

**Coastal acid sulfate soil
processes in Barker Inlet, South
Australia**

Doctor of Philosophy

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September 2010

Chapter Eight

8. Redox chemistry

Redox potentials are one of the most important chemical properties that control a variety of chemical and biochemical processes. Redox conditions are not uniform in soils as they are continually influenced by microbial processes, the concentration of oxygen, organic matter content and types, soil water status, and pH. The fixation of elements in the soils depends on soil redox conditions and pH. In acid sulfate soil environments, the oxidation of sulfide minerals is responsible for sulfuric acid release and increased mobility of metals. At low redox potentials, reduction of sulfate and iron can lead to the formation of iron sulfide minerals and sequestration of metals from soil solution. Redox potential (Eh) measurements enable the oxidation-reduction status of soil and groundwater environments to be characterised for predicting the stability of various minerals and compounds that regulate nutrients and metal availability. Monitoring redox conditions over time provides a diagnostic tool for determining when and where an area is functioning as a wetland or a non-wetland.

In situ redox monitoring was used to assess the soil reduction-oxidation (redox) conditions within tidal environments at St Kilda and Gillman, and non-tidal environments at Gillman. Redox monitoring was also used to gauge the effect that tidal flushing has on soil redox conditions at St Kilda.

This Chapter discusses; **(i)** thermodynamic principles of redox potential in soils, **(ii)** the design, construction and installation of long-term, *in situ* redox monitoring systems at the Gillman and St Kilda study sites and **(iii)** results gained from redox monitoring and their geochemical, pedological and hydrological implications.

8.1. Introduction

Thermodynamic principles of redox potential in soils

Redox potential in soils is a measure of a system's tendency to oxidise or reduce susceptible minerals in compounds (Ponnamperuma 1972; Schlesinger 1997). Oxidation and reduction (redox) reactions are characterised by the loss or gain, respectively, of one or more electrons by an atom or molecule. In soil-water systems an electron cannot exist in a free form (e^-) due to its extremely large charge-to-size ratio (Evangelou 1998; James and Bartlett 2000). Thus oxidation and reduction are simultaneous processes involving electron transfer from an electron donor element or molecular species (reductant) to an electron acceptor element (oxidant). The oxidised and reduced forms of the reacting species are known as redox 'couples'. The tendency for an atom to donate, accept or share an electron is given by the **octet rule**, which states that atoms tend to combine in such a way that they each have eight electrons in their valence (outer) shells, giving then the same electron configuration as a noble gas (Lewis 1916). Redox reactions are thermodynamically possible when two or more active redox couples are in contact. The redox couple with greatest affinity for electrons is reduced and the second redox couple, with a lesser affinity for electrons, is oxidised (Rowell 1981). The energy is released in such a reaction is termed 'Gibbs free energy' (ΔG), and is related to the redox potential (Eh) of each redox couple.

Redox potential (Eh) is an electrical measurement (measured in volts) that shows the tendency of a soil solution to transfer electrons to or from a reference electrode. From this measurement an estimate can be made of whether the soil is aerobic, anaerobic, and whether chemical compounds such as Fe oxides or nitrate have been chemically reduced or are present in their oxidised forms e.g. (Faulkner and Patrick 1992; Vepraskas and Faulkner 2001; Vepraskas *et al.* 2006). By convention, Eh is reported relative to the standard hydrogen electrode (SHE). The SHE is the electrode potential of the hydrogen half cell under standard conditions. Thus, under standard conditions, redox couples that are more reducing than the SHE has a negative electrode potential and those that are more oxidising have positive electrode potentials. Standard redox conditions are rare in nature as geochemical cycles follow basic thermodynamic principles and proceed towards a state of maximal entropy and the most stable mineral phases (Patrick *et al.* 1996). Thus for redox couples under non standard conditions, Eh is related to the

standard redox potential by the Nernst equation (Equation 8-1), which is modified to account for the influence of pH (Atta *et al.* 1996; Connell and Patrick 1968; Rowell 1981).

Equation 8-1
$$Eh(\text{volts}) = E^0 + \frac{RT}{nF} \ln \frac{(Ox) \times (mH^+)}{(Red)}$$

Where:

Eh = electrode potential; E^0 = standard half cell potential; F = Faraday constant; n = number of electrons exchanged in the reaction; R = gas constant; T = the absolute temperature; m is a coefficient (Rowell 1981); H^+ is the activity of protons; and (Ox) and (Red) are the activities of the oxidised and reduced forms of the complex.

This equation shows that Eh increases with increasing activity of the oxidised component (Ox), decreases with increasing activity of the reduced component (Red) and increases with increasing activity of H^+ (Patrick *et al.* 1996). The redox potential (Eh) is commonly reported as 'pe', the measure of electron activity that is analogous to pH (Hostettler 1984; Sigg 2000). However, for the purpose of this study, results will be reported as Eh (in mV relative to the SHE).

Redox potentials in soils

Redox reactions are an important aspect in soil chemistry. Redox reactions change the speciation and solubility of many elements (e.g. Fe^{3+} to Fe^{2+}) create new compounds and minerals; and alter the biochemistry of soils (Patrick *et al.* 1996; Ponnampereuma 1972). Soil redox potential plays a major role in the development of pedogenic features including soil colour, and iron depletions and concentrations (Soil Survey Staff 2010), as well as being a good indicator of nutrient availability and mobility of heavy metals (Sigg 2000). Measurements of redox potential are also used to identify aerobic and anaerobic conditions and in the classification of soils forming under aquic conditions (Soil Survey Staff 2010). This information is also used to characterise environmentally sensitive sites such as wetlands (Faulkner and Patrick 1992; Faulkner *et al.* 1989).

In aqueous systems, the bounds of Eh are dictated by the stability of water. In oxidizing systems the oxidation of water, to molecular oxygen and protons, sets the upper

boundary for Eh (Bohn 1971). Since this reaction yields protons, the stability is a function of pH. At the other extreme of reducing conditions in aqueous systems, hydrogen ion reduction to hydrogen gas is the lower stability of the system (Baas Becking *et al.* 1960; Langmuir 1997; Sparks 1995). Thus the stability limits for Eh are bounded by hydrogen and oxygen gas evolution from water.

Redox reactions between oxidants such as atmospheric oxygen and reductants such as sulfide may proceed by chemical reaction, but they are most often accelerated by many orders of magnitude through enzymatic catalysis in living organisms (Joergensen 1982). Because of the complexity of soils, Eh measurements are composed of mixed potentials and redox couples that are rarely at thermodynamic equilibrium (Owens *et al.* 2005). Thus, redox reactions and redox potentials are not uniform throughout the soil matrix and therefore are best used as an indication or relative status of the soil (Bohn 1971).

Redox potential can be measured in soils using an inert electrode, which readily transfers electrons to or from the soil system but does not react with the soil. When the electrode is coupled with a half cell of known potential (reference electrode), a reducing system transfers electrons to the electrode while an oxidising system takes electrons from the electrode (Patrick *et al.* 1996). The electrode acquires a potential equivalent to the system it is subjected to (Bohn 1968).

The most dominant components in soils, which control the final redox potential are unimolecular and ionic species of oxygen, hydrogen, nitrogen, iron, manganese, carbon and sulfur (Bohn 1971; Ponnampereuma *et al.* 1966). The most common and easily reduced components of soil systems are oxygen, followed by nitrogen, manganese, iron, sulfur and carbon, and are electron acceptors in soil redox processes (Rowell 1981). The reaction rates between redox couples are negligible unless cofactors and enzymes are available to catalyse the reactions. They are most commonly supplied by plant roots and soil microbes (Bohn 1968). Organic matter is the strongest reductant in the aqueous system and thus the major reductant in biological respiration (Langmuir 1997).

Oxygen is the preferential electron acceptor in oxygenated soils (Eh values ranging from +400 to +700 mV), where aerobic bacteria out compete anaerobes and the O₂-H₂O redox couple dominates soil redox potential (Meek and Grass 1975). This is because

oxygen is readily available in the atmosphere and can easily diffuse into aerated soils. As soils become waterlogged, the rate of oxygen diffusion decreases and oxygenated air is replaced by water in soil pores. Remaining oxygen is consumed by aerobic and facultative microbes and roots (Rowell 1981). The decrease in oxygen concentration triggers an increase in facultative and anaerobic microbial activity. Once oxygen is depleted in the soil environment, anaerobic bacteria utilise nitrate (NO_3^-) as the next most available electron acceptor, followed by the redox couples; Mn^{4+} - Mn^{2+} , Fe^{3+} - Fe^{2+} , SO_4^{2-} - S^{2-} and CO_2 - CH_4 (Langmuir 1997). With every shift to next electron acceptor, soil redox conditions become more reducing, lowering Eh values.

The reverse occurs when Eh increases during re-oxygenation of soil (Evangelou 1998). In coastal or tidal marshes it is common for the soils to become sufficiently reducing that microbes utilize sulfate as a primary electron acceptor, and are therefore optimal for sulfidization. If a source of reactive Fe is present in the soil where sulfate reduction is occurring, iron sulfide minerals will form (Rabenhorst and James 1992). If a soil is periodically saturated, mottles (reduced spots, depletions and / or concentrations) may develop. These features are indicators of alternating periods of oxidation and reduction (Faulkner and Patrick 1992), during which Fe and Mn are mobilised by reduction and then immobilised in the form of oxides.

