Coastal acid sulfate soil processes in Barker Inlet, South Australia

Doctor of Philosophy

The University of Adelaide

School of Earth and Environmental Sciences

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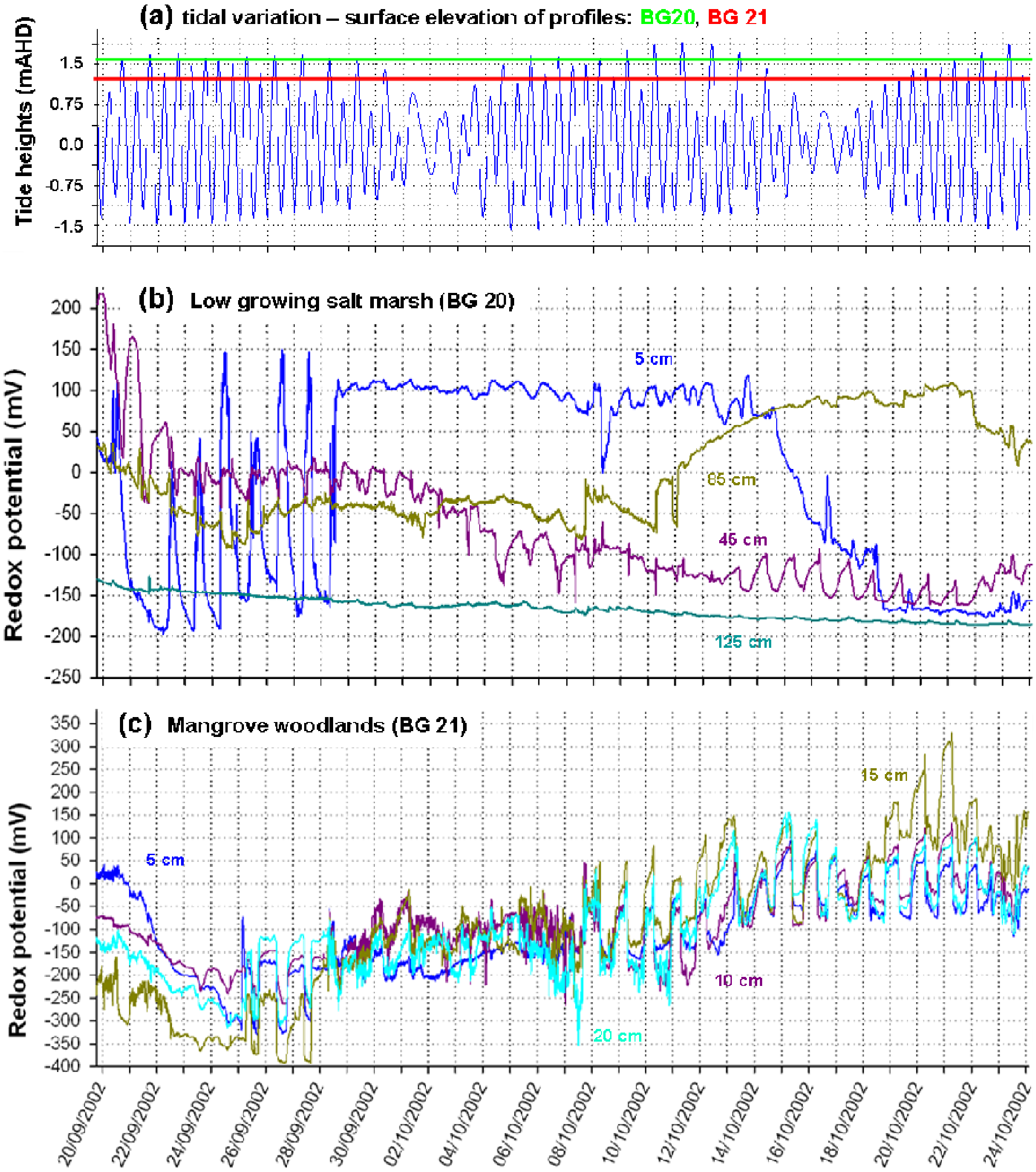


Figure 8-14 Intertidal soils, Gillman Focus area C. (a) tidal fluctuations showing the surface elevation (1.6 m AHD) of the intertidal samphire soil profile (BG 20) and the surface elevation (1.2 m AHD) of intertidal mangrove soil profile (BG 21). Soil redox potentials for 4 depth intervals measured in profiles: (b) BG 20 (5 cm (blue), 45 cm (purple), 85 cm (green) and 125 cm (cyan)), and (c) 4 depths measured in profile BG 21 (5 cm (blue), 10 cm (purple), 15 cm (green) and 20 cm (cyan)).

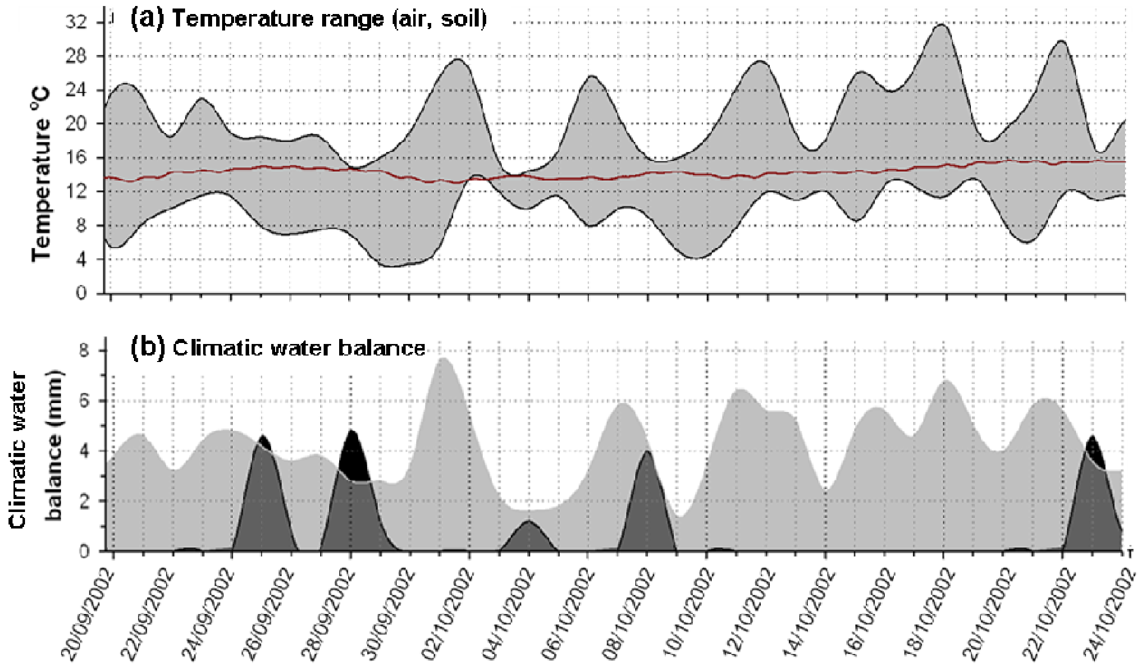


Figure 8-15 Time versus measurements of: (a) air temperature range (light grey shaded area) and soil temperature recorded at 20 cm depth in soil profile BG 21. (b) water balance showing evaporation potential (light grey shaded area) and rainfall (dark grey and black areas).

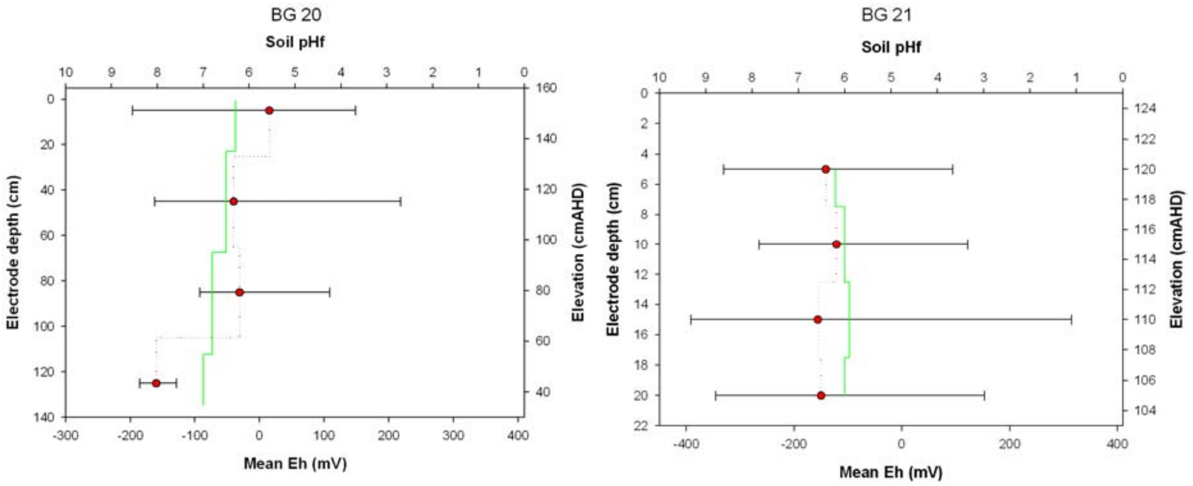


Figure 8-16 Plot of mean redox (red dots) measurement (mV) versus depth (cm) for soil profiles BG20 and BG 21. Error bars show the range of Eh (bottom axis) measurements either side of the mean. Depth is shown in centimetres from the surface (left axis) and as AHD (right axis). The green lines show mean field measured soil pH (pHf).

8.2.2. Redox conditions in non-tidal areas

Low lying, non-tidal soils at Gillman, Focus area C

Soil profiles BG 28 and BG 22.1 were located in a former intertidal area on the southern side of the bund wall at Gillman, Focus area C (Figure 8-13). Soil profile BG 28 was located 20 m south of the bund wall in a slight depression (0.6 m AHD) that was excavated during construction of the bund wall and was covered by a 1-2 mm thick benthic (algal / microbial) mat and salt scalded mud flats. Profile BG 22.1 was located about 50 m south of the bund wall on a slightly elevated (1.2 m AHD) area that was predominantly covered by salt scalded mud flat with sparse stunted samphire vegetation. Soil profile BG 28 was classified as an Epicalcareous, Hypersalic Hydrosol (Isbell 2002). Profile BG 22.1 classified as a Haplic, Hypersalic Hydrosol (Isbell 2002). Redox conditions were recorded at 4 depth increments (5 cm, 45 cm, 85 cm and 125 cm) within profiles BG 28 and BG 22.1 (Figure 8-17 and Figure 8-18).

Soil temperature (at 40 cm depth) was recorded at hourly intervals for a 1 month period, between the 20th September 2002 and the 24th October 2002 (Figure 8-17). As expected, soil profile BG 28 had a constant water table depth of 10 cm and soil profile BG 22.1 had a constant water table depth of 30 cm during the monitoring period, because of minimal rain input and a lack of tidal influence. Profile BG 22.1 was located 50 m north of, and had a very similar morphology to profile BG 22 described previously, although less samphire vegetation covered the surface. Redox potentials took between 3 and 7 days to stabilize at both profiles following installation of Pt electrodes and were then relatively constant during the monitoring period. The deeper electrodes (e.g. at 125 cm) may have taken longer to stabilize due to the oxygen introduced with placement taking longer to be remove because of slower reaction rates at depth (possibly due to cooler, clay soils with little organic matter content).

