types to contaminant sources might be better defined by comparing the types and levels of contaminants occurring within near surface soils of exposed areas to those in soils covered by fill materials, especially where the date of filling is known. This technique would work best where fill material has compressed the original topsoil and maintained it in a moist environment that promoted the formation of sulfides within the buried topsoil layer.

13.3.6. Mineralogy

Evaluate rates and thermodynamic properties (dissolution) of the major minerals identified in salt efflorescences and their contribution to stored acidity.

Investigate the potential for the wide range of minerals identified in salt efflorescences to retain (by binding or inclusion) and release (by dissolution) metals.

Investigate the formation of pyrite and monosulfides under acidic conditions.

Evaluate the effect that hypersaline pore water has on mobility of pyrite oxidation products and stability of sulfide minerals.

13.3.7. Micromorphology

Further investigate the potential for armouring of iron sulfides by the range of minerals identified in the salt efflorescences in this study.

Analyse in more detail the goethite honeycomb structures observed in goethite-rich framboids to delineate the oxidation rate and mineral transformations of pyrite oxidation.

13.3.8. Management of acid sulfate soil in the Barker Inlet

Information presented in this thesis should to be incorporated into a revised version of the Acid Sulfate Soil Management Manual for the Barker inlet (Thomas *et al.* 2004a), such as:

- Updated acid sulfate soil hazard maps.
- Add cross sectional diagrams and soil-regolith models to show the vertical spatial distribution of acid sulfate soil materials and acidity (components of net acidity).
- Add new acid base accounting data.
- Test acid sulfate soil mitigation methods (i.e. those described in Table 12-2).

The Coastal Protection Board Policy documents (Coastal Protection Board 2003) and educational pamphlet on acid sulfate soils for school groups published in 2001 (Thomas 2001); Appendix H) should be updated using modern terminologies, acid sulfate soil maps, popular cross-sectional diagrams (e.g. Figure 8-4) and information produced in this thesis.

13.3.9. Monitoring

The work presented in this thesis provides a baseline for the state of the St Kilda and Gillman study sites from which future changes can be evaluated. The effects of movement of groundwater (some of it acidic) within the soil profile during both: (i) continued oxidation and (ii) re-wetting scenarios should be further tested and monitored for the different soil types.

Monitoring is considered an essential component of acid sulfate soil assessments because of the temporal nature of the processes that occur. A robust monitoring strategy should be instigated in the Barker Inlet and adjacent wetlands, especially during drought and reflooding (re-wetting) phases, when acidity and metal mobilisation are likely to be greatest.

It is recommended that a follow-up survey of the various focus areas studied in this thesis is conducted within 2 years to characterise and identify the changes that are occurring. The intention would be to revisit selected sites sampled as part of this project, with a focus on sites that contained sulfuric material and that have now been covered with fill material as the site is developed. The areas of the Gillman site that are currently being reclaimed using waste derived fill can be seen on the most recent aerial photograph (June 2010) of the site (refer to Appendix A). The chemical and descriptive data collected during this study provide a valuable baseline for assessing the environmental implications of future changes to land use, and the success of burial and loading (compression) as a remediation method for thick, poorly compressible sulfuric materials.

13.3.10. Data Interrogation

The rigorously collected and well distributed data set generated for Barker Inlet has substantial potential for further analysis including:

- Integrating the data with past and future data sets as a baseline to identify changes with time, and then to investigate and explain the processes that cause the change. This would then allow predictive scenarios presented in this thesis to be tested and better developed.

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List of Appendices

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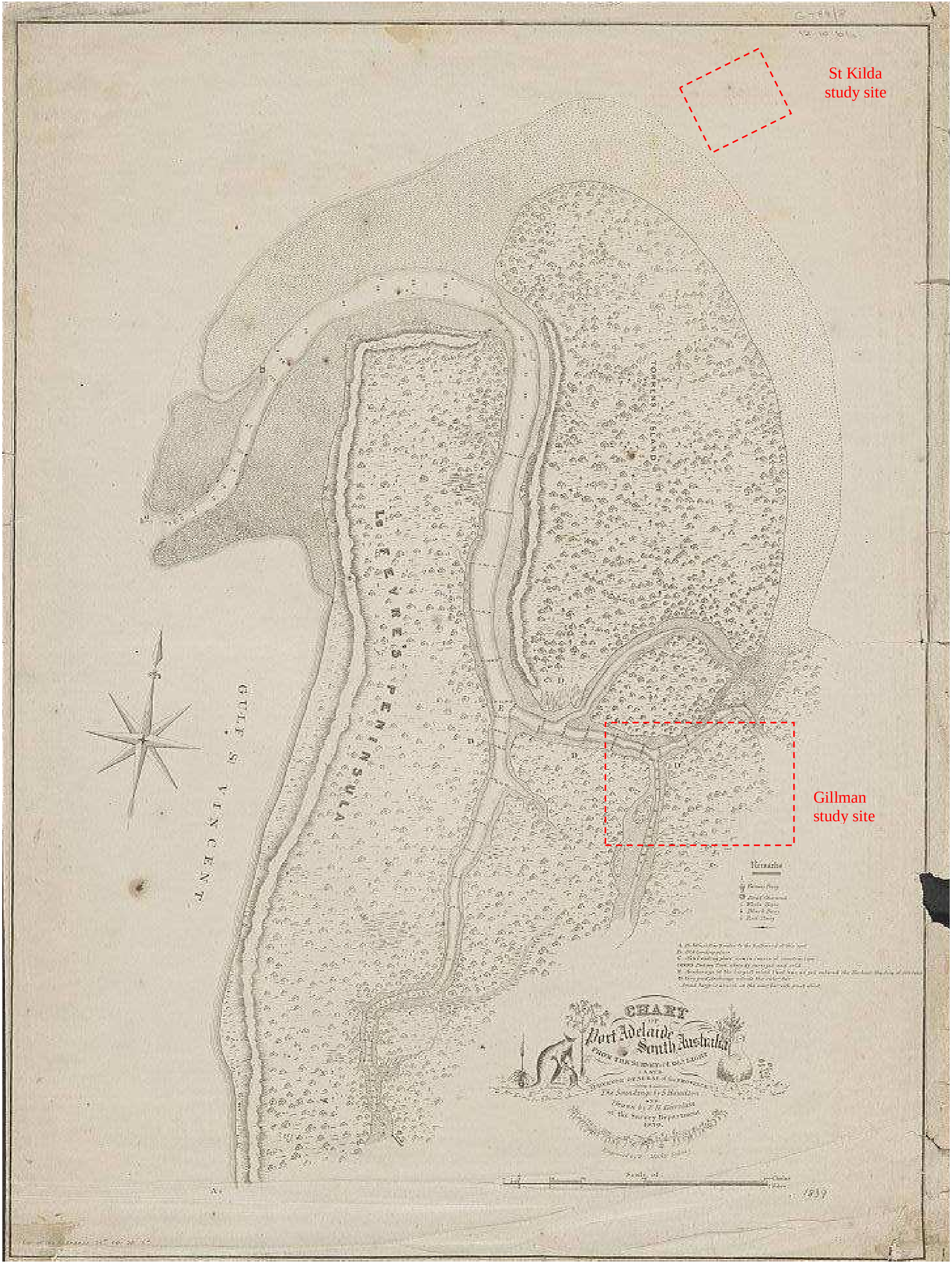
Appendix A

Historical aerial photographs of study sites

Barker Inlet, 1839



Barker Inlet, 2010 (June).

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