System for quasi-continuous simultaneous measurement of oxygen diffusion rate and redox potential in soil

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Abstract

Oxygen diffusion rate (ODR) and redox potential (E_H) are quantitative indices representing oxygen availability and redox status in soils, which is valuable information for better understanding causes and effects of soil aeration. Because these indices are spatially and temporally highly variable, continuous measurements and adequate numbers of repetitions are essential for accurate *in situ* monitoring. Here, we present a new, fully automated recording system for *in situ* measurements where ODR and E_H are measured at the same platinum electrode. The conflict between electrode polarization for ODR and the resulting biased E_H readings is solved by reducing the polarization time and introducing a recovery interval between two consecutive measurement cycles. The shorter polarization time ensures accurate E_H readings. It also results in moderately overestimated ODR readings, but this can be corrected before data analysis. The recovery interval restricts temporal resolution of the E_H-ODR data pairs to 8 h. We illustrate the use of the system with measurements in a field experiment in Zürich, Switzerland. ODR curves at different depths ran roughly parallel to the corresponding curves of O_2 concentration in soil air but ODR was much more sensitive to precipitation. Low ODR was a necessary but not a sufficient condition for declining E_H. E_H ran parallel to O_2 concentration in soil air rather than to ODR. The fully automated system allows for time series of replicate measurements in multifactorial field studies with reasonable labor requirements. It may be particularly suitable for studies examining the effects of soil tillage, compaction, and irrigation, where structure-related soil properties such as porosity, gas permeability, and soil aeration play a dominant role.

Key words: field soil / measurement system / monitoring / soil aeration / soil heterogeneity

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1 Introduction

Continuous measurement of parameters that represent the status and effects of oxygen supply in soils can provide important information for understanding processes and conditions leading to oxygen deficiency in soils. Oxygen deficiency in soils can have negative effects on soil functions and plant growth, since, *e.g*., cellular respiration in soil organisms and plant roots is affected. Cellular respiration follows biochemical redox pathways in which organic nutrients are decomposed and the discharged electrons are transferred to electron acceptors. Molecular oxygen (O_2) is the terminal electron acceptor in aerobic respiration processes and, therefore, O_2 availability in soil is essential for obligate aerobic organisms.

Plant roots and soil microbes are the main consumers of soil O_2 (*Ben-Noah* and *Friedman*, 2018). Oxygen deficiency in soil can restrict shoot and root development, impair plant health, and consequently cause losses in crop yield (*Letey* and *Stolzy*, 1967; *Gliński* and *Stępniewski*, 1985c; *Grassini* et al., 2007; *Balakhnina* et al., 2010; *Ben-Noah* and *Friedman*, 2018). Microbial respiration in soils can follow aerobic or anaerobic pathways. In anaerobic pathways, O_2 is replaced by alternative electron acceptors such as nitrate, manganese oxide, iron (hydr)oxides, sulfate, or carbon dioxide, leading to chemically reduced metabolites. As a result, the redox status of the soil changes to increasingly reducing conditions. Both pathways coexist and their respective contribution to total soil respiration varies spatially and temporally (*Ben-Noah* and *Friedman*, 2018). If the O_2 availability decreases, the contribution of anaerobic respiration increases and the soil is more often in a reduced state. Thus, redox status is the result of respiration activities and indicates changes in O_2-dependent soil processes and soil properties, *e.g*., denitrification activities, evolution of greenhouse gases (nitrous oxide, methane), dissolution of manganese and iron (hydr)oxides, and solubility of nutrients and trace metals (*Gliński* and *Stępniewski*, 1985a).

Most of the oxygen consumed in the soil must be transported from the atmosphere through the air-filled pore space to the site of consumption (*Cook* and *Knight*, 2003; *Ben-Noah* and *Friedman*, 2018). Hence, O_2 availability and associated switches between aerobic and anaerobic respiration are

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controlled not only by the rate of oxygen consumption, but also by spatial and temporal variations in gas diffusivity and air permeability. When assessing the effects of agricultural soil and land management on soil aeration and redox status on field scale, these temporal and spatial variations have to be taken into account (*Fiedler* et al., 2007).

ODR is determined as the rate of oxygen diffusion to a platinum wire placed in the soil, where the oxygen is polarographically reduced. The intensity of the reduction current at the platinum wire is amperometrically detected and related to the oxygen flux.

The reduction current is converted into ODR according to:

$$ODR\left(\mu g\ m^{-2}\ s^{-1}\right) = (I\ M)\ /(n\ F\ A), \quad (1)$$

where I (μA) is the reduction current, M is the molecular weight of O_2 (32 g mol^{-1}), n is the number of transferred electrons per reduced oxygen molecule (*i.e.*, 4), F is the Faraday constant (96.500 C mol^{-1}), and A (m^2) is the area of the reducing platinum electrode surface. Upon commencement of measurement, the reduction current I initially decreases, but stabilizes at a steady state after a few minutes. This limiting current is used for calculating ODR. The value obtained is a quantitative index of the oxygen availability in soil, since the oxygen flux to the platinum wire responds to the same restrictions as the oxygen flux to an oxygen-consuming organism or organ, *e.g.*, a plant root.

E_H is the electrochemical representation of the electron activity in solution relative to a hydrogen reference cell (*Sigg*, 2000). It has frequently been used as a quantitative approximation of the bulk electron activity in soil solution caused by oxidative and reductive soil constituents, and thus as an index for soil redox status. Redox potential can be determined *in situ* using a platinum electrode placed in the soil (*Eshel* and *Banin*, 2002; *Mansfeldt*, 2003).

