

Scientific Registration n° : 2135

Symposium n° : 35

Presentation : Poster

Measurement of Redox Potential (Eh) in Periodically Waterlogged Viticultural Soils

Suivi du potentiel rédox (Eh) dans des sols viticoles à engorgement temporaire

DOWLEY Andrew(1), FITZPATRICK Robert(2,3), CASS Alfred(3), BESZ William(3)

(1) University of Adelaide, P.B. N°1, Glen Osmond, South Australia, Australia, 5064

(2) CSIRO, Land & Water, P.B. N°2, Glen Osmond, South Australia, Australia, 5064

(3) CRC Soil & Land Management, P.B. N°2, Glen Osmond, S.A., Australia, 5064

Most viticultural soils in Australia are characterised by sandy to loamy textured surface horizons often with bleached E horizons overlying heavier textured (25 to 40% clay) natric Btng horizons. Consequently, irrigation and seasonal rainfall may cause waterlogging and salt accumulation. This poses a threat vineyard productivity and to grape juice and wine quality. However, accurate *in situ* measurements and continuous measurement procedures for monitoring degrees of alternating reducing and oxidising conditions in soils with fluctuating watertables have proved to be difficult to achieve in the field. Soil redox potential (Eh) is widely used as an indirect measure of *in situ* soil oxygen status. While it is regarded as being a simpler and more reliable for measuring *in situ* soil oxygen status than other parameters, a number of problems are encountered when long-term and continuous measurement is attempted. Our poster outlines the development of a system for the long term, automated measurement of soil Eh and soil moisture tension in the field. Eh data obtained from a seasonally waterlogged Typic Natraqualf and a poorly aerated Aeric Calciaquert is presented.

Our poster outlines a new method of producing cheap, reliable platinum electrodes for redox measurement that are capable of functioning continuously in the soil for a number of years. A new technique for attaining a reliable, stable and long lasting salt bridge between the redox reference electrode and the soil is presented. The design of a datalogger that is capable of simultaneously monitoring up to 8 Eh electrodes, 8 tensiometers, 8 gypsum blocks, 2 temperature probes and a tipping bucket rainfall gauge is presented. The datalogger is powered by a small, portable solar panel and is capable of storing data acquired six times a day for up to two months. Electronic temperature sensors are installed and output is logged in both the soil and in the salt bridge solution containing the reference electrode. This is done in order to record any redox fluctuations that may be associated with a change in soil temperature or the temperature of the reference electrode.

Duplicate electrodes measured Eh at three depths in a Typic Natraqualf and an Aeric Calciaquert in vineyards in South Australia for a period of two months. The redoximorphic features at the three depths in both profiles closely matched the Eh and rainfall data.

Keywords : Redox potential (Eh), irrigation, waterlogging, sodicity, Calciaquert, Natraqualf, redoximorphic features

Mots clés : potentiel Redot (Eh), irrigation, engorgement, sodicité, Calciaquert, Natraqualf, caractère rédoximorphe

Scientific Registration n° : 2135
Symposium n° : 35
Presentation : Poster

Measurement of Redox Potential (Eh) in Periodically Waterlogged Viticultural Soils Suivi du potentiel rédox (Eh) dans des sols viticoles à engorgement temporaire

**DOWLEY Andrew(1), FITZPATRICK Robert(2,3), CASS Alfred(3), BESZ
William(3)**

- (1) University of Adelaide, P.B. N°1, Glen Osmond, South Australia, Australia, 5064
(2) CSIRO, Land & Water, P.B. N°2, Glen Osmond, South Australia, Australia, 5064
(3) CRC Soil & Land Management, P.B. N°2, Glen Osmond, S.A., Australia, 5064

Introduction

The Australian wine industry is presently undergoing a rapid, export driven expansion. The commercial pressure for increased production has, however, led to the establishment of many new vineyards on seasonally waterlogged Natraqualfs (sandy to loamy textured surface horizons with bleached E horizons overlying heavier textured natric Btng horizons with 25-40% clay), and poorly aerated Aeric Calciaquerts. In many cases, the result has been unacceptably low productivity and fruit quality (Fitzpatrick *et al.* 1993). While there exists a pressing need for greater understanding of grapevine growth responses on these soil types, accurate *in situ* measurements and continuous measurement procedures for monitoring degrees of alternating aerobic and anaerobic conditions in these soils has proved to be difficult to achieve in the field.

