Contemporary and relict processes in a coastal acid sulfate soil sequence: macroscopic and geomorphic features

B.P. Thomas[1], R.W. Fitzpatrick[1], R.H. Merry[1], R.M. Poch[2], W.S. Hicks[3] and M.D. Raven[1]

[1]CSIRO Land & Water/ University of Adelaide, Private Bag No. 2, Glen Osmond, S.A., 5064. Emails: brett.thomas@csiro.au; rob.fitzpatrick@csiro.au; richard.merry@csiro.au; mark.raven@csiro.au
[2]Univerity of Lleida, Catalonia, 25198, Spain, Email rosa.poch@macs.udl.es
[3]CSIRO Land & Water, GPO Box 1666, Canberra, ACT, 2601; Email: warren.hicks@csiro.au

Abstract
Two 4D mechanistic process models were developed to explain the evolution of soil-landscapes in two adjacent and contrasting coastal regions in Barker Inlet, South Australia containing sulfidic materials and sulfuric horizons.

Pedological (morphology), geomorphic, micromorphological, mineralogical (XRD), electron microscopic (SEM and TEM) and geochemical (XRF, ICP, automated redox monitoring) investigations were conducted on soil-sequences in the following two adjacent study sites:

- tidal mangrove soils with sulfidic material (Histic-Sulfidic Intertidal Hydrosols). Recent changes in tidal regime has contributed to a marked increase in supply of nutrients and organic matter causing strongly reducing conditions to develop, which has lead to mangrove deaths; and
- a similar tidal region where seawater was excluded in 1954 when a bund wall was constructed for industrial and agricultural land reclamation. Loss of tidal inundation has caused the formation of sulfuric horizons overlying sulfidic material leading to degraded soils (Sulfuric Hypersalic Hydrosols) and waters in the drained area.

The 4D mechanistic models were developed to illustrate the major geomorphic stages in soil-landscape evolution at different spatial scales. Superimposed on this framework are detailed chemical and physical changes that occur when tidal influences are altered or excluded in these environments. The models also pinpoint how and where acidity and contaminants such as heavy metals and oxyhydroxysulfates are produced in soil layers, their movement and spatial distribution in these settings. This information provides a better understanding of soil-landscape processes to underpin future management of these systems.

Key Words
Redox, eutrophic, sapric and hemic soil materials

Introduction
Setting and general characterisation
The Barker Inlet is located 15 km north of Adelaide and covers an area of about 25 km^2 (Figure 1). The natural elevation of the Gillman area ranges from -1.0 m AHD in creek channels, to 2.5 m AHD on undulating mounds between tidal creeks. The climate of the area is Mediterranean, which is characterised by cool-to-mild, wet winters and extended hot, dry summers. The mean annual rainfall for the area is 470 mm which mainly falls between May and September. The high potential evaporation demand (1,760 mm per year) exceeds rainfall by almost four to one and, accordingly, groundwater movement is predominately vertical, with very low lateral seepage rates of 0.3 to 0.6 m/yr (Pavelic and Dillon 1993).

The recent geological evolution of the area has largely been controlled by global sea level fluctuations (Edmonds 1995). The Holocene St Kilda Formation overlies the Glanville Formation (Pleistocene), which together on-lap the thick alluvial Hindmarsh Clay Formation (Belpario and Rice 1989). Reworking of coastal sediments since sea level stabilisation about 7500 B.P. resulted in the northerly extension of Le Fevre Peninsula and the Port River outlet. The establishment of extensive sea-grass meadows led to the rapid accumulation of marine and estuarine sediments resulting in coastal pro-gradation throughout the late Holocene (Edmonds 1995). Pro-gradation led to the simultaneous back-barrier development of marshes and mangrove swamps parallel to the shoreline. The embayment is now mostly in-filled except for the Port River estuary. The pre-European sedimentary environment of Barker Inlet is shown in Figure 1. Subsidence rates of 1mm per year have been documented in the Barker inlet area (Belpario 1993) and are

attributed to movement along the Para Fault, subsidence due to ground water extraction and consolidation of inter-tidal soils after drying due to bunding (construction of levee banks) (Figure 1).