Near surface Eh measurements in profile BG 28 were basic-moderately reducing and ranged from 175 mV to 125 mV. Eh measured circum-neutral-moderately reducing at 45 cm and 85 cm electrodes and declined gradually from about 75 mV to –50 mV during the monitoring period. Eh measured at 125 cm depth was basic-strongly reducing throughout the monitoring period and ranged from -180 mV to -205 mV (Figure 8-17 and Figure 8-18).

Fluctuations in Eh were minor compared to the intertidal soil profiles described previously. Fluctuations of up to 50 mV were measured by the upper two electrodes (5 and 45 cm) following rainfall events (Figure 8-17). The fluctuations were likely a response to strong winds moving the pole in which the electrodes were implanted rather than to an increase in soil moisture, because the response was always immediate and deep electrodes in profile BG 22.1 were also affected. This response to strong winds was observed at other exposed locations where Pt electrodes were installed into a single, long PVC pole that extended above the ground or water surface (e.g. soil profiles BG 15 and BG P 5).

Soil redox potentials measured at soil profile BG 22.1 decreased with depth and ranged from acidic-weakly reducing at 5 cm, to acidic-strongly reducing at 45 cm and had similar circum-neutral-strongly reducing conditions at 85 cm and 125 cm depths (Figure 8-17 and Figure 8-18). Redox potentials took about 5 to 6 days to stabilize following installation of the Pt electrodes and were then relatively constant during the monitoring period. Eh measured at 5 cm depth was significantly more oxidising than the lower Pt electrodes, with Eh measurements ranging from 480 mV to 570 mV. Eh measured at the 45 cm declined gradually from –28 mV to –90 mV during monitoring. At the 85 cm electrode Eh measurements rose slightly from -140 mV to –90 mV during monitoring while Eh measured at 125 cm depth took longest to stabilize after installation and then rose slightly from -150 mV to -205 mV over the month of monitoring (Figure 8-17).

Fluctuations in Eh measurements were minor at all depths, particularly when compared to the intertidal soils described previously. Cyclic (diurnal) fluctuations of about 20 mV were only recorded by the 5 cm electrode. Slightly larger fluctuations in Eh, ranging from 10 to 50 mV, were measured at all electrodes following rainfall events (Figure 8-17). The sharp, small amplitude peaks recorded during rainfall events were likely induced by disturbance of the Pt electrodes (possibly from wind shaking the exposed electrode poles) rather than rainfall, because the responses occurred simultaneously at all depths and were generally followed by a short re-stabilization period. The 5 cm Pt electrode did show a slight drop in Eh following moderate rainfall events and was likely a response to increased soil moisture content.

Following the recognition of wind induced fluctuations of Eh measurements the design of Pt electrode, as well as their installation technique, was modified. The modified methodology was employed when monitoring redox conditions in soil profiles BG 11, BSK 6, BSK 7 and BSK 8. At exposed sites, rather than installing a ‘bank’ of electrodes for the entire profile, individual Pt electrodes were inserted at each monitoring depth. The electrodes were completely buried, with only the wire tails emerging from the ground, in order to minimise movement by wind or birds perching on the poles. This method also reduced the likelihood of water or air moving down the insertion hole, in non-saturated soils. Most importantly for Gillman study site, this method enabled the electrodes and data logger to be well hidden from vandals and curious animals (foxes, cats and cows) that occasionally chewed on connecting cables.

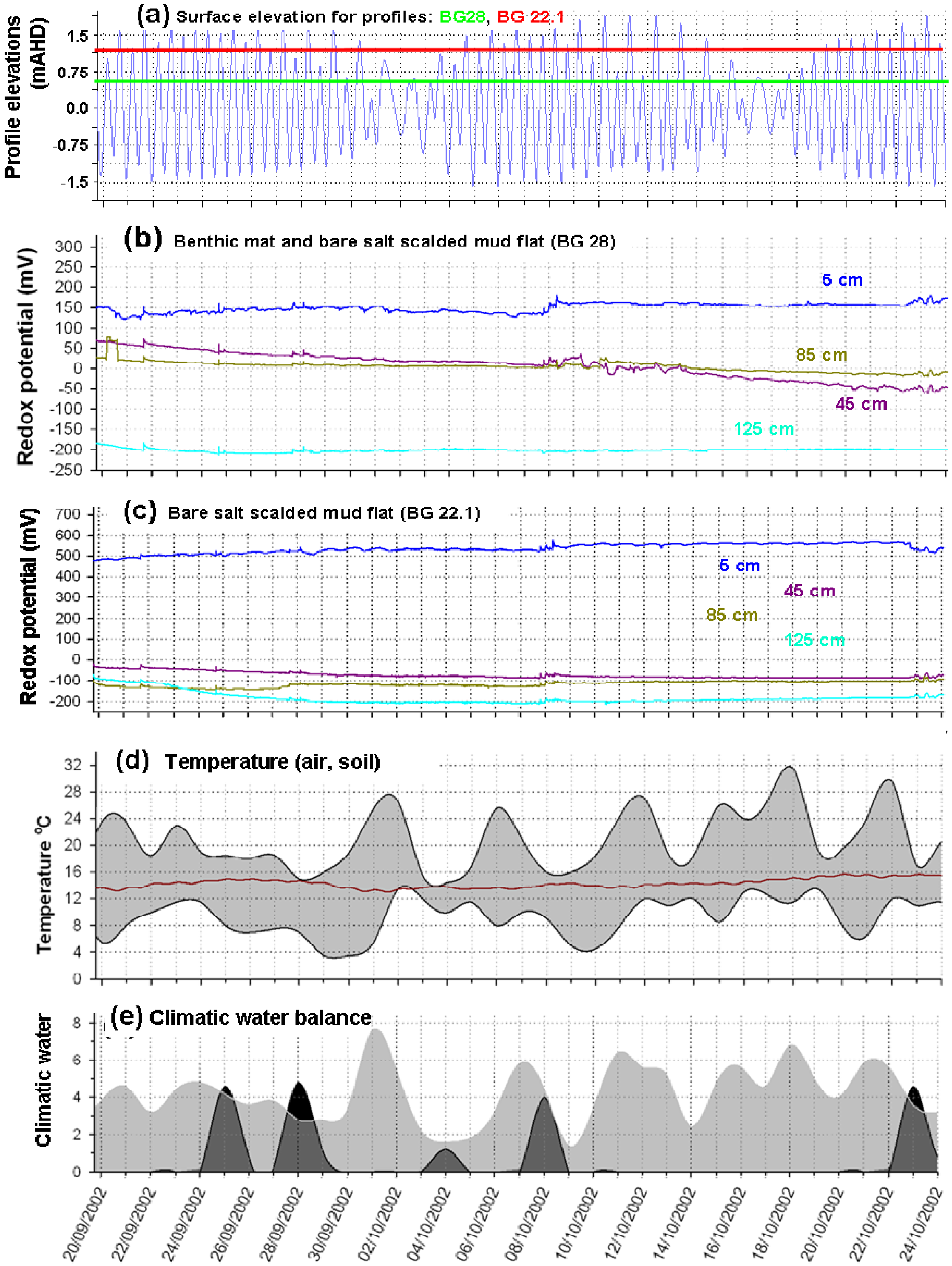
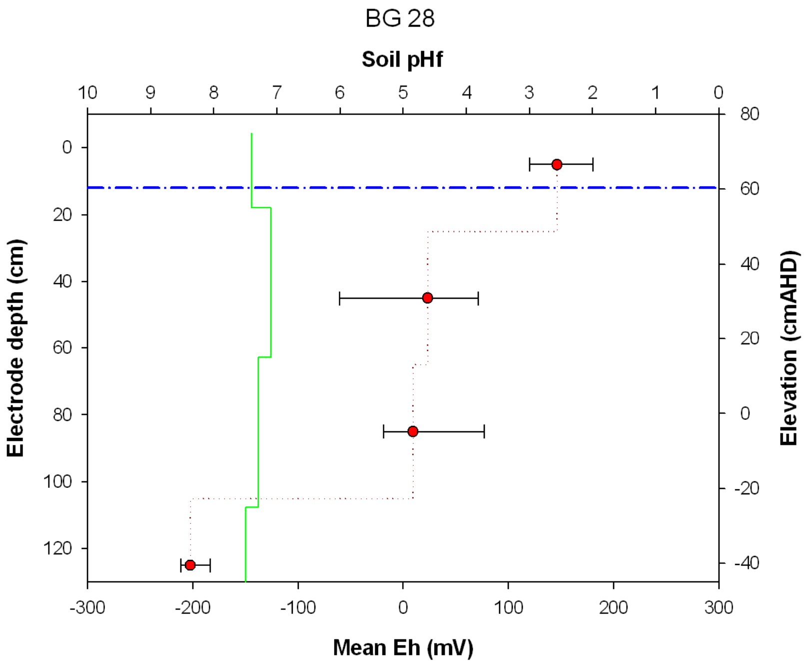


Figure 8-17 Non-tidal soils, Gillman Focus area C. (a) surface elevations (solid lines) for BG 22.1 (1.2 m AHD) and profile BG 28 (0.6 m AHD) showing the *former extent of tidal influence*. Soil redox potentials for 4 depth intervals measured in profile BG 28 (b) and 4 depth intervals measured in profile BG 22.1 (c). Depth intervals were at 5 cm (blue), 45 cm (purple), 85 cm (green) and 125 cm (cyan) for both profiles. Time versus measurements of: (d) air temperature range (light grey shaded area) and soil temperature (brown line) at 15 cm depth, and (e) water balance showing evaporation (light grey area) and rainfall (dark grey areas). Note that 10 ml of rain fell on the 16th to 18th of September 2002, prior to the monitoring period.



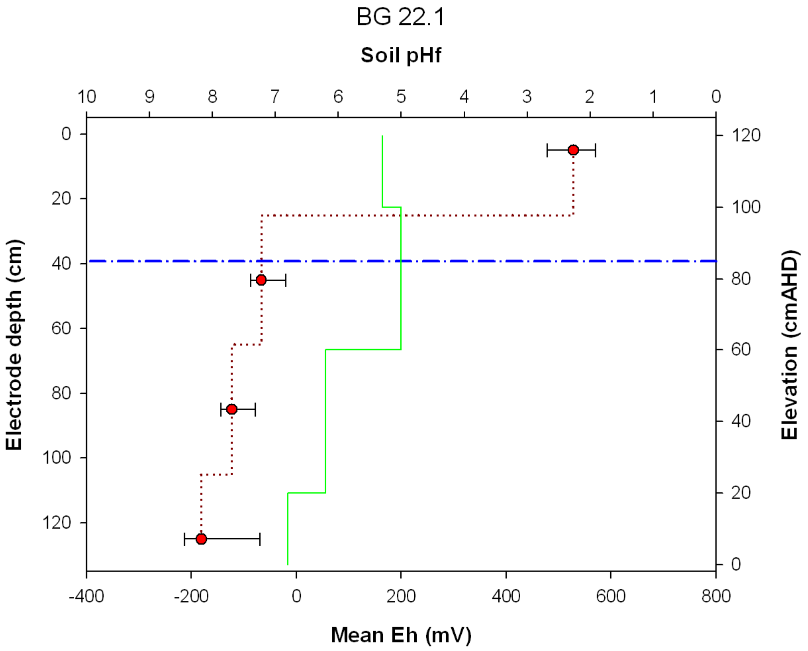


Figure 8-18 Plot of mean redox (red dots) measurement (mV) versus depth (cm) for soil profiles BG 28 and BG 22.1. Error bars show the range of Eh (bottom axis) measurements either side of the mean. Depth is shown in centimetres from the surface (left axis) and as AHD (right axis). The green lines show mean field measured soil pH (pHf). The blue dotted lines indicate watertable height.

