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Comparison between oxygen concentrations and redox potentials measured at the rear of Nordre Bredsgaarden at Bryggen, Bergen, Norway



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#### Summary

The National Museum of Denmark and MVH Consult in the Netherlands have been asked by Riksantikvaren to make a comparison between oxygen concentration and redox potential measurements in the cultural layers at the rear end of Nordre Bredsgården, Bryggen in Bergen. The comparison is part of an evaluation of different monitoring systems for unsaturated urban deposits.

The results show that it is possible to install redox sensors from the soil surface, thus avoiding costly and destructive excavations, but also that it can be difficult to determine exactly which soil layers the sensors are monitoring. The results emphasize the importance of sampling and describing soil during the installation. The results further indicate that pressing or drilling a hole for the probes may create a preferential flow path for percolating rainwater at least for a period of time. The current design of oxygen sensors were too fragile to be installed from the soil surface, so comparison is made to sensors installed in a test pit.

A direct comparison between oxygen concentration and redox potential measured in similar soil strata shows that when oxygen is present the redox potentials are between 600 and 800 mV. When oxygen is not present the redox potentials at this location vary between -200 and 800 mV. This means that it is not possible to evaluate the presence or absence of oxygen from the redox potential alone, as high redox potentials may also be found under anoxic conditions. A first comparison indicates that redox measurements in sand and other permeable deposits in the unsaturated zone are very fluctuating possibly because of their low redox buffer capacity. Redox potentials show a reaction to rainfall events, changes in groundwater level and soil water saturation, but the reactions may differ in different soil layers and are not fully interpreted yet. A comparison between the redox potential and groundwater chemistry should be made at a later stage, when more data are available.

The equipment used for redox potential measurements is sturdy enough to be installed in urban deposits, but it is recommended to continue work on the interpretation of redox potential measurements and how they relate to the decay rate of archaeological remains. These interpretations already exist to some extent for the oxygen measurements, but here it is recommended to develop more robust sensors and monitoring equipment.

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Continuous measurements of redox potential started on 5th of May 2011 and are not explicitly listed here (for depths see Table 1).

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# 1. Introduction

The Norwegian Standard for environmental monitoring and investigation of cultural deposits (NS 9451:2009) describes that monitoring should include continuous measurements of oxygen and/or redox potential in the soil. At the time of writing (2009) the experience with these types of measurements in cultural layers was limited, but during the latest years new equipment and more data has become available. It is thus relevant to evaluate the first experiences with both oxygen and redox measurements – Do the extra expenses give a significantly better evaluation of the preservation conditions? Can the two methods substitute each other or are both types of measurements necessary? Can the results be readily interpreted in terms of decay rate of archaeological material?

The evaluation of the methods was discussed at meetings between Riksantikvaren and monitoring specialists in Copenhagen (15th December 2010) and in Bergen (22nd March 2011). It was suggested that a comparison should comprise three stages: a literature review of both oxygen and redox measurements in cultural deposits; a direct comparison of the two methods in the laboratory; and a direct comparison of the two methods in the field. Laboratory studies will be initiated during the autumn 2012, while this report represents a direct comparison in the field.

Both types of equipment have been installed at Nordre Bredsgården at Bryggen in Bergen. Oxygen sensors were installed in October 2010 in a small test pit (Matthiesen & Hollesen 2012) and redox probes were inserted in May 2011 by pushing a small hole into the deposits (Vorenhout 2011). Almost 1 year of data is available at this point, which will form the basis of the field comparison. At a meeting at Riksantikvaren in Oslo (28th March 2012) it was decided that the comparison should be done stepwise by the following priority list:

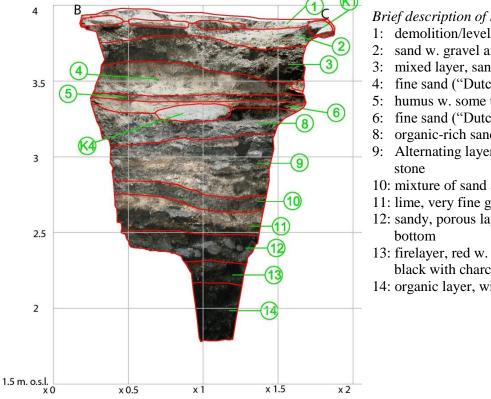
- 1. Validate the positions of the equipment are the oxygen and redox sensors placed in exactly the same cultural layers?
- 2. Validate if installation in a test pit vs. installation by 'Direct Push' technique will influence the results does the installation for instance create artificial flow paths for infiltrating water?
- 3. Make a direct comparison between oxygen and redox values measured at the same depth, in order to check how they correlate and/or supplement each other
- 4. Compare the results to soil moisture, groundwater level and rainfall
- 5. Compare the results to groundwater chemistry
- 6. Discuss implications for preservation conditions

Riksantikvaren has asked the National Museum of Denmark and MVH consult in the Netherlands to make this comparison, putting main focus on point 3.

#### 2. Site description and available data

Comparison of oxygen and redox data is based on measurements at the rear of Nordre Bredsgården, Bryggen, where the groundwater level is low and the upper 3 m of the deposits are unsaturated. Here, a small test pit was established in 2006, and a depth profile of the soil strata from the north-eastern part of the excavation is shown in Fig. 1 (Matthiesen, 2007). The test pit was re-opened in October 2010, and oxygen, temperature and water content sensors were installed directly in the soil profile in the south eastern part of the excavation (Matthiesen and Hollesen, 2012). The depth of each sensor was measured by theodolite, using the lid on MB21 as a reference (2.155 m asl) - the uncertainty is estimated to 1-2 cm. The horizontal position was not measured for each individual sensor, but Figure 2 shows their approximate distribution. The cultural layers around the sensors were described during the installation (Table 1) and may differ slightly from the layering shown in Figure 1.