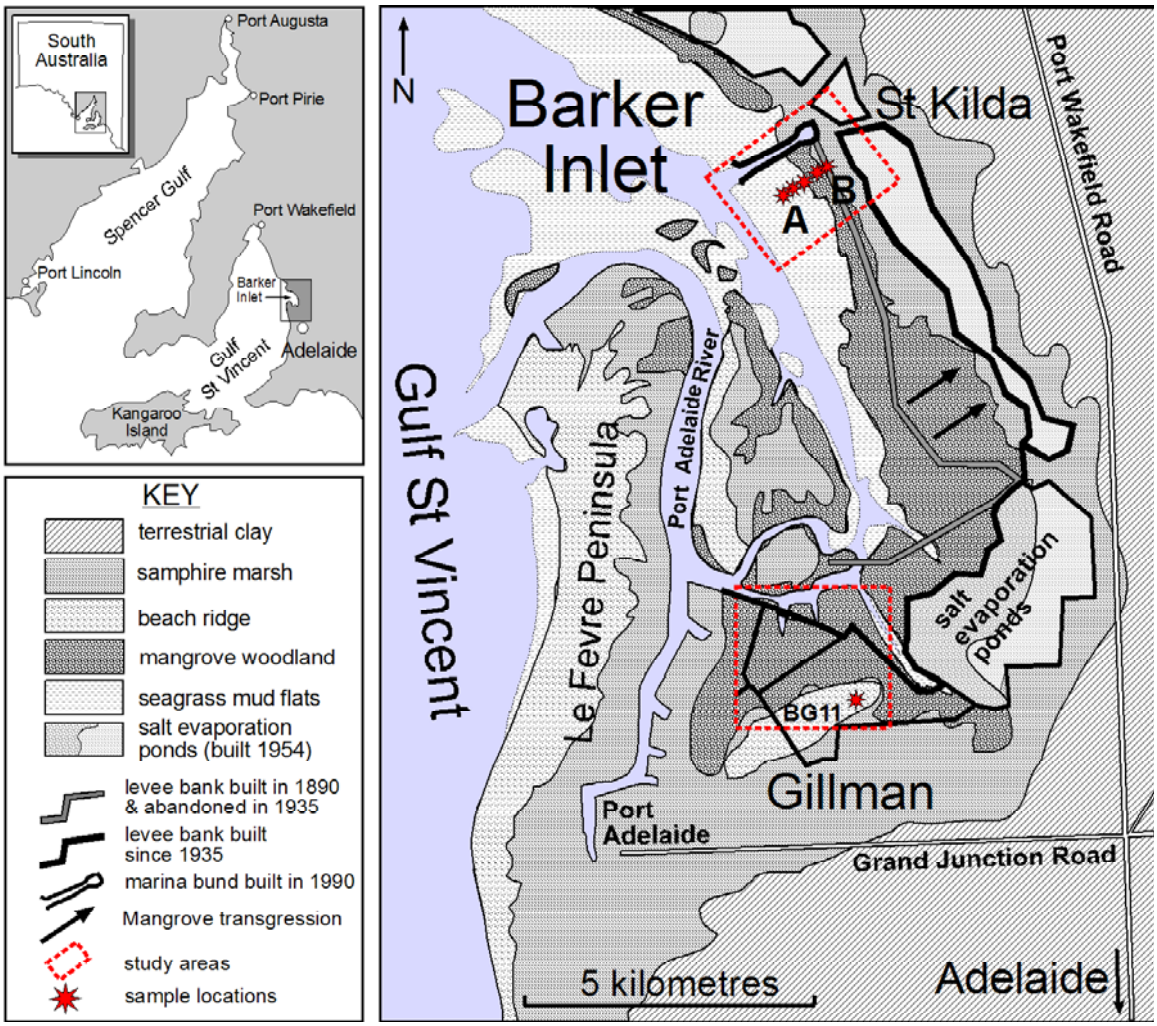


Figure 1. Barker Inlet is a tidal dominated estuary located 20 kms north of Adelaide, South Australia. The levee bank built in 1890 was placed along the landward extent of mangrove woodland. Mangroves have colonised a large area beyond this levee since it was breeched and abandoned in 1935 (arrows show mangrove transgression). The St Kilda study site is "natural" tidal mangrove woodland but tidal-water movement (drainage) was restricted about 12 years ago when the St Kilda marina and channel were constructed (at the north of the St Kilda study area). The Gillman study site was drained in the mid 1950's when a bund wall was constructed in an attempt to reclaim inter-tidal mangroves and samphire salt marsh for agriculture and industry. This land was soon abandoned due to severe acidification, salinity and storm-water ponding. (Modified after Belpario and Rice 1989).