Soil redox potential (Eh) is widely used as an indirect measure of *in situ* soil oxygen status. Although it is regarded as being simpler and more reliable for measuring *in situ* soil oxygen status than other parameters, a number of problems are encountered when long-term and continuous measurement is attempted.

The aims of this paper are to:

- (i) review the limitations associated with redox potential (Eh) measurement in the field,
- (ii) describe a new system that is specifically designed for the long-term, automated measurement and storage of soil redox potential data,
- (iii) present data obtained from a seasonally waterlogged Typic Natraqualf and a poorly aerated Aeric Calciaquert to illustrate the performance of this system in the field.

Limitations to measurement of redox potential in soils

Thermodynamic equilibrium is never reached in natural soil systems. Heterogeneity and thermodynamic instability in natural soil systems result in the measured redox potential

being a mixed potential that does not usually reflect, according to the Nerst equation, the ion oxidation states of present mineral species (Bartlett and James, 1995; Rowell, 1981). Although redox measurements are only semi-quantitative in the sense that the identity of the ions donating or receiving electrons is unknown, redox potentials are still valuable in providing an indirect measure of the soils aeration status for plant growth. Generally aerobic (oxidised) soils suitable for root growth and function have an Eh value greater than +300 mV while anaerobic (reduced) soils have values between +200 mV and -400 mV.

Redox measurements tend to be less stable and less reproducible in oxidising than in reducing environments. This is usually due to the low concentration of redox couples in well aerated soils (Veneman and Pickering, 1983). Nevertheless, even in well aerated soils, there is a close relationship between the soil redox potential and oxygen concentration in the soil atmosphere (Farrell *et al.*, 1991).

A number of practical problems have been encountered using Eh electrodes permanently installed for monitoring redox potential. Redox potential is usually determined by measuring the potential difference (EMF or voltage) between an inert (usually platinum) electrode installed in the soil and a reference Ag/AgCl or calomel electrode at the soil surface (Rowell, 1981). Current leakage from the soil solution to the platinum wire/copper wire junction of the Pt electrodes is a common problem with these measurements. This problem is especially evident when Pt electrodes are exposed to wet or waterlogged conditions for prolonged periods of time (Mann and Stolzy, 1972). Consequently, a rapid method for the construction of platinum electrodes that requires minimal equipment and which produces an essentially leak-proof electrode is required.

A second problem associated with permanently installed systems for monitoring soil redox conditions is the difficulty associated with maintaining a stable, long-term saltbridge connection between the reference electrode and the soil. Commercial reference electrodes generally only have a small salt bridge reservoir that requires frequent refilling. This is impractical in many field monitoring situations. Consequently, as part of this field monitoring system we have endeavoured to develop an enlarged salt bridge that maintains stable, long-term contact between the reference electrode and the soil.

Field redox measurements taken during the dry summer months are often further impeded by desiccated soils. At low soil moisture contents the electric flow rate, between the reference electrode and the soil, is greatly reduced. This results in prolonged stabilisation times or even continuous drifting of the potentiometer (Veneman and Pickering, 1983). The enlarged salt bridge discussed in this report was designed to minimise this problem.

