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Report for Riksantikvaren

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Measurement of oxygen, nitrate, sulphate and redox potential in microcosms with waterlogged organic cultural deposits

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Summary

The National Museum of Denmark and MVH Consult in the Netherlands have been asked by Riksantikvaren (Norway's Directorate for Cultural Heritage) to compare the use of redox potential probes, oxygen probes, and analyses of water/soil chemistry as a way of getting information about preservation conditions and decay rates at archaeological sites. This has been done through field studies at Bryggen in Bergen (Walpersdorf et al 2012), and through laboratory experiments. Initial laboratory work focussed on a direct comparison between oxygen and redox potential under both saturated and unsaturated conditions. Under unsaturated conditions redox potentials were fluctuating and difficult to interpret, but the results were more promising under saturated conditions (Mortensen et al 2013). Oxygen measurements seemed to work under both conditions. This report describes further studies under saturated conditions, and includes the effect of other dissolved oxidants (nitrate and sulphate). The study is made within the frame of Urban Watch, a research project financed by Norges Forskningsråd and Riksantikvaren.

The results and interpretations are to some extent influenced by heterogeneous conditions in the microcosms, which need to be taken into account when comparing different parameters. The results indicate that redox potential measurements are very sensitive and show abrupt increase/decrease when the conditions change. The absolute values can to some extent indicate which oxidants are present and which processes are on-going, but the repeatability is not very good. There is some correlation between the decay rate and the redox potential, with the highest decay rates being measured at the highest potentials, but even below 0 mV vs SHE unacceptable high rates may be found. There is no correlation between the concentration of different oxidants and the redox potential, and the potential may vary by some hundred mV between replicates. Overall, this means that redox potential measurements are useful for showing if the conditions are changing or stable, but interpretation of the absolute values in terms of decay processes is still difficult.

The microcosm study confirms that oxygen is the most reactive oxidant and it is noted that the decay rate under unsaturated conditions is higher than in all other setups (160-330 µg CH_2O /g dry sample/day for highly organic soil at 15 °C). The decay rates shown for saturated soil with dissolved oxygen (40-120 µg CH_2O /g /day) and nitrate (13-70 µg CH_2O /g /day) are also high. The decay rate under sulphate reducing conditions is lower (2-8 µg CH_2O /g /day) but not insignificant. The exact effect in situ will depend on the supply of oxidants. All samples in this study were relatively well preserved, and a lower reactivity may be expected for more degraded samples. It was attempted to measure the temperature dependence of anoxic decay, but the results are uncertain and have to be validated.

Introduction

The National Museum of Denmark and MVH Consult in the Netherlands have been asked by Riksantikvaren (Norway's Directorate for Cultural Heritage) to compare the use of redox potential probes, oxygen probes, and analyses of water/soil chemistry as a way of getting information about preservation conditions and decay rates at archaeological sites. This has been done through field studies at Bryggen in Bergen (Walpersdorf et al 2012), and through laboratory experiments comparing oxygen and redox potential measurements under both saturated and unsaturated conditions (Mortensen et al 2013). The first reports concluded that under unsaturated conditions redox potentials were fluctuating and difficult to interpret. This report takes a closer look on the saturated conditions and how redox potential measurements can reflect changes, different processes, concentrations of different oxidants, and decay rates. The study also gives information on the effect of adding different dissolved oxidants (oxygen, nitrate, sulphate) to waterlogged archaeological soil material, which may be used to discuss the effect of infiltrating different types of water into archaeological deposits. Finally, a small study of the effects of temperature on decay under saturated conditions is included. The study is made within the frame of Urban Watch, a research project financed by Norges Forskningsråd and Riksantikvaren.

Background

Developer-funded monitoring programs in urban cultural layers normally include analysis of soil and groundwater chemistry, and monitoring of the temperature, the groundwater level and/or the water content in different soil layers. The Norwegian monitoring standard (NS 9451, 2009) mentions that monitoring of oxygen and/or redox potential in the soil shall be considered as well, and Riksantikvaren wants to evaluate if these parameters shall be included in standard monitoring programs. Several questions are relevant in this connection: will the extra expenses give a significantly better evaluation of the preservations 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? Riksantikvaren has asked the National Museum, in collaboration with MVH Consult, to address these questions through laboratory and field studies. Furthermore, infiltration of water to reduce the decay of organic archaeological remains is suggested at several sites, most notably at Bryggen in Bergen where infiltration basins ("swales") have already been constructed. Oxygen and redox potential are being monitored in the cultural deposits in connection with this infiltration. However, it is highly relevant to investigate which types of water (in terms of chemical composition and temperature) can be used for infiltration and what is the effect on the decay of the cultural deposits.

There exist a very comprehensive literature on redox potential measurements (e.g. Schüring et al, 2000) and turnover of organic material (e.g. Kirk, 2004) in natural waterlogged soils, but a literature review is not included in this study.

Experimental

Soil samples from Fjellbrønn 3 (FJB3) from Bryggen in Bergen have been used throughout this study (Figure 1). The samples were received approximately one week after the drilling took place in January 2012, and have been kept in the freezer at -20 °C until used in the study.

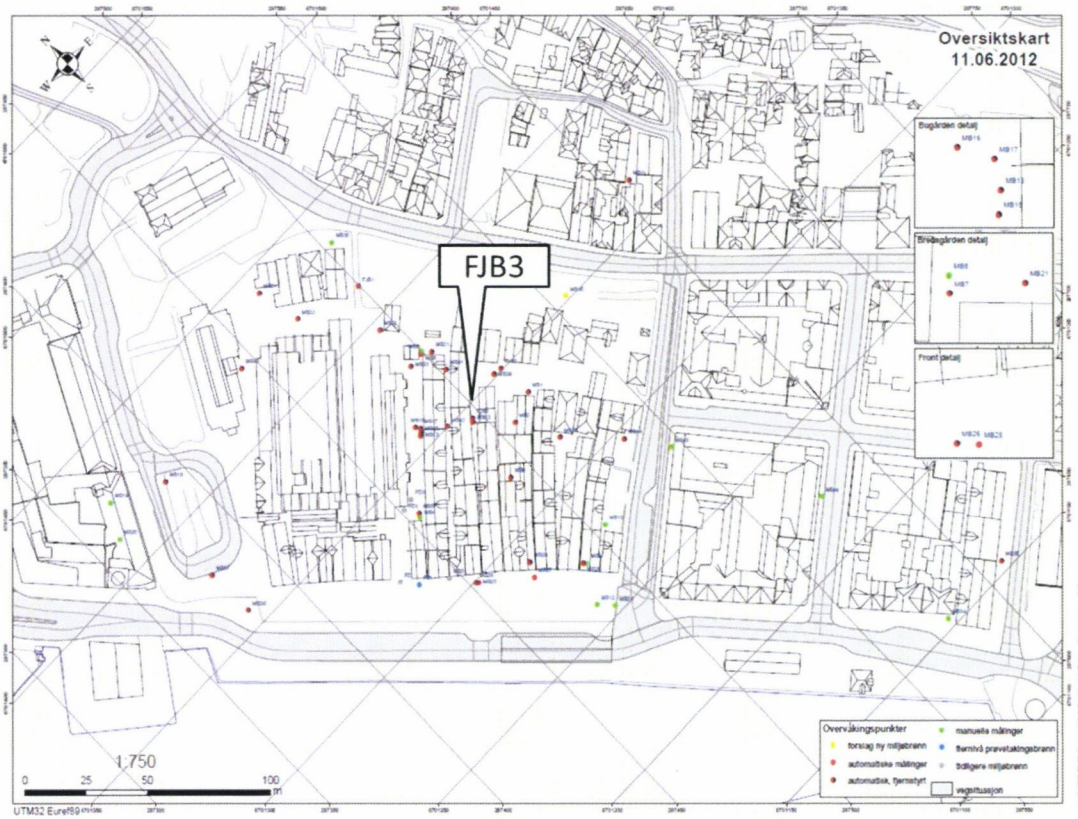

Figure 1. Map showing the location of the Fjellbrønn 3 sampling site on Bryggen.

Samples from four depths have been used. The samples are briefly described in Table 1, and in more detail in Walpersdorf (2013). All samples are from saturated conditions, even if the uppermost sample (FJB3-01) may occasionally have been drained in periods of very low water-table at Bryggen. All samples are relatively well preserved (from medium to excellent state of preservation) and not necessarily representative for the upper, more degraded cultural deposits at Bryggen. The soil surface at FJB3 is at 2.0 m above sea level (asl).