Thus, ODR and E_H are adequate indices to study the dynamics of O_2 availability and redox status in field soils. Yet, the temporal and spatial variability of ODR and E_H requires continuous *in situ* measurements and adequate spatial repetitions. Moreover, to observe processes at microsites, ODR and E_H must be measured at exactly the same spot. This can best be achieved if the two measurement systems use the same platinum electrode. However, the electrode polarization during ODR measurement may result in a memory effect around the electrode resulting in a bias of E_H measurements (*Liu* and *Yu*, 1984).

The aim in the present study was to set up a system for measuring O_2 availability and redox status continuously and in spatial repetitions in field soils. For this purpose, we developed a new system for quasi-simultaneous, continuous measurement of O_2 availability and redox status that combines the techniques for determining oxygen diffusion rate (ODR) (*Gliński* and *Stępniewski*, 1985b) and redox potential (E_H) (*Sigg*, 2000; *Mansfeldt*, 2003), respectively. By using the same platinum electrode for ODR and E_H, we also reduced the number of sensor probes needed by half, thus saving costs of purchase and labor input for installation and maintenance, which makes a difference for studies requiring a large number of sensor banks, *e.g.*, multifactorial studies in the field.

2 Material and methods

2.1 Design of the system

The starting point for combining the two techniques into one system for continuous measurements was *Mansfeldt*'s (2003) method for long-term *in situ* E_H measurement.

For ODR measurements, the current carrying circuitry, including the voltage regulator and the amperemeter (I), was connected to the E_H measurement system (switch closed in Fig. 1).

A brass rod (50 cm length) was used as the current carrying anode (*Gliński* and *Stępniewski*, 1985b). The voltage at the voltmeter (V) was then used as feedback signal for adjusting the O_2 reduction potential at the platinum electrode (–650 mV relative to the calomel electrode). The polarographic ODR current was read at the amperemeter. This generic system was implemented using a measurement and control datalogger (model Campbell CR 1000; Campbell Scientific Inc., Utah, USA) for system control, signal detection, and data acquisition (Fig. 2).

A channel relay multiplexer (MUX) (model Campbell AM16/32B; Campbell Scientific Inc., Utah, USA) was used for processing 24 platinum electrodes in series. The voltage regulator was a four-channel analog output module (model SDM-A04; Campbell Scientific Inc., Utah, USA).

For E_H readings, the 20 GΩ input resistance of the CR 1000 input channel has been proven to be sufficient for accurate measurements (*Rabenhorst* et al., 2009). Therefore, the E_H voltage was read directly in the input channel. The ODR circuitry was galvanically isolated from the rest of the system using two isolating amplifiers [Sineax VS 54 Current shunt/V-I converter (VS 54); GMC-Instruments Schweiz AG, Switzerland]. This precautionary measure was taken to keep the sensitive polarographic currents unaffected by electric fields caused by the 230 V voltage supply or any other instruments used in field experiments. The output voltage of the voltage regulator was converted into an electric current in the first VS 54 and back-converted into a voltage at the resistor R2 = 50 Ω (Fig. 2), before being applied between the platinum electrodes and the brass rod. The induced ODR current (I in Fig. 1) was converted into a voltage at the resistor R1 = 100 Ω (Fig. 2), and amplified in the second VS 54 before it was read in the CR 1000 differential voltage input channel ("ODR signal" in Fig. 2).

The platinum electrodes were custom-made platinum wire glass electrodes purchased from an electrode manufacturer (Willi Möller AG, Zurich, Switzerland). The platinum wire (diameter 1 mm, protruding 10 mm from the glass body) was soldered to the center conductor of a coax cable isolated by a

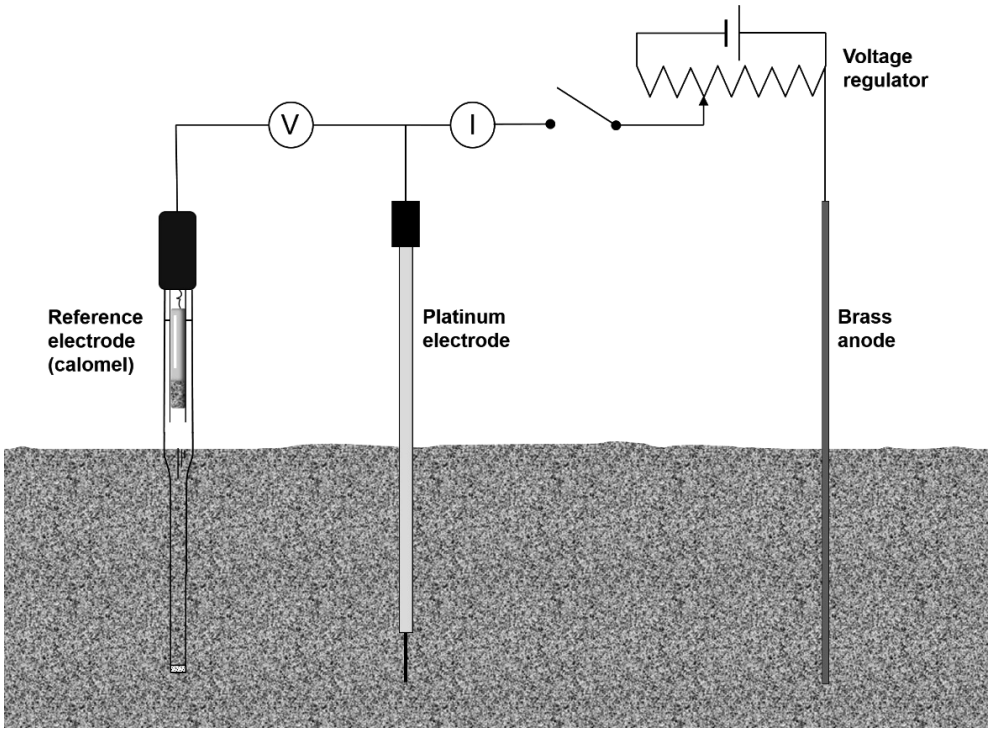

Figure 1: Schematic representation of the system used for simultaneous measurement of redox potential (E_H) and oxygen diffusion rate (ODR). (V) voltmeter for E_H measurements (switch open) and for trigger voltage control during ODR measurements (switch closed). (I) amperemeter for reading ODR current.