Redox potentials in soils are affected by a number of factors (Ponnamperuma 1972; Reddy and DeLaune 2008), such as:

- water table fluctuations (or hydrology) that introduce oxygen to the soil,
- loading of alternate electron acceptors,
- loading of organic matter (electron donor),
- organic matter available in the soil (electron donor),
- microbial biomass (type and size),
- temperature and
- soil pH

***In situ*, continuous field measurements of soil redox potential**

The most common approach for measuring soil redox conditions is to directly measure the potential difference (Eh) between a sensing electrode and a reference electrode

embedded in the soil, using a high-impedance potentiometer (Bartlett and James 1995; Bohn 1968; Patrick *et al.* 1996; Ponnampertuma 1972). Platinum (Pt), gold (Au) and carbon have been used as sensing electrodes but platinum is the preferred material because of its high reduction potential, high electrical conductivity, hardness and rarity in the soil and water environment (Lee *et al.* 2004). Commonly used reference electrodes include: silver - silver chloride (Ag/AgCl/KCl), calomel, and mercury (Hg/Hg₂SO₄) types. Reference electrodes have a known relationship to the standard hydrogen electrode.

A number of practical problems have been highlighted by various workers concerning the reliable construction and application of continuous soil Eh monitoring systems. The main groups of problems highlighted include: (i) poisoning of sensing electrodes, (ii) electrode breakdown and (iii) the heterogeneous nature of soil systems (Devitt *et al.* 1989; Eshel and Banin 2002; Mann and Stolzy 1972; Mansfeldt 2003; Mueller *et al.* 1985; Rabenhorst 2009; Rickman *et al.* 1968; Whitfield 1974).

Despite these practical problems, many workers have reported successful applications of *in situ*, long term redox monitoring in soil, with monitoring times ranging from a few weeks to a few years (Baker 2006; Bochove *et al.* 2002; Childs 1981; Faulkner and Patrick 1992; Fiedler 2000; Fiedler *et al.* 2007; Josselyn *et al.* 1990; Merry *et al.* 2002; Olness *et al.* 1989).

In this study sensing electrodes were constructed using platinum and based on work previously conducted by (Biddle *et al.* 1995) and (Dowley *et al.* 1998). The electrodes were constructed by soldering (using silver solder) a 12 mm length of 1 mm diameter Pt wire to a length of silver plated copper wire. The copper wire was insulated with PTFE (Teflon) for high resistance to UV radiation, oils and acidic and alkaline conditions. The soldered joint was sealed by setting it within a block of epoxy resin, leaving 8 mm of Pt wire exposed. A 1 mL plastic pipette tip was used as a mould for the resin. A 45 cm long, plastic irrigation riser (plastic tube) was threaded over the wire tail and also set into the pipette tip prior to the epoxy curing (Figure 8-1). The pointed pipette tip and sturdy irrigation riser allowed the Pt electrode to be pushed into soft soils with minimal disturbance to the soil.

The set-up was designed to be easily modified to install longer (additional) plastic lengths of tube for deeper penetration of the electrode tip. To simplify field deployment and retrieval of the electrodes, banks of electrodes were placed into one length of PVC tube at designated depth increments (Figure 8-2). An Ionode – Ag/AgCl double junction reference electrode (IJ14) was used as the reference electrode (Figure 8-1). The reference electrode had a potential of 199 mV relative to the standard hydrogen electrode (SHE). Electrodes were tested prior to field installation using Zobell's solution (Nordstrom 1977) and quinhydrone mixture (Owens *et al.* 2005).

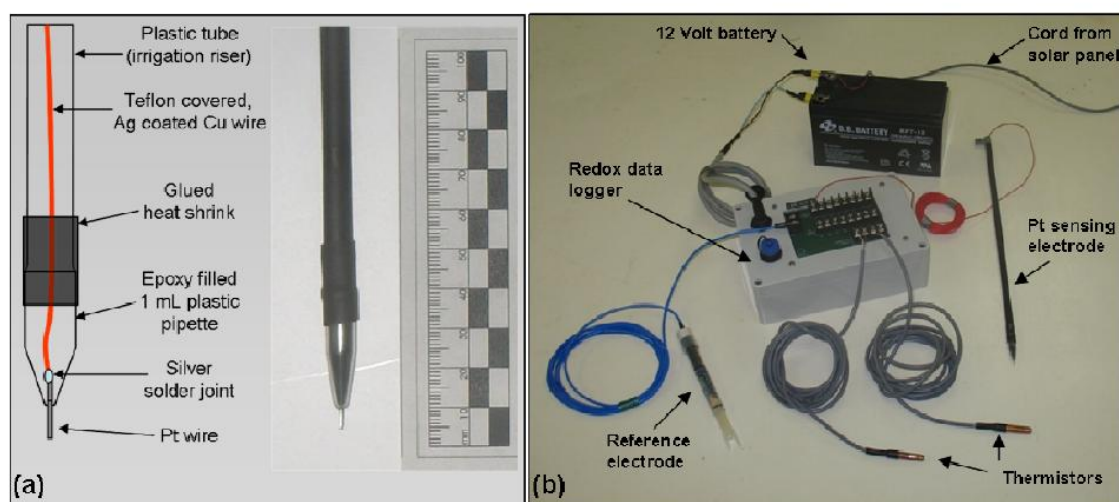


Figure 8-1 (a) photograph and schematic diagram of a Pt electrode. The red copper wire attaches to a data logger. (b) Data logger set up for redox monitoring showing connection to a power supply, Ionode IJ14 (Ag/AgCl) reference electrode, two precision thermistors and one Pt electrode.

Data loggers used to record Eh measurements during this study were based on a prototype developed by (Dowley *et al.* 1998) and Microscan Electronics. The data loggers had 16 sensing electrode channels and one reference electrode channel, as well as two temperature sensing channels (Figure 8-1). They incorporated an ultra high impedance ($> 1 \text{ G ohm}$) voltmeter in series with a $0.1 \mu\text{F}$ shunting capacitor that acted as a low pass, resistive capacitive (RC) filter. The RC filter removed 'noise' from nearby AC sources, such as magnetic fields produced by transmission lines (Dowley *et al.* 1998).

The circuit also incorporated a high speed electronic switch that allowed the potential of the 16 sensing electrode channels to be recorded in series and for the circuit to be closed between readings to limit artificial drift (Dowley *et al.* 1998; Rabenhorst 2009). The

circuit drew less than 10-12 milliamps, ensuring that there was no measurable shift in the potential recorded by the logger from the actual potential at the Pt tip of the sensing electrode (Langmuir 1971).