Materials and Methods

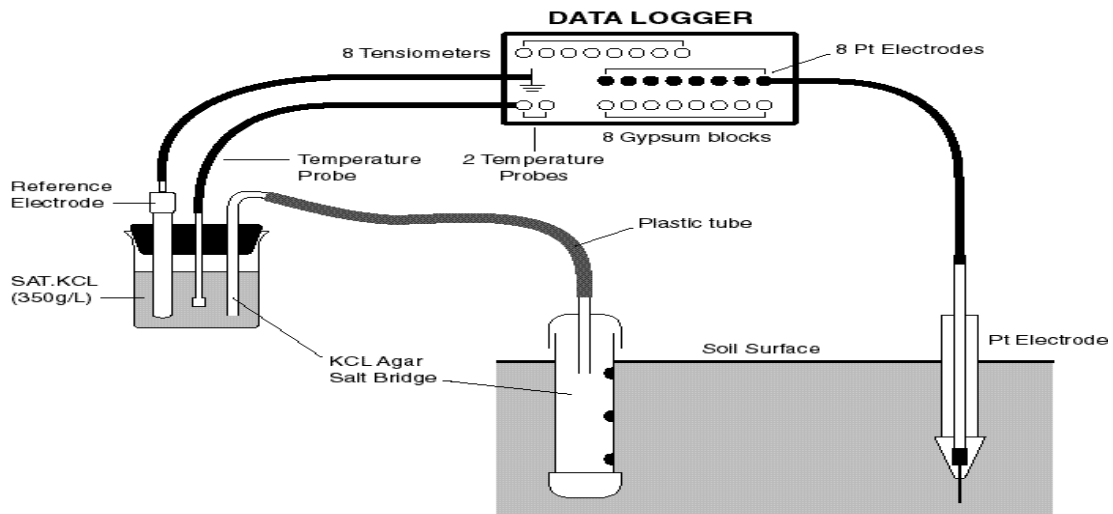
Eh Electrode

Platinum (Pt) electrodes were made by soldering 15mm of 18 gauge (1 mm) diameter Pt wire to 7/0.2 mm silver plated copper wire. Silver solder was used to form a durable, high quality contact between the platinum and silver coated copper wire. The copper wire was insulated with PTFE (teflon) which demonstrates extreme resistance to oils, acids, alkalis and other chemicals, and will not deteriorate in the presence of UV radiation (sunlight). The solder joint was insulated in adhesive lined, heat shrink tubing. The adhesive inner wall of the tubing melts when heated and is forced into component interstices by the shrinking action of the outer wall. This provides for a permanent encapsulation for protection against moisture intrusion into the junction.

Disposable, 1mL plastic pipette tips were then inserted over the solder joint to function as moulds. Leaving approximately 10 mm of platinum exposed, the moulds were filled with neutral-cure epoxy resin. Rigid plastic tubing (6 mm outside diameter (O.D.)) was then fitted over the PTFE coated copper wire and pushed into the resin filled pipette tip. This design ensured a reliable electrode with a junction rigidly encased in heat shrink tubing and resin to prevent penetration of soil solution. The electrode shape also allowed for installation by simply pushing the rigid plastic tubing with pointed pipette tip into the soil like a stake.

Salt Bridge

The salt bridge was constructed using a modification of the technique described in Veneman and Pickering (1983). The salt bridge consisted of a 250ml jar complete with rubber stopper, a bent length of 6 mm outside diameter (O.D.) glass tubing, a length of 6mm (O.D.), flexible, clear plastic tubing and a length of 25 mm (O.D.) PVC tubing, (300-700 mm long), with end caps. Holes (6 mm diameter) were drilled into the PVC tubing at points corresponding with the intended depth of the Pt electrodes that were to be inserted into the soil. The holes were covered with filter paper either glued or taped to the inside of the tube. The PVC tubing (with end cap in place), flexible tubing and glass tubing were then filled with saturated KCL solution (350g/l) containing about 3% by mass laboratory grade agar (Fig.1). To every liter of solution a few grains of phenol were added to prevent microbial growth within the salt bridge. A 6 mm hole was drilled in a second PVC cap which was placed on the top of the tube. The 6 mm agar filled plastic tubing was pushed through this 6 mm hole into the gel in the PVC housing to provide a good electrical contact. The glass tubing, also filled with the saturated KCl-agar gel, was inserted into the free end of the 6 mm plastic tubing (Figure1). Holes were drilled in the rubber stopper in order to fit the reference electrode and the agar filled glass tubing. The jar was filled with saturated KCl solution and the stopper sealed in place.