	Depth (m asl)	State of preserv. (SOPS)	Dry content (% of ww)	Organic content (% of dw)	Nitrogen total (% of dw)	Phosphorus total (% of dw)	Sulphur total (% of dw)	Sulfate (% of dw)
FJB3-01	0.55	Medium	37 (34)	40 (47)	0.99	3.8	0.87	0.026
FJB3-02	-0.45	Medium	24 (24)	47 (54)	1.9	0.64	1.6	0.050
FJB3-06	-3.75	Good	22 (24)	74 (73)				0.052
FJB3-08	-4.75	Excellent	38 (38)	39 (35)	1.6	1.5	1.6	0.027

Table 1. Characteristics of the soil samples used in this study. SOPS is an abbreviation for "State of preservation scale" as described by archaeologist Rory Dunlop from NIKU (Dunlop 2012). ww means "wet weight", dw means "dry weight". Dry content and organic content measured by the authors are listed, numbers in parenthesis correspond to measurements carried out by Eurofins (Walpersdorf 2013).

The procedure for measuring oxygen concentration and redox potential under unsaturated and saturated conditions is described in Mortensen et al (2013) but is repeated here as the same soil samples and setups are used throughout the experiment: Particles such as stones and larger twigs were removed from the soil before it was stirred to homogenize each of the four depths investigated. Soil from each of the four depths was split into three subsamples yielding 12 samples in total, each weighing between 22 and 55 g. Each of these samples was placed in the bottom of a 100 mL screw-cap vial, filling it approximately by two thirds (Figure 2). Optical sensors were installed on the inside of the glass wall, with sensors for carbon dioxide, pH and oxygen in the water filled headspace over the soil sample, and an extra oxygen sensor down in the waterlogged soil (illustrated in Figure 2). The redox potential was measured down in the waterlogged soil using a Pt electrode and a Ag/AgCl reference electrode installed through the lid of the vial (Figure 2, right) and the potentials were monitored by a "Hypnos III datalogger". All equipment for redox potential measurements was provided by Michel Vorenhout from MVH Consult. The optical sensors were monitored using the relevant instruments from PreSens GmBH, namely an OXY-10, an OXY-4, a pCO_2 mini and a pH-1 mini. Most experiments were carried out at 15 °C and the samples were also kept at this temperature in a climate chamber or a water bath in between the experiments.

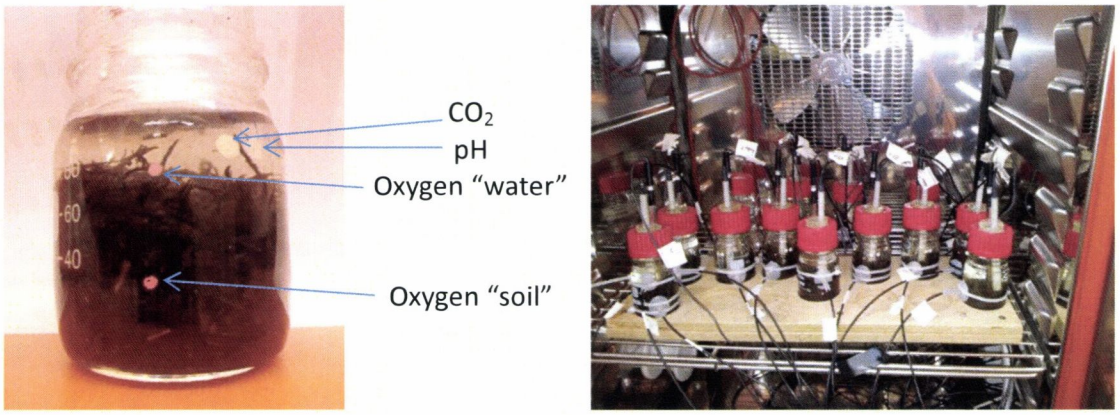

Figure 2. Photographs showing the microcosms. To the left 100 mL screw cap vials containing soil sample and buffer solution; on the inside of the glass wall two oxygen optical sensors, one CO_2 sensor and one pH sensor can be seen as round circles. To the right a picture of the setup inside the climate chamber, redox electrodes are seen protruding through the lids of the 12 vials and optical fibres are fixed to the side of the vials for logging the oxygen concentration. Two hypodermic needles for sampling of water were installed in each lid after the photo was taken.

For the first experiments focusing on oxygen and redox potential (Mortensen et al 2013), the lids of the vials were sealed with aluminium foil, and epoxy was used for gluing the redox electrodes to their holes in the lids in order to make the containers oxygen-tight. The vials with soil were completely filled with aerated 0.0092 M $NaHCO_3$ solution adjusted to a pH of 6.69 with hydrochloric acid - this matches the values found in groundwater and soil samples from FJB3 (Walpersdorf 2013). The lid was refitted in such a way that no air bubbles were trapped in the vial. The redox potential and oxygen concentration in the soil were logged continuously until anoxic and relatively stable conditions were achieved (Figure 3). pH, CO_2 and oxygen in the water were measured manually once per day. In vial 8 the reference electrode broke, so no results are given for this vial.

In the next phase two small holes (Ø=1mm) were drilled in each lid to allow the installation of hypodermic needles for the addition and sampling of water for nitrate and sulphate analysis. 2 mL of de-aerated nitrate solution (0.01 M) was added to each vial using two syringes connected to the hypodermic needles (one syringe for adding the nitrate solution and one for sampling the surplus solution from the vial). Sampling from the vials was made once per day, again using two syringes (one for the sampling and one filled with de-aerated $NaHCO_3$ solution to replace the sampled volume) avoiding the introduction of air into the system. The samples were filtered (0.45 µm) and the concentration of nitrate (as well as chloride and sulphate) was measured on an ion

chromatograph (Figure 4). After the nitrate was consumed, 2 mL sulphate solution (0.014 M) was added using the same procedure as for nitrate (Figure 5).

After the sulphate reduction experiment the samples were exposed to 25-30 °C for a few days (due to problems with the climate chambers), but were else kept at 15 °C. Nitrate was added to the system a second time (Figure 6), as the results from the first nitrate reduction measurements were quite variable. The second time it was attempted to mix the water in the headspace more thoroughly when the nitrate was added and before sampling, to reduce possible concentration gradients. A third study of nitrate reduction was carried out at 5 °C in order to study the temperature-dependence of anoxic processes (Figure 7) – the vials were stabilised at 5 °C for two weeks before nitrate was added.

The consumption rate for nitrate and sulphate was calculated from the decrease in concentration over time:

$$Consumption\ rate = V \cdot (\Delta C / \Delta t) / m \qquad (Eq.\ 1)$$

where V is the volume of water inside the vial (cm^3), $\Delta C/\Delta t$ is the decrease in concentration over time ($\mu g/cm^3/day$), and m is the dry weight of the soil sample (g). For oxygen consumption the calculations are given in Mortensen et al (2013).

Results

Measurements of oxygen and redox potential under both unsaturated and saturated conditions were shown and discussed in Mortensen et al (2013) but the results from saturated conditions are repeated in Figure 3 in a slightly modified version to allow an easier comparison with other results.