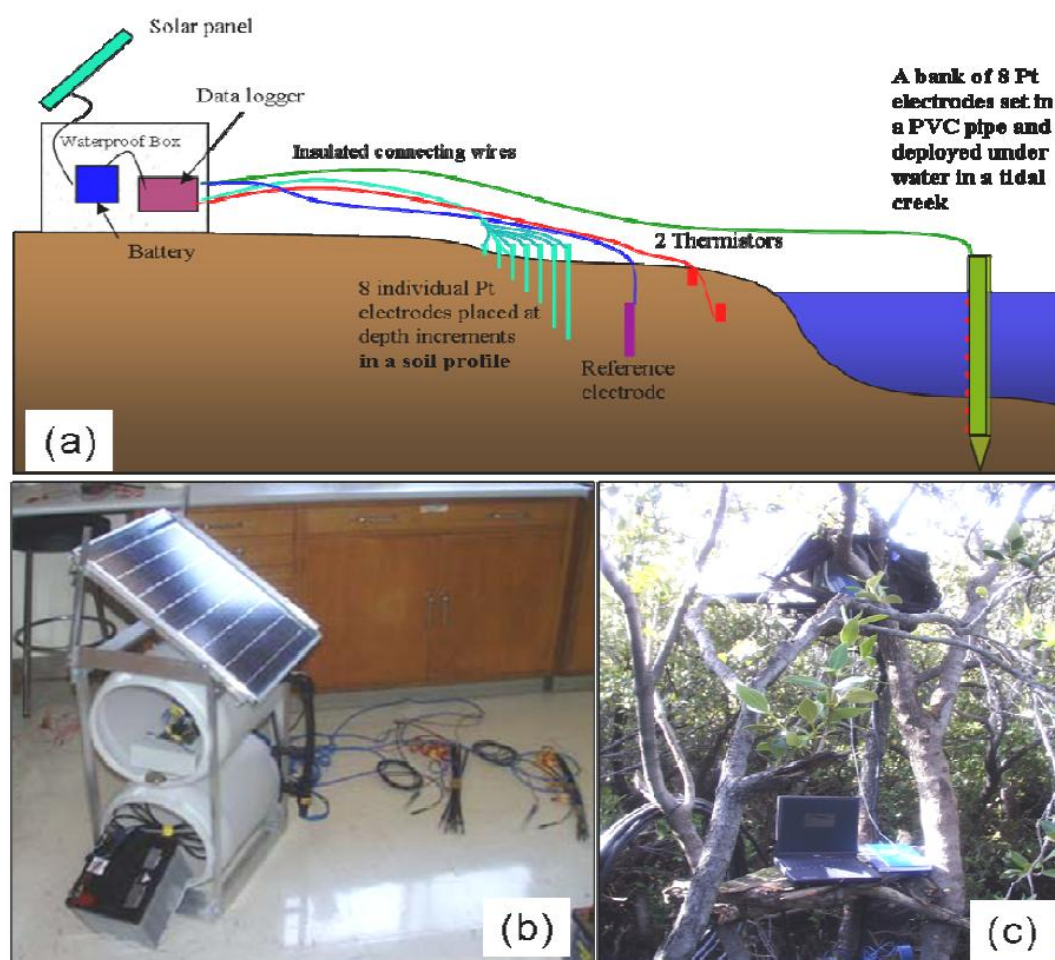


Figure 8-2 (a) Schematic illustration toposequence cross-section showing an example redox data logger system installed in the field for automatic monitoring of redox conditions at the following two locations: (i) 8 depth intervals in a soil profile and (ii) at 8 depth increments through the water column and across the water-sediment interface in a tidal creek. (b) Two data loggers (located in the upper, water tight drum) were connected to a 12 Volt battery (located in the lower drum) that was kept charged by a solar panel. This data logger system was deployed at St Kilda where it was secured in the canopy of a mangrove tree, above the high tide mark (c). Redox data was downloaded to a computer every 2 to 3 months.

8.2. Results and discussion of field redox monitoring

Associations between Eh and the following parameters are discussed in this section: (i) rainfall, (ii) temperature, (iii) depth, (iv) soil morphology, (v) vegetation, (vi) groundwater and (vii) tides. To investigate these associations, redox monitoring systems were installed at representative locations at both Gillman and St Kilda study sites. Five ‘type’ soil profiles were monitored at the St Kilda study site, which were subject to a

range of tidal flooding regimes and had different soil types with associated surface cover / vegetation types. Five ‘type’ soil profiles were also monitored at the Gillman study site. Four profiles were located within Gillman Focus area C, where profiles BG 20 and BG 21 were under tidal influences and profiles BG 28 and BG 22.1 were located in the bunded area that had not received tidal inundation since 1935 due to construction of bund walls to prevent tidal inundation. The fifth soil profile monitored at Gillman (BG 11) was located in the former supratidal area within Focus area A and contrasted with the other monitoring sites as it contained a sandy profile with abundant sulfuric material. Climatic data (air temperature, rainfall and evaporation) were recorded at Torrens Island (BOM site no 23018), about 5 km from St Kilda township and 2 km from the Gillman study site. The climate data was sourced from SILO (Jeffrey *et al.* 2001). Tide heights for the St Kilda field sites were estimated by adding 12 minutes to Port Adelaide (Outer Harbour) tidal predictions (Bureau of Meteorology 2010). The 12 minute delay was imposed following field verification.

Redox conditions measured by a given Pt electrode were representative of only a few cubic millimetres of soil surrounding the electrode tip. For this reason multiple electrodes were installed within the same soil layer at some locations to gain a better understanding of the heterogeneity of the soil and its responses to change. An equally useful method for appreciating this limitation in field redox measurements is to carefully excavate the electrode from the soil, at the end of the monitoring period, to evaluate the morphology of materials in close contact to the sensing tip (Baker 2006). This was done where waterlogging did not prevent it. Furthermore, interpretations of redox data are best based on one or two elements that are abundant in soils and react quickly to changes in redox potential. The Eh measured in natural environments is restricted to a relatively defined Eh-pH range (Figure 8-3). Eh values measured in the natural environment should only be regarded as qualitative due to reliability problems created by mixed potentials and reaction kinetics, the performance of Pt electrode and thermodynamic behaviour of redox monitoring equipment (Baas Becking *et al.* 1960; Sigg 2000; Whitfield 1974). Therefore redox values in this study will be described according to redox “classes”, shown in Figure 8-3, that range from (at pH 7); **(i)** oxidising (>400 mV; O₂ predominant), **(ii)** weakly reducing (400 to 200 mV; O₂, nitrate and Mn (III, IV) reduced), **(iii)** moderately reducing (200 to -100 mV; iron (III) reduced), and **(iv)** strongly reducing (< -100 mV; sulfate and carbon dioxide reduced)

conditions, (adapted from Krauskopf (1967) and Zhi-Guang (1985). Mean soil field pH (pH_f) values were used to assign Eh measurements to redox classes in the following discussion, as pH was not monitored continuously.

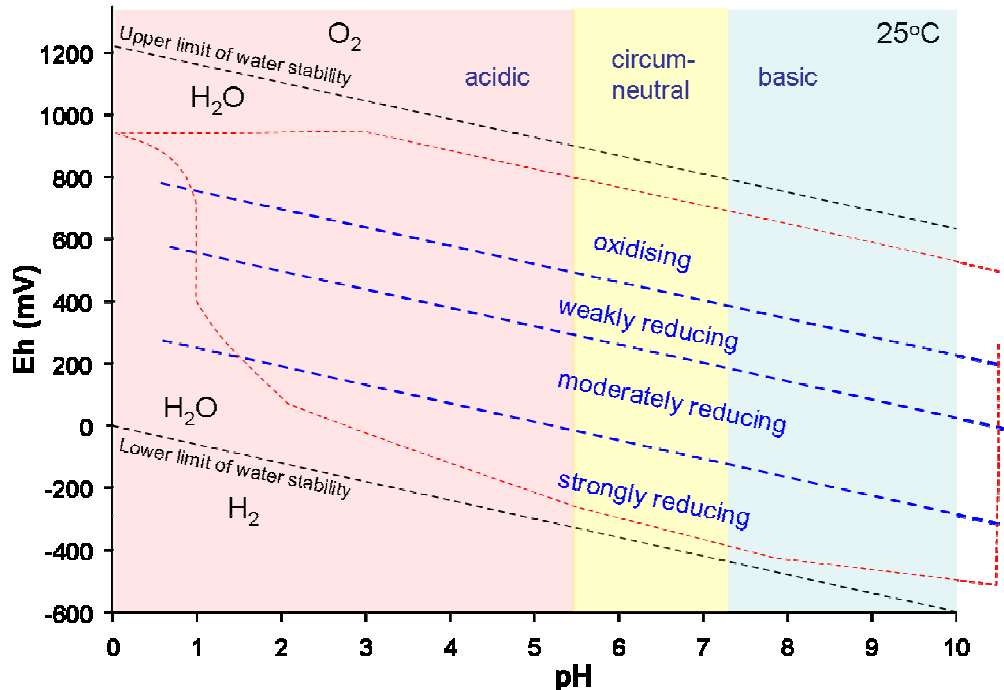
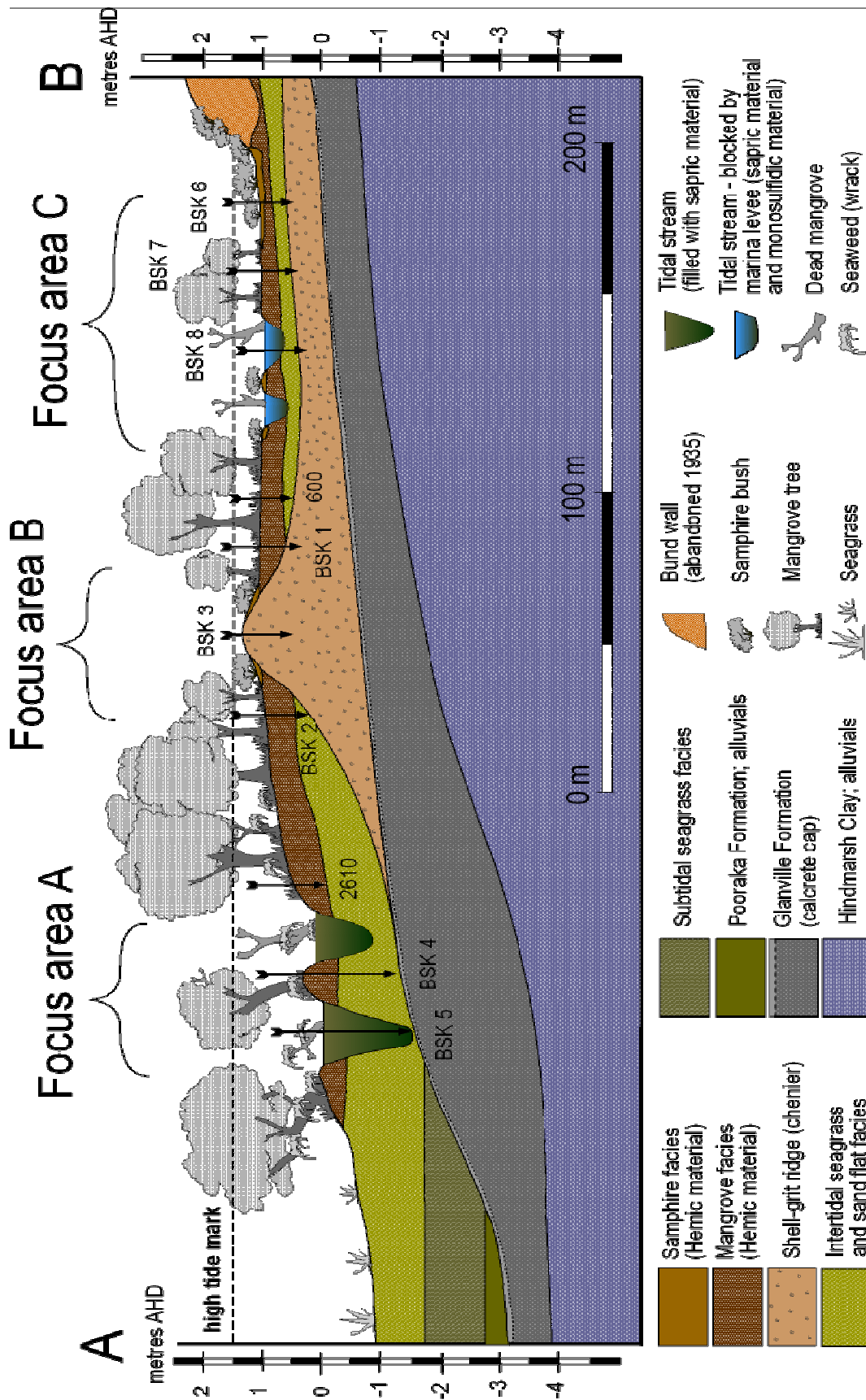


