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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 and oxygen probes as a way of getting information about preservation conditions at archaeological sites. This has been done through field studies at Bryggen in Bergen (Walpersdorf et al 2012) and through laboratory experiments described in this report. Here redox potentials and oxygen concentration and consumption have been measured in soil samples from Bryggen placed under controlled conditions in oxygen-tight containers at the laboratories of the Danish National Museum. In this way rates of oxygen consumption and oxygen concentration could be measured and compared to the measured redox potentials under both saturated and unsaturated conditions. For unsaturated conditions the measurements showed a steady decrease in oxygen concentration in the vials, leading to anoxic conditions after 10-30 days. Measurements were made both above and beneath the soil surface, showing very similar results which indicate that the conditions and decay were not limited by diffusion across the soil surface. Furthermore it demonstrates that the oxygen sensors work in both air and soil. The redox potential measurements were very fluctuating and with a large variation between replicates, possibly due to air-filled pores in the unsaturated soil giving insufficient contact between redox probes and the soil. The potentials measured under oxic conditions varied between 0 and +600 mV vs. SHE, and under anoxic conditions they varied between +300 to -300 mV. The system was vulnerable to static electricity and showed very large variations if the wires were handled.

Under fully saturated conditions the concentration of oxygen, carbon dioxide, pH and redox potentials were logged on the same soil samples as were used in the unsaturated experiments. Redox potential was logged under the soil surface, carbon dioxide and pH were measured in the water-filled headspace over the soil surface and oxygen was measured both below and above the soil surface. The rates of oxygen consumption under saturated conditions are lower than under unsaturated conditions, which is in agreement with previous findings. It was observed that an initial carbon dioxide release coincided with an initial consumption of oxygen and subsequent carbon dioxide release was observed for some but not all samples. One explanation for this could be the release of carbon dioxide from anoxic degradation processes. A pH drop was observed during the experiment; this is likely to be related to carbonic acid formed by the produced CO_2. The redox potentials measured under saturated conditions were less fluctuating and more consistent compared to measurements under unsaturated conditions. The redox potentials remained steady between +400 and +550 mV as long as oxygen was present in concentrations higher than about 5 % saturation, under this value the redox potentials dropped. When all oxygen was depleted the redox potentials

still changed in some instances. This may be due to changes in metabolic pathways taking place under anoxic conditions in the microcosms, changes that cannot be observed through oxygen measurements. Thus under saturated conditions the two methods seem to complement each other, whereas under unsaturated conditions oxygen measurements are preferable as the redox potential measurements were very fluctuating and difficult to interpret. Future work will include more detailed studies under saturated conditions, where the redox potentials are compared to decay rates from different anoxic processes.

Signatures

Martin N. Mortensen Rune V. Zimsen Henning Matthiesen

Introduction

The National Museum of Denmark and MVH Consult in the Netherlands have been contracted by *Riksantikvaren* to make an investigation of the possibilities for using redox potential measurements and/or oxygen measurements for in situ monitoring of cultural layers under both saturated and unsaturated conditions. The comparison comprises both field measurements and laboratory studies, both using material from Bryggen in Bergen. Results from the field studies are reported in Walpersdorf et al (2012); this report shows the results from comparison under controlled conditions in the laboratory; and a third report (forthcoming) will focus on anoxic processes and how they influence redox potentials and decay rates.

Background

Developer-funded monitoring programmes in the unsaturated zone in urban cultural layers normally include monitoring of the temperature and the water content in different soil layers. Riksantikvaren wants to evaluate if the monitoring programs should also include measurements of redox potential and/or oxygen in the soil. 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. 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") are already planned. 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. In the project "Urban WATCH", the National Museum, in collaboration with MVH Consult, NIVA, NGU and TAUW, is going to address this question, using Bryggen in Bergen as example.

Experimental

The experiments carried out during the present work aim at monitoring the changes in certain chemical parameters related to decay processes in soil. The samples investigated were soil samples from *Fjellbrønn* 3 from Bryggen in Bergen (figure 1), sampled at four different depths, namely FJB3-01, FJB3-02, FJB3-06 and FJB3-08 with preservation states (SOPS) rated as medium, medium, good and excellent respectively.

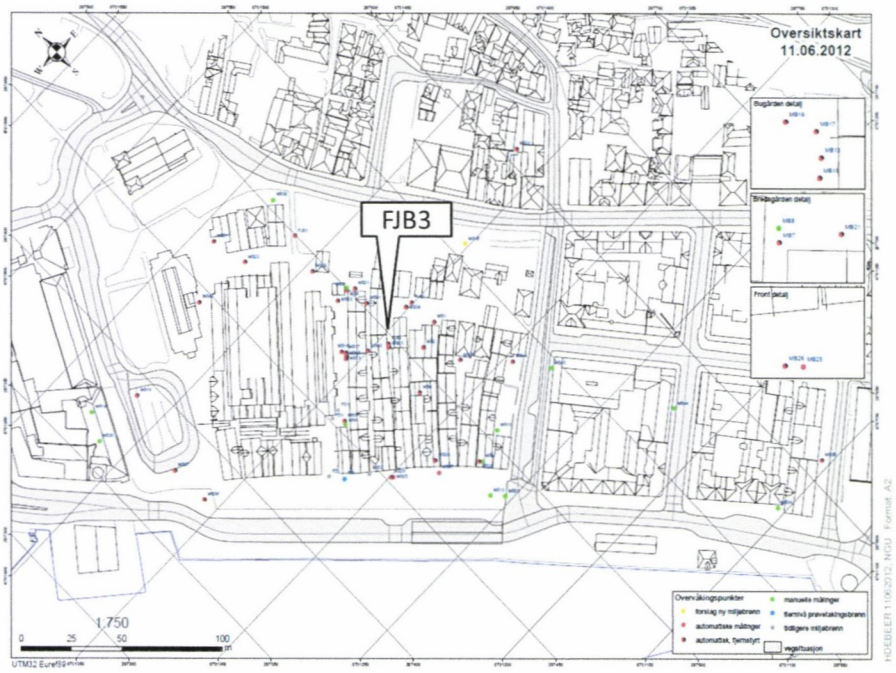

Figure 1. Map showing the location of the Fjellbrønn 3 sampling site on Bryggen.