Redox sensors with built-in temperature sensors (Vorenhout et al., 2011) were installed from the soil surface in May 2011 into pre-pushed holes in the deposits created by Direct Push technique (MVH consult, 2011, Figure 3). The redox sensors were inserted as a bundle of glass fibers with the measuring tips placed in approximately the same depths as the O<sub>2</sub> sensors in the test pit and at 1 m distance from the pit (Figure 2, no. 5, 6). The positions of the redox probes were measured by Multiconsult, and due to the installation technique the uncertainty on the depth of the sensors is estimated to be  $\pm 5$  cm. Unfortunately, detailed information of the different soil strata was not logged during the installation, so instead the soil description from the installation of dipwell MB21 next to the redox sensors is used (Dunlop, 2007).



Brief description of soil strata:

- 1: demolition/levelling deposit
- 2: sand w. gravel and pebbles
- 3: mixed layer, sandy w. decayed wood
- 4: fine sand ("Dutch ballast sand")
- 5: humus w. some thin planks
- fine sand ("Dutch ballast sand")
- organic-rich sandy layer w. timber
- 9: Alternating layers of lime, charcoal and
- 10: mixture of sand and lime
- 11: lime, very fine grained
- 12: sandy, porous layer w. stones at the
- 13: firelayer, red w. sand in upper part, black with charcoal in lower part
- 14: organic layer, with timbers

Figure 1: North-east profile of the excavation. Each individual soil layer has been thoroughly described by archaeologist Rory Dunlop (2007) using a standardized layer recording system. An ultra-short description of the layers is given to the right.

In addition, redox sensors have been installed along a transect from the swales towards the test pit to investigate the lateral effect of the planned infiltration events (Figure 3, no. 1-4) near the sheet piling (at MB13) and in Bryggestredet (at MB39). As a test a few oxygen sensors were installed from the soil surface along with these redox probes. However, almost half of the oxygen sensors were damaged during the installing, showing that the design of the sensors needs to be changed if they shall be used for installation from the soil surface.

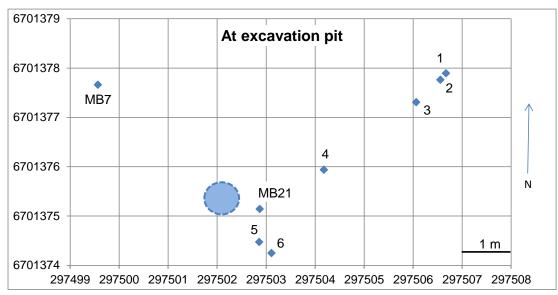


Figure 2: Positions of dip wells MB7 and MB21 and of redox probes installed at the excavation pit. The blue circle indicates the approximate area of  $O_2$ , temperature and water content sensor distribution. Number 5 and 6 mark the position of the redox depth profile included in this study.



Figure 3: Picture of the rig with gauging probe (Direct Push technique)

Table 1 gives an overview of the installed sensors in relation to soil stratigraphy. Dipwells MB7 and MB21 are perforated for water intake at 0.46 to -1.57 m asl and 1.61 to 0.61 m asl, respectively.

Depth	Water	Oxygen	Temperature	Redox-	Soil type
(m asl)	content		•	Temperature	Excavation/MB21
4.14				1	Soil surface*
4.12			Temp 1		Cobblestone
4.04				R41(26)-4.3	Sand
3.92	SM200-4	Oxy 2	Temp 2		Sand
3.79			- I	R40(25)-4.1	Demolition layer
3.68		Oxy 3	Temp 3		Backfill
3.6	SM200-3 <sup>+</sup>				Backfill
3.54				R42(27)-4.2	Sand
3.46		Oxy 4	Temp 4		Backfill
3.31	SM200-2 <sup>+</sup>	Oxy 1			Dutch sand (#6)
3.29	511200 2			R39(24)-4	Dutch sand
3.24				R38(23)-3.7	Dutch sand
3.21		Oxy 5	Temp 5	100(23) 3.1	Backfill
3.09	Theta 1	ONY 5			Organic (#8)
3.05	Theta I	Oxy 6	Temp 6		Organic (#8)
2.8				R15(15)-2.3	Silty/sandy humus
2.77	Theta 2	Oxy 7	Temp 7	K15(15)=2.5	Lime/sand (#9/10)
2.74		OXy /		R37(22)-3.6 <sup>+</sup>	Lime
2.5		Oxy 8	Temp 8	K37(22)-3.0	Lime (#11)
2.49		UXY 0		R13(13)-2.1	Mineral
(6)				K15(15)-2.1	(sand/gravel)
2.37	Theta 3				Gravel (#12)
2.31	Theta 5	Oxy 9	Temp 9		Gravel (#12)
2.3		Uny y		R14(14)-2.2	Mineral
2.0				KI ((1)) 2.2	(sand/gravel)
2.24				R36(21)-3.5	Mineral
					(sand/gravel)
2	Theta 4	Oxy 10	Temp 10		Organic (#14)
1.99				R12(12)-2	Charcoal
1.74				R35(20)-3.4	Timber
1.24				R34(19)-3.3	Mineral (sand/gravel)
0.74				R33(18)-3.2	Organic/timber
0.27				R32(17)-3.1	
-0.26				R31(16)-3	

Table 1: Overview of sensor installations at the excavation

\*surface at excavation, also taken as reference level for conversion of depths below street level to m asl for the redox depth profile (Figure 2). The uncertainty of the depth placement for the  $O_2$  sensors is  $\pm 1-2$  cm, for redox probes  $\pm 5$  cm. + sensors not working. Labelling of redox sensors: Redox ID(logger channel)-temperature ID. For the oxygen sensors the soil type was noted during the installation, and for the redox sensors the soil type is based on the description of samples from MB21 next to the sensors (Dunlop 2007).

In Appendix 1, Table A1, monitoring periods and data availability for the different sensors is described. This report includes continuous redox potential measurements during the first year from May 2011 to April 2012 where the logger stopped.

## 3. Results

The following paragraph gives an overview of the monitoring since May 2011 and the data availability. For direct comparison of all data the average of time intervals of 30 minutes has been calculated.