Elevated, non-tidal soils at Gillman, Focus area A

Redox monitoring system was installed in soil profile BG 11 to monitor redox conditions within the former (drained) supratidal environment. Soil profile BG 11, which classifies as a Sulfuric, Salic Hydrosol (Isbell 2002) was instrumented with 12 Pt electrodes positioned within key soil layers down the profile (Figure 8-19). The profile face was excavated so electrodes could be pushed horizontally into each of the key soil layers to minimise the possibility of contaminating or damaging the Pt electrode tip with foreign materials from overlaying soil layers, particularly organic matter which may serve as an energy source for microorganisms (Figure 8-19) and shell fragments. By this method it was possible to position the Pt electrode 40 to 50 cm away from the exposed pit face. An Ionode Ag/AgCl reference electrode was inserted at the base of the soil profile, below the water table, to maintain contact with soil solution and prevent it from drying out. Once all electrodes were installed the soil profile was systematically back filled to limit oxidation of soil layers and prevent evaporative concentration of salts at the pit face. The Pt electrodes were installed on the 22nd May 2004 at 10, 30, 40, 50, 65, 70, 110, 150, 160, 170, 190 and 200 cm (Figure 8-20). Soil temperature (at 15 cm and 40 cm) and redox measurements were recorded for 23 days at hourly intervals, until the 19th June 2004.

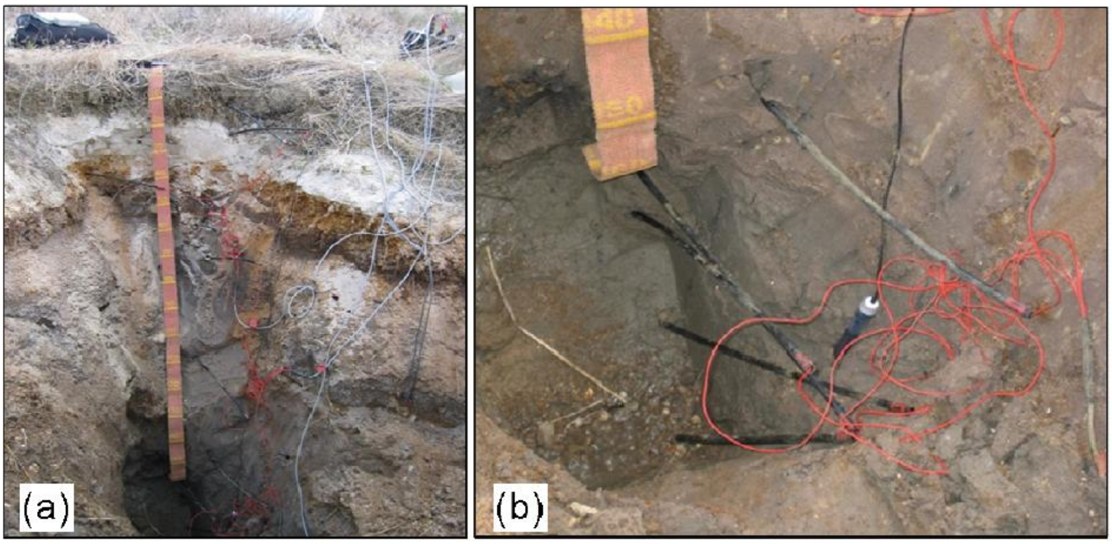


Figure 8-19 (a) platinum electrodes being positioned for installation in soil profile BG 11 (a). Pt electrodes were pushed horizontally into the soil layers in order to minimise cross contamination from the overlaying soil materials. (b) the Ag/AgCl reference electrode was placed at the base of the profile in moist soil.

Redox potentials measured at soil profile BG 11 took between 3 and 6 days to stabilize following installation of the Pt electrodes and were then relatively stable during the monitoring period (Figure 8-20). Eh values ranged from circum-neutral-weakly reducing at 10 cm depth (ranging from 290 to 360 mV) to acidic-strongly reducing conditions at 160 cm depth (ranging from -260 to -110 mV). Eh values generally declined with depth, but increased slightly from below the water table, which occurred at 170 cm (Figure 8-21). As expected, redox conditions were generally more oxidising in the top 50 cm of the profile, where sulfuric materials were identified, than in the deeper hypersulfidic material (Figure 8-20). Eh values throughout the profile were surprisingly low given the drainage history of the site and because it contains sulfuric materials to a depth of 170 cm. Jarosite mottles are common in the sandy soil layers occurring between 65 and 170 cm depth, where conditions ranged from acidic-moderately reducing to acidic-strongly reducing and Eh ranged from 155 to – 260 mV during the monitoring period. These low Eh measurements are likely to be representative of the soil matrix rather than within the jarosite mottles, where acidic-weakly reducing to acidic-oxidising (> 600 mV at pH < 3.8) redox conditions would be expected. Soil colour is a good indicator of redoximorphic conditions (Vepraskas 2001). The low chroma (≤ 2) matrix colours of soil layers below 60 cm in profile BG 11 were reasonably consistent with the redox conditions recorded. The unexpected low Eh measurements may also be due to seasonal variations because redox monitoring at this site was restricted to one wet month in winter.

Cyclic fluctuations in redox measurements were minor compared to the intertidal soil profiles described previously. Low amplitude diurnal fluctuations (ranging from 5 to 10 mV) were recorded by two near surface Pt electrodes (at 10 and 40 cm depths) and were likely to be a response to temperature oscillations and vegetative respiration. This diurnal ‘wobble’ of Eh started to disappear when soil temperature dropped below 15° C. Fluctuations of up to 50 mV were measured by a number of electrodes following rainfall events. Near surface electrodes, at 40, 50 and 65 cm depths, showed a sharp drop in Eh measurement following some rainfall events while deeper placed electrodes (at 160 and 190 cm) recorded a slight rise following rainfall events. The abundant rainfall during the monitoring period caused the water table to rise 10 cm (from 170 cm depth to 160 cm depth) (Figure 8-20). Electrodes positioned below the water table showed a slow decline in Eh over the monitoring period, while those above the watertable (and still within sulfuric materials) showed a rise in Eh. This trend may be a seasonal response (summer to winter) as the groundwater table slowly rises.

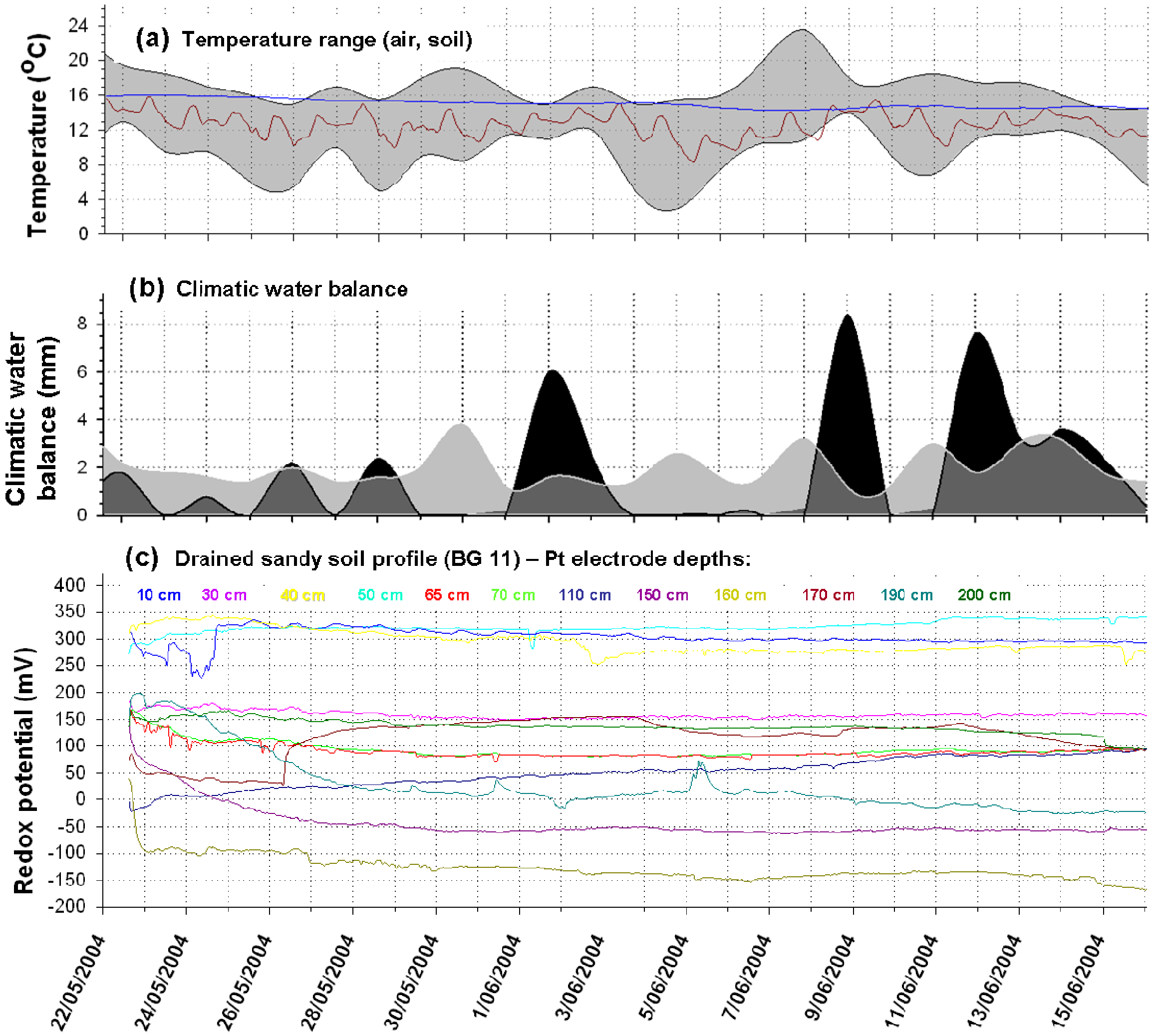


Figure 8-20 Non-tidal soil profile BG 11, with a surface elevation of 2.5 m AHD. Water table was at 160 cm depth during the monitoring period. Time versus measurements of: (a) air temperature range (light grey shaded area) and soil temperature (brown line at 10 cm depth) and the (blue line at 40 cm depth). (d) water balance showing evaporation (light grey area) and rainfall (dark grey and black areas), (c) soil redox potentials for 12 depth intervals measured in profile BG 11. Depth intervals were 10 cm (blue), 30 cm (pink), 40 cm (yellow), 50 cm (cyan), 65 cm (red), 70 cm (green), 110 cm (dark blue), 150 cm (purple), 160 cm (dark yellow), 170 cm (dark red), 190 cm (dark cyan) and 200 cm (dark green).