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. The samples are briefly described in Table 1, and in more detail in Walpersdorf (2013).

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).

	Depth (m asl)	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

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 of these samples was placed in the bottom of a 100 ml screw-cap vial with optical sensors installed on the inside of the glass wall to measure carbon dioxide, pH and oxygen in the headspace over the soil sample and also oxygen in the soil itself (illustrated in figure 2). Carbon dioxide and pH could only be measured under saturated conditions. The redox potential was measured in the soil using a Pt electrode and a Ag/AgCl reference electrode buried in the soil as illustrated in figure 2 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.

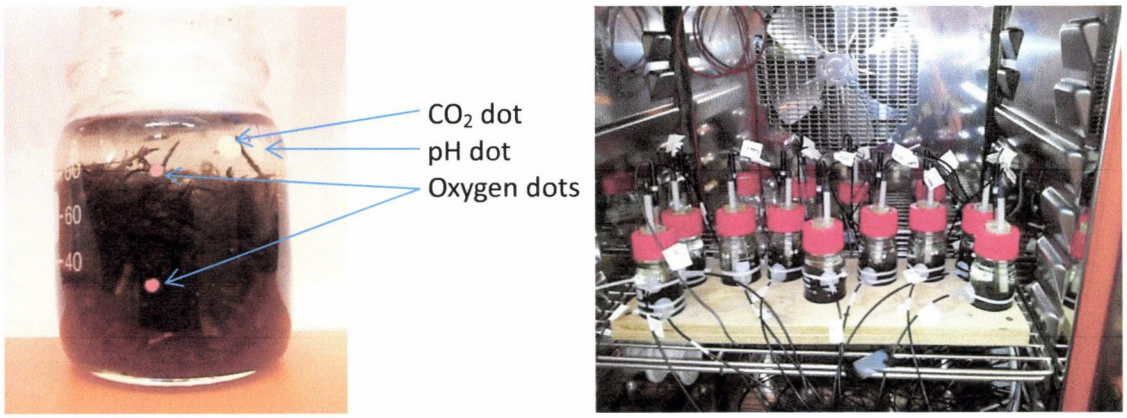

Figure 2. Photographs showing the microcosms. To the left 100 ml screw cap vials containing sample soil and buffer; on the inside of the glass wall two oxygen sensor dots, a CO_2 sensor and a pH sensor can be seen. To the right a picture of the setup inside the climate chamber, redox electrodes are seen in the lids of the 12 vials and fibre optic cables are logging the oxygen concentration in the soil layers of each sample.

The lids of the vials were sealed with aluminium foil and epoxy was used for gluing the electrodes to their holes in the lids in order to make the containers oxygen-tight. All experiments are carried out at 15°C to allow comparison with previous experiments that have been carried out at this temperature.

The oxygen consumption was measured by monitoring the decrease of headspace O_2 concentration and the rate of oxygen consumption calculated as:

$$\textit{Oxygen consumption rate} = V \cdot C \cdot (\Delta O_2 / \Delta t) / m \cdot 100 \qquad (1)$$

where V is the volume of air inside the vial (cm^3), C is the initial concentration of oxygen (mg/cm^3), $\Delta O_2/\Delta t$ is the decrease in oxygen saturation over time (% sat/day – taken as the slope of the oxygen

curves), m is the dry weight of the soil sample (g) and 100 (%) is a scale factor. For experiments under unsaturated conditions, C in the gas phase is calculated from the ideal gas law to 0,284 mg/cm^3 at 15°C. For experiments under saturated conditions, V is the volume of water in the vial, and C is 0.010 mg/cm^3 at 15°C (table value). The procedure has been described previously (Matthiesen 2007).

Results and discussion

Unsaturated soil

A series of measurements was carried out on the soil samples. No moisture was added to the soil samples and thus the water content was the same during the experiment as it was in the ground at the given depth and at the time of sampling. The water content and the content of organic matter were measured by standard procedures before the experiments were started (reported in table 1); the water contents were in agreement with measurements carried out by external laboratories.