Figure 8-3 The Eh-pH ranges found in soil environments at 25°C and one atmosphere pressure, showing the following redox “classes”, divided by the blue dotted lines: (i) acidic-oxidising, (ii) acidic-reducing, (iii) basic-oxidising, and (iv) basic-reducing (adapted from Krauskopf (1967) and Zhi-Guang (1985)). The red dotted line shows the limits of the natural environment in terms of pH and oxidation-reduction potentials, described by Baas Becking *et al.* (1960).

8.2.1. Tidal influences on redox conditions

At St Kilda, soil profiles were selected to: (i) characterise the soil redox states or classes (Figure 8-3) within different map units in an undisturbed tidal environment, and (ii) gauge what effect the strength of tidal flushing has on soil redox potentials. Two soil profiles were monitored within St Kilda Focus area A, which is located near the seaward extent of the mangrove woodland and is subject to strong tidal flushing (Figure 8-4). Three soil profiles were monitored at St Kilda Focus area C, which is located near the landward extent of tidal influence and receives less tidal exchange (Figure 8-4). Focus area B was not monitored continuously and is therefore not discussed in this Chapter.



Strong tidal flows - St Kilda Focus area A

Soil profiles BSK 4 and BSK 5 are approximately 3 m apart and located about 50 m from the seaward fringe of the mangrove forest (Figure 8-4) and were subjected to strong tidal forces and fluctuations (i.e. 1.2 to 0 m). Profile BSK 4 was located on a slight rise at the base of mature mangrove trees (Figure 8-5) and classifies as a Sapric, Histic-Sulfidic, Intertidal Hydrosol (Isbell 2002). Profile BSK 5 was located in a water filled tidal creek depression and classifies as a Sapric, Histic, Intertidal Hydrosol (Isbell 2002). The tidal creek was clogged-up with ‘wrack’ consisting of decaying organic matter (predominantly seagrass, mangrove leaves and sea lettuce) (Figure 8-5). The surface of profile BSK 4 was approximately 40 cm higher than the surface of profile BSK 5. Redox conditions were recorded at 8 depth increments within each of the profiles (Figure 8-6).

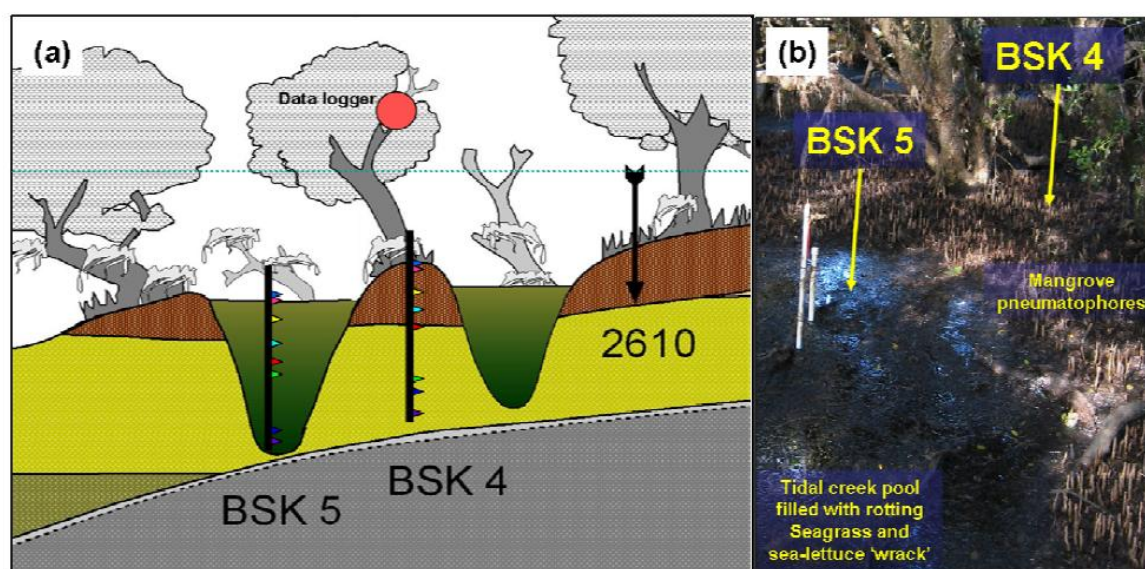


Figure 8-5 (a) schematic cross-section of St Kilda Focus area A showing the location and relative depth of Pt electrodes and redox data logger. The black lines indicate the location soil profiles and the coloured marks represent platinum electrode tips set at specific depth intervals, with colours being applicable to the Eh vs time graphs shown in the figure below. (b) photograph showing redox monitoring sites and equipment installed at the St Kilda Focus area A.

Redox potentials and soil temperature measurements (measured at 10 cm depth) were recorded at 15 minute intervals continuously for a period of 2 months, between the 14th January 2004 and the 10th of March 2004. A two month period was considered sufficient to gauge the effects strong tidal movements will have on soil redox. Barker Inlet and St Vincent Gulf experience daily tidal movements that vary in amplitude from 2.5 m to 0 m, where a tidal cycle is skipped completely (Figure 8-6). The skipping of a tidal cycle is called a ‘dodge tide’ and it occurs approximately once every two weeks.

This unusual tidal cycle made distinguishing the effects of tidal movement apparent from the diurnal effects of temperature and evapotranspiration.

The soil Eh took 4 to 6 days to stabilize following installation of the Pt electrodes within both profiles. Redox measurements revealed values ranging from circum-neutral-oxidising to circum-neutral-strongly reducing (550 mV to – 260 mV) and was generally more reducing with increasing depth (Figure 8-6). Fluctuations in redox potential (of up to 600 mV) were greatest nearer the sediment surface and were related to tidal flooding cycles. For profile BSK 4 (mangrove soil), daily fluctuations in redox were of low amplitude compared to BSK 5 (tidal creek sediment). Near surface Pt electrodes in both profiles became more reducing during tidal flooding and more oxidising as tidal waters receded. Smaller amplitude and longer period fluctuations in soil redox measurements occurred when tidal flushing was minimal and especially during the ‘dodge’ tide. Extended exposure of soils during the dodge tide caused near surface soils to become more oxidised, while deeper soil layers became more reduced. This pattern is evident for the upper 3 Pt electrodes located in the top 30 cm of profile BSK 4, and for the upper 4 Pt electrodes, located in the top 40 cm of profile BSK 5 (Figure 8-6). Soil redox conditions measured in deeper soil layers may become more reduced during dodge tides due to less tidal movement of oxygenated water through the soil profiles (Figure 8-6). Eh measured by the highest placed Pt electrode (+ 2 cm) in soil profile BSK 5 reacted inversely to the other near surface electrodes (blue trace of Figure 8-6). This was because it was located 2 cm above the lowest water mark and was completely exposed to air for the majority of the tidal cycle. When the tide re-submerged this Pt electrode, connectivity was again restored and the electrode measured the redox condition of surface waters (Figure 8-6). A relationship between soil Eh and temperature or rainfall (Figure 8-7) was not evident from these measurements due to the dominance of tidal responses.

Relatively elevated soil redox conditions (circum-neutral-weakly reducing to circum-neutral-moderately reducing), measured by the Pt electrodes placed at 65 cm, 90 cm and 120 cm depths in soil profile BSK 4 (Figure 8-8), may be explained by the abundance of mangrove pneumatophores, which are regularly spaced about 15-30 cm apart and can introduce oxygen to subsurface soils (Scholander *et al.* 1955). A 2-3 m tall *Avicennia* mangrove tree has well over 10,000 pneumatophores (Tomlinson 1986). No live

mangrove pneumatophores were observed in soil profile BSK 5. Eh measurements below 120 cm in profile BSK 4 and below 40 cm in profile BSK 5 remained circum-neutral-strongly reducing for the majority of the monitoring period (Figure 8-8).