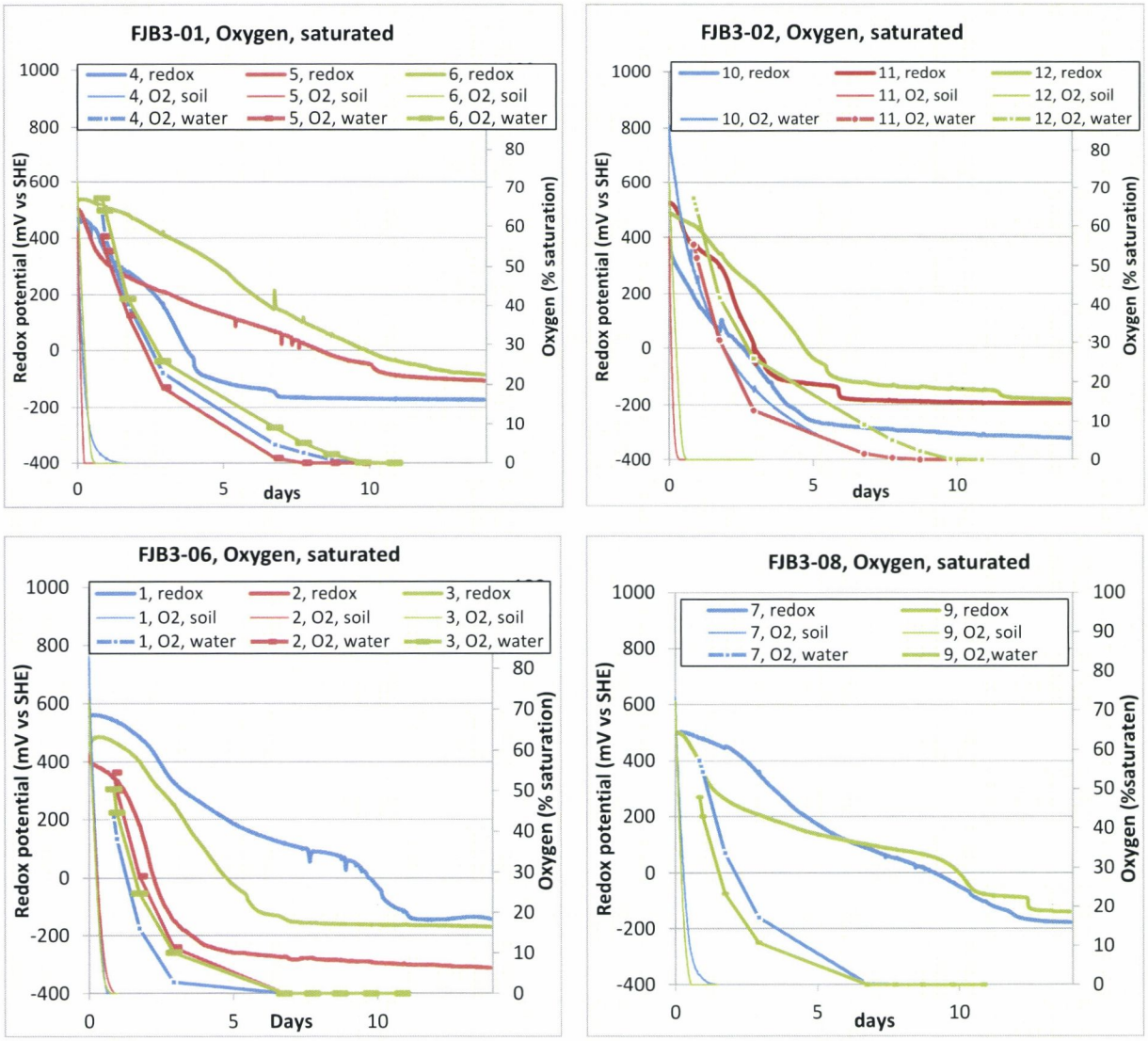

Figure 3: Redox potentials and oxygen concentrations measured immediately after the vials were filled with aerated $NaHCO_3$ buffer at 15 °C (29/10-12/11 2012)

After the oxygen consumption experiments syringes were installed in the lid of the vials. Nitrate was added on the 14/1/2013 and water samples were taken for analysis once or twice per day. Figure 4 shows the results from these nitrate measurements. The sulphate content in the water samples was between 20 and 120 mg/L (not shown) which comes from the soil itself (Table 1, last column). Oxygen was measured continuously for all vials and showed 0% oxygen throughout the remainder of the experiment.

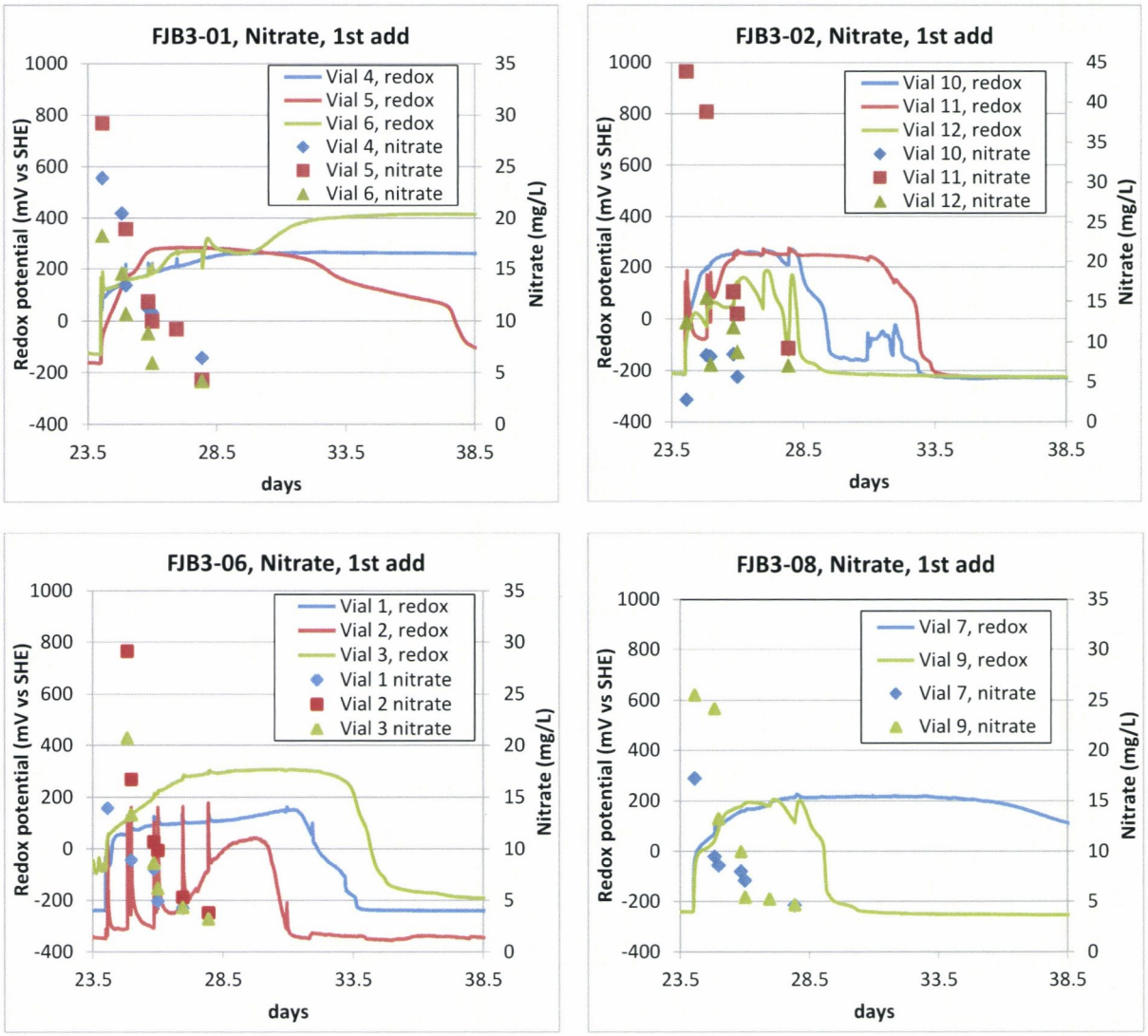

Figure 4: Redox potentials and nitrate concentrations measured after the first addition of nitrate at 15 °C (14/1-19/1 2013)

After the nitrate measurements were finished extra sulphate was added to all vials on the 29/1/2013 and samples were taken at intervals (Figure 5). It was verified that there was no nitrate in any of these samples (not shown)