Methodology

The pedological morphostratigraphy of the St Kilda and Gillman areas was established from 35 backhoe excavations supplemented with pre-existing drill-hole data from Belpario and others (e.g. Belpario and Rice 1989; Pavelic and Dillon 1993; Fitzpatrick *et al* 1996). Acid Sulfate Soil and geomorphic maps were produced from pedological soil profile descriptions. Micromorphological, mineralogical (XRD), electron microscopic (SEM and TEM) and geochemical (XRF, ICP) investigations were conducted on selected soil and pore water samples. Long term, automated redox monitoring was conducted on soil profiles and water columns using platinum electrodes with a Ag/AgCl reference electrode (Ionode IJ14) linked to a 16 channel data logger. Eh values are reported as equivalent to a Standard Hydrogen Electrode.

Results and Discussion

St Kilda

In the 1890s a levee bank was built at St Kilda and extended south along the landward extent of mangrove vegetation. 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 (Belperio 1993). From 1935 to 1979, mangroves (*Avicennia marina*) between St Kilda and Gillman advanced inland at a rate of approximately 17 m per year (Burton 1984) due to localized subsidence expanding the intertidal zone (Figure 1).

The St Kilda study area contrasts the Gillman site in that bunding has caused some areas at St Kilda to become permanently inundated, highlighting just how complex and sensitive these coastal ecosystems are to changes in tidal/hydraulic regime. A marina with a bunded channel that transects the coastal plain was constructed at St Kilda in 1990 (Figure 1). Although the bund wall does not exclude the tide from inundating mangrove soils, it does block a number of northward draining tidal creeks causing them to become flooded pools. The flooded creek depressions have become stagnant as debris (seaweed and wood) accumulates in them, resulting in mangrove deaths (Zone 3 of Figure 2 below). Mangroves are also dying along the seaward extent of the mangrove woodland (Zone 1, Figure 2).