Figure 4 compares the recordings of the temperature sensors built-in in the redox probes (RT) with the temperature sensors placed besides the oxygen sensor tips in the test pit (Temp). There is a good correlation between the two readings of sensors installed in similar depths, but temperature readings from the redox probes are more fluctuating. Both sets of sensors show that the annual variations in temperature decreases with depth, as expected. Temperatures measured by the redox temperature sensor at 4.04 m asl just below the cobblestones closely follow air temperature (not shown).

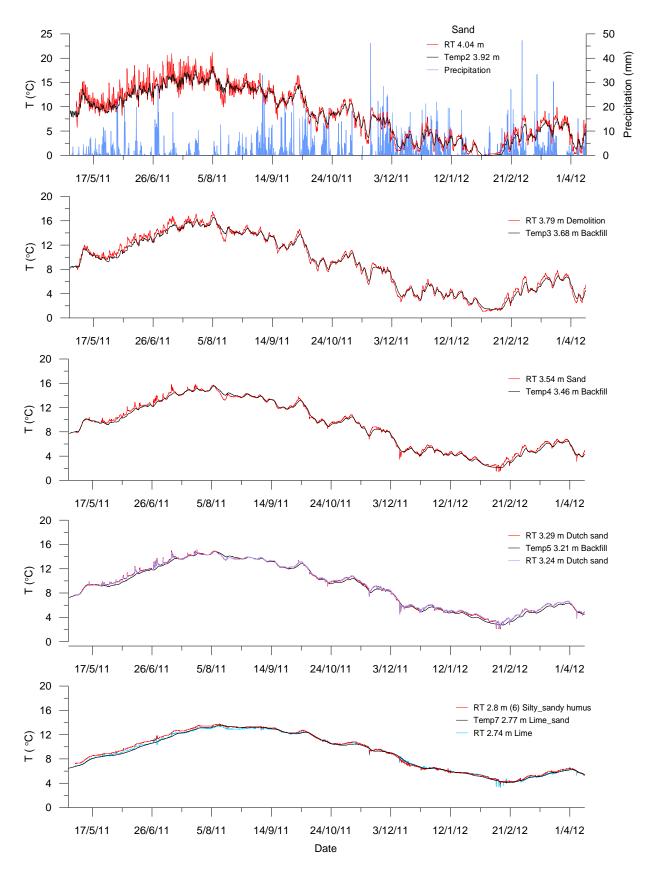


Figure 4: Temperature in different deposits measured with the redox electrodes (RT) at position 5 and 6 and the temperature/oxygen sensors in the test pit (Temp). For comparison rainfall data from the meteorological station Florida and groundwater level at dip well MB21 is included.

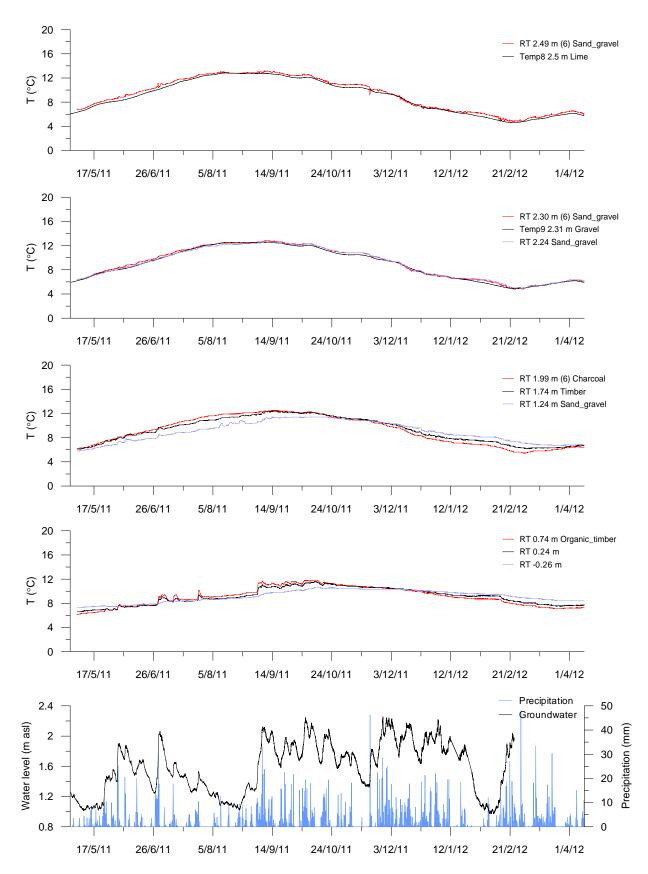


Figure 4 continued: Temperature in different deposits measured with the redox electrodes (RT) at position 5 and 6 and the temperature/oxygen sensors in the test pit (Temp). For comparison rainfall data from the meteorological station Florida and groundwater level at dip well MB21 is included.