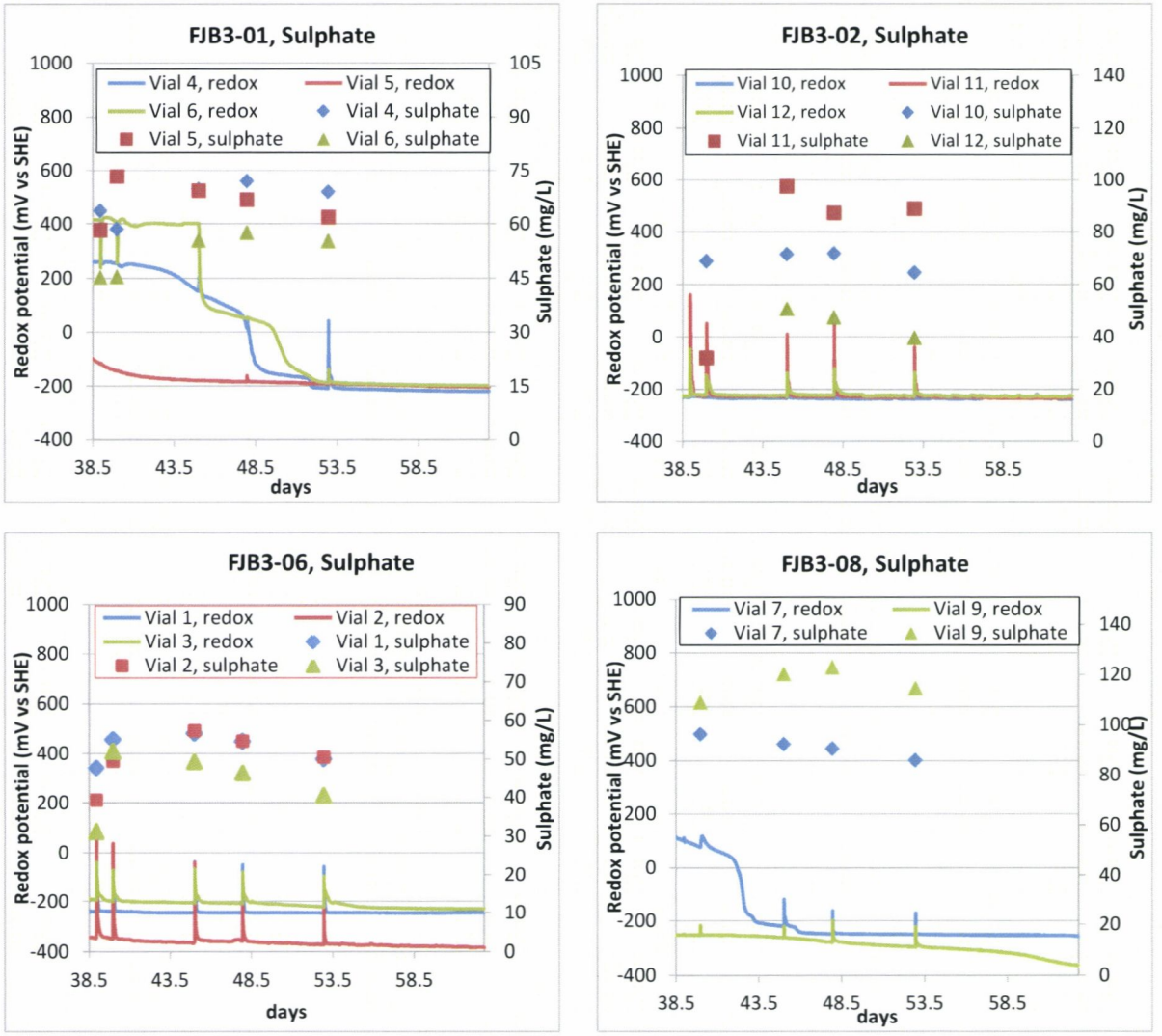

Figure 5: Redox potentials and sulphate concentrations measured after addition of sulphate at 15 °C (29/1-22/2 2013)

The samples were kept at 15 °C from February to April (except for a few days where problems with the climate chamber caused the temperature to rise to 25-30 °C). The samples were transferred to a water bath at 15 °C, and in Mid-April a new redox measurement series was initiated. A new addition of nitrate was made on the 22/4/2013 in order to check the repeatability (Figure 6). At this time the sulphate concentrations in all vials had decreased to less than 2 mg/L (not shown).

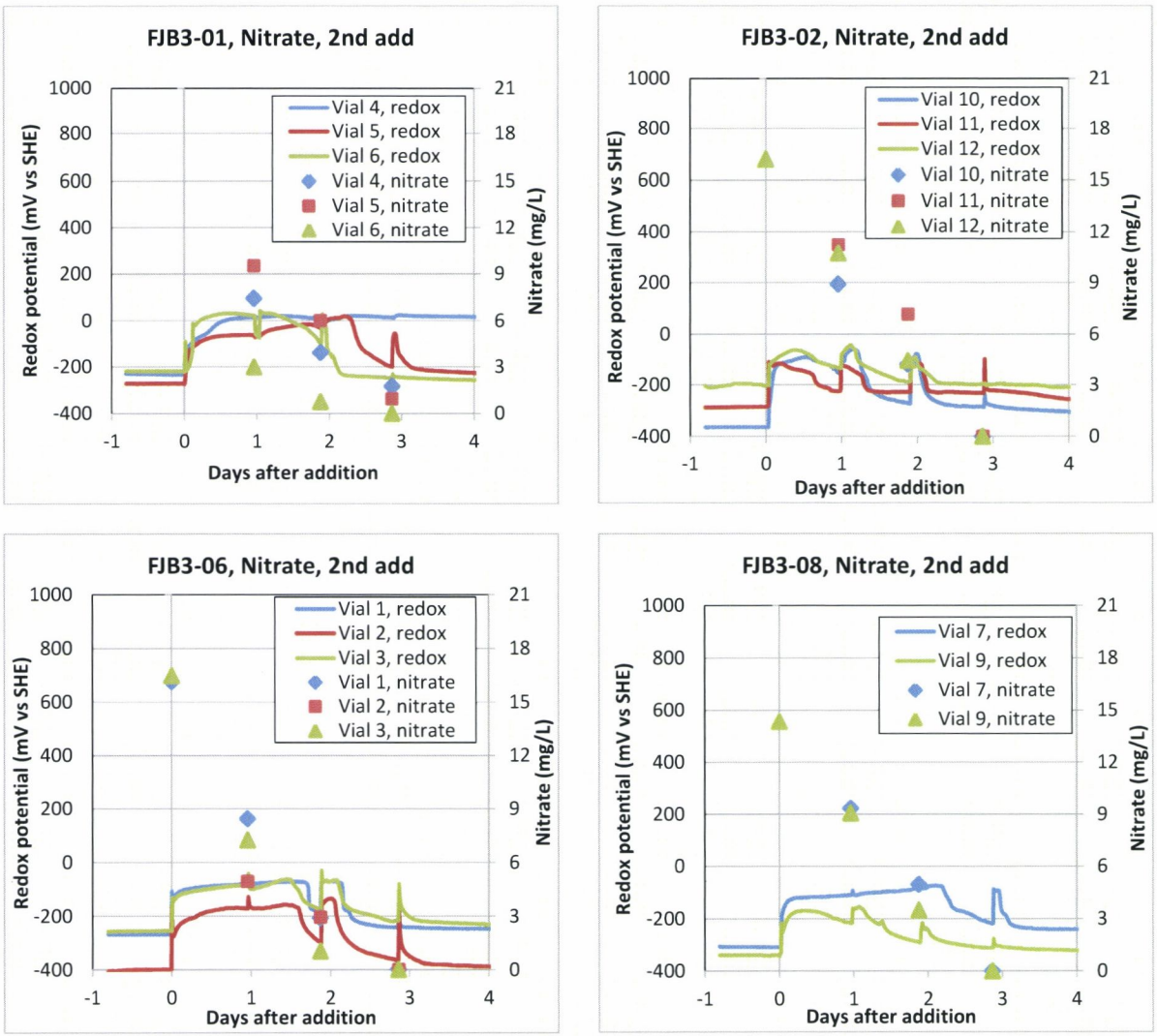

Figure 6: Redox potentials and nitrate concentrations measured after the second addition of nitrate at 15 °C (21/4-26/4 2013)

The samplings were cooled to 5 °C and kept at that temperature for two weeks, before nitrate was added to the vials on the 21/5/2013 (Figure 7). The sulphate concentration was < 2 mg/L in all vials (not shown).