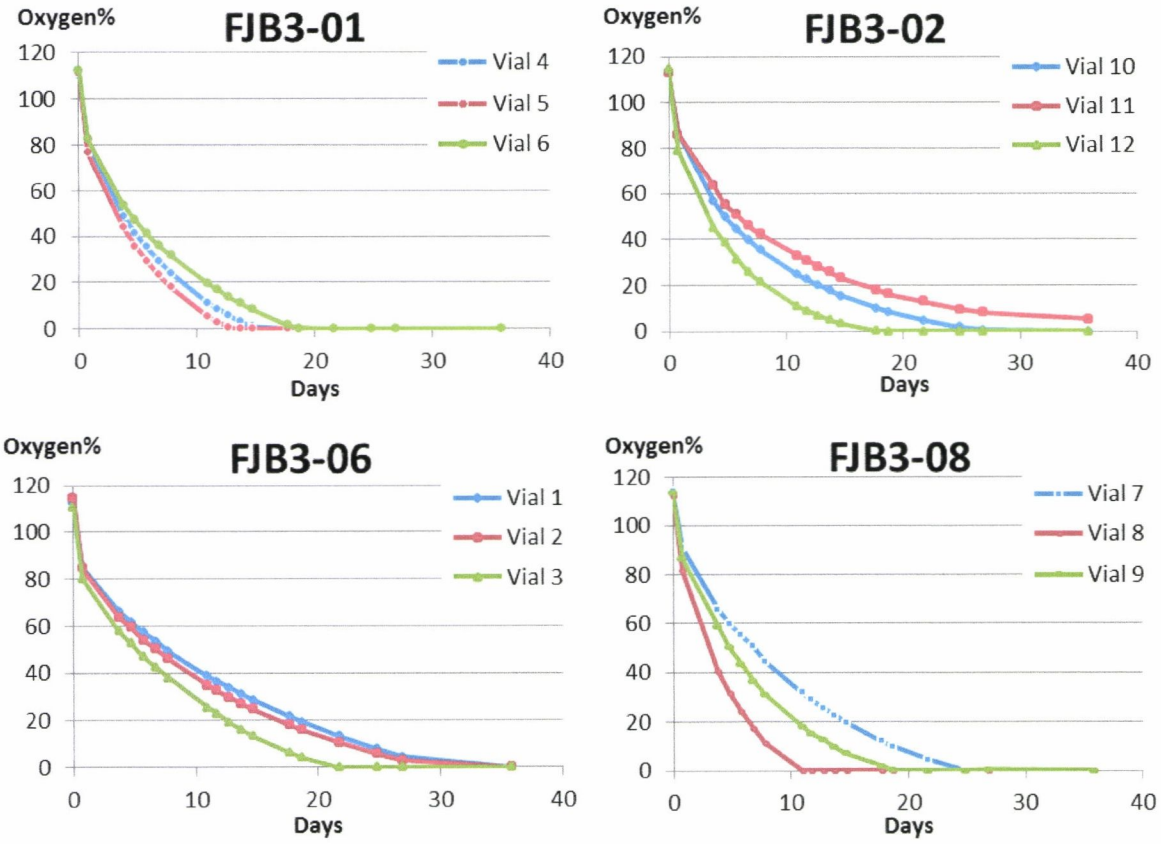

Figure 3. Oxygen concentration (% saturation) as a function of time in the air headspace above the soil surface measured in triplicate for each of the four depths in *Fjellbrønn* 3 (FJB3-01, FJB3-02, FJB3-06 and FJB3-08).

The oxygen concentration in the headspace was measured by a sensor installed above the soil surface inside the oxygen-tight vials at 15°C. This oxygen concentration is plotted as a function of time in figure 3, where it is seen that all oxygen in the headspace is consumed in 10- 30 days by most samples. The dependency of oxygen concentration on time is not linear as seen in figure 3; preliminary tests (data not shown) indicate that the oxygen-consuming reaction may be characterized as half order in oxygen since the square root of the oxygen concentration relates linearly to time. The rate of oxygen consumption has been calculated for the measurements shown in figure 3. This was done by calculating the slope of the curves as a linear least-squares fit to the part of the curve between 100 % and 70 % oxygen saturation and omitting the first data point (as the temperature and system need to stabilize). The headspace of air over the sample was taken into account in the calculation of the rates of oxygen consumption. The average rate was 191 µg O_2/g dry soil/day (standard deviation=12) for the three measurements in FJB3-01, it was 174 µg O_2/g dry soil/day (standard deviation=42) for FJB3-02, 353 µg O_2/g dry soil/day (standard deviation=7.6) for FJB3-06, and 245 µg O_2/g dry soil/day (standard deviation=24) for FJB3-08 (also summarized in table 2). Thus, it is seen that the oxygen consumption, which is related to reactivity, does not strictly follow the depth profile, but other parameters, such as for instance the organic content of the sample, may also influence the reactivity.

The oxygen concentration was also measured in the soil layer itself in the oxygen-tight vials and the redox potential was logged from Pt-electrodes and Ag/AgCl reference electrodes buried 1-2 cm into the soil sample. The photograph in figure 2 shows the 12 microcosms, the results of the measurements are presented in figure 4.

