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Redox changes in a small wetland with potential acid sulfate, saline and sodic soils

MERRY Richard H. (1), **FITZPATRICK Robert W.** (1), **BONIFACIO Eleonora** (2), **SPOUNCER Leonie R.** (1) and **DAVIES Philip J.** (1)

(1) CSIRO Land and Water, PMB No 2, Glen Osmond, South Australia, 5064, Australia
(2) Universita' di Torino, DIVAPRA - Chimica Agraria, Via L. da Vinci 44, 10095 GRUGLIASCO (TO), Italy

Abstract

The study site is a typical, perched wetland in a saline, sulfidic discharge area in the eastern Mt Lofty Ranges near Adelaide, South Australia. The wetland is part of the 10% of strongly waterlogged landscape identified by GIS analysis of a larger 80 km^2 area. Approximately 40% of this area was identified as being poorly drained, but only a small proportion, less than 10%, supports wetland vegetation. The climate is Mediterranean with hot, dry summers and cool, moist winters.

Better management of these wetlands can be attempted if more is known of the redox processes associated with soils in them, their likely response to erosion, drainage, vegetation changes and grazing, and their effect on water quality. Consequently, the objective of this work is to report on redox changes that occur seasonally, diurnally and after rainfall in soils along a 25 m transect with soil conditions that range from sodic (margin area) to saline (seepage area) to potential acid sulfate (marsh area). The transect was instrumented at five points from the margin area (re-vegetated with tall wheatgrass), saline seepage area (little or no vegetation) and marsh area (vegetated with native wetland plants). A data logger recorded Eh from eight platinum electrodes, temperature at two points, and rainfall. The sensors for Eh were placed at 5 and 20 cm depths and for temperature at 5 cm. Data records were captured at six hourly intervals and were accumulated continuously from February 1999 to February 2001.

Daily redox cycles and some seasonal effects measured in the permanently wet marsh soils are thought to be associated with the activity of C^4 plants and oxygen diffusion. Subsoils (at 20 cm) in the marsh remain reduced and sulfidic throughout the year. Eh sensors, either at 5 or 20 cm depths, indicated increasingly reduced conditions as a direct response to rainfall events and, eventually, a greater, lagged decrease to about -200 mV over several days after significant rain events in May that remained reduced until spring (September). Lowering of the groundwater table in summer resulted in oxidation, formation of ferrihydrite, precipitation of sulfate salts and formation of magnesium-substituted calcite in the upper few centimetres of the marsh soil.

Should the marsh erode or drain, there are likely to be significant consequences in the release of salts, iron minerals and protons mobilising toxic metals into drainage lines. The main sources of sulfur are significant sulfide mineralisations that occur in the region. Relict sulfidic wetlands can be recognised in stream lines within the same

catchment. They produce significant acidification on exposure through erosion and are local sources of salinity, generate sodic soils and release iron and aluminium minerals.

Keywords: redox, wetland management, salinity, sulfidic soils

Introduction

GIS analysis of an 80 km^2 area (Davies *et al.,* 2000; Fitzpatrick *et al.,* 1999) in the eastern Mt Lofty Ranges about 50 km north-east of Adelaide, South Australia, indicated that about 10% of the landscape is strongly waterlogged for most or all of each year. Approximately 40% of this 80 km^2 area, including the strongly waterlogged land, was identified as being poorly drained, but only a small proportion, less than 10%, supports wetland vegetation. Better management of these wetlands can be attempted if more is known of their soils, the redox processes associated with them, their likely response to erosion, drainage, vegetation changes and grazing, and their effect on water quality.

The objectives of this study are to: (i) report on redox changes that occur seasonally, diurnally and after rainfall in soils along a 25 m transect through a saline seepage - marsh area with soil conditions that range from sodic to saline to potential acid sulfate, and (ii) interpret the observed physico-chemical conditions with optimum land management.