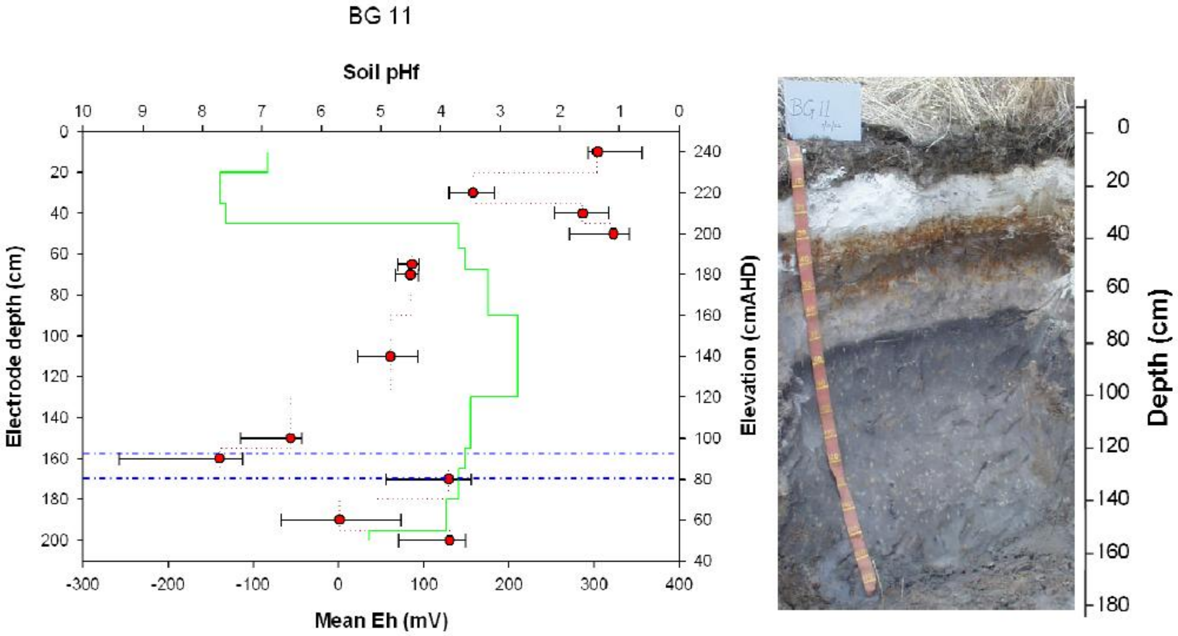


Figure 8-21 Plot of mean redox measurement (mV) versus depth (cm) for soil profiles BG 11. Error bars show the range of Eh (bottom axis) measurements either side of the mean. Depth is shown in centimetres from the surface (left axis) and as AHD (right axis). The green line shows soil pHf measurements. The blue dotted lines at 160 and 170 cm depth indicate the increase in watertable height during the monitoring period. Jarosite mottles are common between 50 cm to 190 cm depths.

Disturbed, elevated, non-tidal soils at Gillman, Focus area A

Redox monitoring equipment was installed in soil profile BG 15 to monitor redox conditions within a severely disturbed (drained) environment. Profile BG 15 was located on the side of a drain that was excavated 16 months prior to the redox monitoring period (Figure 8-22). A pole containing 8 Pt electrodes was inserted vertically into the sloping face of the drain wall. Platinum electrodes were installed on the 15th of December 2003 at 1, 20, 30, 60, 62, 80, 90 and 150 cm (Figure 8-23). Soil Eh measurements were recorded for 3 months at hourly intervals, until the 15th March 2004. Soil temperature was measured at 20 cm depth (Figure 8-23). Salt efflorescences (with pH ranging from 0.8 to 3.0) precipitated on the drain walls, particularly during hotter summer months and were partially washed away during heavy rains. Soil profile BG 15 classified as a Sulfuric, Salic Hydrosol (Isbell 2002) and was described in Table 6-4.

Figure 8-22 Photo (winter 2003) of the drain transecting sulfuric and sulfidic materials at Gillman Focus area A. Soil profile BG 15 is located on the left (western) wall of the drain. The drain was excavated in August 2002 as part of a lime slot remediation trial. The water in the drain had a pH that ranged between 2 and 3. Salt efflorescences (with pH values ranging from 0.8 to 3) precipitated on drain walls, particularly during summer months and were washed away after heavy rains. The drain runs north-west, positioning profile BG 15 in direct sunlight for the greater portion of the day.

Soil redox values in soil profile BG 15 were high, ranging from 200 mV to 1400 mV at depth 120 cm, but were substantially lower at depth below 120 cm to150 cm (Figure 8-23 and Figure 8-24). The mean redox potentials recorded by the upper 5 Pt electrodes (located at 1, 20, 30 60 and 62 cm depths) generally measured Eh values above 1000 mV and were therefore considered to have had poor connectivity with the reference electrode, due to drying of the soils. Connectivity may have been restored following some moderate rain events, causing redox measurements to approach a representative Eh value, however the redox data from these electrodes was not considered reliable and therefore were not interpreted further.

Redox potentials in constantly moist soils (at 80, 90 and 150 cm depths) took about 5 days to stabilize following installation of the Pt electrodes. The water table dropped from 110 to 120 cm depth during the monitoring period. Redox conditions within soil profile BG 15 generally declined with depth and measured acidic-oxidising at 80 cm depth (ranging from 535 to 685 mV), acidic-weakly reducing at 90 cm depth (ranging from 420 to 525 mV) and acidic-moderately reducing at 150 cm depth (ranging from 25 to 190 mV) (Figure 8-23 and Figure 8-24).

Platinum electrodes in soil profile BG 15 responded rapidly to changes in soil saturation following rain events. In a highly oxidised environment the Pt surface absorbs O_2 and thus acts as an oxide electrode that has the function of the hydrogen electrode (Catallo 1999; Whitfield 1969; Whitfield 1974). This causes the Pt electrode to respond to pH rather than O_2 partial pressure, and therefore Eh measurements do not reflect the soil aeration in O_2 environments (Callebaut *et al.* 1982; Fiedler and Sommer 2004). Therefore making interpretation of Eh data obtained under long-term, oxidising conditions difficult. Platinum electrodes located at 80 cm and 90 cm responded to rain events with a sudden increase in Eh measurement (of about 400 mV) followed by a gradual decline back to (nearing) the prior Eh value over a few days to a few weeks. The Pt electrode placed at 150 cm depth also responded, on two occasions, to rainfall events with a sharp decrease in Eh value, which generally took much less time to re-equilibrate (Figure 8-23) and was probably a response to wind induced movement of the pole containing the Pt electrodes. The Pt electrodes at 80 and 90 cm depths responded rapidly to rainfall events because: (i) their real depth (from the drain wall) was about half that of their vertical depth (documented here), and (ii) the soil texture was predominantly a medium sand, which was highly permeable. The fluctuations in Eh measured following rain events was likely a response to pH changes in the soil as rainfall caused the surface salt efflorescences (composed of acidic sulfate salts) to dissolve and transport H^+ ions into the underlying soils. The pH of the drain water dropped by up to 1 pH unit following heavy rains that washed salt efflorescences from the drain walls. The occurrence of salt efflorescence was greatest between 40 cm and 100 cm depth (Figure 8-24) and would therefore have the greatest affect on lower electrodes.

Diurnal fluctuations in Eh readings were obvious throughout the monitoring period (Figure 8-23). Diurnal fluctuations from electrodes placed at 80 and 90 cm depth had large amplitudes (ranging from 10 to 200 mV), peaking in the early to mid morning, which corresponds to profile BG 15 being in direct sunlight. The fluctuations in Eh may have been related to the very high daily temperatures causing very high evaporation potentials, and by activity of aerobic microbes (green algae) that were observed beneath salt efflorescences and within the drain waters. Diurnal fluctuations measured by the Pt electrode placed at 150 cm were of relatively small amplitude (ranging from 10 to 100 mV).

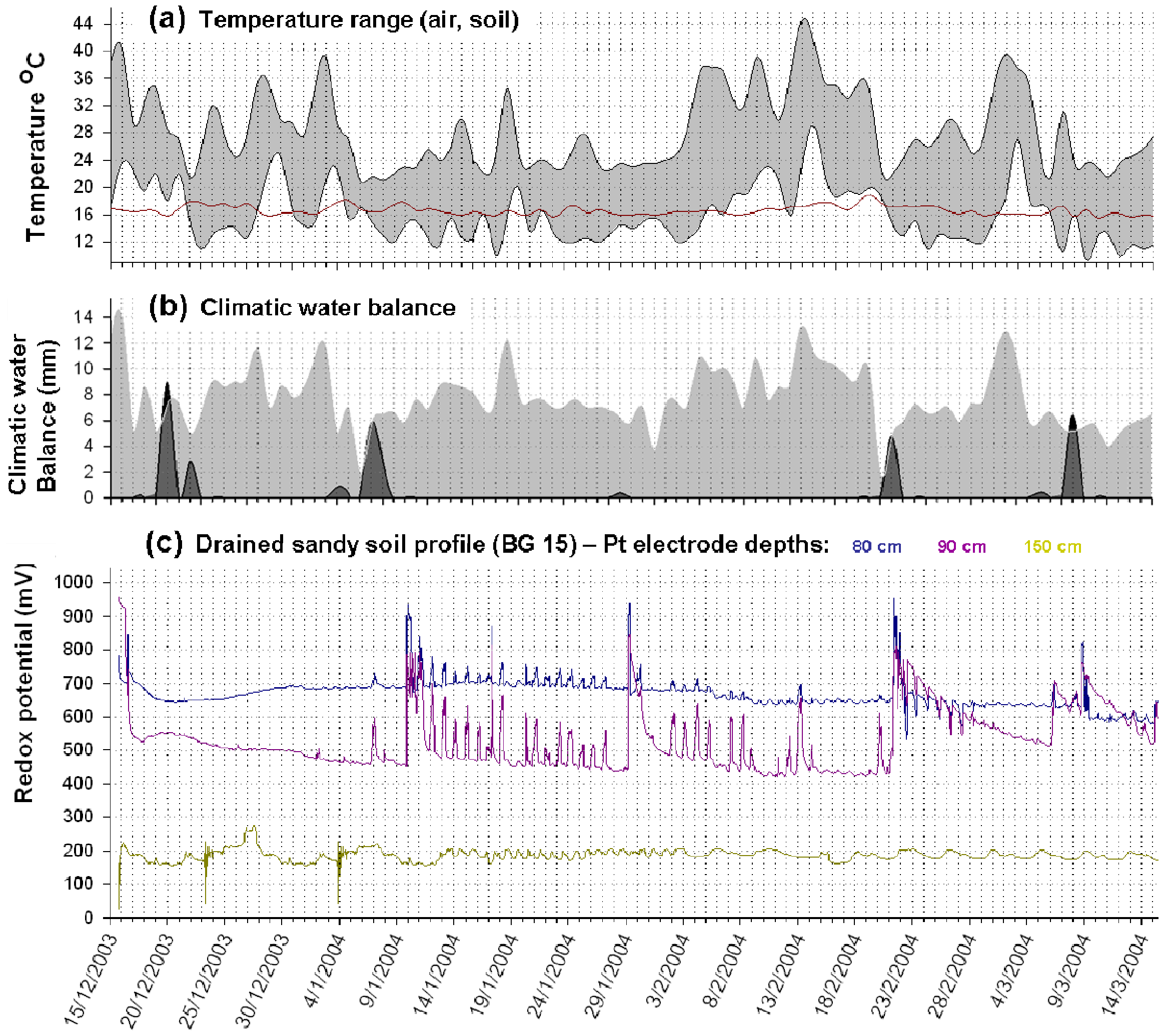


Figure 8-23 Non-tidal soil profile BG 15, with a surface elevation of 2.05 mAHD. Time versus measurements of: (a) air temperature range (light grey shaded area) and soil temperature (brown line at 20 cm depth). (d) water balance showing evaporation (light grey area) and rainfall (dark grey and black areas), (c) soil redox potentials for 8 depth intervals measured in profile BG 15. Depth intervals were 80 cm (dark blue), 90 cm (purple) and 150 cm (dark yellow).