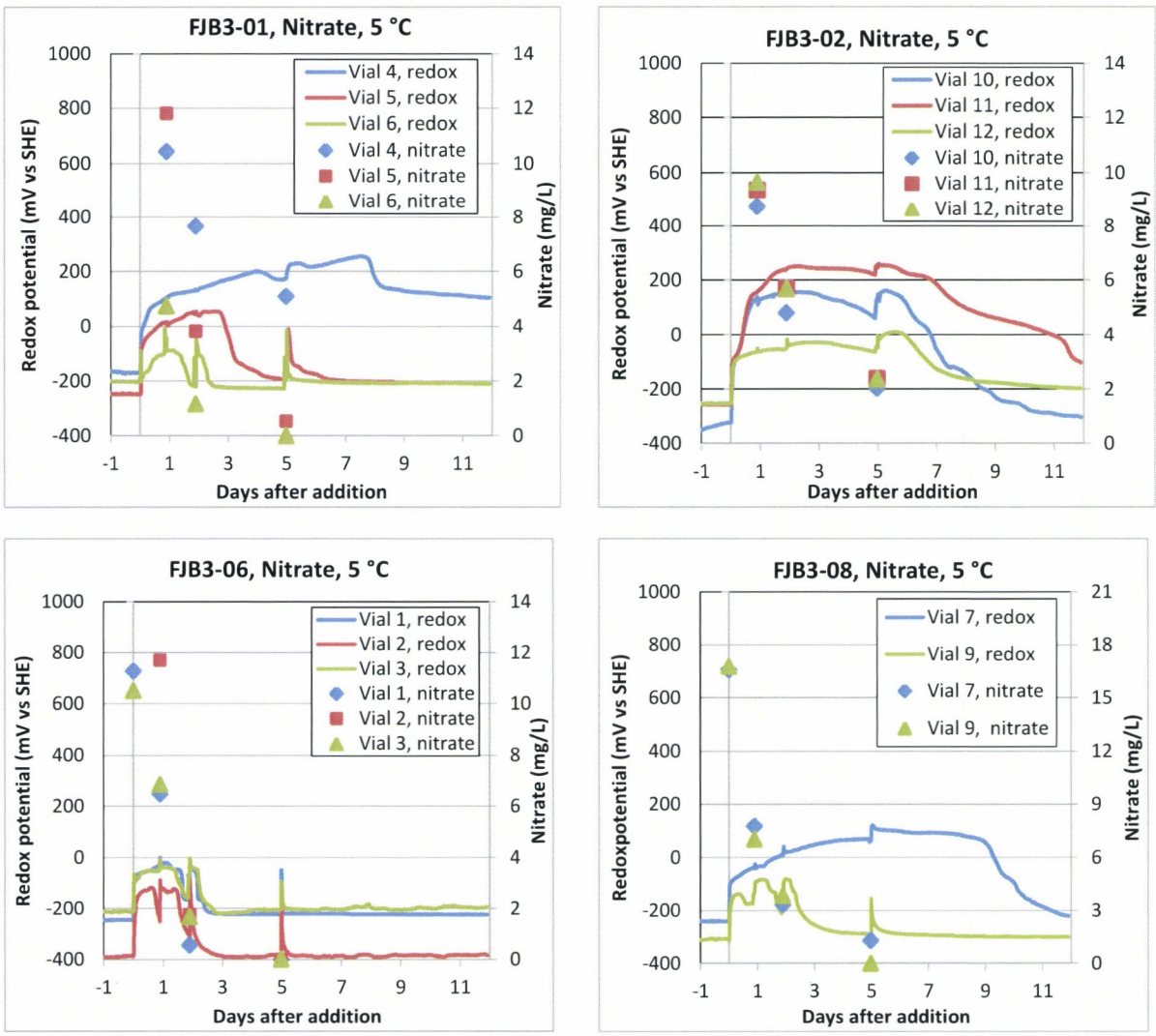

Figure 7: Redox potentials and nitrate concentrations measured during the third addition of nitrate at 5 °C (21/5-3/6 2013)

Measurements of CO_2 and pH were carried out throughout the experiments using a new type of optical instruments. The results indicated some distinct decreases in pH (Mortensen et al 2013, Figure 9) and increases in CO_2 pressure (not shown) during the incubation experiments. An increase in CO_2 pressure was expected due to the degradation of organic material, but in some vials the increases were substantially higher than expected, and the pH lower than expected. At the end of the experiments samples were taken from all vials to check the pH manually with a traditional glass electrode and to make alkalinity measurements. The results from the manual measurements raised some doubt to the absolute values and long term stability of the optical pH and P CO_2

measurements, so these results are not presented or discussed in any detail here. Instead the results from the manual measurements are given in Table 2.

	Buffer	FJB3-01			FJB3-02			FJB-06			FJB3-08	
		4	5	6	10	11	12	1	2	3	7	9
pH	6.69	6.68	6.66	6.77	6.63	6.58	6.56	6.83	6.90	6.87	6.89	6.90
Alkalinity (meq/L)		8.03	7.80	8.27	7.25	7.78	6.81	7.58	7.50	8.03	8.78	9.57

Table 2: Measurements of pH and alkalinity in subsamples from each vial at the end of the experiment. The pH value of the buffer used to fill up the vials initially is shown for comparison.

Discussion

The discussion focuses on the following questions:

Are the samples and microcosms representative?

Are the redox potential measurements sufficiently sensitive, i.e. do the measurements react to changes in the environment?

Are the redox potentials repeatable, i.e. do they give the same results for replicates?

Does the redox potential reflect which processes are ongoing

Does the redox potential reflect the concentration of reactants?

What decay rates for organic matter are found for the different processes?

Does the redox potential reflect these decay rates?

How does the temperature influence decay under waterlogged conditions?

Representativity of samples and microcosms

The samples used were all from a deep drilling FJB3 from Bryggen in Bergen, with medium to excellent state of preservation, and an organic content between 39 and 74%. This is typical for samples from the deep waterlogged deposits at Bryggen, whereas samples from the upper, unsaturated deposits will often have a lower organic content, and be significantly less reactive (Hollesen & Matthiesen, 2011).

A buffer solution with a pH and bicarbonate content similar to in situ conditions was used in the experiments. Measurements in all vials at the end of the study showed very modest changes in the pH and the buffer capacity (alkalinity) was still high (Table 2).

The microcosms have earlier been used to compare oxygen and redox potential measurements under unsaturated conditions (Mortensen et al 2013). Two oxygen sensors in each microcosm (one beneath and one above the soil surface – Figure 2) are used to check if there are any oxygen gradients within the system, and for unsaturated microcosms the oxygen concentrations were equal above and below the soil surface. However, when it comes to saturated conditions the situation is different: Figure 3 demonstrates that the oxygen concentration beneath the soil surface decreases much faster than the concentration in the water above the soil surface (the soil becomes anoxic after

less than one day, while it takes up to a week before the water above is anoxic). This is due to a slow diffusion of oxygen and other dissolved species through water – when oxygen is consumed in the soil, it takes some time before the oxygen is transported down into the soil from the water above.

The redox sensors are placed within the waterlogged soil, and despite the short distance it cannot be excluded that there are some differences between the conditions and concentrations just around the sensors and the conditions in the water above. These limitations need to be taken into account when comparing and discussing the results from the different measurements. The concentrations gradients could be reduced by using continuous stirring of the system, but firstly stirring is difficult due to the presence of redox sensors and reference electrodes in the vials, and secondly stirring might induce unrealistic high decay rates. Thus it was decided not to use continuous stirring during the experiments.

Sensitivity of redox potential measurements

The results from the laboratory study indicate that the redox potential measurements are quite sensitive to changes to the system: E.g. an increase in redox potential is always observed when nitrate is added to anoxic soil systems with redox potentials between -200 and -400 mV vs SHE (Figure 4, 6 and 7). The magnitude of the increase may vary, but some effect is seen for all samples. Furthermore, for some of the anoxic systems even the sampling of water gives rise to short term changes in the redox potentials, seen for instance in Figure 5 (vial 1-3 and 10-12).

Repeatability of redox potential measurements

The repeatability may be evaluated in two ways: By comparing results from the 3 replicates/vials that have been made for each soil layer, and by comparing the results for individual vials when the same manipulation (e.g. nitrate addition) is repeated.

Comparing replicates may be done qualitatively by comparing the three redox curves (red, blue and green) in each of the 4x5 graphs (4 samples and 5 manipulations) in Figure 3-7. As a general picture, the three curves show similar trends in a graph, but for a given sample and manipulation the absolute value of the redox potential can vary by several hundred mV at a given time. E.g. for sample FJB3-06 during oxygen reduction (Figure 3) the redox potential after 5 days varies between +200 and -250 mV vs SHE, and even for the most stable curves (sulphate reduction in Figure 5) the potential varies between -400 and -200 mV vs SHE for sample FJB3-06. Some of this variation will reflect real differences between the vials (i.e. slightly different environmental conditions), and some is due to uncertainty of the redox or reference probes. For instance the redox potential measured in

vial 2 is systematically 100-200 mV lower than in vial 1 and 3 for all experiments, which is probably due to a biased redox or reference probe.

Repeatability may also be discussed by comparing the effect when a given manipulation is repeated. Here, nitrate is added to all vials 3 times. After the first addition (Figure 4) the redox potentials increase to between 0 and +300 mV vs SHE, with most values around +200 mV. After the second addition (Figure 6) the redox potentials only increase to between -200 to 0 mV vs SHE, and after the third addition (Figure 7) the potentials increase to between -100 to +200 mV vs SHE, i.e. the probes behave differently after the three additions. This could be due to a memory effect of the probes, if the platinum in the redox probes is influenced by sulphide produced during the sulphate reduction experiment between the first and second nitrate addition. However, the difference could also be due to changes to the soil that may have become more reduced in the latter two experiments. Overall it is estimated that redox probes placed under (almost) identical conditions can give results that vary by some hundred mV, which is in correspondence with the experience from others (Schüring et al, 2000).