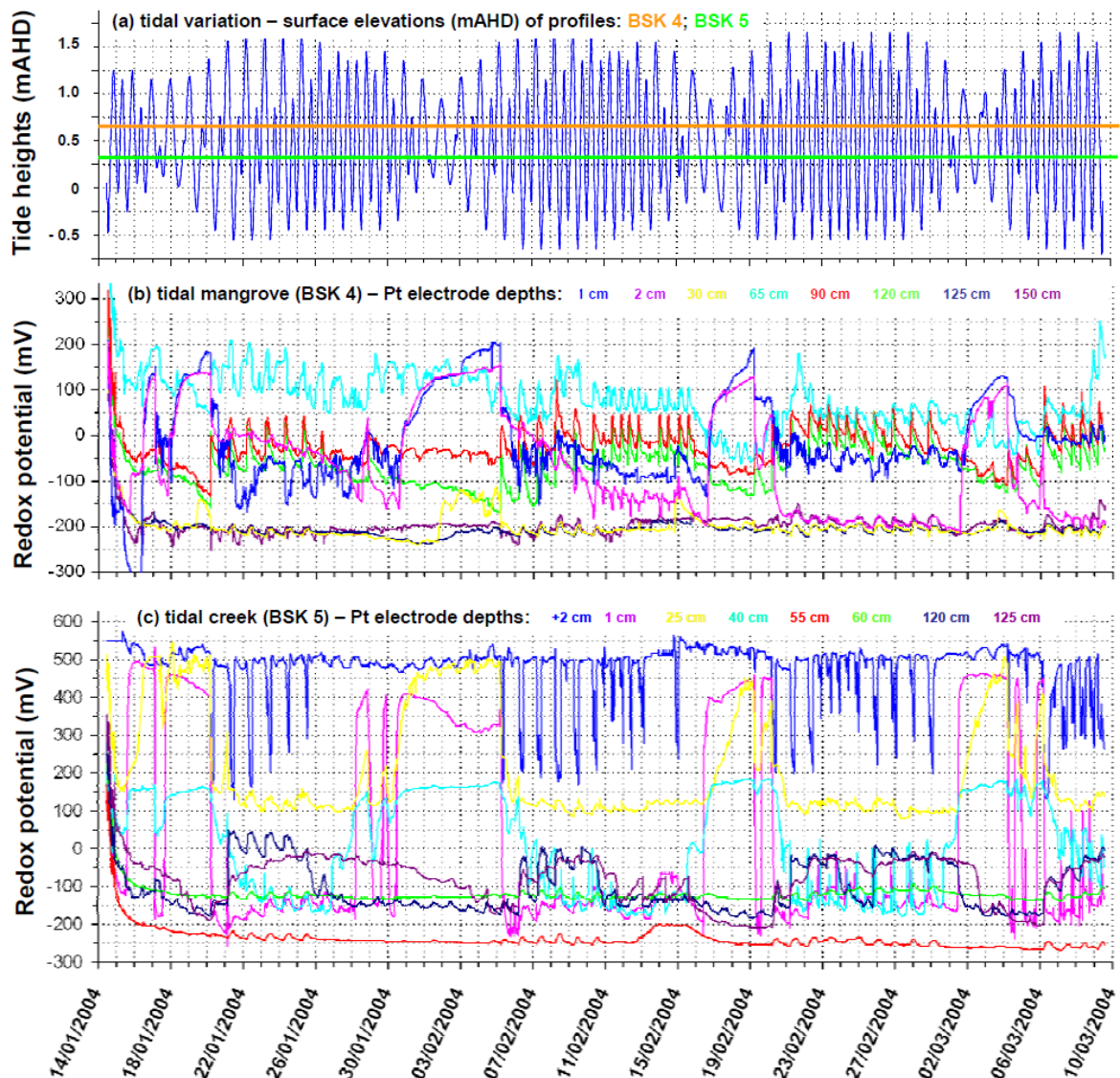


Figure 8-6 Intertidal soils with strong tidal flushing at St Kilda Focus area A. Time (over two months) versus measurements of: (a) tidal fluctuations showing the surface elevation (0.3 m AHD) for soil profile (BSK 5) in an eroded tidal creek and the surface elevation (0.5 m AHD) for soil profile (BSK 4) within intertidal mangrove woodland. Note that four dodge tides occurred during the monitoring period. Soil redox potentials for 8 depth intervals measured in profile BSK 5 (b) and eight depth intervals measured in profile BSK 4 (c).

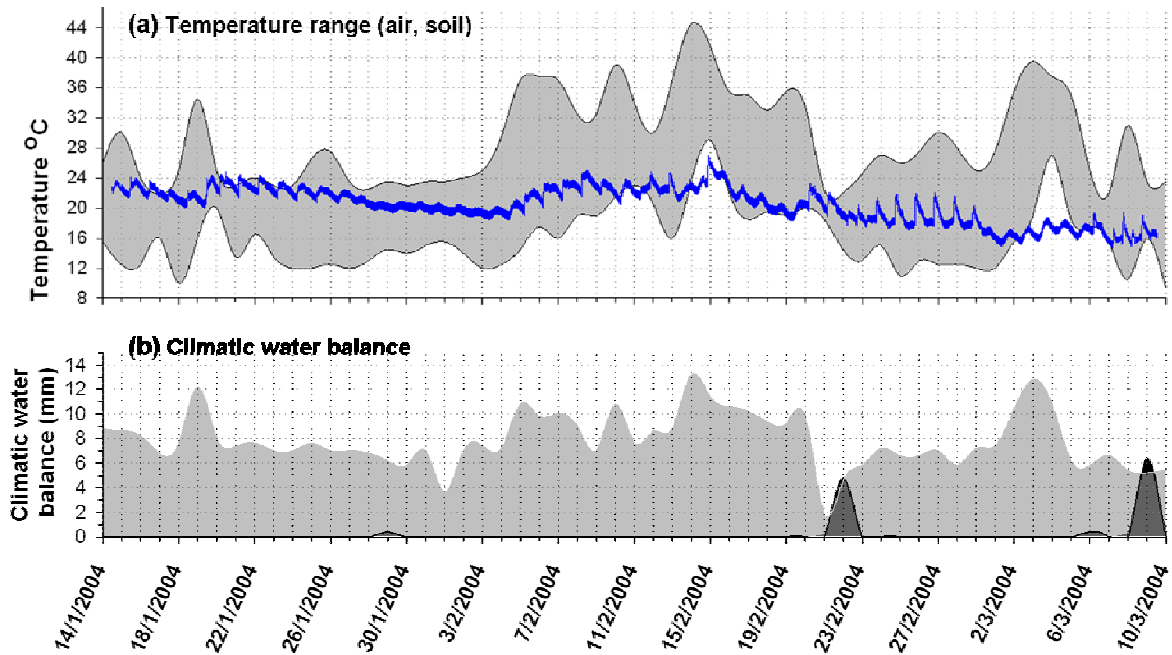


Figure 8-7 (a) range of daily air temperature (light grey shaded area) and soil temperature at 10 cm depth (blue line), (b) daily climatic water balance indicating rainfall (dark grey) and evaporation (light grey).

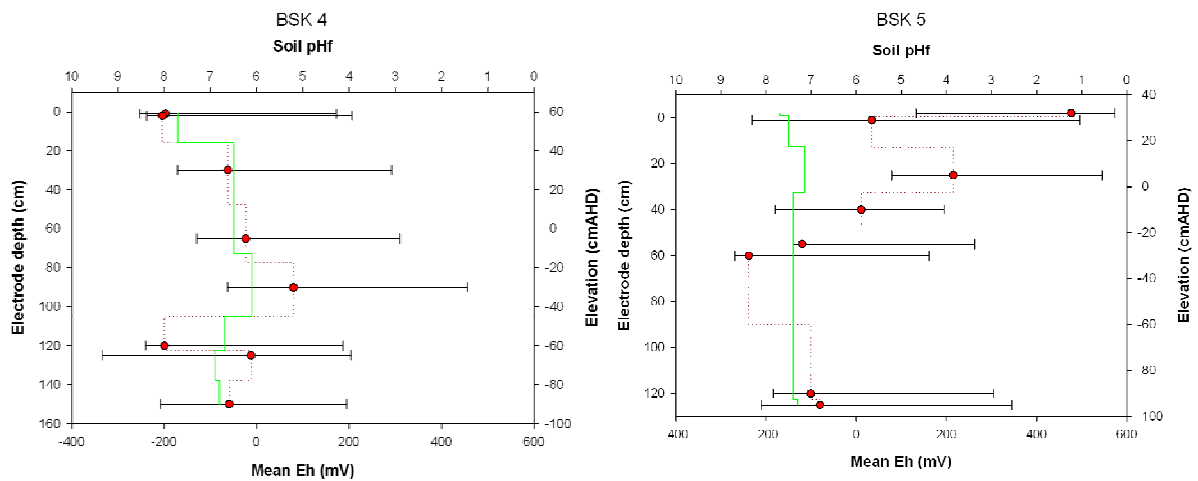


Figure 8-8 Plot of mean redox (red dots) measurement (mV) versus depth (cm) for soil profiles BSK 4 and BSK 5. Eh (mV SHE) is displayed on the bottom axis, with error bars showing the range of measurements either side of the mean. Depth is shown in centimetres from the surface (left axis) and as AHD (right axis). The horizontal blue dotted line indicates surface water height at low tide. The green lines show mean field measured soil pH (pHf).