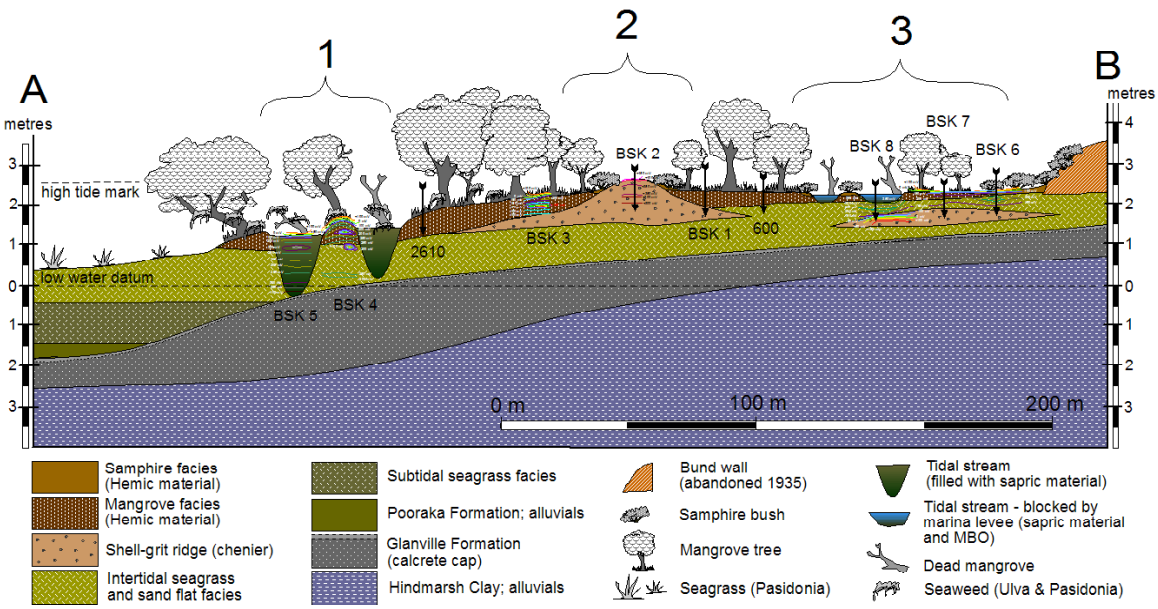
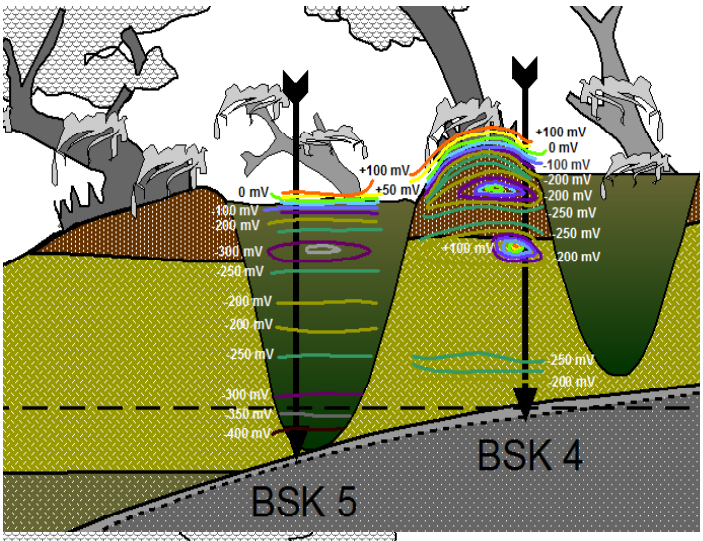


Figure 2. A schematic illustration of the local geomorphology and location of soil profiles and monitoring sites. Zones 1, 2 and 3 are described in table 1.

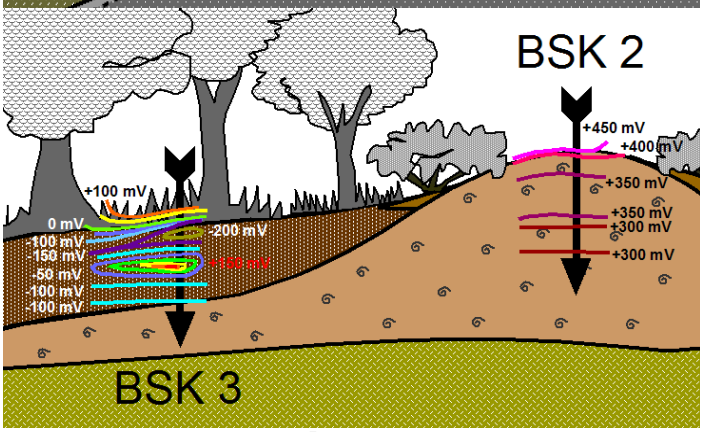
In Zone 1 healthy mangrove soil is slowly being eroded away by outward flowing water through the tidal creeks. The creeks are filled with rotting organic matter such as sea-grass and sea-lettuce (sapric soil material) that is causing extremely reducing conditions (Eh values down to –410mV). These soil conditions become toxic to mangrove pneumatophores when H_2S concentrations are high. The pneumatophores retreat to higher ground (less reducing soils) leaving the creek banks susceptible to erosion and further restricting the area in which pneumatophores can survive. When these areas become too small, the trees become unstable and are easily knocked down during storms, killing them. The dead trees in the sea-ward fringe of mangrove forest (Zone 1) are not being replaced as seedlings are continually smothered by sea-lettuce and seagrass.

Changes to the hydraulic regime of a mangrove woodland at St Kilda, through both natural (subsidence) and anthropogenic (blocking of tidal creeks) processes has caused the eutrophication and erosion of tidal creeks and mangrove deaths. Extremely low redox conditions lock up nutrients in the soil effectively starving the trees. As land subsidence continues, the mangroves along the seaward fringe will die and mangrove soils will eventually erode to form seagrass and mud flats. The mangrove forest will encroach landward and onto higher shell-grit ridges, reducing the area currently occupied by samphire vegetation. The landward retreat of samphire to higher ground however is impeded by the levee bank surrounding the salt evaporation ponds. The construction of a drain along the southern side of the marina bund wall to intersect the stranded tidal creeks could greatly enhanced the tides ability to “flush” nutrients from the stagnant pools and help remediate the effects of continual inundation.