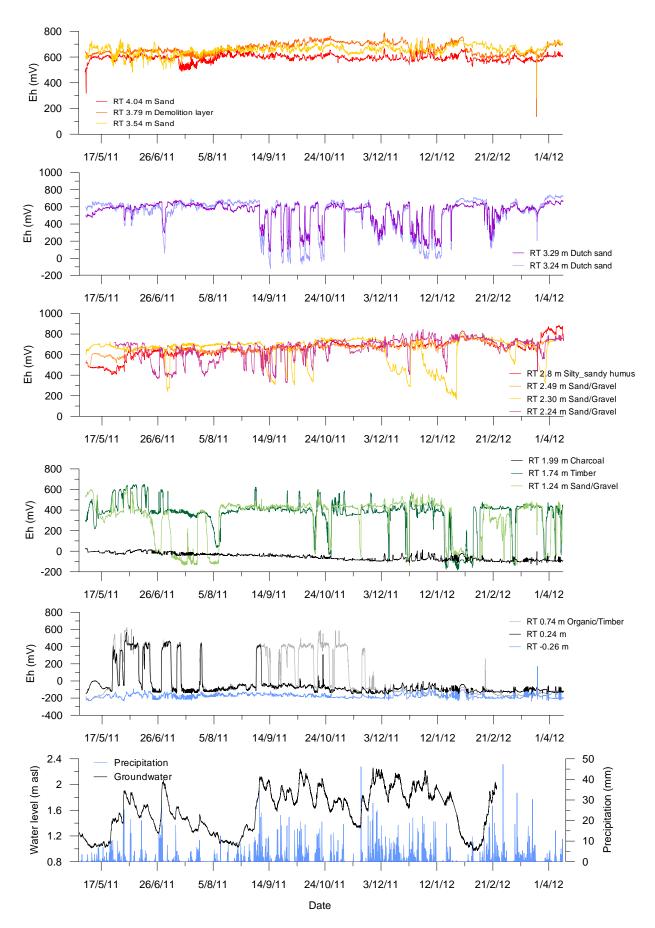


Figure 5: Redox potential (Eh) in different soil depths. For comparison rainfall data from the meteorological station Florida and groundwater level at dip well MB21 is included.

Redox potential (Eh) measurements are summarized in Figure 5. Values are corrected to standard hydrogen electrode potentials (SHE). Aerobic soils can become anaerobic and then reduced within a few minutes to hours of saturation due to a decreased  $O_2$  diffusion rate. A commonly used classification to describe the redox status by Mitsch and Gosselink (2007) is shown in Table 2.

Element	Oxidized Form	Reduced Form	Approximate Redox Potential	Degree of reduction
			for Transformation (mV)*	
Oxygen	O <sub>2</sub>	H <sub>2</sub> O	600 to 400	Oxidising
Nitrogen	$NO_3^-$ (nitrate)	$N_2O, N_2, NH_4^+$	250	Weakly reducing
Manganese	Mn <sup>4+</sup> (manganic)	Mn <sup>2+</sup> (manganous)	225	
Iron	Fe <sup>3+</sup> (ferric)	Fe <sup>2+</sup> (ferrous)	+100 to -100	Moderately reducing
Sulphur	$SO_4^{2-}$ (sulphate)	S <sup>2-</sup> (sulphide)	-100 to -200	Strongly reducing
Carbon	CO <sub>2</sub> (carbon	CH <sub>4</sub> (methane)	Below -200	
	dioxide)			

Table 2: Oxidized and reduced forms of several elements and approximate redox potentials for transformation in wetlands (modified after Mitsch and Gosselink (2007))

\*These potentials may vary as pH and temperature also affect the rates of transformation.

There exist other schemes applying different thresholds based on previous field observations or theoretical equilibrium thermodynamics. According to Schüring et al. (2000) in natural waters and at a pH between 7 and 8 oxidising conditions prevail from ca. 700 to >800 mV, nitrate reduction is dominant at around 700 mV, manganese reduction between 400 and 600 mV, iron reduction from 100 to -200 mV followed by sulphate reduction and methanogenesis below -200 mV and fermentation below -400 mV.

In archaeological deposits redox potentials in the range of the classification by Mitsch and Gosselink (2007) are normally observed (M. Vorenhout, pers. comm.), and thus their classification is used in the following. Applying this scheme to our study site, strongly oxidizing conditions (median 600 to 700 mV) prevail in the upper 1.9 m of the depth profile (or down to 2.24 m asl) in mostly permeable, sand or gravel containing layers. Frequent periods of weakly to moderately reducing conditions occur during autumn and winter in the Dutch sand (in 3.24 to 3.29 m asl). In the meter underneath (1.2 to 2.2 m asl) the system becomes more reduced and median redox levels decrease to ca. 400 mV corresponding to weakly reducing conditions, but in periods conditions may vary between oxidizing and strongly reducing. An intercalated layer of charcoal at 1.99 m depth continuously exhibits moderate reducing conditions (median -53 mV). In the permanently saturated zone from 0.74 m asl median redox potentials become negative (around -100 mV), but also here occasionally oxidising conditions are observed (> 500 mV). The lowest redox potential occurs just below sea level at a depth of -0.26 m asl with a median of -178 mV indicative of sulphate reduction.

Oxygen concentrations (Figure 6) are dynamic with a high temporal variation. The concentrations are near to 100% saturation in the uppermost sand layer and decrease to ca. 20% saturation on average in backfill material in 3.21 m depth (ca. 0.93 cm below the surface). Below that depth oxygen is generally absent (< 0.2%), except of two short events occurring on a few days in May and December where  $O_2$  concentrations rapidly increase to ca. 20-25% both in an organic layer in 3.06 m asl and a gravel layer at the upper border of the ground water table. No oxygen was present in a layer of backfill material in 3.46 m depth indicating a reducing environment.

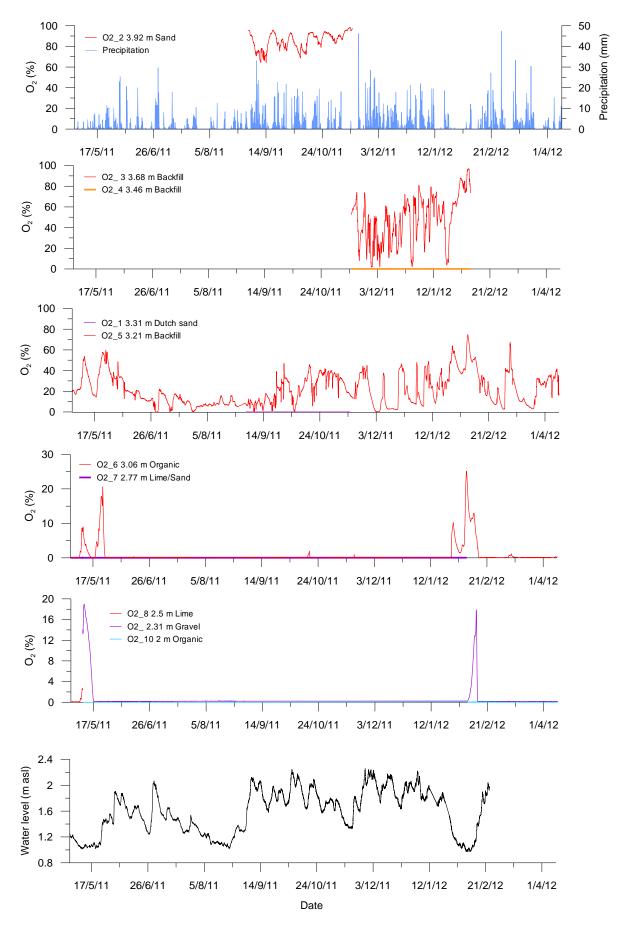


Figure 6: Oxygen concentrations in different soil depths. Note the different scale of the y-axis. For comparison rainfall data from the meteorological station Florida and groundwater level at dip well MB21 is included. Note different y-axis on the different graphs.