Moderate tidal flows – St Kilda Focus area C

Soil profiles BSK 6, BSK 7 and BSK 8 are located about 280 m from the seaward fringe of the mangrove forest (Figure 8-4) and are subjected to considerably lower tidal forces than soils within Focus area A. Profile BSK 6 is located on a slightly elevated position (1.2 m AHD) covered by short samphire vegetation. Profile BSK 7 is located at a slightly lower elevation (about 30 cm) amongst young mangrove trees, near the bank of a permanent tidal creek. Profile BSK 8 is a subaqueous soil profile located within the tidal creek and is covered by 40 cm of water during low tide (Figure 8-9). Soil profiles BSK 6 and BSK 7 both classify as Hemic, Histic-Sulfidic, Intertidal Hydrosols (Isbell 2002), while profile BSK 8 classifies as a Sapric, Epicalcareous, Intertidal Hydrosol (Isbell 2002).

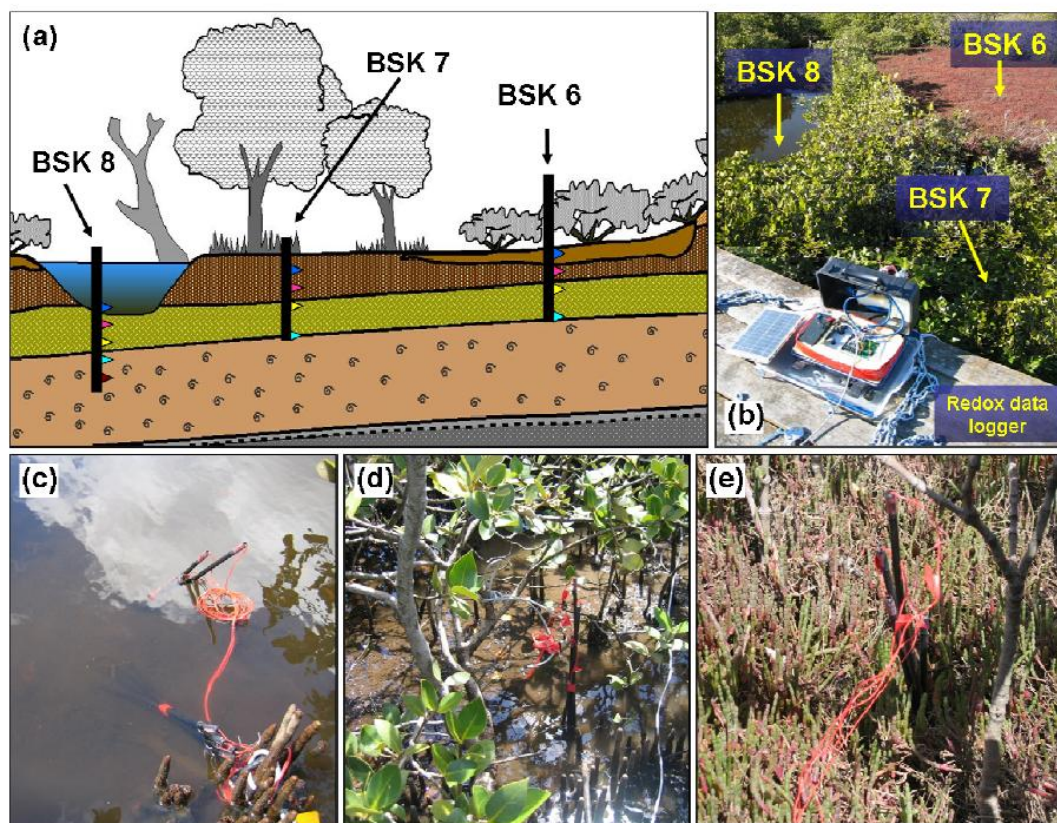


Figure 8-9 (a) schematic cross-section of St Kilda Focus area C showing the location of soil profiles and position of and relative depth of each Pt electrodes within the profiles. The colours representing the platinum electrode tips are applicable to the Eh vs time graphs shown in the figure below. (b) photograph showing the very portable redox data logger and location of profiles. (c), (d) and (e) are photographs of Pt electrodes installed at sites (c) BSK 8, (d) BSK 7 and (e) BSK 6.

Tidal flooding of sub-aerial sites generally occurred daily, except during dodge tides when minimal tidal movement occurred. The surface of profiles BSK 6 and BSK 7 are exposed for up to 4 consecutive days during the dodge tide period (Figure 8-10). Redox conditions were recorded at 4 depths within profiles BSK 6 and BSK 7, and at 5 depths

in profile BSK 8 (Figure 8-10). Redox and soil temperature (measured at 10 cm and 40 cm depths) measurements were recorded at hourly intervals for a period of 20 days, between the 9th March and 29th of March 2004 (Figure 8-11). This period covered one dodge tide event to gauge the effects tidal flooding on soil redox conditions. Redox potentials took between 2 and 3 days to stabilize following installation of the Pt electrodes. BSK 6 is covered by samphire vegetation and Eh measurements ranges from circum-neutral-strongly reducing (-50 mV) at 10 cm depth to circum-neutral-strongly reducing (-400 mV) at 20 cm depth. Redox potentials were not related to depth in any of the 3 soil profiles, with the deepest Pt electrodes often measuring relatively high Eh values. This is likely due to differences in soil layer morphology because the lower electrodes at all 3 sites were placed into a buried shell grit layer (Figure 8-9). Fluctuations in Eh measurements were evident in all soil profiles and were synchronised with tidal oscillations. These regular fluctuations were recorded by Pt electrodes placed at 10, 20 and 40 cm and varied between 50 to 150 mV. The near surface Pt electrode (5 cm) in profile BSK 6 consistently measured basic-strongly reducing conditions (-240 mV) with only minor diurnal fluctuations (Figure 8-10). It is surprising that near surface electrodes did not become more oxidising during low tide or during the dodge tide when the surface layer was not inundated for about 4 consecutive days. This may have been due to the high clay content of the near surface soils causing wet to pool and stay wet (Figure 8-9). The dodge tide period appears to have caused a slight rise in Eh at the 10 cm electrode and a slight decrease in Eh at the 20 and 30 cm electrodes. The lack of tidal movement during the dodge tide allowed redox conditions to become more oxidising and stable within the lower and more porous peaty soil layers, within soil profile BSK 6 (Figure 8-10).

Soil profile BSK 7 is covered by mangrove vegetation and is inundated for slightly longer during each tidal cycle than profile BSK 6 due to its lower elevation (Figure 8-9 and Figure 8-10). Redox potential measurements in profile BSK 7 were circum-neutral-strongly reducing to basic-strongly reducing at (Eh ranging from -115 mV at 5cm depth to -205 mV at 20 cm depth). Fluctuations in Eh measurements corresponded to tidal movements and were greatest at the 5 cm and 30 cm electrodes. The regular fluctuations in Eh measured by the 30 cm deep electrode may indicate that tides strongly influence ground water movement through the course shell grit layers. This condition was recorded within the shell grit layer at all three soil profiles (Figure 8-10 and Figure

8-12). The Pt electrodes at 10 and 20 cm depths in profile BSK 7 consistently measured circum-neutral-strongly reducing and basic-strongly reducing conditions respectively (< -180 mV) with only very minor cyclic fluctuations.

The variability of redox conditions was measured by 4 replicate electrodes placed within the top 2 cm sediment in subaqueous profile BSK 8 (Figure 8-9). The replicate electrodes all recorded circum-neutral-strongly reducing conditions, although with large fluctuations in Eh, ranging between -100 mV and -450 mV (Figure 8-10). Although this variation was statistically large, the redox measurements over time showed reasonably consistent responses to tidal variation, particularly when considering the Pt electrodes were placed in a soft, organic rich 'peat' (containing 0.19% AVS). The mean Eh value, of the 4 replicates, was used to represent the 2 cm depth redox data for soil profile BSK 8 in Figure 8-10 and Figure 8-12. Redox conditions at 10 and 20 cm depths in profile BSK 8 were similar (strongly reducing) to that measured at 2 cm, but were much less variable, which is likely due to the soil being more coherent, with higher clay content. More oxidising conditions were, surprisingly, measured deeper in the soil profile, at 30 cm and 40 cm depths, and ranged from basic-moderately reducing conditions to basic-weakly reducing conditions (Figure 8-10 and Figure 8-12). The relatively high Eh values measured at these depths may be due to the Pt electrodes being placed within a coarse shell grit layer. Cyclic fluctuations measured at 10 and 20 cm depths in profile BSK 8 were minor, being similar to the same depth intervals in profile BSK 7 (Figure 8-10). Cyclic fluctuations were much more pronounced at the 30 and 40 cm depth intervals. The dodge tide period appears to have caused only a slight stabilization in Eh conditions at the 30 cm electrode and a slight decrease in Eh at the 2 and 40 cm electrodes. It was not possible to associate Eh trends to variations in temperature or rainfall events at this location due to the dominance of tidal influences (Figure 8-11).