Fitzpatrick/Dowley fig. 1/12/97/1011/GER.

Figure.1: Schematic diagram of the automated redox monitoring assembly.

A further refinement to the reference electrode assembly was the addition of a temperature sensor to the salt-bridge reservoir (250ml jar) in which the reference electrode was inserted. This temperature sensor was set to record the temperature of the solution at the time that Eh measurements were recorded. With this addition the Eh of the reference electrode could be corrected for temperature (t) according to the equation ($Eh=206-0.7(t-25)mV$). Temperature sensors were also placed in the soil to delineate any correlation between profile temperature and Eh.

The salt bridge was installed in the field by hand auguring a 40mm diameter hole to the required depth. After the PVC housing had been inserted into the hole, the hole was back filled with a slurry of kaolinite and soil. This ensured a good electrical contact between the salt bridge and the soil. By this method a continuous and long lasting salt bridge had been constructed between the reference electrode and the depth in the soil of each installed platinum (Pt) electrode.

Datalogger

The datalogger was constructed to simultaneously monitor up to 8 Eh electrodes, 8 tensiometers, 8 gypsum blocks, 2 temperature sensors and a tipping bucket rainfall gauge. The datalogger was powered by a small, portable solar panel and was capable of storing 360 data sets (ie. 6 readings per for 60 days). Electronic temperature sensors were installed and the output logged in both the soil and in the salt bridge solution containing the reference electrode. This was done in order to record any redox fluctuations that may be associated with a change in soil temperature or the temperature of the reference electrode.

A schematic view of the system including Pt electrodes, salt-bridge assembly and datalogger is shown in Figure 1.

Results

Site and Soil Descriptions

Data from two sites is discussed in this paper. The two soils are representative of the major types of seasonally waterlogged or poorly aerated soils found in the viticultural regions of South Australia. Site 1 is located in the Barossa Valley and site 2 in the Coonawarra wine district in the south-east of South Australia (Table 1).

Table 1: Site and soil description of monitored sites

Site	1	2
District	Barossa Valley	Coonawarra
Grapevine Variety	Shiraz	Pinot noir
Soil Taxonomy (Soil Survey Staff, 1996)	Typic Natraqualf	Aeric Calciaquert

The Natraqualf at site 1 has a bleached E horizon overlying a gleyed (chroma of <2) and mottled Btng horizon. These morphological features are good indicators of seasonal waterlogging. Gleying also occurs in the Bssg1 horizon of the Calciaquert at site 2. Bright yellow coloured mottles and coatings on calcite nodules occur at the Bssg1/ Bk2 horizon boundary.

Redox Potential and Rainfall

Duplicate Eh electrodes were installed at the two sites at three depths. Redox potential (Eh) and related rainfall results obtained from the two sites are presented in Figures 2 and 3. Data presented here were collected over a period of 6 weeks during early spring when the soil conditions are expected to be wet.

Discussion

The Eh data for the Natraqualf indicates that different redoximorphic environments exist at different depths in the soil profile. The E horizon remained aerobic (oxidising) (>300 mV) throughout the spring of 1997 (Figure. 2). The redox conditions in the shallow clay horizon (Btng), however, fluctuated from aerobic to strongly anaerobic (reducing) (<0 mV with minimum value of -280 mV). These fluctuations in redox potential appeared to be associated with large rainfall events as is indicated by the rainfall data (>50 mm). The redox conditions in the Bt2 horizon remained reduced (<200 mV) for the entire season. Differences between the duplicate Eh electrodes at the same depths probably reflect slightly varying redox conditions.