The reason for this can be impermeability of this layer or a higher organic matter content and increased microbial decay, all reflecting an inhomogeneous composition of the backfill material.

#### 4. Discussion

The results are discussed according to the 6 different points mentioned in the introduction.

#### 4.1 Validation of the position of the equipment

The soil profile description from the test pit (Figure 1) shows some inhomogeneity of the distribution of the single deposits, but there is a good agreement with the soil description for MB21 (Table 1). Temperature readings of the two sets of sensors are very similar despite a difference in installation depth of 1-12 cm. However, the depth assignment (Table 1) shows that not all redox sensors are installed in the same deposit as the oxygen probes and that sensors installed in the same depths might not measure in the same deposit, e.g. at 2 m depth asl. A comparison of oxygen and redox measurements is possible for the topmost sandy layer (Oxy 2 – R41), the sensors in the demolition/backfill layers beneath (Oxy 3 – R25), in Dutch sand (Oxy 1 – R23/24), in gravel and sand/gravel layer (Oxy 9 – R14/R21) and, with some constraints, in organic material and charcoal (Oxy 10 – R 12). The lime layer is excluded due to a malfunctioning redox sensor (R22).

#### 4.2 Validation of the installation method (test pit versus installation from the soil surface)

The advantage of establishing a test pit is the possibility to properly characterize the deposits and insert sensors horizontally to minimise preferential flow effects on the measurements. On the other hand, refilling of the hole is artificial and has been shown to facilitate percolation of rainwater and penetration of oxygen for some weeks due to less dense packing. In many places, this method is not convenient or applicable and installation of sensor probes into pre-pushed holes from the surface is the preferred and least destructive method. The redox sensors have been inserted using this technique which can also provide information of the penetrated soil type (not logged during the process). However, vertical installation could induce some preferential water transport along the probes due to the lack of collapsing of the created hole. Temperature may be used as an indicator for preferential flow, as a fast percolation of rain water will be reflected in rapid temperature changes affecting several depths simultaneously. In soils with a slow percolation of water the soil temperature will change through heat conduction which gives a more time delayed depth propagation and a smoothed amplitude.

Comparing the temperature measurements from the redox probes (RT) with the sensors installed in the test pit (Temp) show some distinct differences (Figure 4): There is some correlation between precipitation and temperature for both types of sensors in the upper sandy soil layers, where rainwater may infiltrate rapidly. However, the RT data are more fluctuating showing rapid "peaks" especially in the unsaturated zone to 3.24 m asl and particularly in the first months after installation. For comparison the Temp sensors installed directly in the test pit give smoother temperature graphs. There may be a small hardware effect (if the two types of sensors have different sensitivities) but more likely it indicates preferential flow along the RT probes.

In order to study the timing further, the RT data are presented for selected periods in Figure 7: During relatively dry periods rainfall events of > 10 mm per 6 hours indeed cause an immediate reaction throughout the upper deposits of the unsaturated zone (Figure 7 a, I, II). Here, the sandy layers beneath the demolition layer at 3.79 m asl and above the silty/sandy humus layer at 2.8 m asl always express stronger temperature fluctuations in response to the rain events, in particular when they last for a couple of days as from 27 - 29 June (Figure 7 II). In winter these fluctuations are also visible and coincide with thawing events following stable and low surface temperatures with snow cover (from 6 - 11 December 2011 and 3 - 14 February 2012) and a groundwater table minimum (Figure 7 III, IV) but most of the time temperature effects are less pronounced (Figure 7 V).

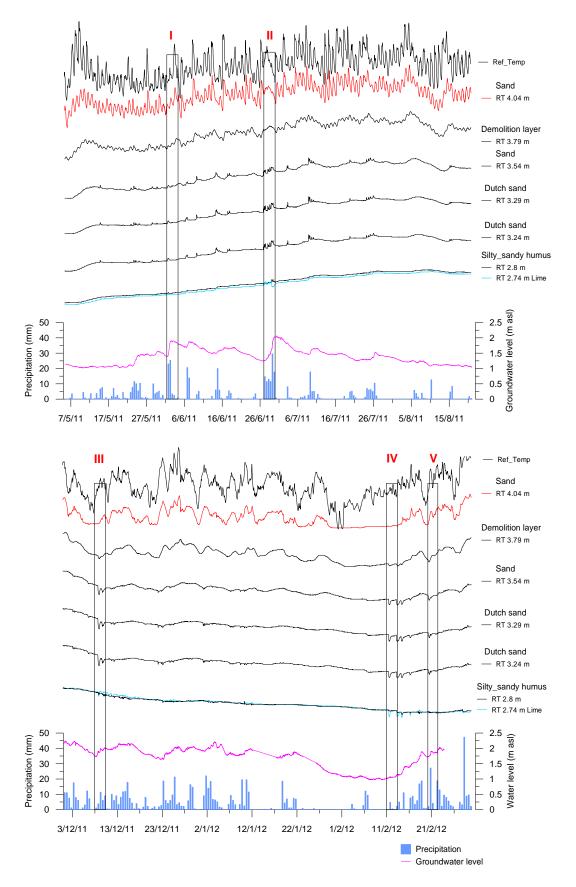


Figure 7: Temperature fluctuations in the unsaturated zone in a dry period (upper graph) and a wetter period in winter (lower panel). Scaling of the temperature graphs for comparison is 0-25 °C for the reference temperature(ref\_temp) inside the logger-box (upper panel) and 4.04 m, for all others 0-20 °C. Bars and numbers highlight the events discussed in the text. Only temperature data from the redox probes in the unsaturated zone are shown as the deeper installed sensors or sensors from the test pit do not show this fluctuation in the measurements.