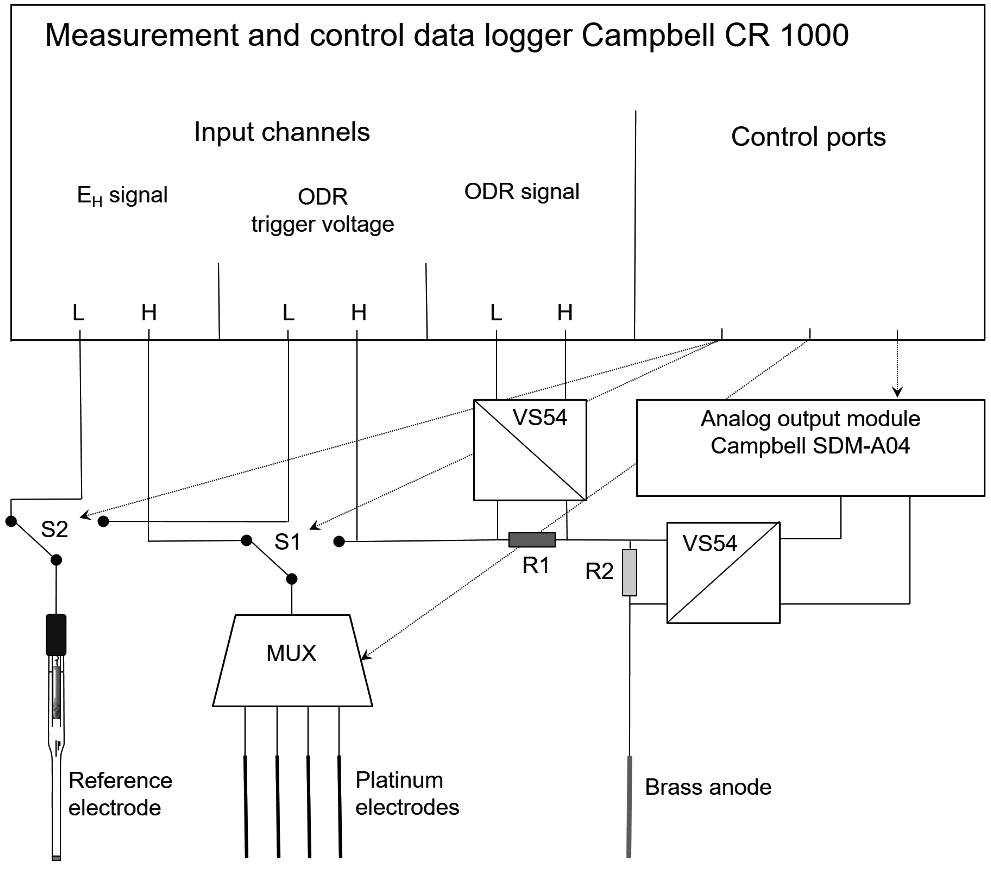

Figure 2: Schematic representation of the automated recording system for combined quasi-continuous measurement of redox potential (E_H) and oxygen diffusion rate (ODR). (L) low, (H) high differential analog input channels; (MUX) channel relay multiplexer Campbell AM16/32B; (R1) 100 Ω, (R2) 50 Ω resistor; (S1, S2) switches for switching between E_H and ODR modus; (VS54) Sineax VS 54 Current shunt/V-I converter.

PTFE dielectric (type RG 316 U, Huber+Suhner AG, Pfäffikon ZH, Switzerland). The solder joint was sealed in the glass body using a waterproof resin, while the gap between the coax cable and the rear of the glass body was sealed with a hot-glue coated heat shrink tube. The platinum tip was then polished in-house in two steps to obtain a smooth surface, us-

ing a 1 μm and a 0.3 μm polish (Luxor® type grey and white, Merard, Arnad, France), respectively, in order to minimize catalytic activity. Thereafter, the platinum tip was washed in analytical grade methylene chloride using an ultrasonic bath. This basic glass electrode was mounted in a customized PVC tube (diameter 10 mm i.d. × 12 mm o.d.; Debrunner Acifer AG, Wettingen, Switzerland). The glass body was fixed in the PVC tube with silicon tube rings, which protected against mechanical forces. Both ends of the PVC tube were then sealed with hot-glue coated heat shrink tubes, letting the platinum tip-bearing end of the glass body protrude 3 mm. Before use, all platinum electrodes were tested in a redox test solution (Metrohm Schweiz AG, Zofingen, Switzerland) against a custom-made conventional calomel reference electrode (Willi Möller AG, Zurich, Switzerland) in a solution of 3 M potassium chloride (KCl).

In the field, the same type of calomel reference electrode was part of the reference system, which was adapted to the unsaturated conditions in agricultural soil (Fig. 3).