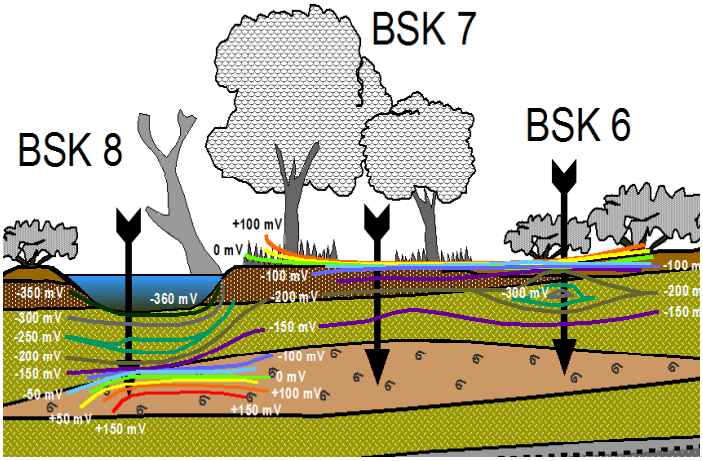
Table 1. Eh values of soil profiles at St Kilda.



Zone 1: Profiles BSK 4 and BSK 5 are 2.0 m thick and located 50 m from the low tide mark from the seaward fringe of the mangrove forest. BSK 4 classifies as a Histic-Sulfidic Intertidal Hydrosol (Isbell, 1996) with hemic soil material and is equivalent to profile 2610 described in Poch *et al.* 2004 of this publication. Eh values range from -250 mV at >1.8m depth to +100 mV near the surface. Positive Eh values were recorded where live pneumatophores introduce oxygen into the soil. The tidal creeks (profile BSK 5) are filled with rotting organic matter such as sea-grass and sea-lettuce (sapric soil material) that is causing extremely reducing conditions (Eh values down to –410mV). BSK 5 classifies as a Histic-Sulfidic Intertidal Hydrosol with sapric soil material.



Zone 2: BSK 2 is a 0.7 m thick soil profile through a shell grit ridge (chenier) and has far higher Eh values than BSK 3 due to its high porosity, elevation and relatively low organic matter content. Eh values for BSK 2 range from +300 to +450mV. BSK 2 classifies as a Salic Epicalcareous Intertidal Hydrosol. Profile BSK 3 is representative of a healthy mangrove soil and classifies as a Histic-Sulfidic Intertidal Hydrosol with hemic soil material. The profile is 0.6 m thick and located 500 m from the low tide mark and the seaward fringe of the mangrove forest. BSK 3 is equivalent to soil profile 600 described in Poch *et al.* 2004 of this publication.



Zone 3: Profiles BSK 6 and BSK 7 are 0.4 m thick and both classify as Histic-Sulfidic Intertidal Hydrosol with hemic soil material. BSK 6 is covered by samphire vegetation and Eh ranges from -300 mV at depth to +100 mV near the surface. BSK 7 is covered by mangrove vegetation and Eh Ranges from -200 mV at 0.2 m depth to +100 mV near the surface. BSK 8 is a 0.4 m thick profile in a tidal creek channel that is unable to drain completely at low tide as a bund wall blocks its seaward flow. Eh ranges from -360 mV in the top 5 cm of sediment and is -200 mV at 30 cm depth. Eh increases markedly to +150 mV at 40 cm depth because of occurrence of shell grit layers. BSK 8 is a Histic-Sulfidic Intertidal Hydrosol with sapric material and MBO.