In conclusion, under unsaturated conditions at low water table or times with intense rainfall some facilitated percolation might occur along the redox probes in non-collapsed holes in coarse deposits. In this case the pre-pushed hole was a few centimetres wide and approximately half-filled by the redox sensors which will have further delayed the collapsing of the hole in the uppermost sandy layers.

#### 4.3 Comparison between oxygen and redox measurements

In the following a rough comparison of oxygen and redox potential measurements is done to evaluate if the two parameters correlate. The oxygen concentration is a well-defined variable. In contrast, redox potential measurements represent a bulk measurement of oxidation and reduction processes (mixed potential) which might not represent equilibrium conditions due to slow kinetics. In well-drained soils presence of oxygen can result in high redox potentials (> 400 mV). However, also in the oxidized zone partly reducing or reducing conditions might occur in microenvironments. Under saturated conditions redox potentials decrease when oxygen is consumed and organic matter decay continues via the step-wise less energy-gaining processes of microbial catalysed nitrate, manganese, iron, and sulphate reduction, but transitional zones can occur where two or more species are simultaneously reduced.

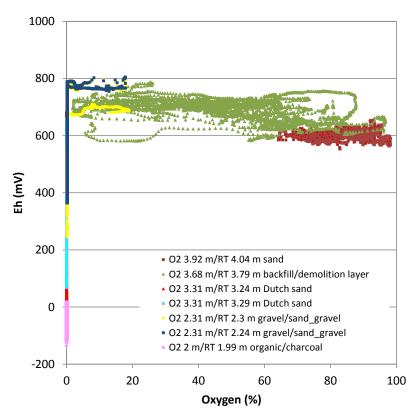


Figure 8: Comparison of oxygen and redox potential measurements in similar depths and soil types.  $O_2$  measurements in 3.31 and 2.31 m are compared with two redox sensors in the same deposit to take the uncertainty in depth location of the redox sensors into account.

Figure 8 shows a direct comparison between oxygen concentration and redox potentials measured in comparable soil layers, as defined in chapter 4.1. Some data have been discarded for the comparison: For the redox sensor at 2.24 m asl there is an initial phase after the installation where the redox potential is low, despite the presence of oxygen, but it is assumed that this is an effect from the installation.

The relation of oxygen and redox potential in Figure 7 indicates that the presence of oxygen always gives a high redox potential, but that there are also periods with high redox potential where there is no oxygen

present. Thus there is no unambiguous relation between  $O_2$  concentrations and redox potential that applies to the sand, gravel and backfill containing soil layers:

In the upper sand and demolition/backfill layers from 4.1 to 3.5 m asl (dark red and green dots in Figure 7 and upper panel in Figure 5) oxygen is always present and a high redox potential between 580 and 800 mV is measured. Surprisingly, there seems to be a slight negative correlation, i.e. the highest redox potentials are found at the lowest oxygen concentrations.

Below follows a zone from ca. 3.30 m asl to 2.24 m asl (the upper border of the groundwater table) where the median redox potential remains at  $\geq 600$  mV but decreases in response to intense rainfall events to a minimum between 200 and -100 mV in the Dutch sand (3.29 and 3.24 m asl, light blue and red dots), corresponding to the above mentioned weakly to moderately reducing conditions due to ongoing nitrate, manganese and iron reduction or downward flow of reduced interstitial water. No O2 was recorded during such a period of fluctuating redox potential from September to November 2011. In the sand/gravel layers in 2.3 and 2.24 m asl (yellow and blue dots in Figure 7 – the initial measurements at 2.24 m asl have been discarded) changes of redox potential did not occur simultaneously despite the short vertical distance between the sensors. This may indicate a mixed impact of rain and groundwater or very local differences in soil compaction around the sensors. Redox potentials remained above 300 mV for most of the time in these more permeable layers. Oxygen was measured at 2.31 m asl and during the monitoring period oxygen was only present on two occasions when groundwater level was at a minimum, which coincides with periods of high redox potential. However in about 90% of the time no oxygen was detected in this depth. It can be concluded that in the deeper deposits from 3.3 to 2.24 m asl (ca. 1 m above the groundwater oscillating zone) redox potentials can vary between -100 and 800 mV also when no oxygen was measured and assuming that both sensors measure in the same soil material.

The groundwater oscillation zone from 0.9 to 2.0 m asl is characterized by a lower median redox potential of around 400 mV (weakly reducing conditions) in permeable timber (1.74 m asl) and sand and gravel (1.24 m asl) containing layers, varying between maximum values of ca. 600 mV, mainly within the first two months, and a minimum close to -200 mV. Unfortunately no O<sub>2</sub> measurements are available for comparison. The deepest O<sub>2</sub> sensor was placed in an organic layer in a depth of 2 m asl where no oxygen was detected during the monitoring period. Correspondingly, a charcoal layer in 1.99 m depth showed lower and less fluctuating redox potentials of 0 to -100 mV (pink dots).

In depths below groundwater level but above sea level, median redox potentials were at -100, but also here higher redox potentials of 400-600 mV indicate the possible occasional presence of oxygen or other oxidizing species in the groundwater.

At this stage, it has to be mentioned, that the used thresholds for the assignment of redox potentials to dominant reduction reactions are derived from measurements in more homogeneous organic-rich and finegrained wetland soils and reactions are temperature and pH controlled. They therefore might not describe the true redox conditions in the unsaturated zone at the study site and should be validated.