Redox potential and processes

Redox potential measurements are often used as an indicator to which redox processes are dominating in the soil or groundwater. Different interpretation schemes are used by different researchers, but the exact interpretation can be difficult as there are often several processes taking place simultaneously. In these laboratory experiments with controlled additions of oxygen, nitrate and sulphate and frequent measurements of the same species, we have some idea of the dominating processes, even if we haven't studied processes such as iron reduction, manganese reduction and methanogenesis during the experiments. Table 3 and Figure 8 sums up the redox potentials measured under different conditions, leaving out apparent outliers such as for instance high redox values measured at the beginning of the sulphate reduction experiments (Figure 4, vial 4, 6, 7) that may be due to a slow adaption of the electrode to the environment. The soil samples contained some sulphate before the experiments were initiated (Table 1) whereas the nitrate content hasn't been measured in the soil itself.

Conditions	Dominating process	Potentials measured	Oxygen	Nitrate	Sulphate
Unsaturated (Mortensen et al, 2013)	Oxygen reduction	0 to +600	+	?	+
Saturated, oxygen present in soil (fig 3)	Oxygen reduction	+400 to +600	+	?	+
Saturated, oxygen absent, nitrate present (fig 4)	Nitrate reduction	0 to +300	-	+	+
Saturated, nitrate absent, sulphate present (fig 5)	Sulphate reduction	-400 to -200	-	-	+
Saturated, nitrate present, sulphate absent (fig 6)	Nitrate reduction	-200 to 0	-	+	-
Saturated, nitrate present, sulphate absent, 5 °C (fig 7)	Nitrate reduction	-100 to +200	-	+	-

Table 3: Redox potentials measured under different conditions. The potentials are given as typical ranges. For each oxidant is indicated if it is present (+), absent (-) or unknown (?)

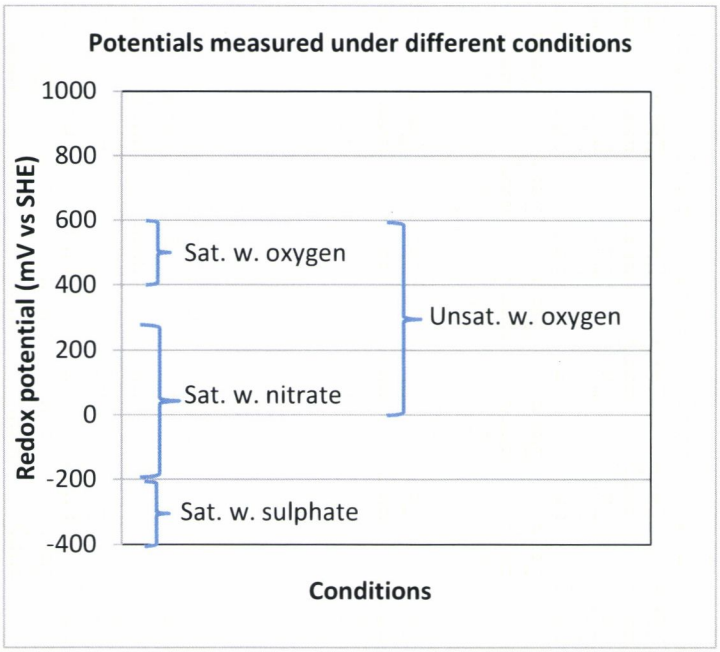

Figure 8: Graphical presentation of the redox potential ranges given in Table 3.

The redox potentials for saturated conditions with oxygen present varies from 400-600 mV vs SHE, which is the same range given by e.g. Mitsch & Gosselink (2007).

The potential under saturated conditions with nitrate added varies from +300 to -200 mV vs SHE. This is a very large range, and the potentials are somewhat lower than what is normally stated by others (e.g. Kofod (2000) give values from +225 to +500 mV for nitrate reduction based on several

papers, and Mitsch & Gosselink (2007) gives a value of +250 mV). This could to some extent be due to mixed potentials (i.e. the potential reflect several processes taking place simultaneously), or concentration gradients within our microcosm (if the nitrate reduction mainly takes place above the redox sensors). On the other hand it is clear from the graphs in Figure 4, 6 and 7 that the potentials are influenced by the nitrate additions, indicating that some nitrate does reach the sensors.
The potentials under saturated conditions with sulphate added vary between -400 and -200 mV vs SHE, with most values near -200 mV. This is in good correspondence with Mitsch & Gosselink (2007) that give values between -200 to -100 for sulphate reduction.
Overall, the results from saturated conditions show some correlation between the on-going processes and the measured potentials, even if the potential ranges are somewhat broad especially for nitrate reduction.
The potentials measured under unsaturated conditions with oxygen present shows a very large variation in redox potential from 0 to +600 mV vs SHE (Figure 8).

Redox potential and concentrations

Having identified the correlation between the redox potential and the presence/absence of different oxidants, the next natural step is to investigate if there is also a correlation between the concentration of these oxidants and the redox potential, i.e. if the measured potentials can be interpreted in more detail. Figure 9 shows the redox potentials relative to the concentrations of different oxidants in the various phases of the experiment:

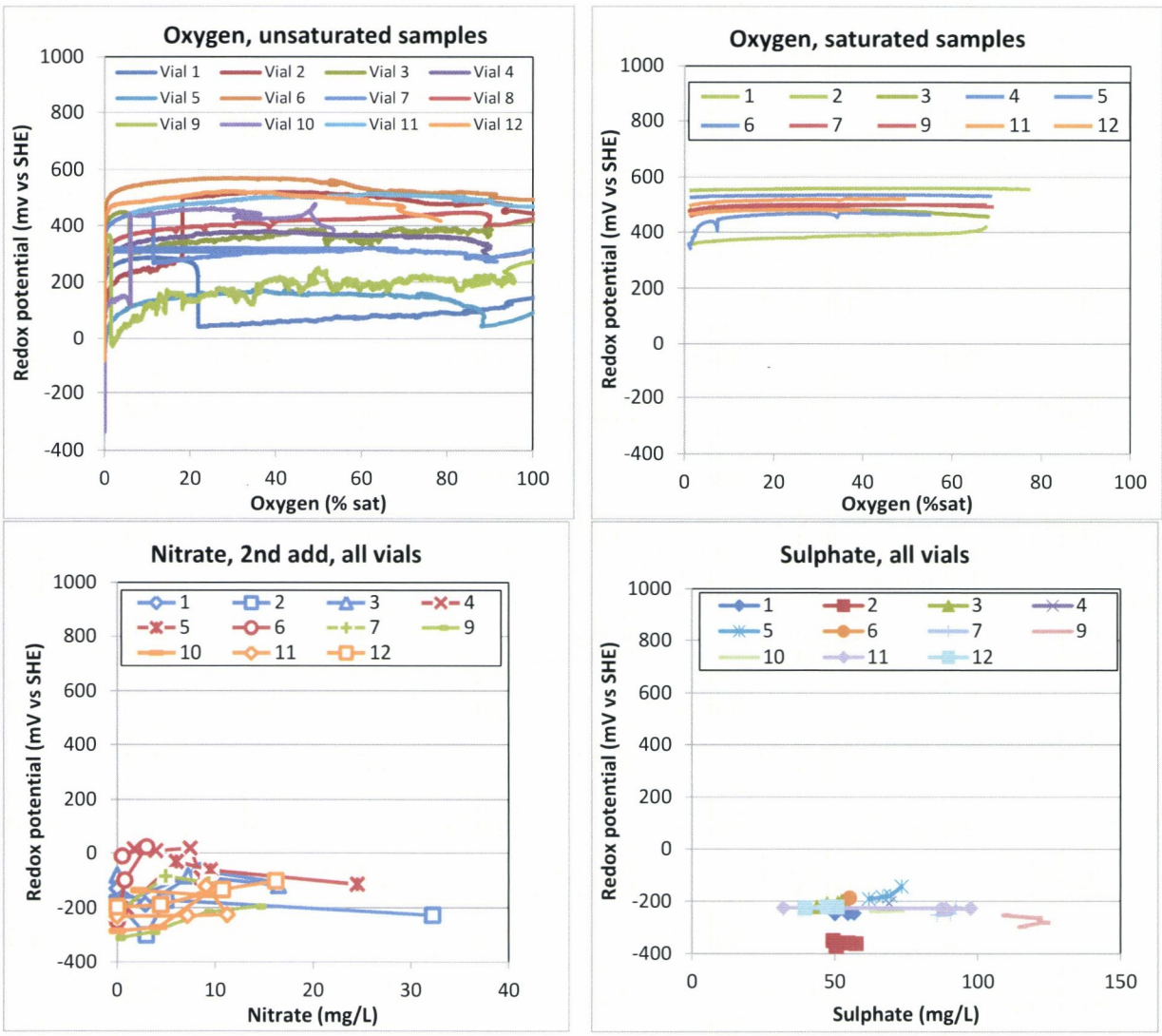

Figure 9: Comparison between redox potentials and concentrations of different oxidants. The results for unsaturated samples (upper left) are from Mortensen et al (2013).