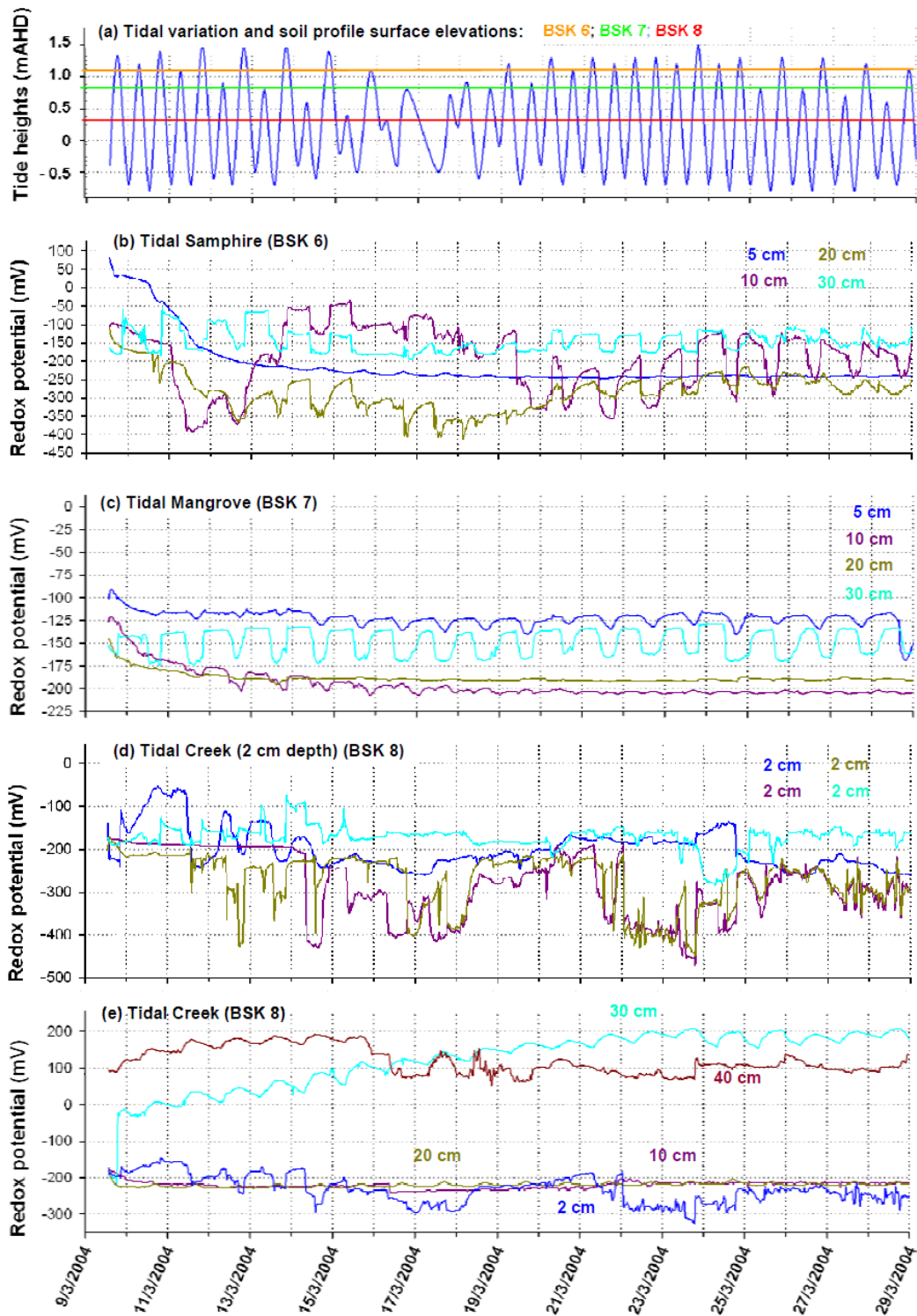


Figure 8-10 (a) tidal fluctuations and surface elevations of 3 intertidal soils profiles with small tidal influence at St Kilda Focus area C. Time (20 days) versus measurement of: (b) soil redox potentials for 4 depth intervals measured in profile BSK 6 covered by samphire vegetation, (c) BSK 7 (four electrodes) covered by mangrove vegetation and (e) 5 electrode depths within profile BSK 8, a subaqueous soil located in a tidal creek. (d) variability in redox conditions within the 0-2 cm depth increment of subaqueous profile BSK 8.

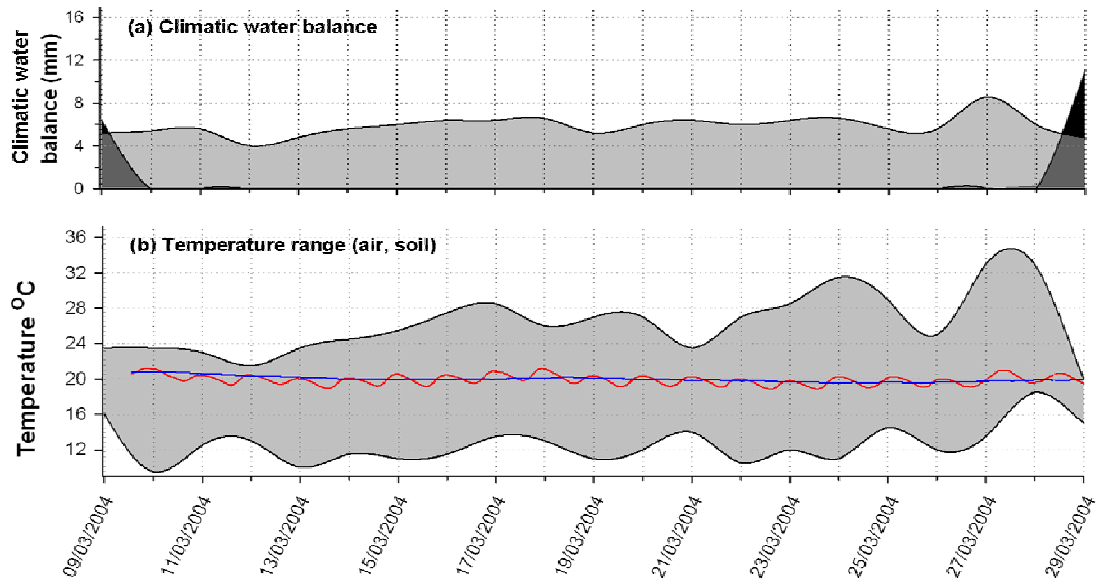


Figure 8-11 (a) daily climatic water balance indicating rainfall (dark grey and black) and evaporation (light grey). (b) range of daily air temperature (light grey area), soil temperature at 10 cm depth (red line) and 40 cm depth (blue line).