Gillman

Before the bund wall was constructed, the Gillman study area consisted of intertidal mud-flats, mangrove muds and supra-tidal samphire sediments. These soil conditions were conducive to sulfate reduction, with sufficient organic matter to produce anoxic conditions and sulfate from seawater. Terrigenous iron was also available to form sulfide minerals and tidal flushing both replenished the sulfate pool and removed the bicarbonate produced by sulfate reduction, resulting in the formation and accumulation of sulfidic material. The soil pH in this anaerobic environment was above seven. These sulfidic soils would classify as Histic-Sulfidic Intertidal Hydrosols.

After the area was drained in 1954, acid sulfate soils formed. Soil profile BG11 is representative of a typical acid sulfate soil at Gillman (Figure 3). The development of this soil profile is described in figure 4 below. BG11 formed as beach sand was deposited on the Hindmarsh Clay and Pooraka Formations about 6600 B.P. (Bowman and Harvey 1986), forming a back-barrier sand ridge. This sand ridge is the most prominent landform at Gillman (2-3 m AHD), and covers about 1.6 km^2. Mangroves were prevalent at

this time of deposition and verified by vertical pneumatophores being preserved as vertically elongate jarosite mottles. From 5800 B. P., the northward development of Le Fevre Peninsula provided BG11 with shelter from wave activity, allowing a fine clayey mangrove peat to deposit in a back-swamp environment. A period of high wave / storm activity deposited a clean sand layer with almost no organic matter, which raised the land surface, allowing samphire vegetation to establish in a supra-tidal environment.

The loss of tidal inundation has dried these coastal soils causing oxidation of sulfide minerals and acidification of soil layers and groundwater. Approximately 4 km^2 of soil in the Gillman area now contain a sulfuric horizon that ranges from 0.2 m to 3.0 m thick and is generally underlain by sulfidic material (Figure 3). These soils are classified as Sulfuric Hypersalic Hydrosols.

The back barrier sand has developed a 2 m thick sulfuric horizon because pyrite framboids within preserved mangrove pneumatophores have oxidised to form yellow jarosite mottles (Figure 4). About 85% of sulfides within the oxidation front of BG11 have oxidised over the past 50 years, producing about 520 000 tonnes of H_2SO_4 (Thomas *et al.* 2003). The sands have limited acid neutralising capacity and the pH of soil solution is generally less than 2.5. Redox monitoring indicated that the large seasonal variation in watertable height (> 1m) may contribute 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.

Most of this acid is still contained within the profile due to the low hydraulic gradient of the area. The levee banks prevent it being discharged into the Barker Inlet at any significant rate as the bunded area acts as an evaporation basin (Figure 3). Thick accumulations of Mono-sulfidic black ooze (MBOs) have formed in drains, tidal creek depressions and low lying, permanently waterlogged areas and act as a sink for metal contaminants (Harbison 1986, Thomas *et al*. 2001).

However, when a drain is excavated within this area, alumino-sulfo salts (e.g. tamarugite), iron oxyhydroxy-sulfate salts (e.g. sideronatrite) and salt efflorescences (e.g. starkeyite) precipitate on the soil surface along the drain edge. These soluble salts dissolve during rain events and contribute to acidity and metal content in drainage waters (Ahern *et al*. 2000). These processes are collectively summarised in the evolutionary and predictive model shown in figure 4.