The calomel electrode was placed in an electrolyte reservoir containing the 3 M KCl solution, which was kept in contact with the soil pore water through a ceramic diaphragm in the electrolyte reservoir. A water-filled interface (adapted tensiometer) linked the reference electrode to the contact site in the subsoil at a depth of about 50 cm, where the water in the interface was in contact with the soil pore water through a porous ceramic cup mounted at the lower end of the interface tube. On the top of the protruding end, an airtight container carrying the reference electrode was attached. Tap water was used as a surrogate for soil pore water in the interface, since tap water in Switzerland originates from aquifers or freshwater lakes. Contact with the soil pore water was enabled by leak flow through the interface from a tap water reservoir controlled by a flow-restricting capillary. The accuracy of the reference potential was monitored using a platinum electrode in the redox test solution, which was linked to the reference system by a 3 M KCl-gel containing plastic tube (Fig. 3). The KCl solution in the electrolyte reservoir and the redox test solution were renewed at least once a month.

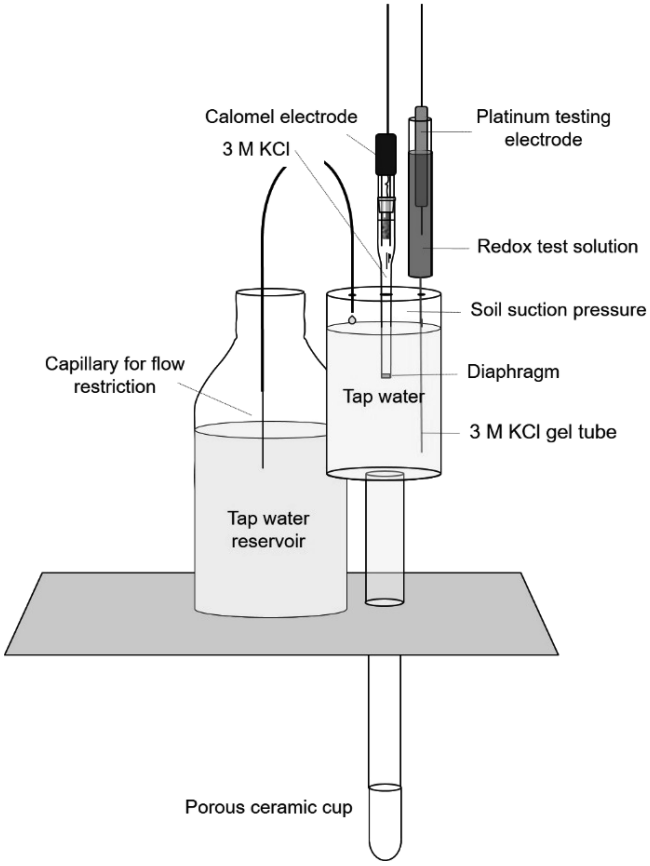

Figure 3: Reference system used for linking the calomel reference electrode to pore water in unsaturated soils.

2.2 System operation

The measuring sequence implemented in the CR 1000 control module comprises the following steps (Fig. 2):

E_H readings:

1. Switches S1 and S2 connect the MUX and the reference electrode to the input channel "E_H signal" and the MUX is switched on.
2. E_H readings are taken consecutively from each platinum electrode (including that in the redox test solution) by switching the MUX channels. A delay time of 1 s is set before each reading. After the last electrode is read, the MUX is switched off.

ODR readings:

3. Switches S1 and S2 connect the MUX and the reference electrode to the ODR circuitry. The MUX is switched on and connects the first platinum electrode to the system.
4. An initial voltage of –300 mV is set at the SDM-A04 output and immediately downregulated to provoke the final –650 mV at the "ODR trigger voltage" channel.
5. After the holding time to the steady state of the polarographic current, the ODR signal is read at the "ODR signal" channel.
6. The voltage at the SDM-A04 output is set to zero, the MUX switches to the next platinum electrode and the ODR measurement cycle loops back to step 4. This ODR measurement loop ends after reading the last platinum electrode.
7. To end the E_H-ODR reading cycle, the MUX is switched off (all platinum electrodes disconnected).

The E_H readings obtained were corrected for the difference between the calomel electrode in 3M KCl and the standard hydrogen electrode, by adding 256 mV (*ISO*, 2002).

After ODR measurements, the previously polarized platinum electrodes yield biased E_H readings, since the polarization relaxes relatively slowly (*Liu* and *Yu*, 1984). Therefore, an adequate relaxation time was required before the next E_H-ODR reading cycle could be started with step 1. In this respect, the polarization for ODR measurements in step 5 is a conflicting procedure that may lower the accuracy of the E_H measurements in step 2 of the subsequent reading cycle if it is started too early. Conversely, long relaxation times impair the temporal resolution of the E_H-ODR data pairs. Therefore, laboratory experiments were conducted (experiments 1 and 2, described

in supplementary information) in order to optimize polarization conditions and relaxation time. As a result, the system was run applying a reduced holding time of 2.5 min instead of 5 min in step 5 and a relaxation time of 8 h between two consecutive measurement cycles (supplementary information, Figs. S2 and S4). The ODR results were corrected for the bias of 11% relative to results obtained with holding times of 5 min (supplementary information, Tab. S2).

2.3 Performance demonstration in the field

Automated ODR-E_H recording systems were installed in the long-term "Soil Structure Observatory (SSO)" for monitoring post-compaction evolution of soils structure [for details, see *Keller* et al. (2017)]. The ODR-E_H probes were installed in all experimental plots of block A and C in the SSO. However, in this study we focus on one plot to illustrate the potential of the system. We pitched on the sensor bank in the soil of the control plot under permanent ley (grass–clover–lucerne mixture) in block A (soil properties shown in Tab. 1) and on the period from July 2015 to July 2016, that comprised typical events of restricted soil aeration and distinct response of redox status. The full dataset of the SSO will be published in upcoming papers.