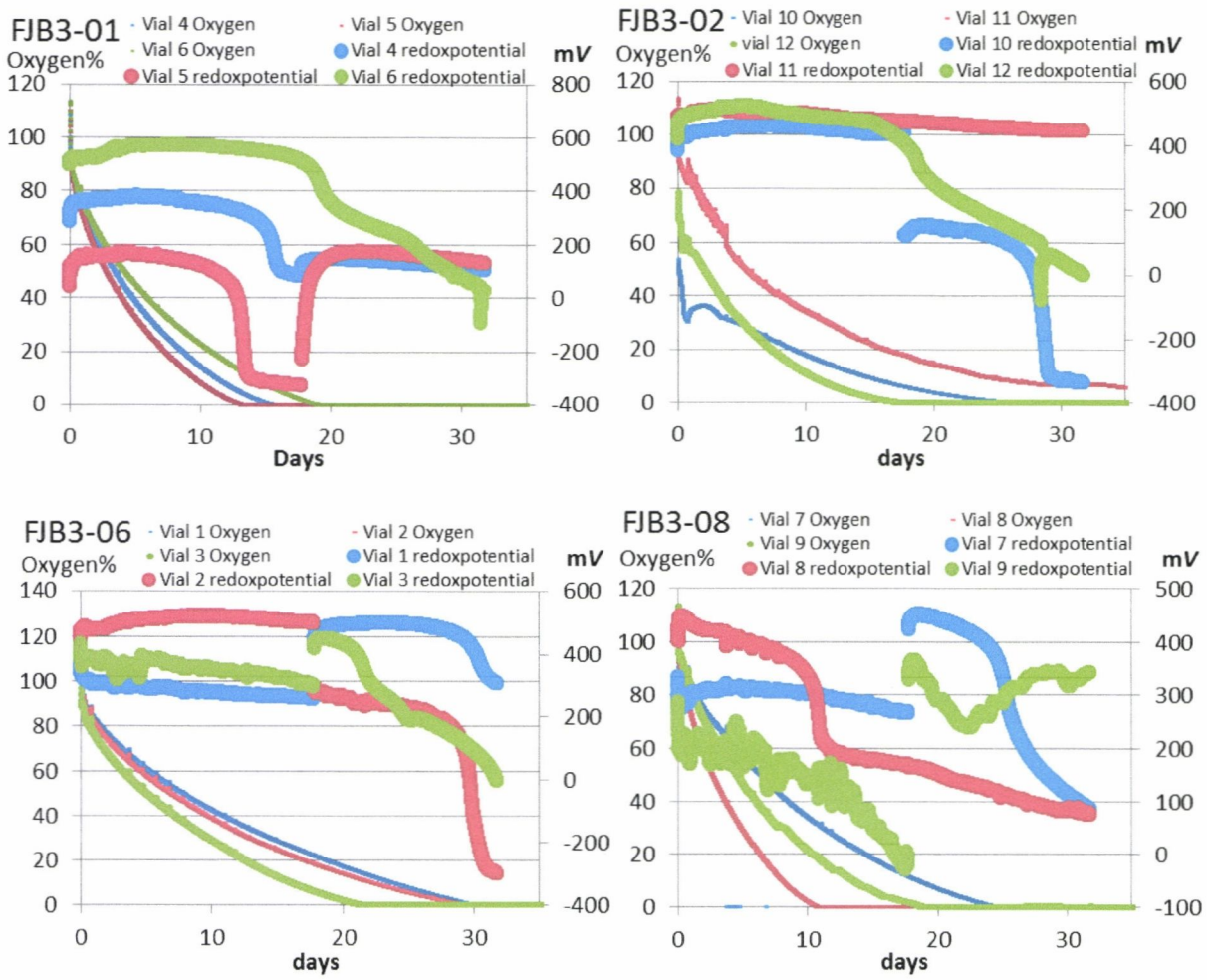

Figure 4. Redox potentials in mV relative to the Standard Hydrogen Electrode (SHE) and oxygen concentration (% saturation), both measured under the soil surface, are plotted as a function of time for triplicate samples from each of the four depths of *Fjellbrønn* 3 (FJB3-01, FJB3-02, FJB3-06 and FJB3-08).

Here the redox potential and the oxygen concentration in the soil are plotted as a function of time for the triplicate measurements of each sample (FJB3-01, FJB3-02, FJB3-06 and FJB3-08) as indicated in the figure. It is seen that the oxygen concentration decreases with time and reaches zero after 10-30 days in most samples. The oxygen concentrations measured in the headspace (Figure 3) and in the soil (Figure 4) are very similar, indicating that the conditions in the soil are not limited by oxygen diffusion across the soil surface in these experiments carried out under unsaturated conditions. Furthermore it demonstrates that the oxygen sensors work in both air and soil. The redox potentials all stabilize within a day; however, not all of the potentials stabilize on the same value. For instance the three measurements of FJB3-01 settle on approx. 200, 400 and 600 mV vs. SHE even though they contain the same sample material and the oxygen curves are similar. In FJB3-02 on the other hand the potentials all stabilize between approx. 400 and 500 mV. It is seen

that the redox potentials drop steeply when the oxygen concentration approaches zero. This occurs after about 12 days in vial number 5, 14 days in vial 4 and 18 days in vial 6 in FBJ3-01 in figure 4. This phenomenon can also be observed on the other curves in figure 4 except for vial 11 FJB3-02 because this sample has not reached sufficiently low oxygen levels, and vial 9 FJB3-08 where the redox potential decreases at a lower rate and at higher oxygen concentrations than for the other measurements. On day 17 the wiring of all the redox electrodes was disconnected and later reconnected to the logger unit under the supervision of Michel Vorenhout who visited the laboratory. This resulted in a sudden jump in some, but not all, of the potentials when the wires were reconnected. Some potentials increased, some decreased, and others did not change. No conclusive explanation has been found for this phenomenon, but it may be connected to insufficient contact between the electrodes and the soil. If this is the case then only four vials have proper electrical connection between the electrodes and the soil, namely vial 6 (containing FJB3-01), vial 11 and vial 12 (containing FJB3-02) and vial 8 (containing FJB3-08). This emphasizes that it can be difficult to obtain a sufficient soil contact and good redox potential measurements in unsaturated soil, where some of the soil pores are filled with air.

One of the main objectives of the present study is to compare redox potential and oxygen measurements in soil. In figure 5 the redox potentials that were also shown in figure 4 are plotted against oxygen concentration. The redox potentials shown in figure 4 may be erroneous due to air in the unsaturated soil as explained. This will clearly reflect on a plot of potential versus oxygen concentration as in figure 5. There is a tendency for redox potential in individual samples to remain relatively constant for oxygen levels between 100-5 % and drop steeply when the oxygen concentration reaches low levels (<5 % O_2 sat), so there is some reaction to changes in the environment. However, when comparing different samples the redox potentials are highly variable, showing levels between 0 mV and 600 mV when the oxygen levels are higher than 5 % O_2. Thus in summary it can be said that redox potentials are difficult to measure and interpret under unsaturated conditions, possibly due to air-filled pores in the soil giving contact problems.