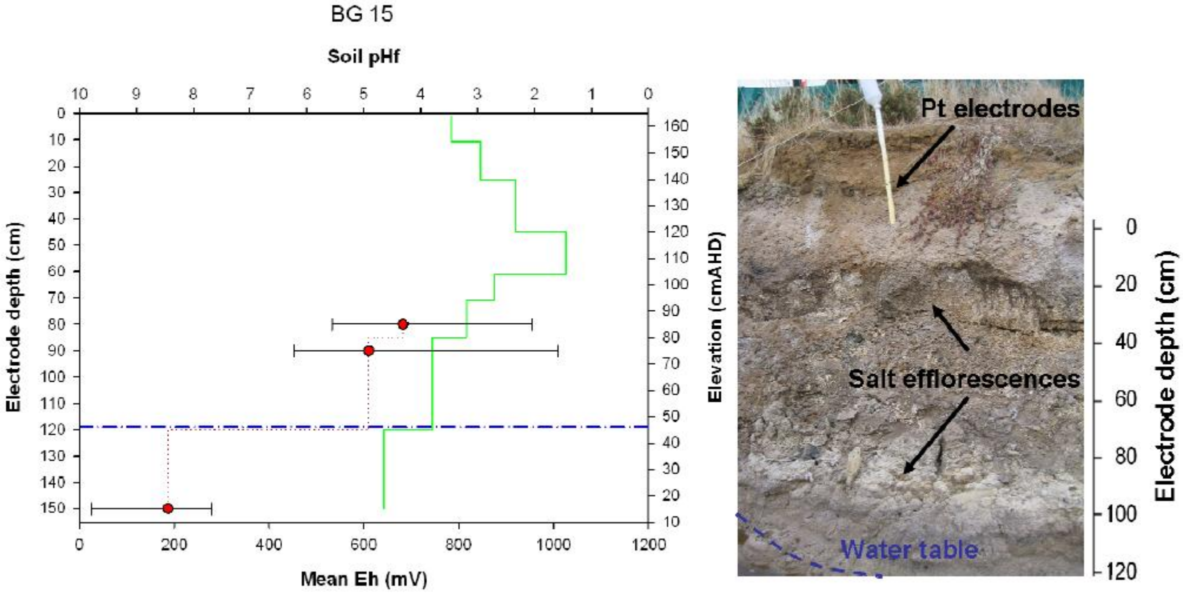


Figure 8-24 Plot of mean redox measurement (mV) versus depth (cm) for soil profiles BG 15. Error bars show the range of Eh (bottom axis) measurements either side of the mean. Depth is shown in centimetres from the surface (left axis) and as AHD (right axis). The green line shows soil pHf measurements. The blue dotted line at 45 cm AHD indicates the watertable height. Redox status: oxidising (> 400 mV); weakly reducing (400 to 200 mV); moderately reducing (200 to -100 mV); strongly reducing (< -100 mV). Photo (summer 2004) of profile BG 15 is located on the side of a drainage channel that was excavated 12 months prior to the monitoring period. A pole containing 7 Pt electrodes was inserted vertically into the sloping face of the drain. Salt efflorescence (with pHs ranging from 0.8 to 3) precipitated on the drain walls, particularly during summer months and were washed away after heavy rains.

8.2.3. Redox conditions in non-tidal, subaqueous environments

Submerged, non-tidal soils at Gillman, Focus area A

Redox data logger was installed within subaqueous sediment profile BG P 5 to monitor redox conditions within the water column and sediments of a storm water ponding basin containing monosulfidic materials. Profile BG P 5 was located at Gillman Focus area A (Figure 6-9), within a storm water ponding basin that was excavated during the construction of the Range Wetlands in 1996 (Figure 3-2). Soil profile BG P 5 classified as a Sodosolic, Salic Hydrosol (Isbell 2002) and is described in Table 6-6.

A pole containing 8 Pt electrodes was inserted vertically into the bottom of the pond on the 5th of October 2002. The pond contained 65 cm of water during the monitoring period. Three Pt electrodes were located within the water column at 20, 40 and 60 cm above the sediment-water interface, and 5 Pt electrodes were located at 1, 20, 22, 40 and 60 cm below the sediment-water interface (Figure 8-25 and Figure 8-26). Measurements were recorded for 4 weeks at 30 minute intervals, until the 1st of November 2002. Soil temperature was measured at 5 cm below the water-sediment interface. Measurements were discontinued due to the monitoring equipment being vandalised on the 1st of November 2002, which was a constant occurrence at all Gillman study sites. Redox potentials took about 1 to 2 days to stabilize following installation of Pt electrodes.

Redox conditions within the water column were more oxidising than within the soils, and fluctuated (diurnally) from circum-neutral-oxidising to circum-neutral-moderately reducing at all three Pt electrodes (located at 20, 40 and 60 cm above the sediment-water interface) (Figure 8-25 and Figure 8-26). Eh values measured within the water column had a similar, but large diurnal fluctuation, which was greatest nearest the water surface (ranging from 545 mV to 45mV). Redox conditions within the soils profile were most reducing immediately below the sediment-water interface and became more oxidising with increased depth. Redox conditions fluctuated diurnally from circum-neutral-moderately reducing to circum-neutral-strongly reducing at Pt electrode depths 20, 22, 40 and 60 cm below the sediment-water interface. Soil redox conditions remained circum-neutral-strongly reducing at 1 cm below the sediment-water interface (ranging from -210 to -85 mV, and is where monosulfidic materials were most concentrated (Figure 8-25 and Figure 8-26).

Cyclic fluctuations in Eh measurements were of considerably larger amplitude in the water column (60 cm depth) compared to the soils. The fluctuations were comparable to intertidal profiles described previously. In the water column Eh fluctuated by 150 to 300 mV, on a diurnal cycle, where the trough generally occurred in the early morning and the peak occurred mid to late afternoon, synchronised with air temperature as well as solar radiation. In the water column the fluctuations in Eh are therefore likely to be a response to microbial respiration and temperature. In the soil fluctuations of Eh measurements had smaller amplitudes and were out of phase by about half a day with the fluctuations measured in the water column. Fluctuations in the soil were more oxidising at night and when temperature was lowest, and was likely a response to activity of anaerobic microbes in the soil (Figure 8-25). The sharpness of the peaks and troughs was likely influenced by electrode depth, being related to the rate at which the soil or water changes temperature, with sharp transitions indicating a rapid temperature change (and a subsequent rapid microbial response).

One notable rainfall event occurred on the 24th of October 2002 that caused an immediate drop in Eh within the water column and a delayed drop (by 2 days) in Eh measured in the underlying soil (Figure 8-25). Monosulfide content within the top 5 cm was of soil high (measuring 1.14% AVS) and was likely dispersed into the water column by water runoff and wind induced wave action during the rain event. Monosulfidic materials can rapidly consume oxygen from the water column when disturbed and suspended (Burton *et al.* 2009; Bush *et al.* 2004b; Smith and Melville 2004; Ward *et al.* 2004).

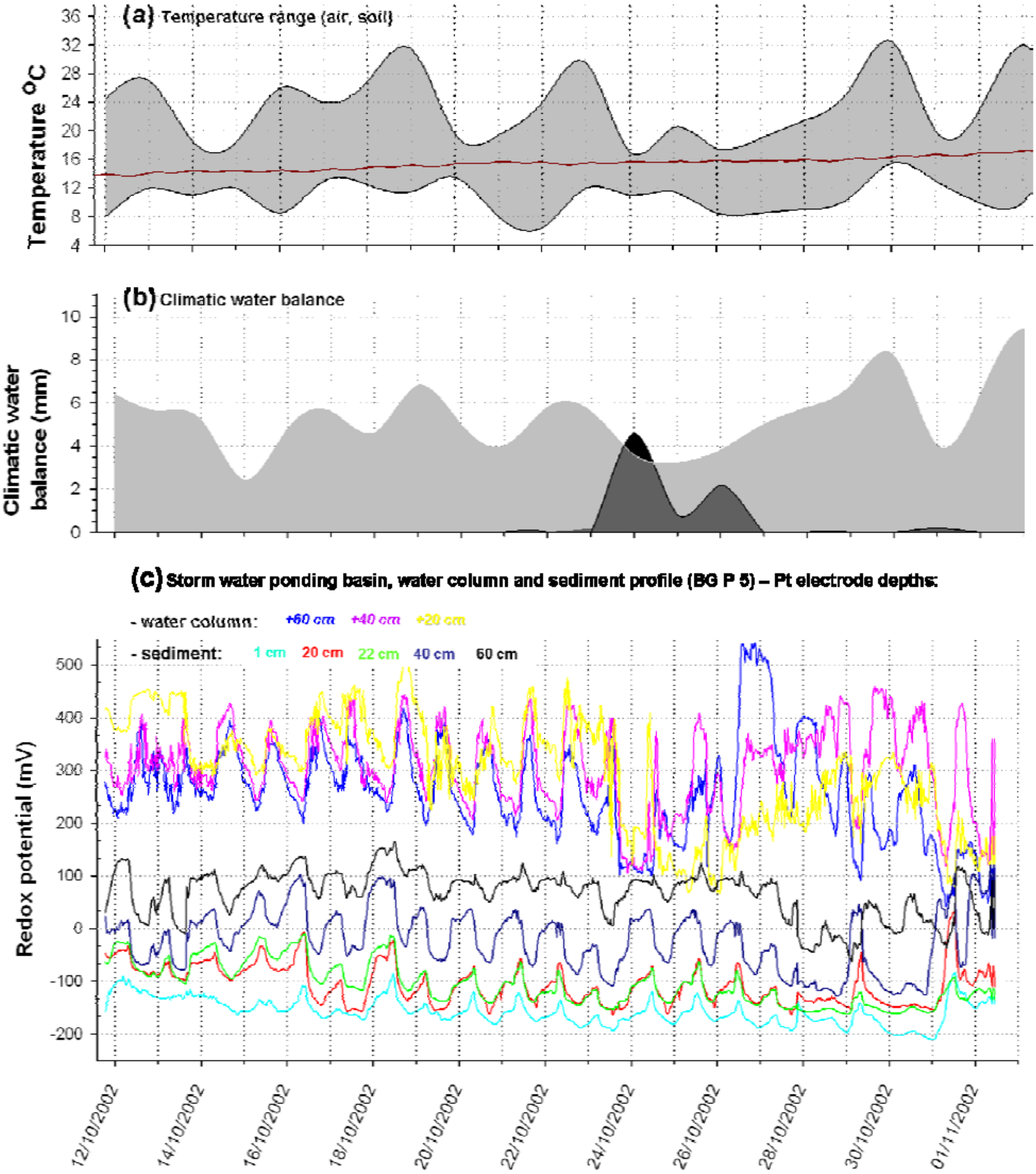


Figure 8-25 Time versus measurements of: (a) air temperature range (light grey shaded area) and soil temperature (brown line at 10 cm depth within soil sediment); (d) water balance showing evaporation (light grey area) and rainfall (dark grey and black areas); (c) soil redox potentials for 5 depth intervals measured within subaqueous soil profile BG P 5 and 3 depth intervals within the overlaying water column (storm water ponding basin). Redox measurements were recorded at 1 cm (cyan), 20 cm (red), 22 (green), cm 40 cm (dark blue) and 60 cm (black) below the sediment-water interface., and at 20 cm (yellow), 40 cm (pink) and 60 cm (blue) above the sediment-water interface. Water depth was 65 cm.