The sensor bank consisted of twelve platinum probes that were installed horizontally from a pit outside the experimental plot, in replicates of four at 10, 20, and 40 cm below the surface. The four replicates per depth were installed at a lateral distance of 20 cm from each other, with the platinum tips positioned 80 cm within the plot. Installation was done by first drilling a hole to the measuring site of the same diameter as the outer diameter of the probe. At the end of the hole, the platinum tip was gently pressed into the soil in order to maintain the soil structure in the best possible manner. After installation of all probes, the pit was refilled with the previously excavated soil. The distance of platinum tips from the pit wall (80 cm) was at least twice the distance from the soil surface to the platinum tips (10, 20, and 40 cm, respectively, for the three installation depths). Thus, we consider effects of unwanted oxygen intrusion from the atmosphere through the pit wall unlikely. The reference electrode-carrying interface (Fig. 3) was installed from above ground at a distance of about 100 cm from the sensor bank by first drilling a hole to 50 cm below the soil surface. The interface was then inserted, bringing the ceramic cup into close contact with the soil structure at the bottom of the hole.

In addition to ODR-E_H measurements, the O_2 concentration in soil air was measured using a technique similar to that devised by *Phene* (1986) and as described in *Weisskopf* et al. (2010). Two replicate soil air access tubes were horizontally installed in the same sensor probe bank at the same depths as the platinum probes. The head of each access tube was a chamber made of a 5 mm thick gas-permeable membrane (40 mm inner diameter, 120 mm length). The air in the chamber was periodically analyzed for oxygen using a conventional electro-chemical oxygen sensor for air samples. Readings were taken every 30 min. Meteorological data were retrieved from the weather station of the Swiss automatic monitoring network (Federal Office of Meteorology and Climatology MeteoSwiss) located within 300 m from the experimental plot.

Table 1: Basic soil properties at the Soil Structure Observatory, block A, Zurich, Switzerland (*Keller* et al., 2017).

Property	Topsoil 0–0.2 m	Subsoil 0.3–0.5 m
Clay ($g\ g^{-1}$)	0.25	0.31
Silt ($g\ g^{-1}$)	0.52	0.49
Sand ($g\ g^{-1}$)	0.23	0.20
Organic C ($g\ g^{-1}$)	0.018	0.008
pH ($CaCl_2$)	6.3	6.6

3 Results

Records of mean values of the four replicate measurements per depth of ODR and E_H, respectively, are depicted in Fig. 4. Variations in ODR (Fig. 4b) were governed by precipitation (Fig. 4a). The path of the ODR curves at the different depths ran roughly parallel to the path of O_2 concentrations in soil air. However, ODR was much more sensitive to precipitation and its variation was considerably larger. The response of O_2 concentration in soil air to decreasing ODR values was delayed and the concentration decreased markedly only after long or repeated periods of low ODR. On the other hand, increasing ODR values were accompanied almost immediately by increasing O_2 concentration in soil air.

The redox potential (E_H) decreased only during periods of low ODR between January and July 2016 (Fig. 4c), although the effect was considerably smaller in the period January-May compared with the period June–July, while ODR was similar.

The advantage of using the identical platinum electrode for ODR and E_H measurements was revealed by comparing the changes at individual probes (Fig. 5). For example, probes #1 and #2 (20 cm depth) at a lateral distance of 20 cm showed differing behavior. Rainfall at the end of May caused ODR values to decrease from about 30 to 8 $\mu g\ m^{-2}\ s^{-1}$ at both probes (Fig. 5b). The E_H values responded immediately at probe #2, whereas at probe #1 E_H remained almost unaffected. After the end of the rainfall event, ODR recovered at probe #1 but fluctuated thereafter with further rainfall events until June 11, whereas ODR remained low and even dropped further at probe #2. In contrast, E_H fluctuated corresponding to wet and dry periods. The E_H values at probe #1 dropped only during the wet period in the second half of June, interestingly under the same ODR conditions as at the end of May when E_H remained almost unaffected.

After the fifth year of use, we have no evidence for electrode malfunction in our soil and under our climatic conditions, even though the electrodes were left in place without cleaning. Readings vary still in the same ranges as at the beginning of the measurements (Fig. 6). ODR recorded between September 2014 and June 2019 had even a tendency to increase (Fig. 6a), possibly due to slow improvement of soil structure under long-term ley. E_H remained approximately constant under oxidizing conditions and peaked off in the same range during reducing conditions except during the extremely wet period in June–July 2016 (Fig. 6b).