Materials and Methods

Work was carried out in the Herrmann's catchment (139^o 01' E; 34^o 53' S; area about 2 km^2) near Mt Torrens in the Mt Lofty Ranges, about 50 km north-east of Adelaide, South Australia (Fitzpatrick *et al.,* 1996). The undulating, hilly landscape of the Mt Lofty Ranges, with altitudes in the range 400 to 500 m and local relief about 30 to 50 m, supports agriculture varying from predominantly extensive grazing to minor viticulture with a variety of soil and groundwater processes. The climate of the area is Mediterranean, with a pronounced maximum of rainfall in winter (May to August) and hot, dry summers (December to February) and an annual rainfall of 6-700 mm.

The marsh area is approximately circular and about 40 m in diameter. A saline seepage area surrounds the marsh, which is situated upslope from the confluence of what are now two incised streams (see Figures 2 and 6 for site 2 in Fitzpatrick *et al.,* 1996). As the existing vegetation is fairly typical of marsh areas in the region, it is likely that the site has been wet for a long period. However, rising saline water tables have resulted from decreased water use efficiencies of the annual agricultural plant species that have replaced native, perennial plants and this has resulted in a significant increase in size of the surrounding saline seepage, over the past decade or two. The effects of increasing sodium concentrations in the soils has resulted clay dispersion and decreased hydraulic conductivities. What was originally a valley floor wetland has migrated upslope and is now perched above the two incised streams (see Figure 2 for site 2 in Fitzpatrick *et al.,* 1996).

Soils of the study site (Table 1) have developed on lower slopes in Quaternary valley sediments derived from Cambrian metasediments containing pyrite. Hydrology at the site is described by Fitzpatrick *et al*. (1996). In marsh areas, water permanently ponds at the surface - and the pressure of the groundwater aquifer is higher in the marsh than the saline seepage area. Water levels in the shallow wells and deep piezometers are similar and fluctuate in the A and E horizons during periods of wetting and drying and indicate the both the groundwater tables from the upslope soils, water storages and fractured Cambrian sediments discharge via the wetland, typically with electrical conductivities of 5 to 10 dSm^{-1} (see Figure 5 in Fitzpatrick *et al.,* 1996). The sodic soils in the area vegetated with tall wheatgrass (*Thinopyrum ponticum* (Podp.) Barkw and D.R. Dewey) immediately adjacent to the wetland show much lower salinities. These salinities increase in summer and from the subsoil to the soil surface due to concentration by evapotranspiration processes.

Table 1 Properties of the three areas of the wetland transect.

Transect length	0 – 8 m		8 – 16 m		16 – 25 m	
Area	Margin		Saline seepage		Marsh	
Soil condition	Sodic		Saline		Potential acid sulfate	
Main Vegetation	Tall wheat grass *Thinopyrum ponticum*		Mimulus and bare ground *Mimulus repens*		Reeds and rushes *Juncus* spp, *Typha sp*	
Surface condition	Hard setting		Seasonally dry, with halite, gypsum crust		Wet, algal growth, highly organic, ferrihydrite slicks	
Soil classification	[1] Mollic Natraqualf [2] Mesotrophic, Mottled-Subnatric Sodosol		[1] Typic Natraqualf [2] Mottled Salic Hydrosol		[1] Typic Sulfaquent [2] Sulfidic Salic Hydrosol	
Soil Depth (cm)	0- 5	5-10	0- 5	5-10	0- 5	5-10
pH_{ca}	6.64	6.6	7.65	8.01	6.73	8.09
[3] EC (dSm^{-1})	2.9	5.1	80.0	12.0	25.0	18.0
C (%)	2.0	1.4	1.7	0.86	13.0	2.7
S (%)	0.025	0.015	0.085	0.005	0.49	0.94
[3] SO_4 (mmol L^{-1})	2.0	1.5	34.3	4.7	25.9	33.1

[1] Soil Survey Staff (1999)
[2] Isbell (1996)
[3] Determined on a saturated paste