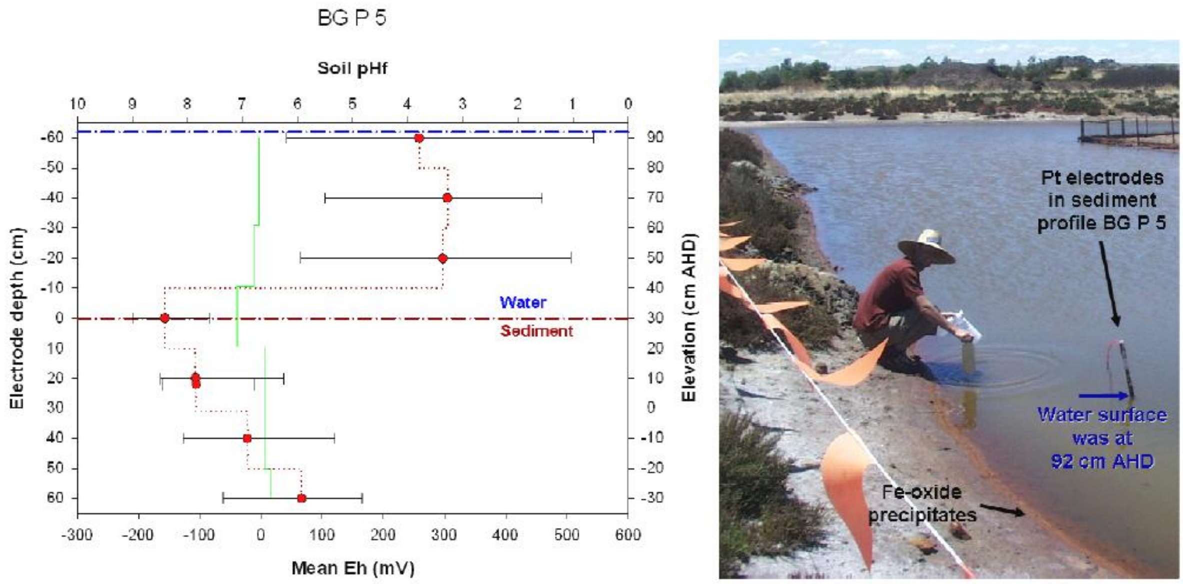


Figure 8-26 Plot of mean redox measurement (mV) versus depth (cm) above and below the sediment-water interface for soil profile BG P 5. Error bars show the range of Eh (bottom axis) measurements either side of the mean. Electrode depth is shown in centimetres from the surface (left axis) and as AHD (right axis). The green line shows soil pH measurements (field pH). The blue dotted line at 95 cm AHD indicates the water height. The red dotted line at 30 cm AHD indicates the elevation of the sediment-water interface.

8.2.4. Summary

Redox monitoring was used to gauge the influence of **(i)** tidal flooding, **(ii)** diurnal and seasonal temperature change, **(iii)** rainfall events and **(iv)** map units, occurring within different hydromorphic zones at the St Kilda and Gillman study sites (Figure 6-1). The redox data were also used to validate geochemical results and mineralogy of salt efflorescences explained in Chapter 10 and micromorphological studies described in Chapter 11.

The *in situ* soil and water redox monitoring systems were developed with the following requirements: minimal maintenance for long term deployment, easy installation and removal from the harsh intertidal and non-tidal wetland environments. The redox data loggers were relatively inconspicuous once installed to minimise tampering by the public. The loggers could be left functioning for many months, depending on battery life, or years if a solar panel was used, however reference electrodes should also be checked and refurbished or replaced regularly (every 4-6 months).

Platinum electrodes typically required between 2 to 7 days to stabilize, within either reduced or oxidised soil environments. Duplicates and closely positioned Pt electrodes were found to show good correlation with similar responses to changes in environmental conditions, particularly in strongly reduced soils. Redox measured by replicate Pt electrodes placed within the water column or at the sediment-water interface showed less correspondence but fluctuations could generally be related to changes in environmental conditions. Based on Eh data from this investigation, the use of at least 4 replicate electrodes is recommended to measure the dynamic redox conditions within aquic environments at and above the sediment-water interface. Closely spacing single electrodes or deploying replicate electrodes in duplicate should suffice in less dynamic, reducing environments. This is because long term 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 the Pt electrode tip provides valuable additional information for interpreting soil redox data. That is the proximity of the Pt electrode to soil materials and features which influence redox measurements can be accounted for (e.g. organic matter, pores, redoximorphic features, soil texture and live roots). Interpretations of Eh data obtained during long term monitoring were also improved by regular site visits to observe the general operation of the monitoring system and environment, particularly within the more dynamic, intertidal settings. For example, in tidal environments water often flows differently during tidal flooding (low energy sheet flooding) compared to when it drains as the tide retreats (higher energy drainage via channels).

Tidal influences

At tidally influenced sites, temporal variability in Eh was generally in phase with tidal cycles. Redox potentials responded rapidly and significantly to tidal drainage and flooding cycles, which in turn altered oxygen supply to the soils and therefore varied biological activity. Areas subject to strong tidal flow rates showed greater variation in Eh measurements within the near surface soils (Figure 8-27 and Figure 8-28). The mean Eh values measured at the near surface of intertidal soil profiles were generally more reduced at the more elevated sites, due to slower tidal flows and limited tidal exchange / flushing (Figure 8-30). This contrasted with non-tidal environments where soil redox conditions were generally more stable and became more oxidising with increased elevation, consistent with soil moisture status (Figure 8-29 and Figure 8-30). Large cyclic (diurnal) variations in Eh measurements appeared to be characteristic of subaqueous environments, but particularly of intertidal soils. In tidally influenced environments the regularity and strength of tidal flushing influenced the amplitude of fluctuations in Eh and mean soil redox conditions (Figure 8-30). Lower amplitude diurnal fluctuations that were out of phase with tides were likely related to changes in temperature and solar radiation, varying the activity of soil microbes and productivity of vegetation. The nature of oscillations in Eh would not have been easily interpreted if monitoring intervals were greater than hourly.

Dissolution of trace elements in these environments would vary diurnally in response to the measured diurnal fluctuations in Eh. Diurnal variations in stream water trace element concentrations have been coupled to diurnal fluctuations in pH (of up to 1 pH unit) arising from changes in photosynthetic and biological activity and light intensity (Bourg and Bertin 1994; Fuller and Davis 1989). This has implications for modelling trace element mobilities and sulfide oxidation rates in these environments through Fe cycling. McKnight *et al.* (1988) found that photoreduction of dissolved Fe^{3+} may be four times faster during daylight hours in streams affected by acid mine drainage, while Wieder (1994) found the opposite effect due to daytime oxidation by algae.

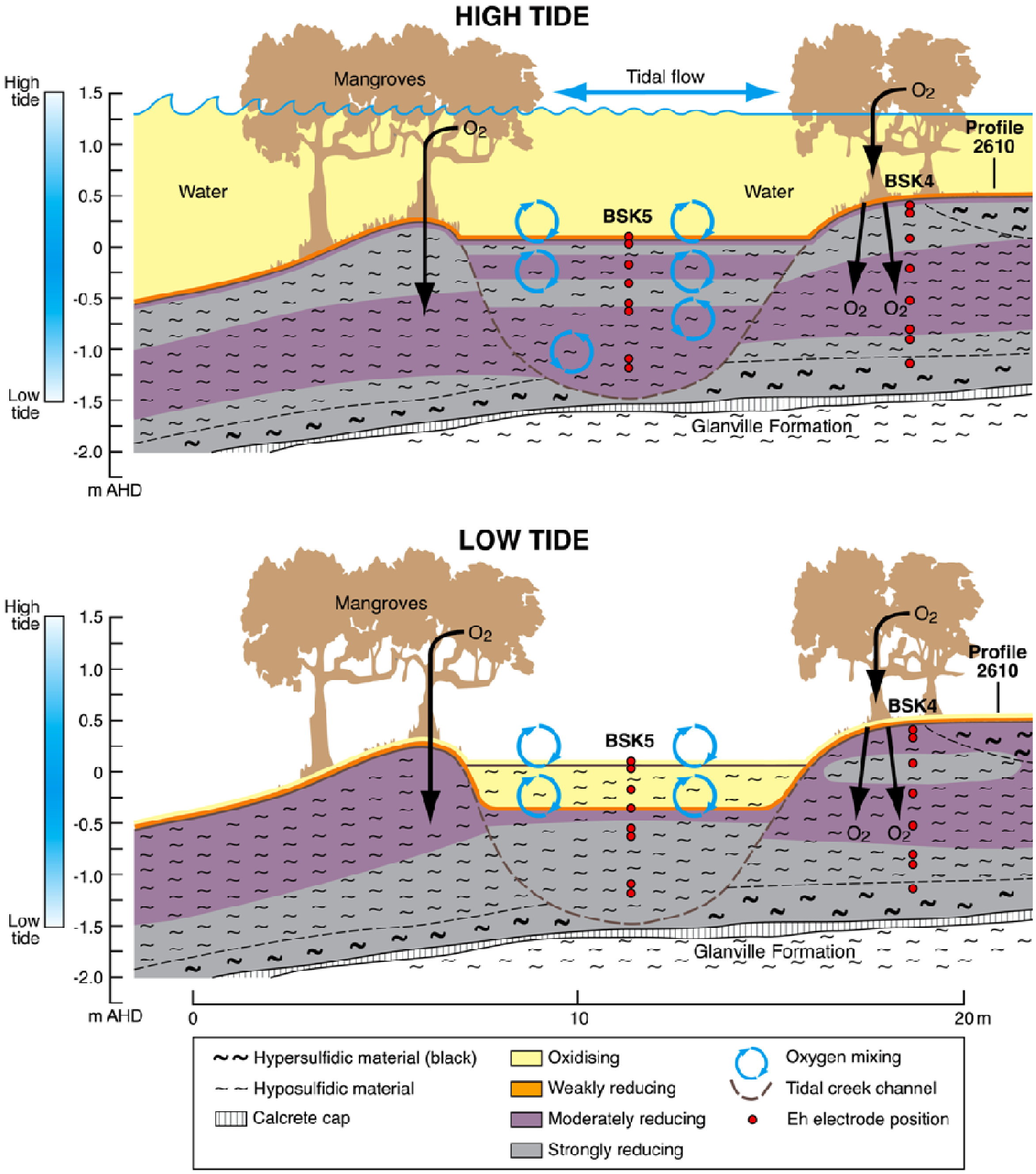


Figure 8-27 Descriptive soil-regolith toposequence model of St Kilda focus area ‘A’ showing changes in redox classes from high tide (hyposulfidic subaqueous organic soil) to low tide (hyposulfidic organic soil). At low tide soils become more oxidising near the surface (i.e. change from strongly reducing to moderately reducing). However, at depth in the tidal creek channel (BSK 5) deeper soils become more reduced at low tide. At high tide there is more movement and mixing of oxygenated water in the tidal creek depression (BSK 5) with sapric materials compared with the adjacent mangrove soils (BSK 4) with hemic materials. During low tide the water drains more freely from the mangrove soils compared to the tidal creek, where the deeper soil layers become strongly reducing as there is less water movement and mixing.