# 4.4 Compare the results to soil moisture, groundwater level and rainfall

Figure 5 shows that the redox potential changes at moments of rainfall and groundwater level fluctuation. As this will also affect the water saturation of the soil, it was investigated if the water content could explain some of the observed behavior of the redox sensors. Is there a critical water content above which the sensor measures a high redox potential although  $O_2$  is absent? Earlier studies with soil material from the study site have indicated that oxygen is measured as soon as the air-filled pore space of the soil increases above 12-15% vol.

From the first year of parallel water content, redox potential and oxygen measurements data are available for 3.92 m, 2.31 m and 2 m asl (Figure 9 and 10). In the sand at 3.92 m asl oxygen and redox measurements follow the same pattern, but Eh is much more fluctuating and make a direct comparison to changes in water content difficult. Water content varies between 20 and 32% vol (Figure 10a) compared to a porosity of 39% vol and under these conditions redox potential is generally > 570 mV (Fig. 10b). Oxygen concentrations, in contrast, decrease from near 100 to 80% with increasing water content.

In the deeper soil in 3.06 m and 2.31 m asl presence of oxygen is clearly related to longer periods (2-3 weeks) of lowered water content (Figure 9). This is also observed in the redox potential measurements, but these are more variable and values return to a high and oxidizing level also during periods with higher water content when no oxygen is measured. In 2.31 m asl oxygen occurs first at a water saturation of ca. 34% vol whereas redox potential is high already from ca. 44 % vol (Fig. 9 d and e, red dots) and only at water contents close to and at saturation (44-48%) a reaction towards lower redox potentials is visible.

Redox potential is always low (< 20 mV vs. SHE) in the groundwater impacted zone at 2 m asl in organic material (Figure 9 and 10f) indicating moderately reduced conditions and water content is high with 66-69 % vol. Water content was not measured in the same layer as the redox measurements but the results might be representative for organic-rich layers at this depth.

The redox potentials in the uppermost sandy layers are surprisingly high and constant (600-800 mV). One explanation of these high potentials could be the low buffering capacity of the sands and a bad contact of the probe with the surrounding soil/deposit material.

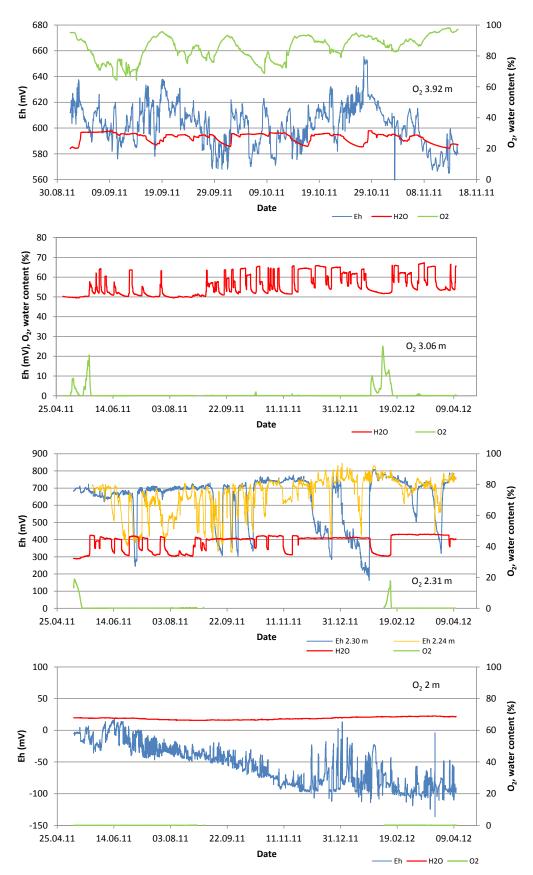


Figure 9: Time course of water content, oxygen concentration and redox potential (Eh) in sandy surface deposits (3.92 m asl), an organic layer (3.06 m asl), gravel and sand/gravel containing layers (2.31 m asl) and organic ( $O_2$ ) and charcoal (Redox) material (2 m asl). The depth of the  $O_2$  sensor is indicated.

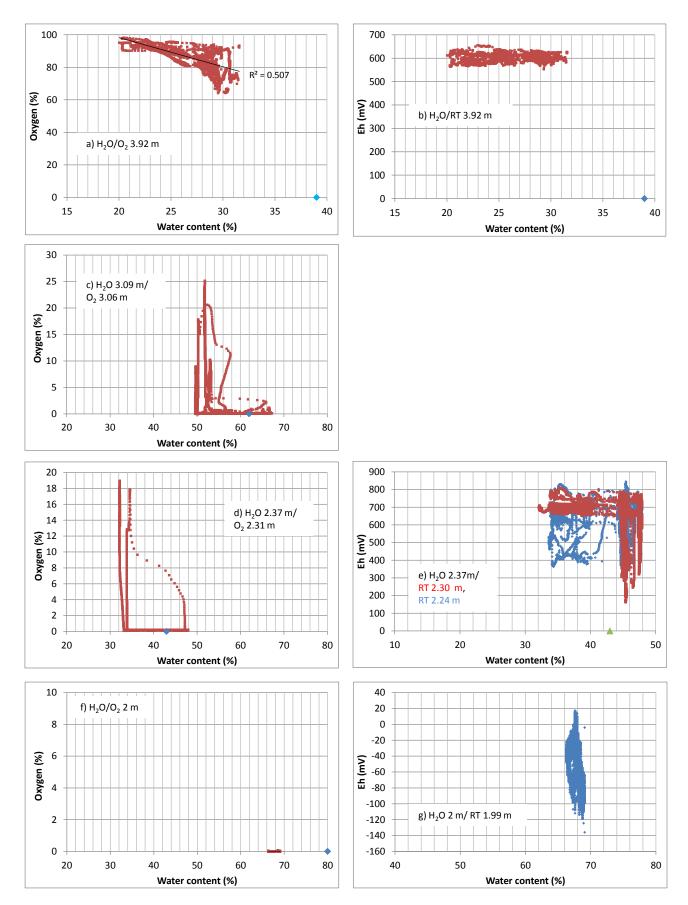


Figure 10: Correlation of water content, redox potential and oxygen in selected depths where data were available. The single symbol (blue or green) marks the water-filled porosity. The inhomogeneous material makes an exact determination of porosity in the laboratory difficult and in situ water content measurements indicate that porosity can be underestimated.