The transect was instrumented (Figure 1) over a distance of 25 m and recordings made continually at six hourly intervals. Times are recorded here in days after 1st January 1999. The "dry" margin (0 m) is re-vegetated with tall wheatgrass (Table 1), to approximately 8 m. The growth of tall wheatgrass in this environment is analogous to that described by Bleby *et al*. (1997). The soils are sodic with a strong clay increase at 20 cm (Natraqualfs). From 8 to about 16 m is without vegetation or sparsely vegetated with tall wheat grass or *Mimulus repens*, a small, salt tolerant plant. The surface of soils in this area become strongly encrusted with salts (halite and gypsum) on drying during summer and may be surface eroded. Some soils develop thin sulfidic horizons, but the soils are predominantly saline Natraqualfs. From about 16 to 25 m, the true wetland is vegetated with native wetland plants, principally *Juncus* spp. and *Typha* sp., and algal growth may be active in summer. The wetland is constantly wet from groundwater discharge and may have a centimetre or more of free water at the surface in winter or during rainy periods. The soils are sulfidic, organic (to about 13% C) and saline, and are underlain below about 25 cm by heavy, sodic clays (Typic Sulfaquent). In this soil the source of sulfur is principally from groundwaters draining the pyritic parent rocks, concentrated by evapotranspiration. During summer there are periods of oxidation of the sulfidic materials resulting in formation of ferrihydrite slicks. Magnesium substituted calcite has formed in the upper few centimetres of the sulfidic soil.

The hydrology of the soils of the dry end of the transect (0 m) is as expected for this soil type. Water flows vertically through the A horizon and laterally through the E horizon above the clayey B horizon. Water will perch on the B horizon following saturation and it is likely that there is or has been some groundwater influence as the soil is sodic, but electrical conductivity levels are lower (Table 1) than the other parts of the transect. The wetland and marginal areas with sparse vegetation are affected by discharge of groundwater under pressure, the wetland being continually wet and the marginal area drying out in summer (Fitzpatrick *et al.* 1996). In the latter, the seasonal salt accumulation discourages the growth of all but salt tolerant plants, in this case mainly *Mimulus*. The soils tend to seal and this may result in restricted oxygen diffusion.

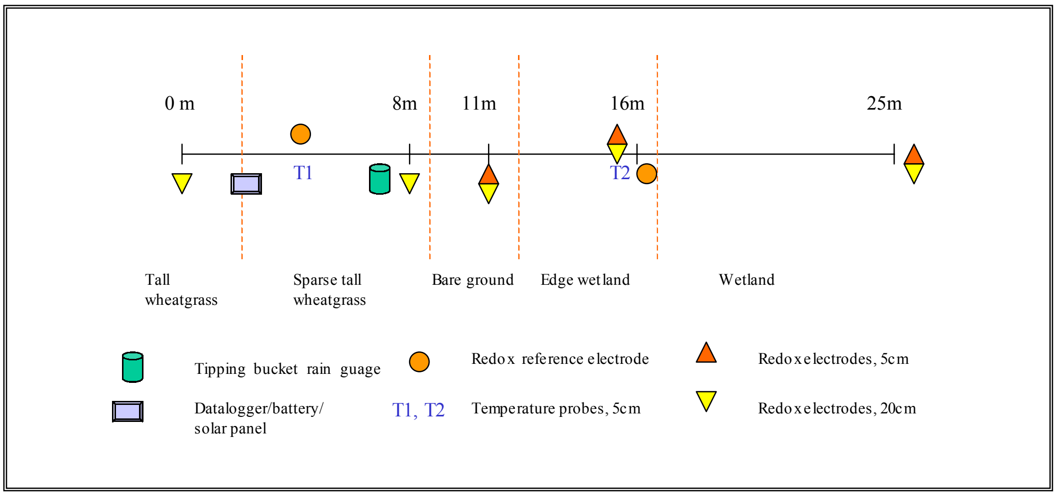

Figure 1 Layout of sensors and vegetation classes across the wetland transect.

A data logger recorded Eh from eight platinum electrodes, temperature at two points, and rainfall using a tipping bucket rain gauge (Figure 1). The platinum electrodes for recoding Eh were placed at 5 and 20 cm depths, but only at 20 cm at the 0 m and 8 m points. Two calomel reference electrodes were used and the voltages recorded on the data logger were corrected to a standard hydrogen electrode by adding 244 mV. The system for recording redox and environmental conditions has been described by Dowley *et al.* (1998). Temperature was recorded at 4 and 16 metres with the probes placed at 5 cm depth. The data records were captured at six hourly intervals from mid-day and were accumulated continuously from February 1999 to February 2001. It appears that the eight platinum electrodes took from two to about eight days to reach an apparent equilibration, depending on the environment of placement and the unknown effect of antecedent conditions and disturbance. Generally the electrodes placed at 20 cm equilibrated within a few days. None of the electrodes were replicated at any of the specific points on the transect so the continuous record was used to attempt to interpret processes operating points along the transect.