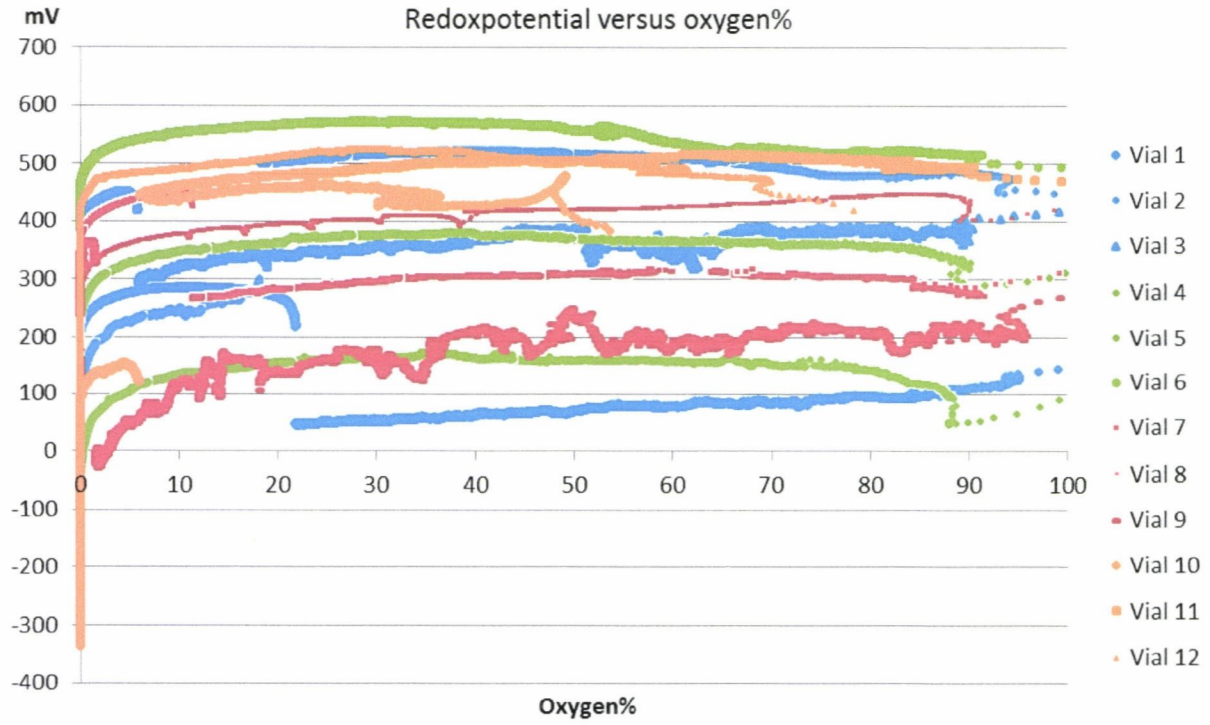

Figure 5. Redox potential in mV relative to the Standard Hydrogen Electrode (SHE) measured in the unsaturated soil and plotted as a function of oxygen concentration in % saturation in the multiplicate measurement on the four depths investigated in *Fjellbrønn* 3 (FJB3-01, FJB3-02, FJB3-06 and FJB3-08) also shown in figure 4.

Saturated soil

When the unsaturated experiments described above were terminated the vials were opened and filled up with an aqueous solution of $NaHCO_3$ (0.0092 M) with a pH of 6.49 adjusted using hydrochloric acid. This carbonate content and pH was chosen to match the values found in groundwater and soil samples from *Fjellbrønn* 3 (Walpersdorf 2013). The lid was refitted in such a way that no air bubbles were trapped in the vial. Redox potential and oxygen content in the soil, and pH, CO_2 and oxygen in the liquid above the soil, were then monitored at 15°C. The results are shown in figure 6, where a graph is presented for each of the four depths of *Fjellbrønn* 3 showing oxygen concentration in the soil, oxygen concentration in the liquid and redox potential in the soil for all replicates in each depth. The oxygen content in the soil drops to zero within the first two days and the oxygen in the liquid above is consumed within 10 days. This delay is due to a limited diffusion of oxygen from the water-filled headspace down into the waterlogged soil. The redox potentials are shown as well; the potentials start between 550 mV and 650 mV and then they decrease to levels between -322 mV and -85 mV at day 14; in some cases the potential still decreases at this point. During this time period the redox potential makes several sudden "drops". It

may be possible to associate one of these with the oxygen concentration reaching zero; however, on most of the redox curves three sudden drops can be identified. The present experiment does not hold information about the identity of these changes but it is possible that they reflect the type of microbial metabolism going on in the soil. For instance sulphate reduction (SO_4^{2-}/HS^-) is known to take place at potentials a little lower than -200 mV (vs. SHE) at pH 7 (Sigg 2000).

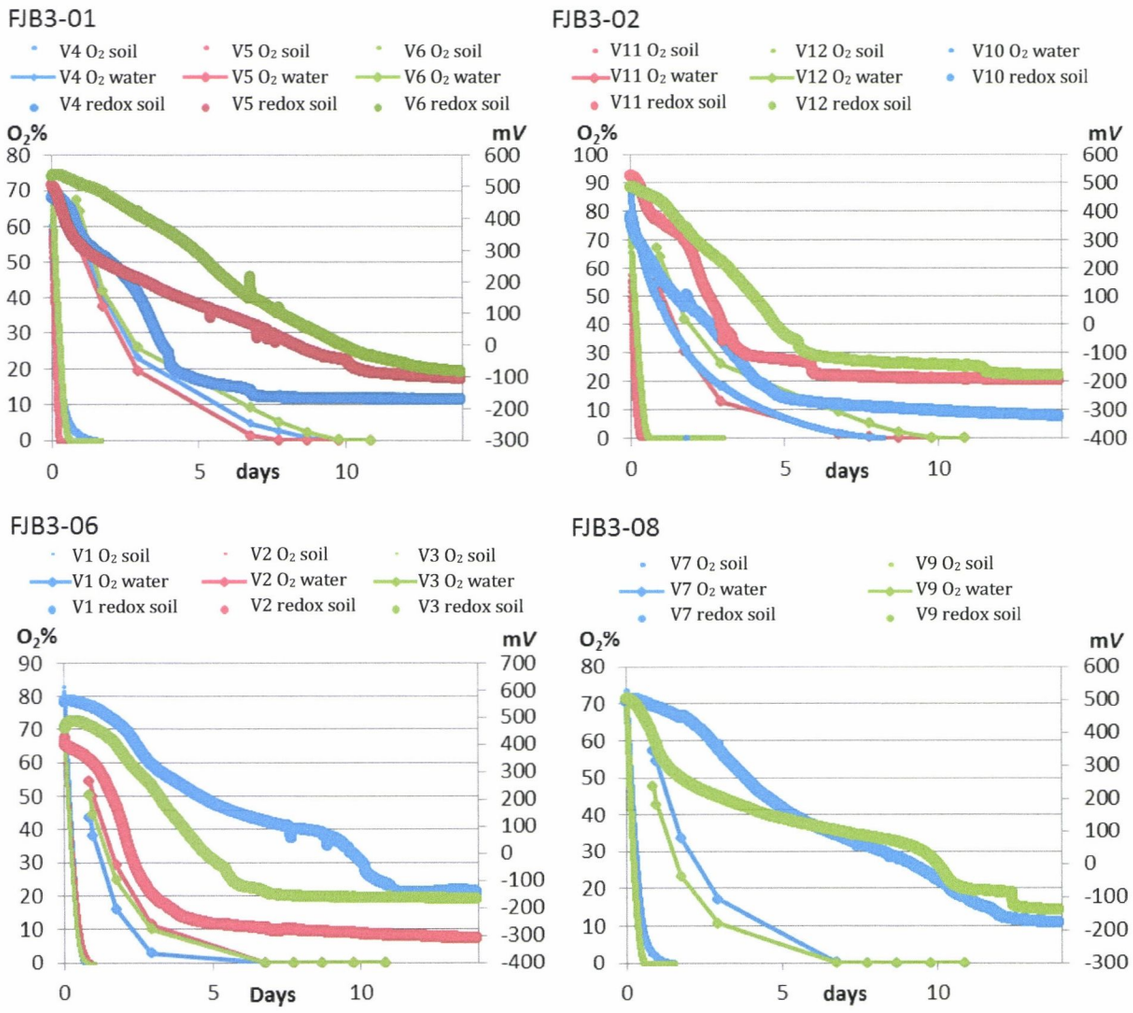

Figure 6. Oxygen concentration in the soil, redox potential (in mV vs. SHE) in the soil and oxygen concentration in the water-filled headspace above the soil plotted as a function of time for the multiple measurements of the four sampling depths of *Fjellbrønn* 3 (FJB3-01, FJB3-02, FJB3-06 and FJB3-08).