#### 4.5 Comparison to ground water chemistry

The measured redox potentials and oxygen concentrations may be compared directly to the groundwater chemistry at the site, as measured in water samples from dipwells. Dipwells MB7, MB8 and MB21 are situated next to the monitoring equipment and have their water intake in relevant soil strata: MB7 has a filter from -1.54 to +0.46 m asl, MB8 has a filter from 0.26 to 2.26 m asl, and MB21 has a filter from 0.61 to 1.61 m asl. On September 2nd, groundwater was sampled from these dipwells for full groundwater analysis (Matthiesen 2012) and again on May 22nd for a partial analysis. However, there are no redox data from the second sampling round as the logger had stopped in April. New water samples will be taken at 1½ months interval for the rest of 2012, and it is recommended to postpone the comparison between redox measurements and groundwater chemistry to the end of 2012 when more data are available.

#### 4.6 Implications for preservation conditions

*Time hasn't allowed a discussion of this point. During the autumn 2012 laboratory studies will be conducted* to study the decay rate of cultural deposits in relation to  $O_2$  and redox potential changes. Implications for preservation conditions will be discussed in that context.

# 5. Conclusions

- It is possible to install redox probes from the soil surface as a relative easy, fast and much less destructive alternative to excavation. However, during the installation it is highly recommended to take soil samples or make in situ measurements for characterization, in order to know the exact character of the soil surrounding the probes.
- During the installation of redox probes no soil samples were taken. This makes it difficult to assure that the oxygen and redox probes are placed in exactly the same soil strata and to directly compare them.
- Probes pressed or drilled down into the soil may to some extent create preferential flow paths for percolating water and give artificially dynamic conditions. The results indicate that the flow path closes, at least partly, after a period of time, but a longer monitoring period is necessary to confirm this.
- A direct comparison between oxygen and redox potential measured in the same soil strata shows that when oxygen is present the redox potentials are between 600 and 800 mV. When oxygen is not present the redox potentials vary between -200 and 800 mV. Thus it is not straightforward to evaluate the presence or concentration of oxygen from the redox potential, or, vice versa, to evaluate the redox potential from the oxygen concentration. This might be a result of the installation in a comparably wide pre-pushed hole and a limited contact of the soil/deposit material with the redox sensors. But the low buffer capacity of the deposits might be the most important factor.
- Both oxygen and redox potential measurements show some correlation to precipitation, water table and soil water content at the site, which need further investigation.
- The redox potential measurements indicate dynamic conditions in the deeper deposits down to 0.2 m asl, but there are no oxygen sensors installed for comparison at these depths.
- Redox measurements seem most reliable in less permeable and organic deposits, which are also less affected by preferential flow. But during the first year of parallel measurements not many sensors in such deposits could be compared.
- It is too early to try to relate the redox potential to the groundwater chemistry at this stage, as the potential is very variable, and groundwater has only been sampled near the redox sensors on one occasion during the monitoring period.
- The results indicate that the two methods cannot substitute but rather supplement each other.

# 6. Future work

- It is suggested to carry out a new comparison between oxygen and redox potential when more data are available, for instance 2013 when oxygen has been measured simultaneously on all 10 oxygen sensors for a period of time.
- It is suggested to compare the redox potential with groundwater chemistry when more water samples have been analysed.
- It is recommended to continue work with the interpretation of redox potential measurements and how they relate to decay rates for the archaeological remains.
- It is recommended to develop more sturdy oxygen sensors that can be installed from the soil surface.
- It is suggested to carry out a literature survey of comparisons between oxygen and redox potential measurements at other sites and in other soil types.

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# Appendix 1

Table A1: In situ monitoring periods and data availability at the excavation pit. Continuous measurements of redox potential started on 5 May 2011 and are not explicitly listed here (for depths see Table 1).

Depth	Period*						
(m asl)	17/3-9/5/11	9/5-19/5/11	19/5-26/8/11	26/8-1/9/11	1/9-14/11/11	14/11/11-7/2/12	
4.12	Т	Т	Т	Т	Т	Т	
3.92	H <sub>2</sub> O, T	H <sub>2</sub> O, T	Т	Т	$H_2O, O_2, T$	H <sub>2</sub> O, T	
3.68	Т	Т	Т	Т	Т	O <sub>2</sub> , T	
3.6	H <sub>2</sub> O	H <sub>2</sub> O	-	-	-	-	
3.46	Т	Т	Т	Т	Т	O <sub>2</sub> , T	
3.31	-	-	-	-	O <sub>2</sub>	-	
3.21	O <sub>2</sub> , T	O <sub>2</sub> , T	O <sub>2</sub> , T	Т	O <sub>2</sub> , T	O <sub>2</sub> , T	
3.09	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	
3.06	O <sub>2</sub> , T	O <sub>2</sub> , T	O <sub>2</sub> , T	Т	O <sub>2</sub> , T	O <sub>2</sub> , T	
2.77	H <sub>2</sub> O, O <sub>2</sub> , T	H <sub>2</sub> O, T	H <sub>2</sub> O, T	H <sub>2</sub> O, T	H <sub>2</sub> O, T	H <sub>2</sub> O, T	
2.5	O <sub>2</sub> , T	Т	Т	Т	Т	Т	
2.37	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	
2.31	Т	O <sub>2</sub> , T	O <sub>2</sub> , T	Т	Т	Т	
2	H <sub>2</sub> O, T	H <sub>2</sub> O, O <sub>2</sub> , T	H <sub>2</sub> O, O <sub>2</sub> , T	H <sub>2</sub> O, T	H <sub>2</sub> O, T	H <sub>2</sub> O, T	

\*since start of redox measurements