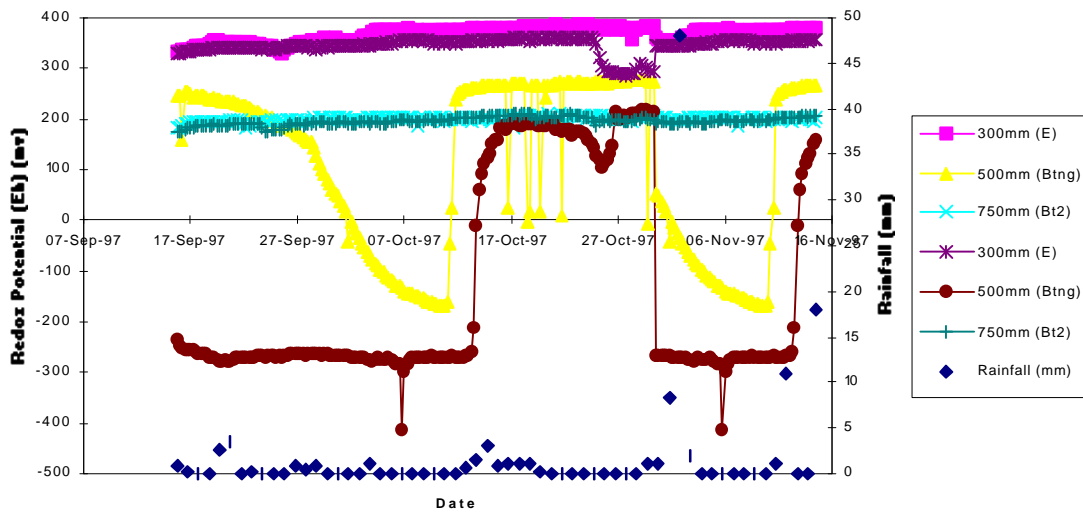


Figure. 2: Redox Potentials recorded in duplicate at three depths in the Natraqualf. Daily rainfall data is also presented.

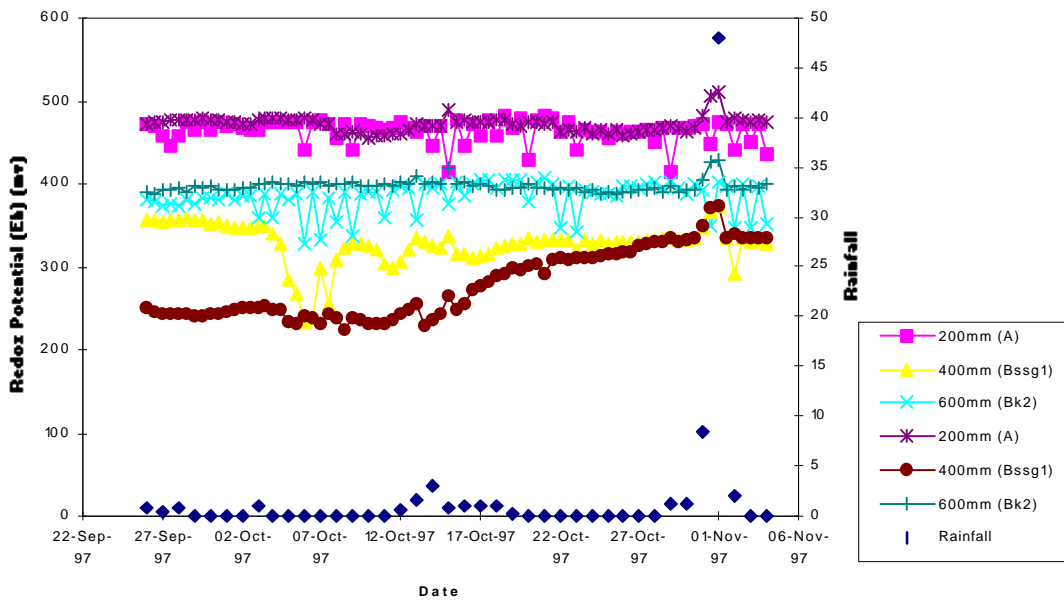


Figure. 3: Redox Potentials recorded in duplicate at three depths in the Aeric Calciaquert. Daily rainfall data is also presented.