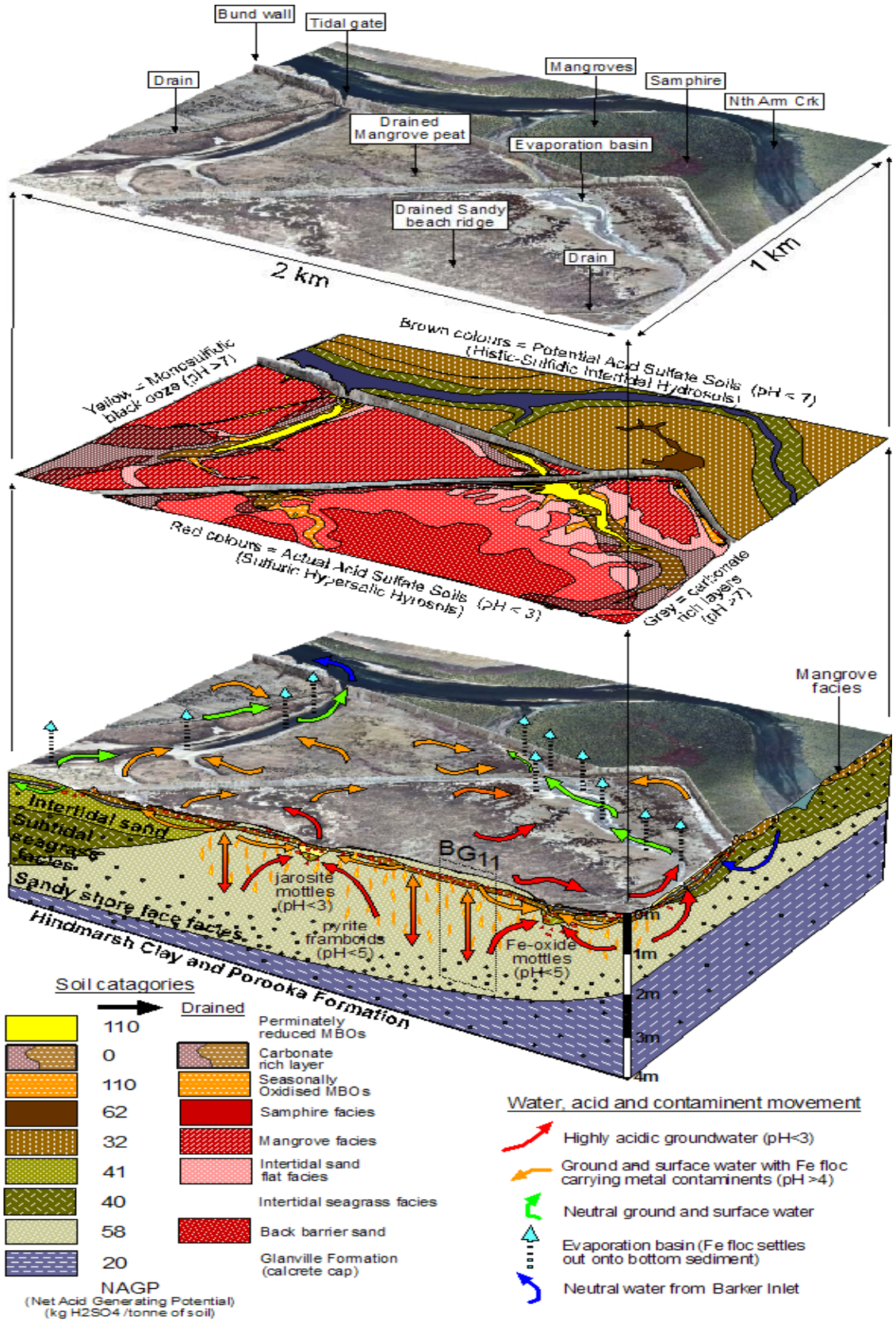


Figure 3. This geomorphologic-landscape (descriptive) model shows the contrasts between tidal and drained coastal landscapes (aerial photograph DEM drape - top layer). Soil acidity is shown by the middle layer (ASS risk map). The bottom layer shows the depositional facies and location of pyrite oxidation and the movement of acidic ground water/contaminants (Fe flock) within the site. The arrows represent the flow path of ground and surface water. Soil profile BG 11 is described in detail by Poch *et al.* (2004), this publication.