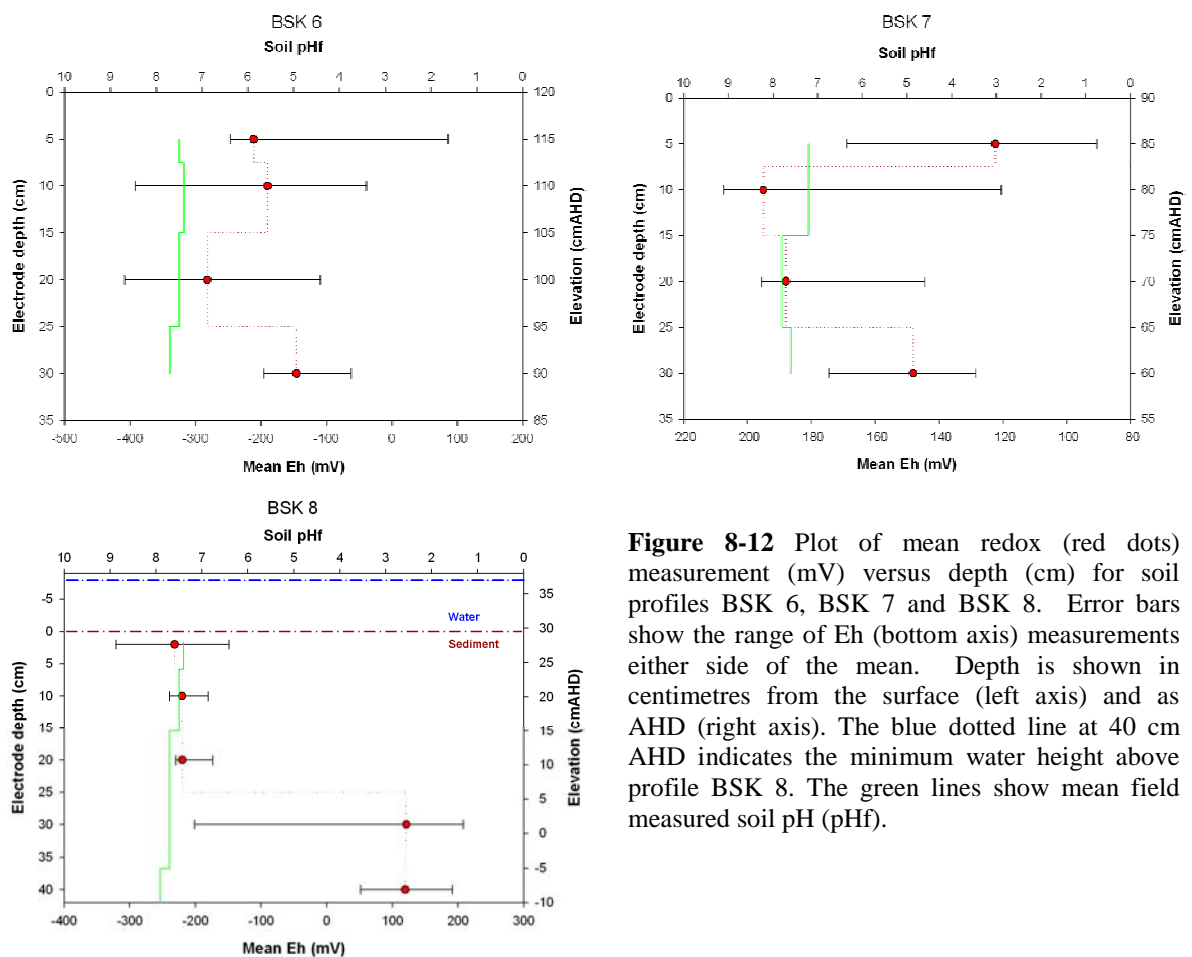


Figure 8-12 Plot of mean redox (red dots) measurement (mV) versus depth (cm) for soil profiles BSK 6, BSK 7 and BSK 8. Error bars show the range of Eh (bottom axis) measurements either side of the mean. Depth is shown in centimetres from the surface (left axis) and as AHD (right axis). The blue dotted line at 40 cm AHD indicates the minimum water height above profile BSK 8. The green lines show mean field measured soil pH (pHf).

Intertidal soils at Gillman, Focus area C

Soil profiles BG 20 and BG 21 were located about 250 m from North Arm Creek within the intertidal zone at Gillman, on the northern side of the bund wall (Figure 8-13). Soil profile BG 20 was covered by thick samphire vegetation and subjected to small tidal influences due to its slightly elevated position (1.6 m AHD). Profile BG 21 was located at a slightly lower elevation (1.2 m AHD) amongst dense mangrove trees. Soil profiles BG 20 and BG 21 were both classified as Hemic, Sulfidic, Intertidal Hydrosols (Isbell 2002). Profile BG 20 was generally flooded once a day but only for short periods due to its elevation near the upper tidal extent. During a period of small amplitude tides, profile BG 20 was exposed for 6 consecutive days (Figure 8-14). The surface of profile BG 21 was submerged by tides almost twice as often as profile BG 20 and was only exposed for 4 consecutive days during the same period, between the 15th and 19th of March (Figure 8-14). Redox conditions were recorded at 4 depths within profiles BG 20 and BG 21 (Figure 8-14 and Figure 8-16). Redox and soil temperature (at 20 cm) measurements were recorded at hourly intervals for a 1 month period, from the 20th September to 24th of October 2002 (Figure 8-15).

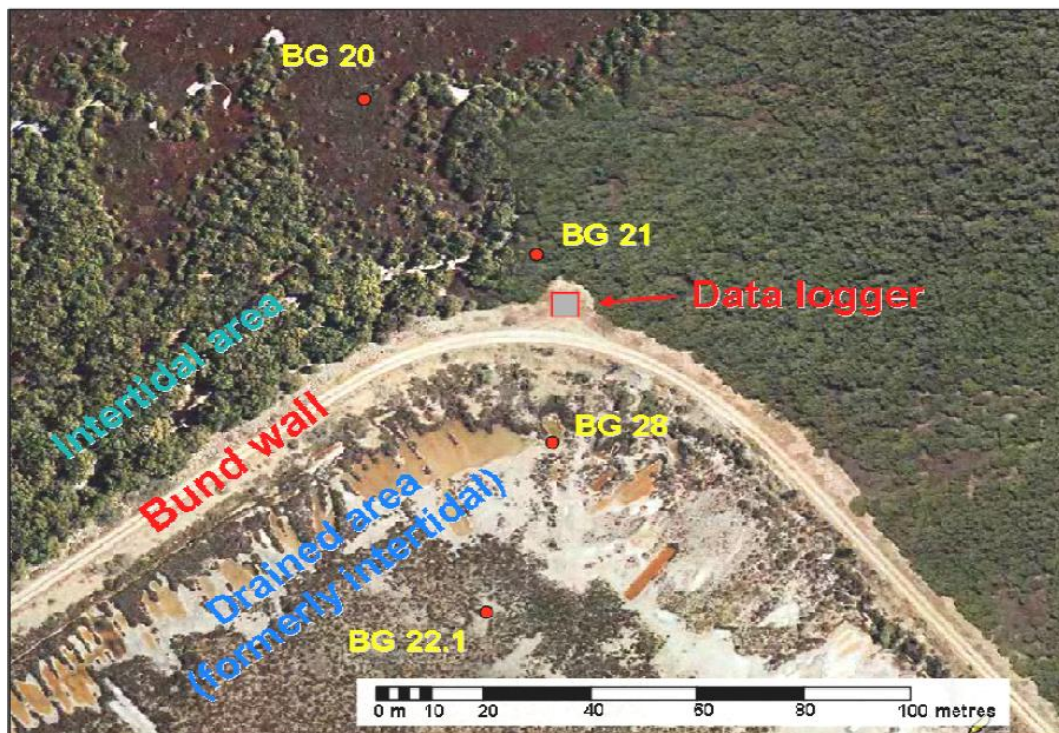


Figure 8-13 Aerial photograph of Gillman Focus area C. Soil profiles BG 20 and BG 21 are located in the undisturbed intertidal zone. Soil profiles BG 28 and BG 22.1 are located behind a bund wall that was constructed in 1935. The bund wall excluded tidal influences to this former intertidal zone. North Arm Creek is located about 600 m to the north of profile BG 21.

Profile BG 20 is covered by samphire vegetation and Eh measurements ranged from circum-neutral-moderately reducing to circum-neutral-strongly reducing (Figure 8-14 and Figure 8-16). Redox potentials took between 3 and 4 days to stabilize following installation of the Pt electrodes. Redox potentials initially decreased with increasing depth, as did the size of fluctuations that occurred. Fluctuations in redox measurements were generally synchronous with the tidal cycle and were largest in the near surface electrodes (with a range of about 300 mV). Eh measured at 5 cm depth were more oxidising (up to 150 mV) during periods of exposure and became more reducing (< -150 mV) following subsequent tidal flooding (Figure 8-14). The deepest Pt electrode (at 125 cm) in profile BG 20 measured circum-neutral-strongly reducing conditions that consistently declined over time (from -140 mV to -180 mV during the monitoring period). During the first dodge tide period the surface of profile BG 20 was not flooded for 6 consecutive days, where exposure caused Eh measurements to increase and stabilize slightly. Redox potentials dropped slightly at 45 cm and stabilized at 85 cm, during the first dodge tide period, with no response observed at 125 cm. This contrasts with the redox conditions following the second dodge tide period where the near surface soils became more reducing (measured at the 5 cm Pt electrode) and more oxidising at the 85 cm electrode (Figure 8-14). This may have been a response to warmer air temperatures causing increased microbial activity, and decreasing the Eh at the surface. Temperatures above 12-14°C degrees are also likely to increase botanical respiration, introducing more oxygen to soils.

Soil profile BG 21 is covered by mangrove vegetation and is inundated for slightly longer periods during each tidal cycle than profile BG 20 due to its lower elevation (Figure 8-14 and Figure 8-16). Redox potentials took between 4 and 5 days to stabilize following installation of the Pt electrodes. Once stabilised, redox measurements were circum-neutral-strongly reducing at all electrodes (ranging from -180 mV at 10 cm depth to -350 mV at 20 cm depth). Eh measured at all electrodes gradually rose during the course of the 1 month monitoring period to circum-neutral-moderately reducing, ranging between 150 mV at 20 cm to -10 mV at 5 cm (Figure 8-14 and Figure 8-16).

Fluctuations in Eh measurements were very consistent with tidal movements and were similar in magnitude (about 150 mV) at all four depth electrodes. The similarities between redox measurements are likely due to the close depth intervals, within similar

clayey peat soil material. Under stable tidal conditions, during the dudge tide period, soil redox conditions within profile BG 21 became more stable (Figure 8-14). Larger amplitude tidal fluctuations caused larger fluctuations in soil redox measurements.

Four moderate rainfall events occurred during the monitoring period (on the 25th and 28th of September and 8th and 23rd of October) but a response in redox potentials was not evident at either of the soil profiles, due to frequent tidal flooding (Figure 8-14 and Figure 8-15). A correlation between rainfall and Eh measured in tidal soils would be small compared to tidal influences and could attributed to longer flooding periods caused by storm tides during the rain events (longer than that predicted by the published tidal data).