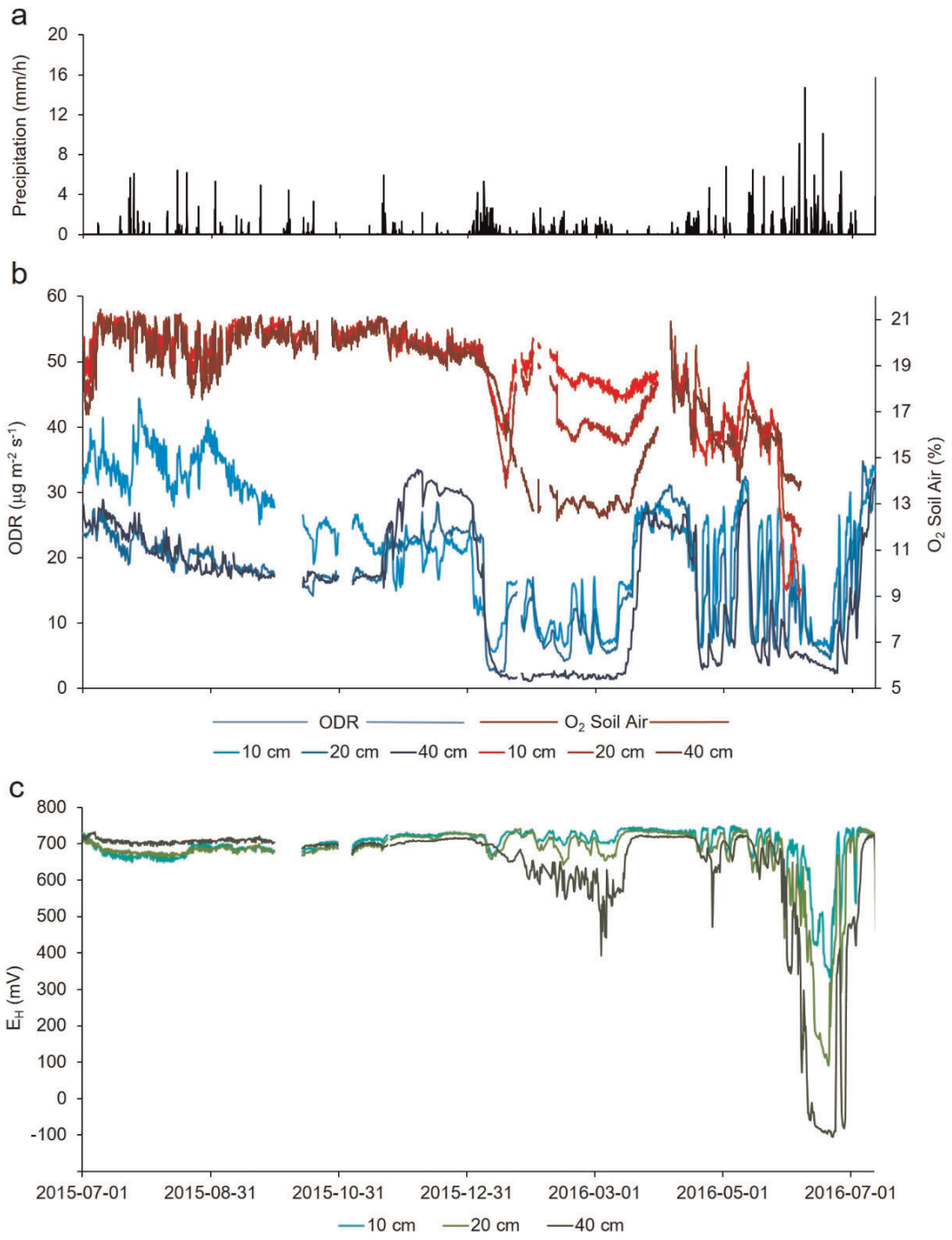

Figure 4: (a) Amount of precipitation recorded at a meteorological station near the measuring site and temporal change at 10 cm, 20 cm, and 40 cm below the surface of a Gleyic Cambisol under ley in (b) oxygen diffusion rate (ODR; mean of 4 probes) and oxygen concentration in soil air (O_2 Soil Air; mean of 2 probes), and (c) redox potential (E_H; mean of 4 probes).

4 Discussion

4.1 System performance in the field

The results obtained with the system for quasi-continuous simultaneous measurement of ODR and E_H allowed for interpreting various cause and effect relationships. For example, the immediate response of ODR to precipitation (Fig. 4a, b) confirms the finding that ODR decreases due to restricted diffusive O_2 transport if the pore space is water-filled (*Wolińska* et al., 2011; *Morales-Olmedo* et al., 2015). The delayed response of O_2 concentration in soil air to decreasing ODR values (Fig. 4b) indicates presumably the time lag of the O_2 concentration in response to O_2 consumed by soil organisms and plant roots after air exchange with the atmosphere has been restricted. Hence, low ODR is not necessarily the