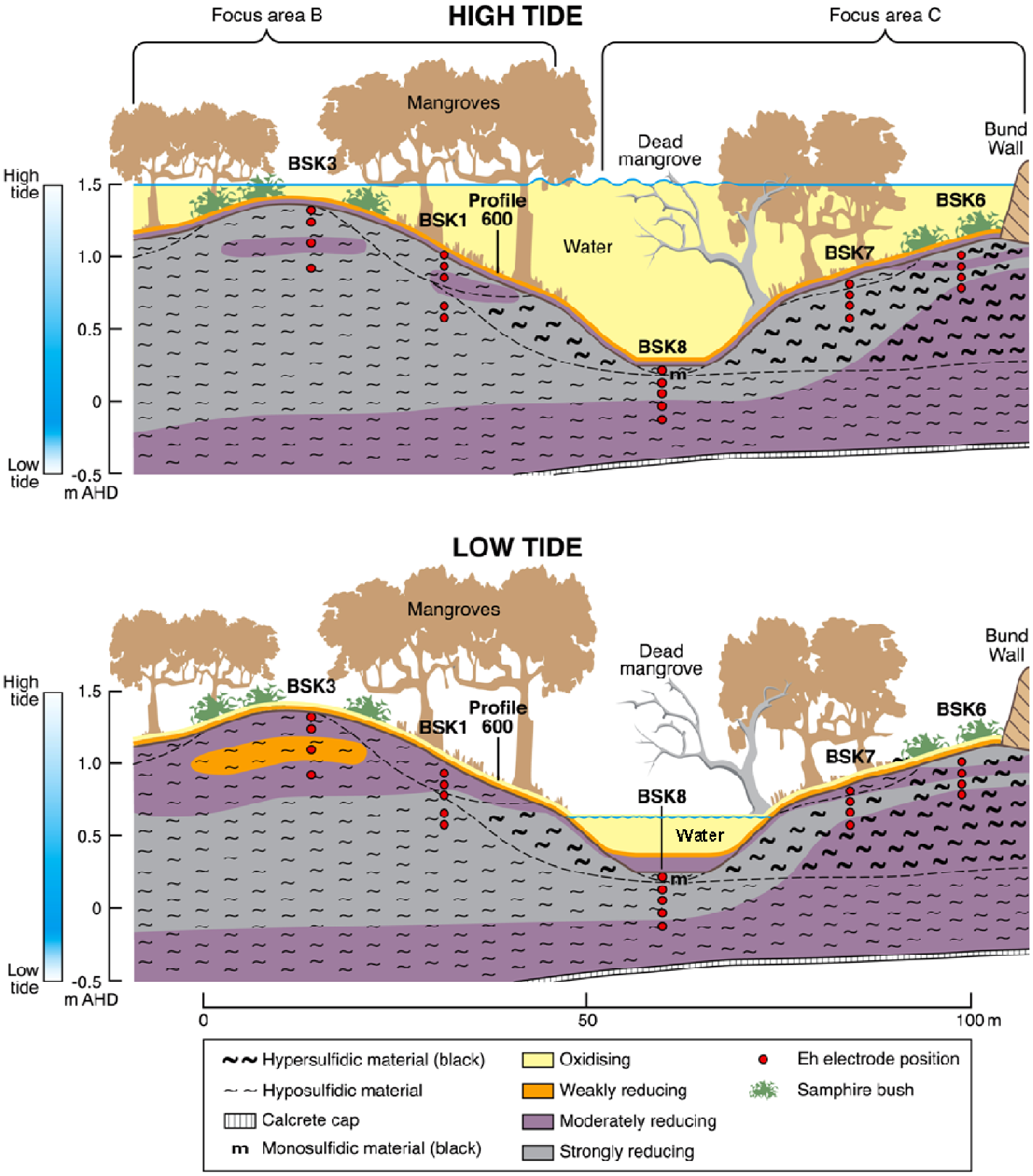


Figure 8-28 Descriptive soil-regolith toposequence model of St Kilda focus area ‘B’ and ‘C’ showing changes in redox classes from high tide to low tide. In focus area ‘B’ soils change from hyposulfidic subaqueous organic soil with strongly reducing redox conditions at high tide to hyposulfidic organic soils with moderately to weakly reducing conditions at low tide. In focus area ‘C’ soils under samphire and mangrove vegetation change from hypersulfidic subaqueous organic soils at high tide to hypersulfidic organic soils at low tide, and become slightly more oxidising in the process. In the tidal creek channel (BSK 8) soils remain as hyposulfidic subaqueous organic soils with monosulfidic materials during high tide and low tide situations. However deeper soils within the tidal creek become more reduced at low tide as there is less water movement and mixing occurring.

Non tidal areas

Non-tidal soils at Gillman had a similar range of mean Eh values and soil pH than for intertidal environments at St Kilda and Gillman (Figure 8-30). Eh measurements in non-tidal, sub aerial environments were characterised by relatively minor diurnal fluctuations. Rainfall events produced the most dramatic responses in Eh measurements, particularly in the upper portion of sub aerial profiles which became more reducing when wetted. 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 of the stormwater pond (profile BG P 5) became more reducing when monosulfide rich bottom sediments were disturbed during a rainfall / storm event. Synchronous monitoring of soil pH values with Eh would be a useful additional characterisation tool for soil geochemical conditions as soil pH may fluctuate by up to 0.5 units over a tidal cycle (Catallo 1999) or can vary substantially as sulfuric materials are re-flooded, and surface waters may acidify if monosulfidic materials are suspended in an oxygen rich environment (Burton *et al.* 2006a; Johnston *et al.* 2004).

Redox conditions within sulfuric materials were generally oxidising (Figure 8-29 and Figure 8-30). However, acidic-strongly reduced redox conditions were measured within sulfuric materials for profile BG 11 (Figure 8-29). These Eh values were lower than expected and were likely due to: **(i)** seasonal variation in groundwater heights and **(ii)** heterogeneity of soil redoximorphic conditions (and features) within the soil profile. Seasonal variation in ground water table height at Gillman (of up to 1 m) may contribute to the reformation of pyrite and the consumption of acidity within re-submerged sulfuric materials during the wetter months, in areas where soil organic matter content is still adequate for strongly reducing conditions to return (Figure 8-31). The variability in redoximorphic features, namely the jarosite mottles within profile BG 11, likely influence (acidified) the soil pH within some soil layers that had a predominantly strongly reduced matrix, during winter. This variation could be better appreciated by installation of multiple Pt electrodes into redoximorphic features and by careful excavation of Pt electrodes (where possible) to describe the micro-environments surrounding the Pt tip. Redox conditions measured in sulfuric materials on the side of a recently excavated drain were considerably more oxidising (e.g. BG 15; Figure 8-27 and Figure 8-28).

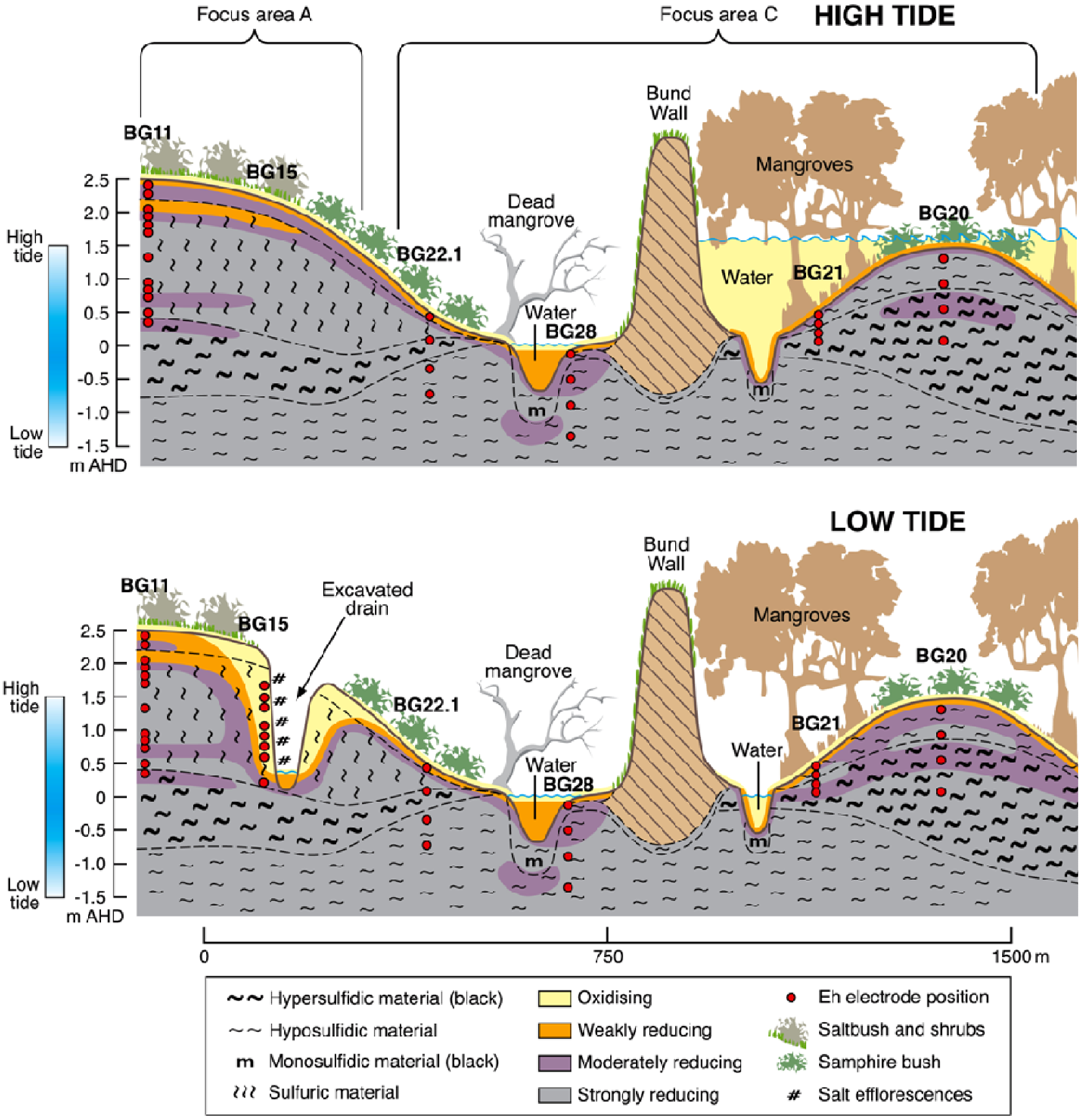


Figure 8-29 Descriptive soil-regolith toposequence model of the Gillman study site, specifically focus areas ‘A’ and ‘C’, showing changes in redox conditions under modified hydromorphic (focus areas ‘A’) and tidal (focus areas ‘C’) conditions. Gillman focus area ‘A’ contained sulfuric sandy soil materials that were dominated by strongly reducing conditions during wet winter months. The soils redox conditions became significantly more oxidising following excavation of a drain within the sulfuric materials. Tidal influences at Gillman focus area C change from hyposulfidic subaqueous organic soil dominated by strongly reducing redox conditions at high tide to hyposulfidic organic soils dominated by moderately reducing conditions at low tide.