The plot of redox potential versus oxygen concentration in the saturated experiment shown in figure 7 has got the same overall shape as in the unsaturated experiment. The potentials do not change much when oxygen concentration changes between 5 % and 95 %, but when the oxygen gets below 5 % saturation the redox potentials drops too.

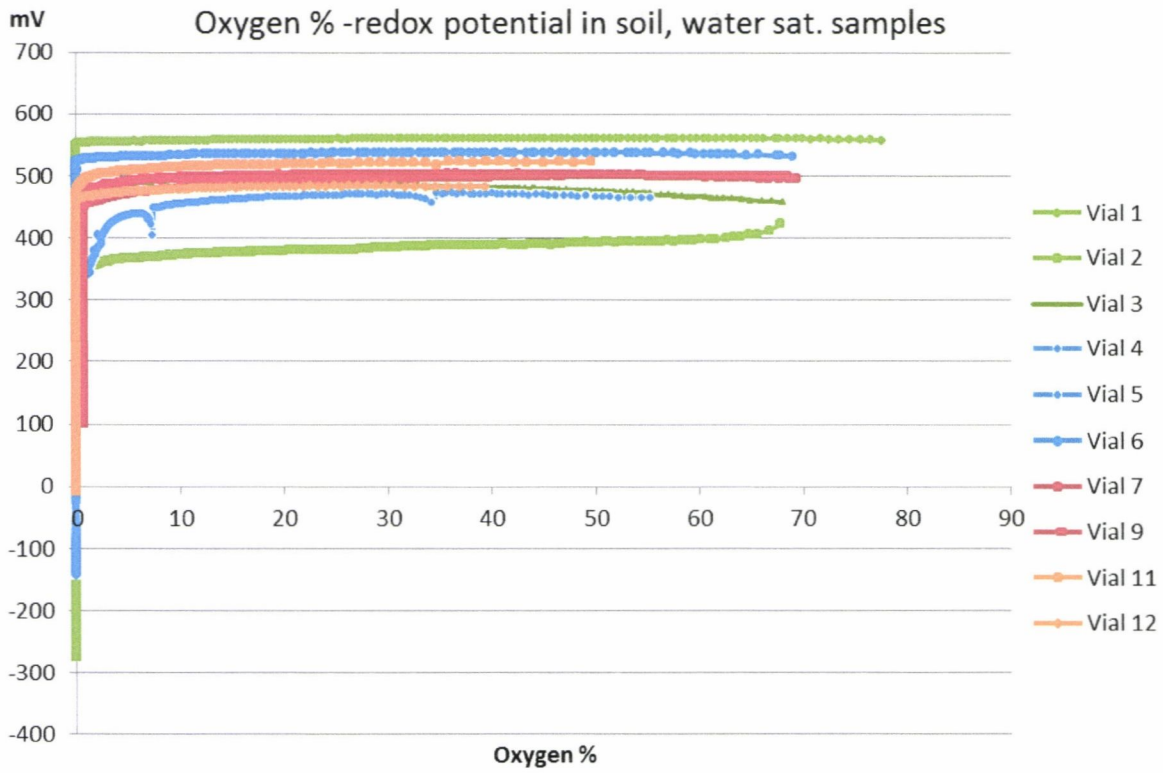

Figure 7. Redox potential in mV relative to the Standard Hydrogen Electrode (SHE) measured in water-saturated samples and plotted as a function of oxygen concentration in % saturation measured in the soil in the multiplicate measurement on the four depths investigated in *Fjellbrønn* 3 (FJB3-01, FJB3-02, FJB3-06 and FJB3-08) also shown in figure 6.

The level of the potential is between 400 mV and 550 mV when the oxygen concentration is higher than 5 %. This variation between samples is significantly lower compared to the measurements under unsaturated conditions (Figure 5). The concentration of CO_2 was measured in the water-filled headspace over the soil during the experiment with saturated soil, which is plotted as a function of time in figure 8. The CO_2 level is not zero to begin with as a HCO_3^-/H_2CO_3 buffer was used to saturate the samples. The CO_2 concentration increases with time for all of the samples, at a high rate to begin with and at a lower rate after about three weeks.