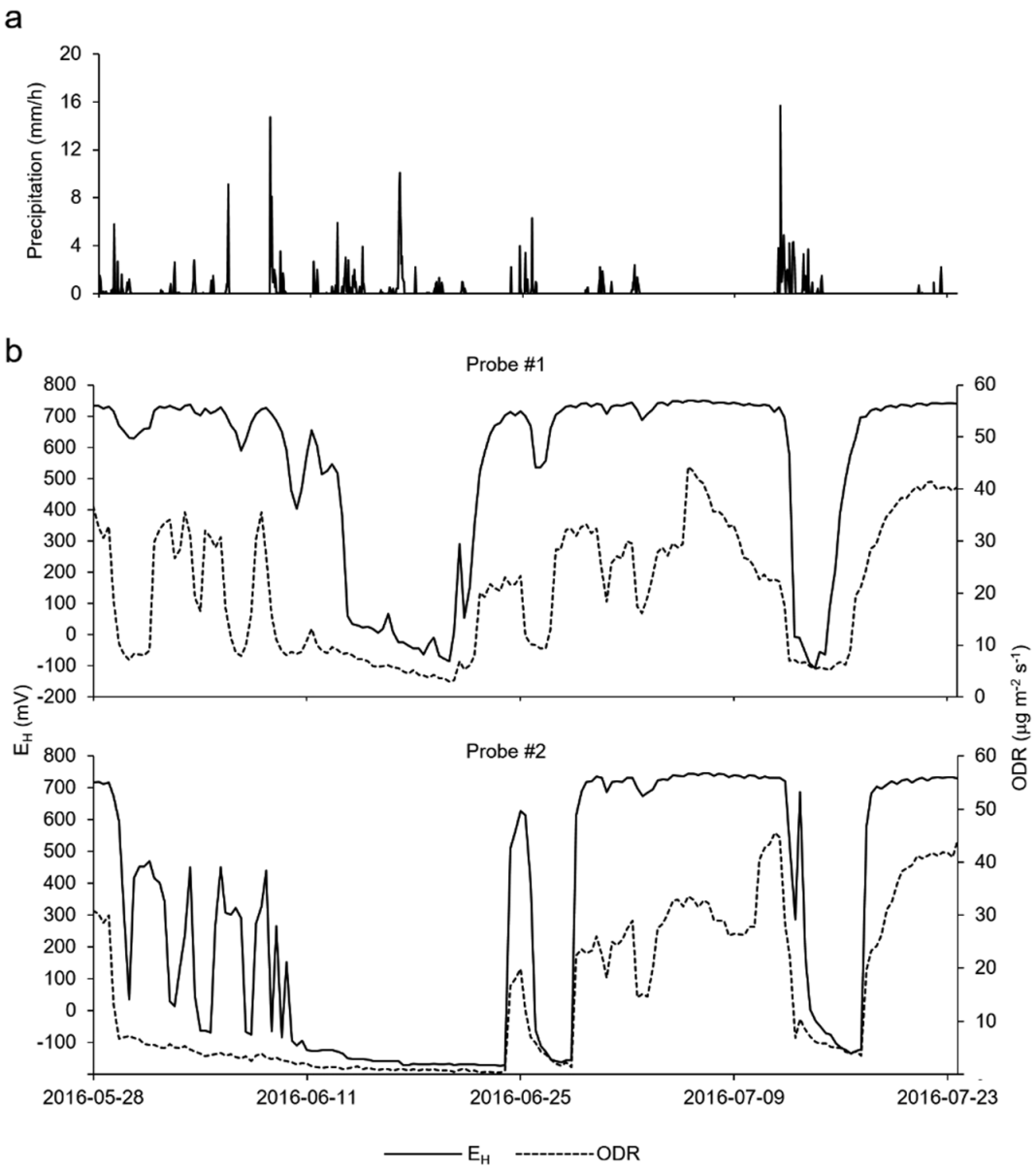

Figure 5: (a) Amount of precipitation recorded at a meteorological station near the measuring site and (b) temporal change in redox potential (E_H) and oxygen diffusion rate (ODR) at probe #1 and probe #2 (20 cm apart), located 20 cm below the surface of a Gleyic Cambisol under ley .

consequence of low oxygen concentration in soil air, but rather indicates the reduced oxygen availability at the site of consumption if infiltrated water becomes a barrier to gas diffusion in the pores and disrupts the pathway to the O_2 reservoir in the soil air. On the other hand, simultaneous increase of ODR and O_2 concentration indicate that the previously depleted O_2 in soil air was renewed by regained exchange of soil air with the atmosphere upon drying and that this O_2 was readily available for consumption since much of the pore space was air-filled.

The stronger response of E_H to low ODR in the period June-July 2016 compared to the period January–May (Fig. 4c) can be attributed to higher O_2 consumption by plant roots and soil microbes. Higher microbial activity can be expected in consequence of increased supply of degradable organic matter under the plant canopy and of higher soil temperature during summer months. Under similar conditions of oxygen availability, E_H-lowering microbial processes were apparently occurring only during periods of intensive microbial activity. The occurrence of intensive microbial activity under restricted oxygen diffusion is corroborated by the sharp decrease in oxygen concentration in soil air when E_H began to drop at the end of May. Interestingly, the trend of oxygen concentration with depth then reversed relative to that in the period of low oxygen concentration between January and March. This indicates that the highest activity occurred in the topsoil, where readily degradable organic matter was probably most available and the soil temperature was more favorable for microbial activity. In contrast, E_H followed ODR and decreased with