Results and Discussion

The complex changes in redox condition at sites along the transect have been interpreted through the influences and interactions evident considering soil depth, vegetation, groundwater, rainfall, and temperature. The effects show consistent patterns at the sites along the transect. The record is complex as the causes of change interact, but can be summarised as follows:

Soil depth and materials

Electrodes placed at 5 cm depth showed redox changes that were more variable than those placed at 20 cm. Changes in redox on a daily cycle (see below, and Figure 2) were clearly evident in the electrodes with shallow placement and occasionally evident at 20 cm, usually with a time lag of 6 to 12 hours, especially during the warmer parts of the year. The two electrodes placed at 5 cm in the wetland proper (at 16 and 25 m) remained oxidised (+550 to +600 mV) during the cold months of the year (Figure 3) with the electrode placed at 25 m becoming more reduced during the warmer months, suggesting an effect of increased biological reduction or oxygen consumption at this time. The amplitude and cyclic nature of these changes also suggest that they result from biological activity as they were not concordant with daily soil temperature changes (see below) and ceased when daily minimum soil temperatures fell below 12^{o}C. Electrodes placed in sulfidic horizons remained reduced (0 to –200 mV, Figure 2) most of the time, but showed some perturbations associated with rainfall events. The electrode placed at 20 cm (at 0 m along the transect) close to the boundary of the E and Bt2 horizons and below tall wheat grass was oxidised for much of the year (Figure 2), but became reduced for a period of about four months from May to September (Figure 3).

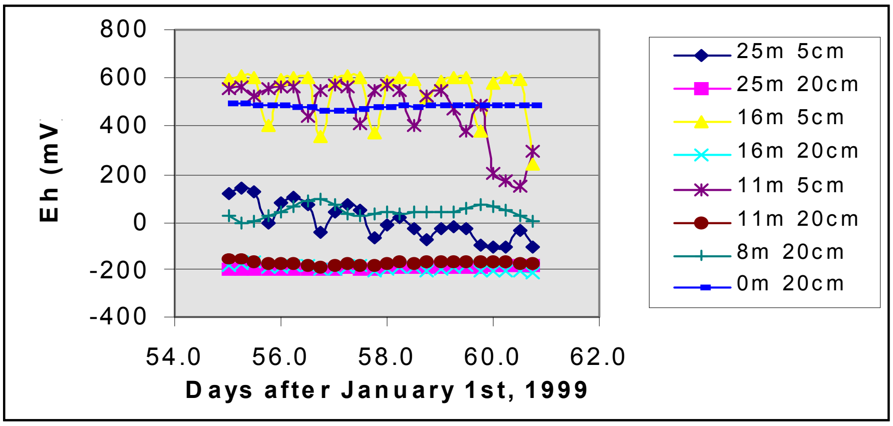

Figure 2 Soil redox status at five locations and eight depths along the wetland transect in summer. Four millimetres of rain fell late on day 59.

Vegetation/biology

It may be expected that there are specific effects of plants on soil redox condition. During the warmer part of the year (October to April), daily cycles in redox potential were observed (Figure 1). In the near surface soil layers of (particularly) the wetland, a sharp decrease in Eh of up to 200 mV was usually recorded at about 1800 hrs. Similar decreases in oxygen occurred at 20 cm and at the 11 m point, but usually damped. These cycles were not time concordant with the recorded daily soil temperature cycles, did not usually occur on rainy days when temperatures did not peak and ceased altogether (Figure 3), remaining relatively oxidised, when minimum soil temperatures at 5 cm dropped below about 12°C (about day 140 of the year) and recurred when temperatures rose above this level at about day 260. The wetland plants *(Juncus*, etc.) are predominantly C^4 and sensitive to low ambient temperatures. A possible explanation of why the daily cycling ceased in winter is that these plants became metabolically inactive at low temperatures and oxygen diffusion into the soils was then not limiting. The daily reduction "spike" on hot, sunny days may have resulted from increased oxygen supply being limited by diffusion rates which returned to adequacy in the evening and night when temperatures dropped and biological demand decreased. The detailed effects of the wetland plants, algal growth and other biota on soil redox condition in these soils require further investigation.