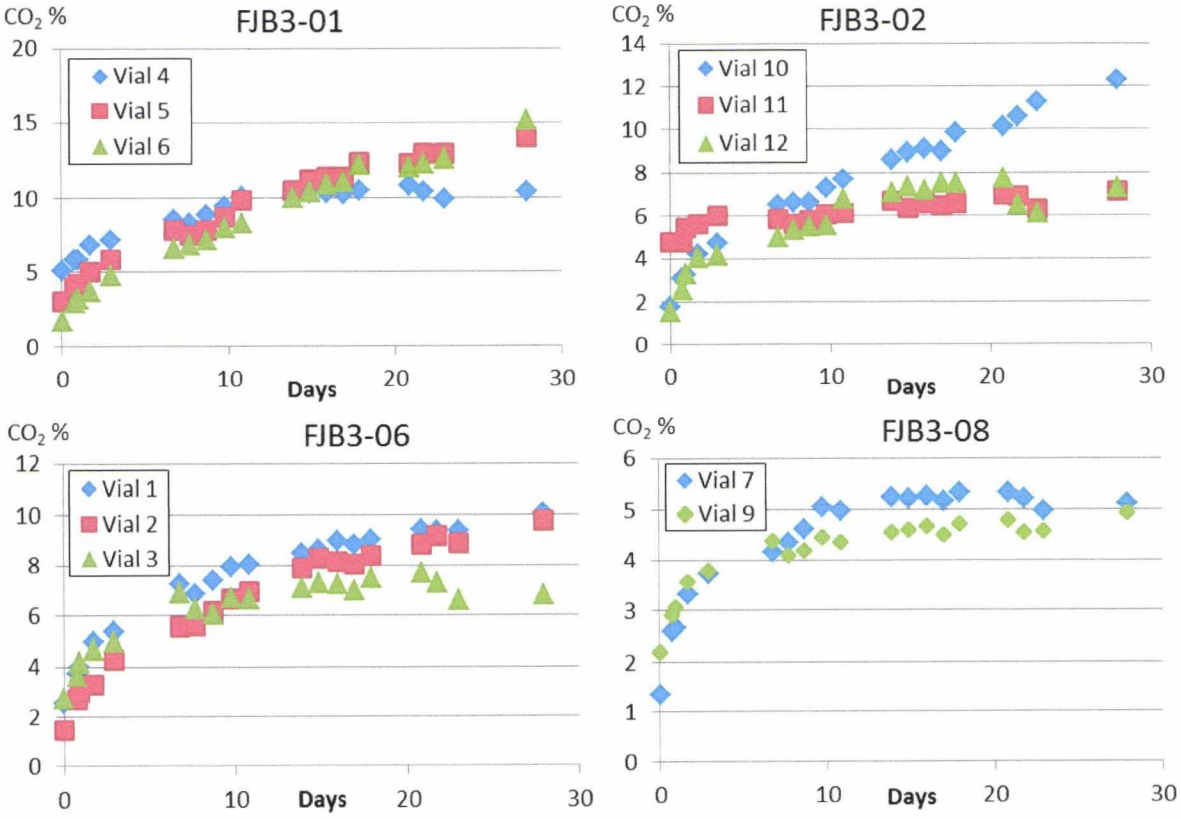

Figure 8. Concentration of carbon dioxide in % saturation measured in the liquid headspace above the soil sample as a function of time for the two (FJB3-08) or three (FJB3-01, FJB3-02, FJB3-06) replicate measurements of the four sampling depths of *Fjellbrønn* 3.

Some samples continue to produce CO_2 at a low rate after the initial fast CO_2 production has levelled off, whereas other samples seem to stop the production completely. A likely explanation for the initial fast release of CO_2 could be that the oxygen available in the liquid is consumed in a fast reaction where organic matter in the soil is oxidized to CO_2. After this, slower anaerobic processes take over also releasing CO_2. Besides measuring CO_2 throughout the experiment, pH was measured too, as illustrated in figure 9. It is seen that the measured pH is close to 8 at the outset of the experiment; it is also clear that it decreases as the experiment progresses. Thus, after a month the pH has dropped to values between 5.3 and 6.9, due to the CO_2 and other acids produced during the experiment.

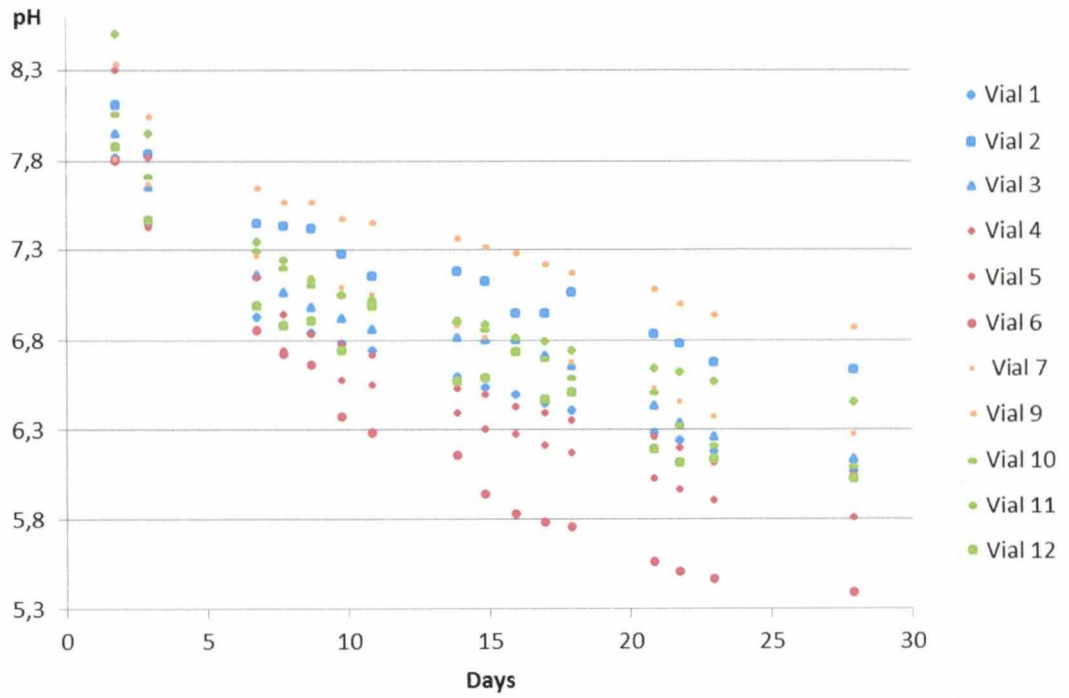

Figure 9. pH logged using PreSens optodes in the water-filled headspace over the soil samples plotted versus time for the multiple measurements carried out on the different depths of *Fjellbrønn* 3 (FJB3-01, FJB3-02, FJB3-06 and FJB3-08).

Comparisons and rates

The results presented above are mostly in the form of logger data and graphs. In order to be able to compare oxygen consumption for different samples the rates have been calculated. As mentioned in the materials and methods section this is done by calculating the slope of the plot of oxygen concentration versus time and correcting using the content of oxygen in the headspace. The slope is calculated as a linear least-squares fit to the data between 100 % and 70 % saturation, thus yielding initial rates. The curves can also be fit as ½-order kinetics covering the whole curve from 100 to 0 % saturation. Rates calculated this way are similar to the initial rates presented here.