The Aeric Calciaquert was generally more oxidising than the Natraqualf although a similar pattern between the two soils emerged. Both soils have an intermediate gleyed (Btng or Bssg) soil horizon that was reduced but with more oxidised horizons occurring both above and below. Consequently, the Ap and Bk2 horizons in the Calciaquert remained aerobic throughout spring (September to November), although the Ap horizon

was more oxidising than the Bk2 horizon. The gleyed Bssg1 horizon was partially reduced, ie. varied between 200 and 300 mV in some locations, during the spring but was aerobic at the end of winter. This was attributable to the low rainfall over the winter, followed by the wetter spring.

The bright yellow coloured mottles and coatings on calcite nodules at the Bssg1/ Bk2 horizon boundary is caused by the recent precipitation of goethite. This observation is confirmed by the redox data which suggest that partial reducing conditions in the Bssg1 (redox depletion zone) contributes to the formation and mobilisation of ferrous iron and precipitation of goethite in the more oxidized underlying Bk2 horizon (redox concentration zone). The redoximorphic features together with the measured redox conditions validate the «Aeric» subgroup classification of this soil (Soil Survey Staff, 1996).

Conclusions

An automated system for the monitoring of up to 8 Eh electrodes, 8 tensiometers, 8 gypsum blocks, two temperature probes and a tipping bucket rainfall gauge has been developed. Included in this system is a rugged, multi-channel data logger, cheap, easily constructed and reliable (Pt) electrodes and a semi-permanent salt bridge between the reference electrode and the soil. Early results indicate that the system can be used for the reliable, long-term, automated measurement of redox potential at multiple depths in seasonally waterlogged soils. Small, inexpensive tensiometers have also been developed. Further testing of these tensiometers is still required.

References

- Bartlett R.J., and James B.R. 1995. System for Categorising Soil Redox Status by Chemical Field Testing. *Geoderma* 68: 211-18.
- Farrell R.E., Swerhone G.D.W., and van Kessel C. 1991. Construction and Evaluation of a Reference Electrode Assembly for Use in Monitoring in Situ Soil Redox Potentials. *Commun. Soil Sci. Plant Anal.* 22, no. 11&12: 1059-68.
- Fitzpatrick R.W., Wright M.J., and Stevens R.M. 1993. Drainage, Sodicity and Related Problems of Vineyard Soils. *Proc. Eighth Australian Wine Industry Technical Conference*, Eds. C.S. Stockley, R.S. Johnstone, P.A. Leske, and T.H. Lee, 38-43. Adelaide: The Australian Wine Research Institute.
- Mann L.D., and Stolzy L.H. 1972. An Improved Construction Method for Platinum Electrodes. *Soil Sci. Soc. Amer. Proc.* 36: 853-854.
- Rowell D.L. 1981. Oxidation and Reduction. *The Chemistry of Soil Processes*, Eds. D.J. Greenland, and M.H.B. Hayes, 401-461. John Wiley & Sons Ltd.
- Soil Survey Staff. 1996. *Keys to Soil Taxonomy*. Seventh Edition. USDA Washington. USA.
- Veneman P.L.M., and Pickering E.W. 1983. Salt Bridge for Redox Potential Measurements. *Comm. Soil Sci. Plant Anal.* 14: 669-677.

Keywords : Redox potential (Eh), irrigation, waterlogging, sodicity, Calciauert, Natraqualf, redoximorphic features
Mots clés : potentiel Redot (Eh), irrigation, engorgement, sodicité, Calciauert, Natraqualf, caractère rédoximorphe