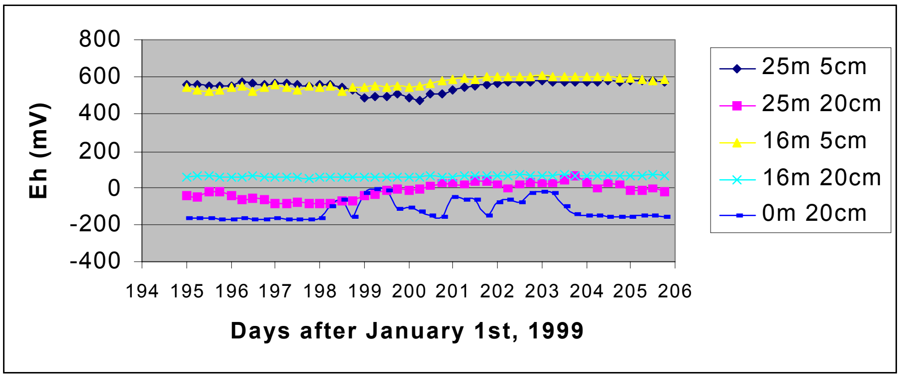

Figure 3 Soil redox status at three locations and five depths along the wetland transect in winter. Thirty nine millimetres of rain fell late on days 198 to 200. This figure has been simplified by removal of data for some electrodes.

Rainfall and groundwater

The effects of rainfall events are evident on the Eh record. Daily temperature cycles (not shown) are damped on rainy days and on fine days, the specific effect of rain the daily redox cycles observed in summer may be more difficult to observe because of the presence of these cycles. Electrodes that recorded oxidised conditions (+400 to +600 mV) showed concurrent decreases of tens of mV at the same time that rain was recorded, returning to the previous condition when the rain ceased. The inverse effect was observed on electrodes that were recording reduced conditions (+100 to –200 mV) where an increase of tens of mV was recorded (Figure 3). This suggests that rain falling perturbs the oxygen diffusion rates, causes a mixing of soil water of different redox status or reflects the rainwater itself. The electrode placed at the E/B horizon boundary below tall wheatgrass (0 m, 20 cm) shows interesting responses not evident in the wetland (blue line, Figure 4). During the warmer months of the year the redox potential is oxidised and stable (about +500 mV). As the soil saturates in autumn, it becomes increasingly reduced as oxygen is excluded or used biologically either by rising (reduced) groundwaters or by water perched on the sodic B horizon. Initially, before day 170, this electrode became reduced to about -200 mV over periods of 3 to 7 days after more prolonged rainfall events and re-oxidised over periods as short as 6 to 12 hours as oxygen re-entered the system. However, after day 170, the soil became saturated and remained reduced (about -200 mV) until day 290 (spring) after which it oxidised initially to +300 mV and slowly rose to +640 mV. Presumably this increase coincided with the removal of the perched water or lowering of the groundwater level.

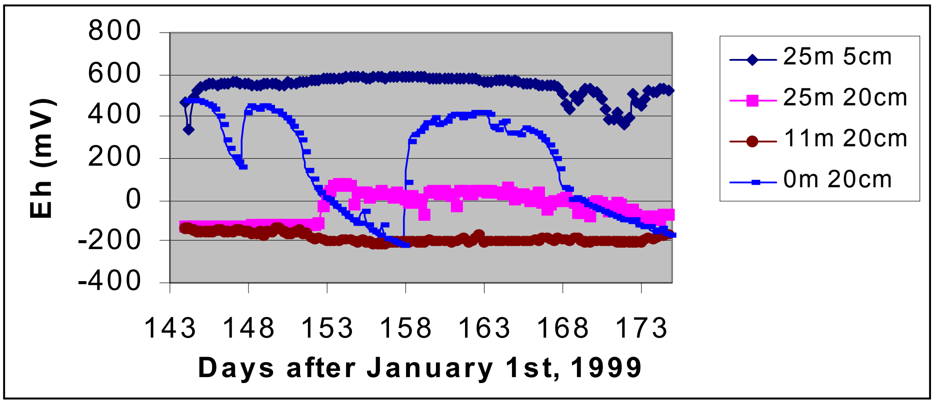

Figure 4 Soil redox status at three locations and four depths along the wetland transect in early winter. Eighteen millimetres of rain fell late on days 143 to 144, 21 mm from days 148 to 150, 2 mm on day 155, 34 mm from days 163 to 165 and 9mm on day 167. This figure has been simplified by removal of data for some electrodes.