If all other parameters were equal, one would expect to see increasing potentials with increasing concentration of oxidants. Figure 9 demonstrates that this is not the case, i.e. it is not possible to estimate concentrations from the measured potentials. Still it is possible to some extent to evaluate the presence or absence of different oxidants from the potentials.

Decay rates

It was planned to estimate the decay rate for organic material in the microcosms in two ways: from the production of CO_2 and from the consumption of the different oxidants added. The CO_2 production was measured with a new type of optical CO_2 sensors that indicated a continuous CO_2 production during the experiments. However, further check of the results raised some doubt about the long term stability of the sensors and the absolute values of the CO_2 pressure. The sensors and

data need to be further evaluated, so the following discussion is mainly based on the consumption of oxidants.

The consumption of oxygen has already been calculated and discussed in Mortensen et al (2013) – these results are considered fairly reliable as they are based on continuous logging of the oxygen concentration in the vials that all show a consistent decreasing concentration.

The consumption of nitrate has been calculated according to Equation 1, using linear regression to find the decrease in concentration over time ($\Delta C / \Delta t$). These results have a higher uncertainty as the calculations are based on a few data points and the decrease in concentration is not always linear.

The consumption of sulphate is also calculated according to Equation 1 and using linear regression, and also here there is some uncertainty.

Consumtion of oxidants	FJB3-01			FJB3-02			FJB3-06			FJB3-08		
Vial	4	5	6	10	11	12	1	2	3	7	8	9
Oxygen, unsaturated	202	178	195	219	135	169	353	361	346	249	268	219
Oxygen, saturated, in soil	48	65	40		143	115	103	98	90	41		43
Nitrate, saturated, 2nd add	21	27	19	42	36	36	147	58	144	54		49
Sulphate	2	4	2	5	4	7	13	13	13	7		5
Nitrate, saturated, 5 °C	8	14	27	12	10	9	119	196	82	29		57

Table 4: Consumption rate for different oxidants during the experiment, in µg/g dry sample/day. Blanks indicate that no measurements were made.

The results for different processes cannot be compared directly, as the consumption of 1 µg oxygen, nitrate and sulphate does not result in the same oxidation. In order to compare the different oxidants on an equal basis, the numbers are recalculated to the amount of organic material (represented as CH_2O) they may oxidise (Table 5)

Oxidation of organic matter	FJB3-01			FJB3-02			FJB3-06			FJB3-08		
Vial	4	5	6	10	11	12	1	2	3	7	8	9
Oxygen, unsaturated	189	167	183	205	127	158	331	338	324	233	251	205
Oxygen, saturated	45	61	38		134	108	97	92	84	38		40
Nitrate, saturated, 2nd add	13	16	11	25	22	22	89	35	87	33		30
Sulphate, saturated	1	2	1	3	3	4	8	8	8	4		3
Nitrate, saturated, 5 °C	5	9	17	7	6	6	72	118	50	17		35

Table 5: Theoretical oxidation of organic matter during the experiment, in µg CH_2O /g dry sample/day. Blanks indicate that no measurements were made

The values are presented graphically in Figure 10 and the average values for each soil sample are presented in Table 6.

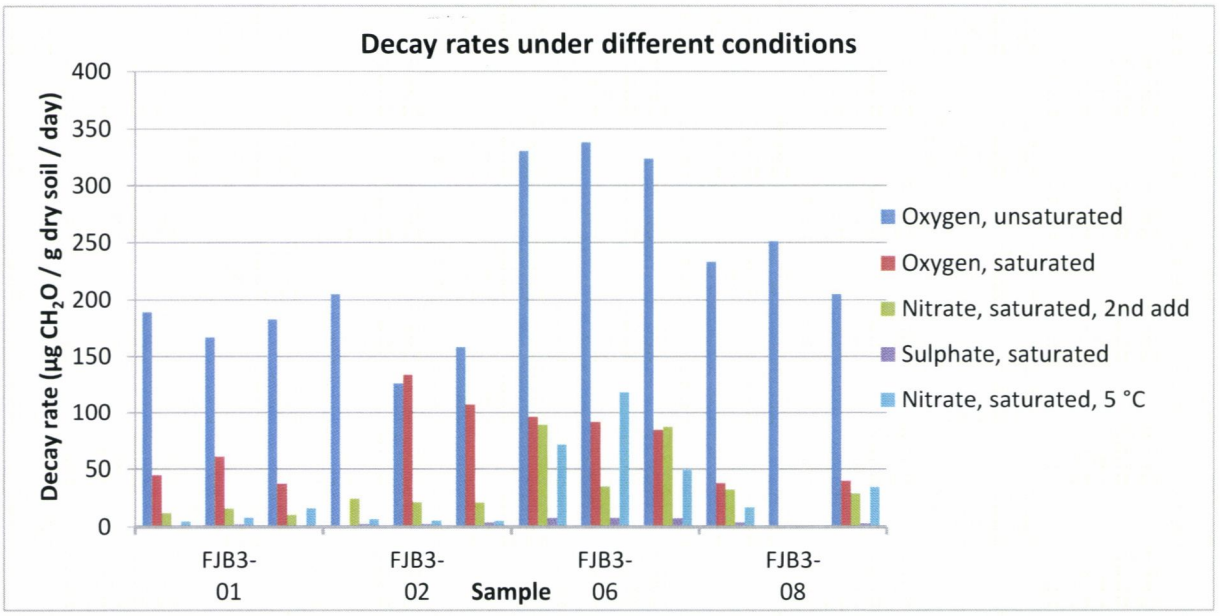

Figure 10: Graphical presentation of the decay rates under different conditions, calculated from the consumption of oxidants.

Average values	FJB3-01	FJB3-02	FJB3-06	FJB3-08
Vial	4-6	10-12	1-3	7-9
Oxygen, unsaturated	180	163	331	230
Oxygen, saturated	48	121	91	39
Nitrate, saturated, 2nd add	13	23	70	31
Sulphate	2	3	8	4
Nitrate, saturated, 5 °C	10	6	80	26

Table 6: Average decay rates for each soil sample, in µg CH_2O /g dry sample/day, based on the results in Table 5

The results confirm earlier studies of soil samples from Bryggen (Hollesen & Matthiesen 2012): Oxygen is the most reactive oxidant and it is noted that the decay rate under unsaturated conditions is higher than in all other setups (i.e. "any water is better than no water"). Still the decay rates shown for saturated soil with dissolved oxygen or nitrate are also high, whereas the decay rate under sulphate reducing conditions is comparably low, but not insignificant. To put the numbers into perspective the soil samples used here are quite organic rich and contain 390-750 mg organic matter per g dry weight (Table 1). This means that e.g. a decay rate of 10 µg CH_2O /g dry sample/day (equal to 3.65 mg CH_2O /g dry sample/year), would correspond to a yearly loss of ½-1 % of the organic matter.

All these measurements have been carried out under "unlimited supply" of the different oxidants, whereas in situ the supply of the different oxidants can vary significantly and they may only be present in limited concentrations or for a limited period. For instance a groundwater sample from

FJB3 from March 2012 showed no oxygen, no nitrate, and a fairly low concentration of sulphate (13 mg/L), meaning that decay in situ takes place at a low rate despite the high reactivity of the soil. Thus, a full evaluation of the results in Figure 10 and Table 5-6 requires knowledge about the supply, presence and concentrations of the different oxidants.

Redox potential and decay rates

In previous sections were shown how the conditions and ongoing processes influence both the redox potentials and the decay rates. It is of great interest how good this correlation is, i.e. if the redox potentials can be directly interpreted in terms of ongoing decay. To study the relation in a bit more detail it is necessary to compare the redox potential and decay rates directly. To that end, the average redox potentials measured in each vial during the different processes are summarized in Table 7. These potentials can be compared to the decay rates for the same vials and processes in Table 5. This is done graphically in Figure 11.