Vegetation

Surface vegetation type and cover can affect soil redox conditions diurnally and seasonally as changes in temperature and solar radiation alter the productivity of vegetation and microbial populations (Figure 8-30 and Table 8-1). For example, there will be diurnal cycling in evapotranspiration (water uptake by the plant), movement of oxygen to the roots, general plant metabolism as well as the activity of organisms around the roots. Mangrove and samphire vegetation likely introduced oxygen to soils during low tides, increasing redox conditions at depth. This effect was less obvious in non-tidal environments, and was decreased dramatically during winter months when soil and air temperatures dropped below 15° C. Soils containing microbial mats (e.g. subaqueous sediments and mud flats) became more reduced during the day as the activity of sulfur reducing bacteria increased in response to warmer temperatures. Surface waters became more oxidising during the day due to algae photosynthesis. Algae may have also been responsible for moist sulfuric materials being more oxidising during the day than at night.

The theoretical relationship between Eh and the redox state of sulfur compounds and minerals can be summarised as shown in Figure 8-31. This figure shows the redox-pH effect on the stability of iron minerals. Superimposing on Figure 8-31 the observed values for intertidal and non-tidal profiles shows that near surface sediments were dominated by goethite dissolution. In tidally influenced environments goethite stability may be controlled by oxygen introduced by vegetation, and infiltrating surface waters. Iron sulfide dissolution predominated at depth were redox conditions were more reducing (Figure 8-31). Redox conditions measured in low lying (subaqueous and hydromorphic soils) within non tidal profiles showed similar trends to intertidal soil profiles. Only one of the two elevated, non tidal soil sediment profiles (BG 15) which contained sulfuric materials reached the jarosite stability zone. Jarosite mottles were observed in this profile. Soil profile BG 11 also contained sulfuric material (and jarosite mottles) but redox measurements did not reach the jarosite stability field during the monitoring period (Figure 8-31). This was likely due to seasonal variations in and to soil heterogeneity as redox monitoring at profile BG 11 was only carried out during one wet winter period.

Table 8-1 Selected soil profiles from the St Kilda and Gillman study sites that were monitored for redox conditions. The table summarises characteristics of; (i) tidal exchange, (ii) redox condition, (iii) map units, (iv) water status and soil drainage (v) soil classification and (vi) and acid sulfate soil materials. Symbols are for reference to Figure 8-30 and Figure 8-31.

Soil profiles (colour coded for figures)		**Redox classes from mean Eh values (range for soil profile)**	**Map unit no.**	**Water state, ponding / drainage**	**Aust. Soil Classification (Isbell 2002)**	**Acid Sulfate Soil materials**
Former intertidal to supratidal areas (Gillman study site)						
BG P 5	⚫	Circum-neutral-weakly reducing to circum-neutral-strongly reducing	**1.** Water	Wet – subaqueous	Sodosolic, Salic Hydrosol	Hyposulfidic, monosulfidic
BG 28	🟣	Basic-moderately reducing to basic-strongly reducing	**2.** Benthic mat and bare salt scalded mud flats	Wet (winter) poorly drained – inundated seasonally / storm event	Epicalcareous, Hypersalic Hydrosol	Hyposulfidic, monosulfidic
BG 22.1	🟤	Acidic-oxidising to circum-neutral-strongly reducing	**4.** Dense low heath - samphire shrublands	Moist (winter), moderately well drained	Haplic, Hypersalic Hydrosol	Hyposulfidic, monosulfidic (minor)
BG 15 (open drain)	🟡	Acidic-oxidising to acidic-moderately reducing	**5.** Open low scrub and grasses	Moist (winter), moderately well drained	Sulfuric, Salic Hydrosol	Sulfuric, hypersulfidic, hyposulfidic
BG 11	🔴	Basic-weakly reducing to acidic-strongly reducing	**6.** Open grass plain and scrub	Moist (winter), well drained	Sulfuric, Salic Hydrosol	Sulfuric, hypersulfidic, hyposulfidic
Undisturbed intertidal areas (Gillman and St Kilda study sites)						
BSK 5 (strong tides)	◼	Basic-weakly reducing to basic-strongly reducing	**9.** Water	Wet, poorly drained	Sapric, Histic, Intertidal Hydrosol	Hypersulfidic, hyposulfidic, monosulfidic
BSK 8 (modest tides)	🟦				Sapric, Epicalcareous, Intertidal Hydrosol	
BSK 4 (strong tides)	🟫	Circum-neutral-moderately reducing to basic-strongly reducing	**10.** Mangrove woodland	Wet, moderately to poorly drained	Hemic, Histic-Sulfidic, Intertidal Hydrosol	Hypersulfidic, hyposulfidic, monosulfidic (minor)
BG 21 (modest tides)	🟩				Hemic-Sulfidic, Intertidal Hydrosols	
BSK 7 (modest tides)	🟪					
BG 20 (minor tides)	🟩	Circum-neutral-moderately reducing to basic-strongly reducing	**11.** Low growing salt marsh plants	Wet, poorly to moderately well drained	Hemic-Sulfidic, Intertidal Hydrosol	Hyposulfidic, monosulfidic
BG 6 (minor tides)	🟦				Histic-Sulfidic Intertidal Hydrosol	

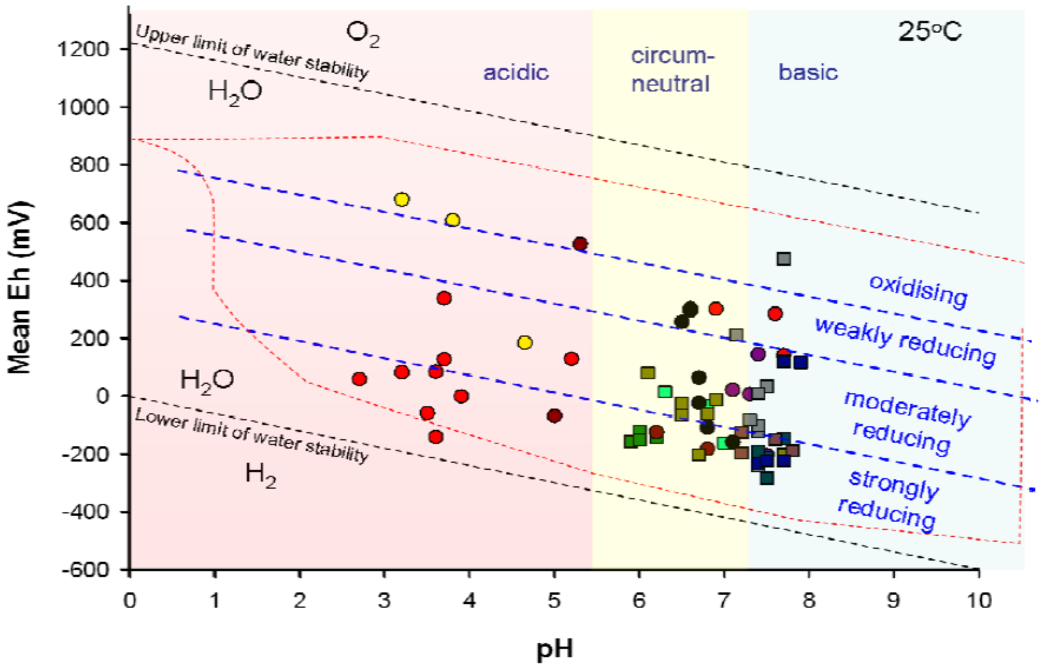


Figure 8-30 Idealised Eh versus pH diagram showing the redox "classes", divided by blue dotted lines (adapted from Krauskopf (1967) and Zhi-Guang (1985)). Mean Eh vs pH of intertidal soil profiles are plotted as square points and non tidal soil profiles are plotted as circular points. Red dotted line indicates the constraint line for natural environments (after Baas Becking *et al.* (1960)). Soil profiles are colour coded – refer to Table 8-1.

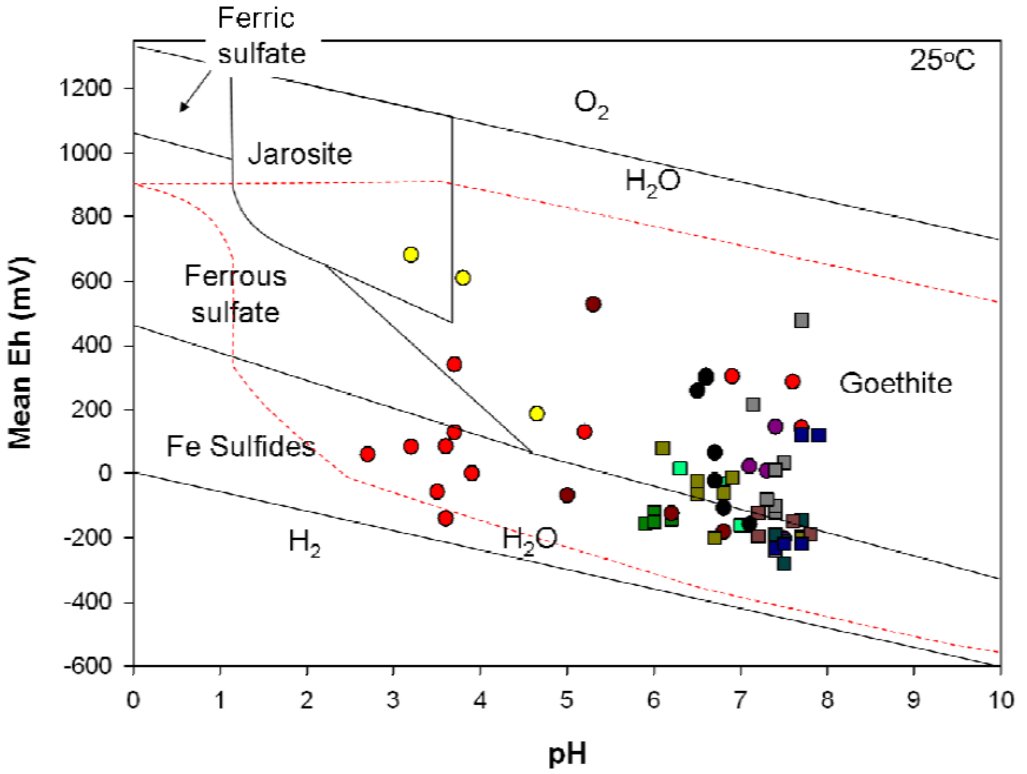


Figure 8-31 Idealised Eh/pH diagram for the Fe-S-O system showing mineral phases that might be expected to be stable under various conditions (after van Breemen (1988)). Red dashed line indicates the constraint line for natural environments (after Baas Becking *et al.* (1960)). Mean Eh/pH of intertidal soil profiles (square points) and non tidal soil profiles (round points) represent measurements taken in soils from the Gillman and St Kilda study sites. Soil profiles are colour coded according to Table 8-1.