In summary, daily redox cycles measured in the wetland soils are most probably associated with the activity of the wetland C^4 plants. Subsoils (at 20 cm) in the wetlands remain reduced and sulfidic throughout the year. Eh sensors, either at 5 or 20 cm depths, indicated altered conditions as a direct response to rainfall events. Several electrodes, but particularly the one placed at 20 cm below tall wheatgrass, indicated the onset of reducing conditions after significant rain events in autumn that eventually decreased to about -200 mV over several days and remained reduced until spring (September). Lowering of the groundwater table in summer resulted in oxidation, formation of ferrihydrite, precipitation of sulfate salts and formation of magnesium-substituted calcite in the upper few centimetres of the wetland soils.

Conclusions

This paper shows the complex interactions of soil, vegetation and hydrology with rainfall and ambient temperature that control the redox condition along a 25 m transect extending from sodic (margin area) to saline (seepage area) to potential acid sulfate soils (marsh area) with saline groundwater discharge area. The processes observed are dynamic and are affected by seasonal conditions and vegetation. Future work should include monitoring at time intervals shorter than six hours to enable more detailed observation of the processes operating. The observations have contributed to a better understanding of the establishment and maintenance of the wetland system and to their likely response to environmental change such as the consequences of drainage and lowering of the groundwater table with subsequent need for rehabilitation to manage salinity, oxidation of pyritic materials and acidification, and development of sodic soils.

Better knowledge of the wetland system has enabled the recognition of relict sulfidic materials from former wetlands exposed in eroded streamlines in the same catchment and elsewhere. On exposure they produce significant acidification and are local sources of salinity, generate sodic soils and release iron and aluminium minerals.

Acknowledgements

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References

Bleby, T.M., M. Aucote, A.K. Kennett-Smith, G.R. Walker and D.P. Schachtman. 1997. Seasonal water use characteristics of tall wheatgrass (*Agropyron elongatum* (Host) Beauv.) in a saline environment. Plant, Cell and Environment 20:1361-1371.

Davies, P.J., R.W. Fitzpatrick, D.A. Bruce, L.R. Spouncer and R.H. Merry. 2000. Use of spatial analysis techniques to assess potential waterlogging in soil landscapes. *In* J.A. Adams and A.K. Metherell (eds.). Soil 2000: New Horizons for a New Century. Australian and New Zealand Second Joint Soils Conference. Volume 3: Poster Papers. 3-8 December 2000, Lincoln University. New Zealand Society of Soil Science.

Dowley, A., R.W. Fitzpatrick, A. Cass and W. Besz. 1998. Measurement of redox potential (Eh) in periodically waterlogged viticultural soils. Proceedings of the International Soil Science Society Congress, Montpellier, France. 20-26 August, 1998. Symposium No. 35, p 12. CD ROM

Fitzpatrick, R.W., D.A. Bruce, P.J. Davies, L.R. Spouncer, R.H. Merry, E. Fritsch and D.J. Maschmedt. 1999. Soil landscape quality assessment at catchment and regional scale. (Mt Lofty Ranges Pilot Implementation Project, National Land and Water Resources Audit) CSIRO Land and Water Technical Report 28/99, July 1999, 69 p. (Also http://www.clw.csiro.au/publications/ technical99/ tr28-99.pdf).

Fitzpatrick R.W., E. Fritsch and P.G. Self. 1996. Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V Development of saline sulfidic features in non-tidal seepage areas. Geoderma 69:1-29.

Isbell, R.F. 1996. The Australian Soil Classification. CSIRO Australia. 143 p.

Soil Survey Staff. 1999. Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys. Second Edition. 869 p.