Average redox potential	FJB3-01			FJB3-02			FJB3-06			FJB3-08		
Vial	4	5	6	10	11	12	1	2	3	7	8	9
Oxygen, unsaturated	367	152	553	452	504	507	294	505	368	305	401	187
Oxygen, saturated	427	489	534		513	476	559	377	482	492		487
Nitrate, saturated, 2nd add	-2	-49	-52	-228	-174	-185	-106	-208	-111	-111		-44
Sulphate	-50	-184	16	-233	-225	-221	-244	-364	-211	-198		-291
Nitrate, saturated, 5 °C	176	-51	-116	-137	82	130	-59	-150	-69	-36		-92

Table 7: Average redox potentials (mV vs SHE) measured in each vial during the different decay processes.

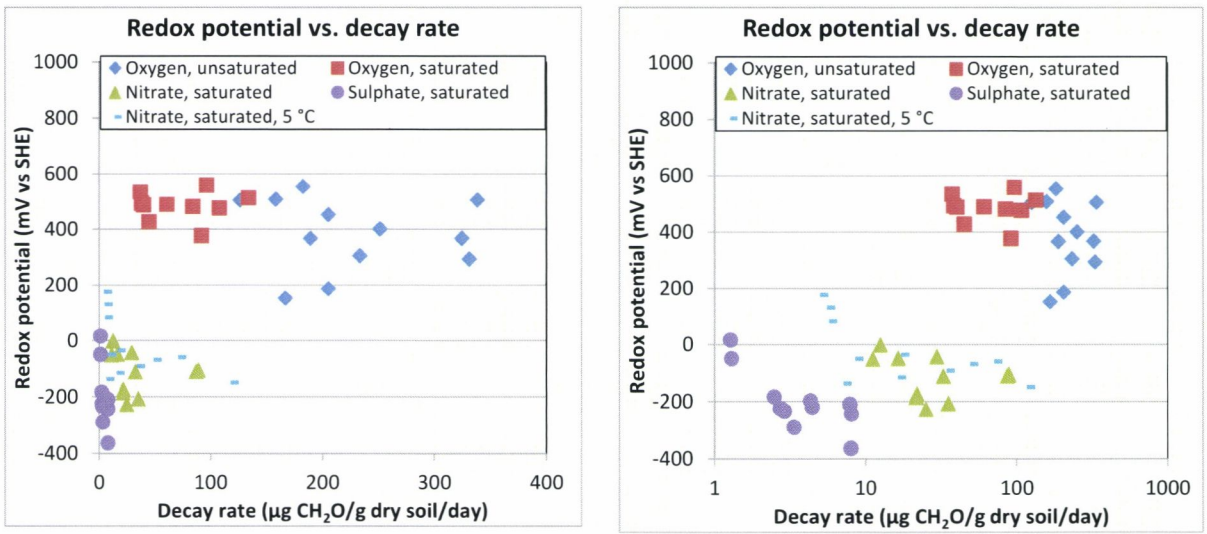

Figure 11: Comparison between the decay rates and redox potentials measured in all vials under five different conditions. Note log-scale on the figure to the right

Figure 11 indicates some correlation between decay rate and redox potential, i.e. the highest decay rates are indeed found at the highest redox potentials (above 0 mV vs SHE). Still, even below 0 mV vs SHE decay rates up to 100 µg CH_2O /g dry sample/day may be found, and the potential must be below – 230 mV vs SHE before the decay rate is consequently below 10 µg CH_2O /g dry sample/day for these samples. At the other end of the scale the data in Figure 11 seem to indicate that the decay rate is always high (> 40 µg CH_2O /g dry sample/day) for redox potentials above 400 mV vs SHE. However, this depends on the samples studied and for instance it has been found that samples from the upper unsaturated soil layers are significantly less reactive than the samples used here. Decay rates as low as 10 µg CH_2O /g dry sample/day have been measured for such samples even under unsaturated conditions with oxygen present (Hollesen & Matthiesen, 2012, Table 3). Thus it is not possible to evaluate decay rates from potential measurements alone - they need to be combined with other studies (as is also the case for e.g. oxygen measurements).

Decay rates and temperature

The correlation between temperature and decay has earlier been studied for unsaturated conditions by comparing the oxygen consumption at 5, 10, 15 and 20 °C (Hollesen & Matthiesen, 2011). This showed that the decay rate increased by 100 to 180% when the temperature was increased by 10 °C. It was planned to make a similar study under saturated conditions by comparing the CO_2 production at 5, 10, 15 and 20 °C for selected samples. However, problems with the CO_2 quantification made it necessary to take another approach that is to compare the nitrate consumption of the samples at 5 and 15 °C (Table 8).

Oxidation of organic matter	FJB3-01			FJB3-02			FJB3-06			FJB3-08		
Vial	4	5	6	10	11	12	1	2	3	7	8	9
Nitrate, saturated, 5 °C	5	9	17	7	6	6	72	118	50	17		35
Nitrate, saturated, 15 °C	13	16	11	25	22	22	89	35	87	33		30
Relative increase (%)	150	91	-32	249	280	287	24	-70	75	89		-15

Table 8: Reaction rate (µg CH_2O /g dry sample/day) for nitrate reduction at 5 and 15 °C. Lower row shows the relative increase (%) in reaction rate when the temperature is increased by 10 °C (from 5 to 15 °C)

The relative increase in decay rate is very variable, ranging from an increase of almost 300%, to a relative decrease in rate. The latter is considered quite unlikely and is probably due to erroneous measurements. The calculation of decay rates is based on relatively few nitrate measurements, which gives an increased uncertainty of the rates. Furthermore, measurements should be carried out at more temperatures (e.g. 10 and 20 °C) to get a good measure of the temperature dependence – this was originally planned, but turned out not to be possible within the time frame of this project, as the nitrate measurements are much more time consuming than the planned CO_2 measurements. Renewed and more comprehensive measurements will be necessary to get a good picture of the influence from

temperature on the decay of cultural deposits under saturated conditions. Until then, some literature values may be used: Scanlon & Moore (2000) studied CO_2 production from peat soil and give a Q10 value of 2.0 for oxic and 2.7 for anoxic conditions, which is equal to a 100% and 170% increase in the production for a 10 °C temperature increase. Jørgensen et al (2009) studied nitrate reduction in anoxic groundwater sediment, and found a Q10 value of 1.8, corresponding to a 80% increase when the temperature increases 10 °C. Bak & Pfennig (1991) studied sulphate reduction in sediments from Lake Constance and found a Q10 value of 2.25 corresponding to a 125% increase when the temperature increases 10 °C, and Urban et al (1994) made a similar study of sulfate reduction in a lake from Wisconsin and found a Q10 value of 2.6 corresponding to a 160% increase when the temperature increases 10 °C. Overall, these literature values indicate that the temperature dependence of anoxic processes is similar to what we have observed for decay under unsaturated conditions in Hollesen & Matthiesen (2011).

Conclusions

To sum up the results from this study:

- The samples used are considered representative for the deeper deposits at central Bryggen, whereas samples from the upper, unsaturated zone will be less reactive
- The microcosms are well suited to measure redox potential and decay processes under controlled conditions, but for studies of waterlogged soil concentration gradients may occur within the microcosms.
- The redox potential measurement are very sensitive and react to even minor changes in the environment
- The redox potential measured may vary by some hundred mV between replicates
- The redox potential can to some extent indicate which oxidants are present and which processes are ongoing. Under waterlogged conditions with oxygen reduction the potentials varied from +400 to +600 mV vs SHE, under conditions with nitrate reduction the potentials varied from +300 to -200 mV vs SHE, and under conditions with sulphate reduction the potentials varied from -400 to -200 mV vs SHE.
- There is no correlation between the concentration of individual oxidants and the redox potential
- There is some correlation between redox potentials and decay rates measured, and the highest decay rates are found at potentials higher than 0 mV vs SHE. Still, for some samples

unacceptable high decay rates are found even at low potentials between -200 and 0 mV vs SHE.

- Overall, the redox potential measurements work better under saturated than unsaturated conditions. They are especially suited for showing if conditions are stagnant or dynamic, but interpretation of the absolute values is still difficult.
- Oxygen is the most reactive oxidant and the decay rate under unsaturated conditions (160-330 µg CH_2O /g dry sample/day) is higher than in all other setups (i.e. "any water is better than no water"). The decay rates shown for saturated soil with dissolved oxygen (40-120 µg CH_2O /g /day) and nitrate (13-70 µg CH_2O /g /day) are also high. The decay rate under sulphate reducing conditions is lower (2-8 µg CH_2O /g /day) but not insignificant. Decay rates in situ will depend on the supply of these oxidants, which may be highly variable.
- Measurements of pH and CO_2 with new types of optical sensors were only partly successful, and more work is necessary to interpret the data.
- It was attempted to measure the temperature dependence of anoxic decay, but the results are uncertain and need to be validated. Literature values from natural systems are given instead.

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