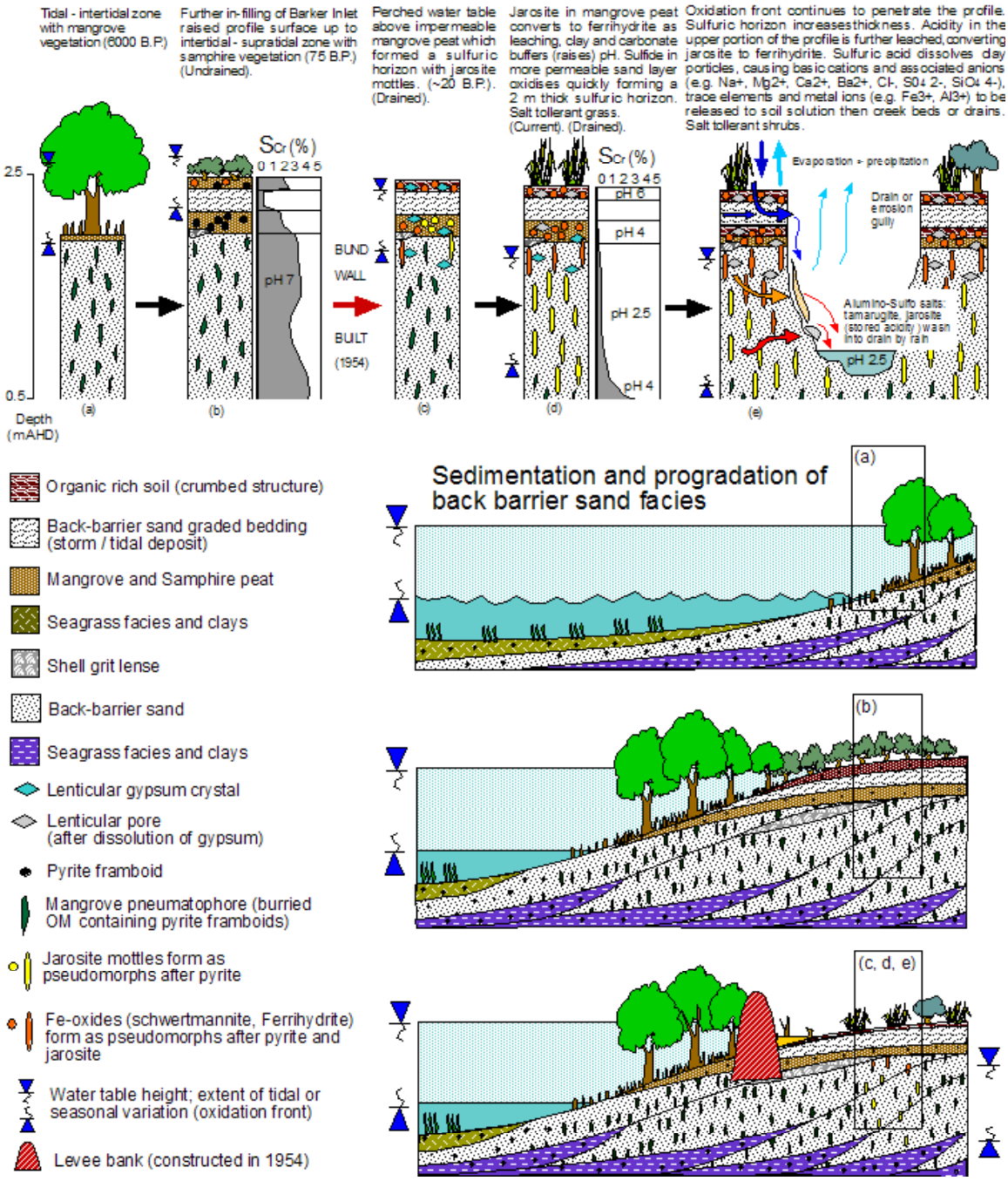


Figure 4. Evolutionary and predictive soil model. If there is no change to the current land management and drainage regime the oxidation front will deepen and pyrite oxidation will continue to produce H_2SO_4. The acid currently stored in the back barrier sand is unlikely to move off site unless the hydraulic or drainage regime of the area is changed. Acid and metal export loads to Barker Inlet are low due to their containment within the Gillman site by bund walls, low hydraulic gradient, carbonate rich horizons fringing the main acid store and occurrence of MBOs within the ponding / evaporation basins.

Conclusions

The loss of tidal inundation caused a lowering of the watertable, enabling oxygen to diffuse into the sulfidic soils which caused pyrite oxidation and soil acidification. The descriptive and mechanistic models 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. The models also pinpoint how and where acidity and contaminants such as heavy metals and oxyhydroxysulfates are produced in soil layers, their movement and spatial distribution in these settings. This information provides a better understanding of soil-landscape processes to underpin future management of these systems. Understanding the distribution, evolution, nature and inter-relationships of the coastal sediments is vital for effective planning of ASS management and selection of appropriate

remediation options. However, the development plans for land influenced by ASS will also dictate the remediation options available to achieve a desired environmental outcome.

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