The rates are listed in table 2 for the triplicate measurements of each of the four depths of *Fjellbrønn* 3. Under unsaturated conditions the triplicate measurements averaged 191 µg O_2/g dry sample/day, 174 µg O_2/g dry sample/day, 345 µg O_2/g dry sample/day and 245 µg O_2/g dry sample/day for depths 1, 2, 6 and 8 respectively of *Fjellbrønn* 3. The standard deviation within these triplicates is moderate, in most cases around one tenth of the average, except for the FJB3-02 samples where the deviation is close to one third of the average; the FJB3-02 samples may have had a little bit of water added by accident before the experiment was started but it seems unrealistic that

this should have anything to do with the higher deviation in this set of measurements. However, the slightly irregular shape of the oxygen consumption curves observed for FJB3-02 may relate to this. It is seen that the rates only vary with a factor two between the 12 subsamples, with the highest rates being found at FJB3-06. This is also the sample with the highest organic content (73 % - Table 1). Apart from that there is no clear correlation between the oxygen consumption and other parameters such as sample depth or state of preservation.

The rate of oxygen consumption is significantly lower in the saturated experiment, which is in agreement with previous studies (Hollesen 2012): when using the oxygen concentrations measured in the water-filled headspace, average oxygen consumption rates between 17 and 55 µg O_2/g dry sample/day may be calculated for the four samples (Table 2). Somewhat higher rates, between 42 and 129 µg O_2/g dry sample/day, are found when using the oxygen concentrations measured directly in the soil. Still they are lower than the 174 to 353 µg O_2/g dry sample/day measured under unsaturated conditions (Table 2). Oxygen diffusion through water is much slower than through air, and especially for oxygen in the water-filled headspace it takes some time before it diffuses down in the soil, where it is consumed.

Table 2. Initial rates of oxygen consumption calculated for the measurements under saturated and unsaturated conditions. The rates are given as micrograms oxygen consumed per gram dry soil sample weight per day (µg O_2/g dry sample/day).

	FJB3-01			***FJB3-02***			***FJB3-06***			***FJB3-08***		
Vial	4	5	6	10	11	12	1	2	3	7	8	9
O_2 consumption unsaturated soil (µg/g/day dry weight)	202	178	195	219	135	169	353	361	346	249	268	219
Average	191			174			353			245		
Standard deviation	12			42			7.6			24		
O_2 consumption in liquid over saturated soil (µg/g/day dry weight)	29	22	36	18	19	15	63	55	48	51		39
Average	29			17			55			45		
Standard deviation	7.0			2.2			7.2			8.2		
O_2 consumption in liquid in the saturated soil pores (µg/g/day dry weight)	48	65	40		143	115	103	98	90	41		43
Average	51			129			97			42		
Standard deviation	13			20			6.3			2.0		

Discussion of redox versus oxygen

The aim of the present work is to compare measurements of redox potential and oxygen as techniques. Do they give similar information, or do they complement one another? The first series of measurements carried out under unsaturated conditions worked well with respect to the oxygen measurements using PreSens optodes. The oxygen concentration was measured in the headspace of air as well as in the soil without any problems. Measuring redox potentials were more problematic in the unsaturated experiment. During installation of the electrodes in the soil it was attempted to establish as good contact between soil and electrodes as possible. However, even though the electrodes gave relatively stable readings for the first few weeks (figure 4), some readings changed dramatically when the wiring was adjusted and it is difficult to be sure which of the readings are most correct. Thus even though a few electrodes may have been showing real values all along, measuring redox potential under unsaturated conditions is risky because it is difficult to decide which readings are reliable and which are influenced by a bad soil contact due to air-filled pores in the unsaturated soil.

Under saturated conditions both oxygen and redox measurements performed well (figure 6 and figure 7). Clearly electrical contact cannot be an issue when the whole system is under water. In general the experiments showed that the redox potentials were high (app. 500 mV +/- 50 mV) when oxygen was present (5 % - 100 % saturation) and dropped to low potentials (< -100 mV) a while after the oxygen concentration had dropped to low values (<5 %). Thus, in most of the region where oxygen sensors are sensitive the redox electrode is insensitive and only in the lower region of the oxygen spectrum does the redox potential shift to a different value and continue to drop. This was observed in figure 6, where several steps were observed in the plot of potential versus time. In theory these steps could be due to a change in degradation mechanism (Sigg 2000) such as the transition from aerobic degradation to a different type of degradation such as for example nitrate reduction, sulphate reduction or methane production. In some cases there was a bad odour (hydrogen sulphide?) when the vials were opened after the experiments had finished. This would agree with anaerobic degradation processes and so would the steps observed for the redox potentials. However, further investigation is necessary in order to demonstrate such a relationship. Nonetheless, changes in the redox potential readings were observed a long time after the oxygen had been depleted. This suggests that measuring redox potentials may hold information about active anaerobic degradation processes under conditions where oxygen measurements are insensitive. Thus the two techniques may be complementary.

Conclusions

Under unsaturated conditions rates of oxygen consumption and concentrations of oxygen in the soil and in the air-filled headspace could readily be measured inside sealed vials containing soil samples from Bryggen. The rates of oxygen consumption fall within the range of previous measurements. Redox potentials were measured too, but the results were very fluctuating and seemed unreliable probably due to poor contact between soil and electrodes.

Under saturated conditions it was shown that oxygen concentration, CO_2 concentration and pH could be monitored in the water-filled headspace, and oxygen concentration and redox potential could be monitored in the soil inside oxygen-tight containers. The rates of oxygen consumption under saturated conditions are lower than under unsaturated conditions, in correspondence with previous measurements. An initial CO_2 release coincides with an initial consumption of oxygen, subsequent CO_2 release is observed for some but not all samples. One explanation for this could be that CO_2 is released as a result of anaerobic degradation processes. A pH drop was observed during the experiment; this is likely to be related to carbonic acid formed by the produced CO_2. The redox potentials measured under unsaturated conditions seem reliable. They remain steady as long as oxygen is present in concentrations higher than about 5 %; below this value the redox potentials drop. When all oxygen has been depleted the redox potentials still change in some instances. This may be due to changes in metabolic pathways taking place under anoxic conditions in the microcosms. Further investigations will be conducted under the project "Urban WATCH" to study the relationship between different anoxic processes, decay rates and redox potentials.

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