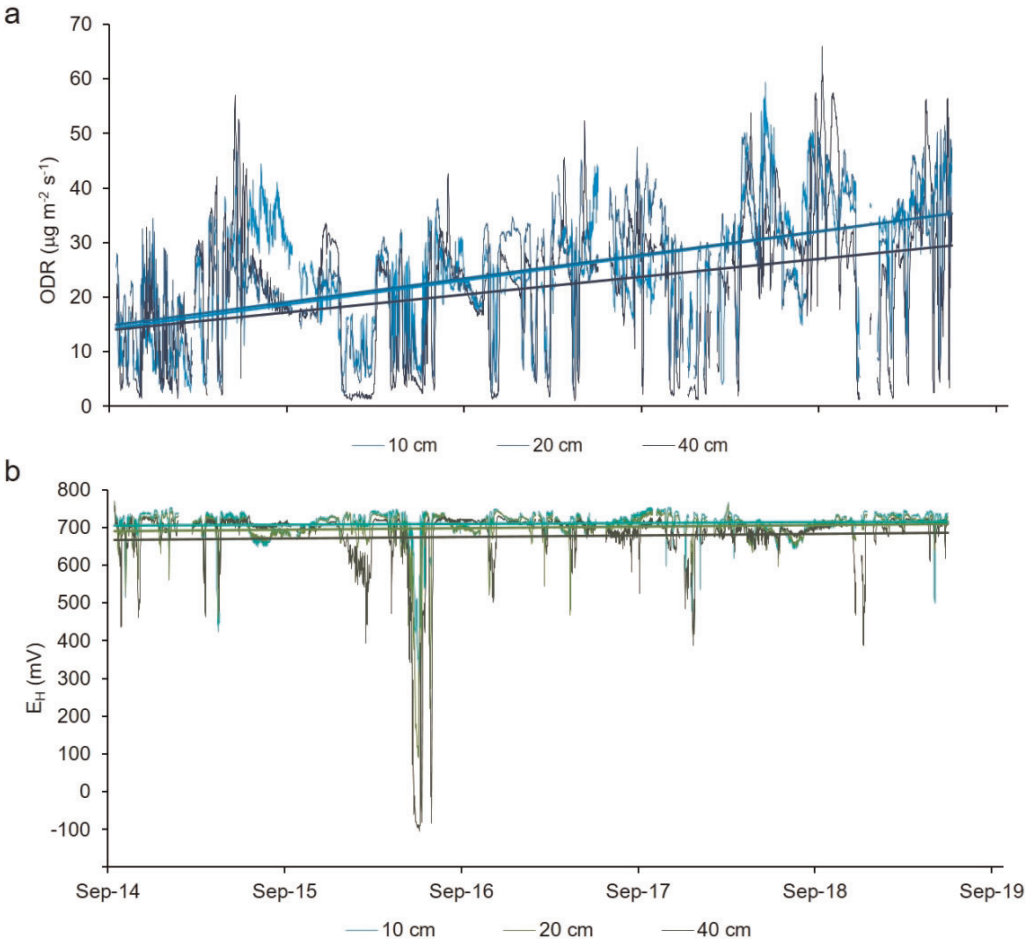

Figure 6: Temporal change (mean of 4 probes) and linear slopes at 10 cm, 20 cm, and 40 cm below the surface of a Gleyic Cambisol under ley in (a) oxygen diffusion rate (ODR) and (b) redox potential (E_H) measured between September 2014 and June 2019.

increasing depth in the period June–July 2016, indicating that changes from aerobic to anaerobic respiration in soil was triggered by oxygen availability at the site of consumption rather than by oxygen concentration in soil air.

4.2 Interpretations of ODR-E_H data pairs from individual probes

The differing behavior of ODR and E_H at two neighboring individual probes (Fig. 5) reflects small-scale variations in soil aeration and redox status and is well in agreement with the findings by *Dorau* et al. (2018). They demonstrated small scale variations in re-oxidation (increasing E_H) of microsites and a close linkage between E_H and air-filled pore volume (ε) in structured soil cylinders during air drying of the previously submerged soil samples. Critical ε values were presented that characterize the tipping point from reducing towards oxidizing soil conditions. Records of ODR–E_H data pairs obtained with our system can directly be interpreted as reflecting differences in causes and effects regarding oxygen availability and E_H response. In general, an ODR of $< 10\,\mu g\,m^{-2}\,s^{-1}$ appeared to be a precondition for declining E_H at both sites. However, between end of May and June 11 incoming O_2 during dry periods was presumably sufficiently active to re-oxidize reduced soil constituents at probe #2, but its availability was too low to increase ODR. This low O_2 availability at probe #2 may have been an effect of restricted diffusion, combined with rapid consumption of oxygen by highly reactive reduced soil constituents such as Fe^{2+}. At probe #1, there were presumably no reduced soil constituents and thus ODR responded to incoming O_2. The E_H drop at probe #1 in the second half of June can be attributed to either increased O_2 consumption by plant roots and soil microbes at this site or to exhausted redox buffering, *i.e.*, exhausted E_H stabilization by electron acceptors such as nitrate (*Abbasi* and *Adams*, 1999; *Mansfeldt*, 2004). Alternatively, it could reflect the end of a lag phase for the microbes before they adapted to anaerobic conditions (*DeAngelis* et al., 2010; *Peralta* et al., 2014). These suggestions are supported by the immediate E_H drop under the same ODR conditions in mid-July. At that time, O_2 consumption was presumably high, the redox buffers were already exhausted, and the microbial community was adapted to anaerobic conditions.

Higher temperatures and longer dry periods may have caused the closer correlation between ODR and E_H from mid-June onwards at both probes. On the one hand, E_H

responded more often to reduced ODR at probe #1. On the other hand, air filling of the pore space was presumably more rapid, reached higher levels, and thus caused more rapid and stronger soil aeration, so that ODR responded along with re-oxidation and increasing E_H also at probe #2 after wet and anoxic periods.

4.3 Limitations of the system

The temporal resolution of the recorded ODR–E_H data pairs is restricted to 8 hours. Consequently, diurnal E_H and ODR patterns cannot be recorded and thus short-term changes of the redox conditions (*Dorau* and *Mansfeldt*, 2016) and soil aeration on an hourly basis cannot be captured. For example, redox conditions can change dramatically within hours in temporarily waterlogged horizons of wetland soils. To identify biogeochemical processes in such soil environments, it may be necessary to monitor E_H and ODR on an hourly basis. Furthermore, the ODR values were approximately 11% higher than values obtained using the conventional method (*Gliński* and *Stępniewski*, 1985b), since the polarization voltage was held for only 2.5 min, instead of 5 min, before the ODR current was read (supplementary information). It has to be noted, however, that in practice different holding times are used. Readings are normally taken after a holding time of 4 to 5 min (*Drewry* et al., 2001; *Feng* et al., 2002; *Simojoki* et al., 2008; *Włodarczyk* et al., 2008; *Balakhnina* et al., 2010; *Wolińska* et al., 2011). Other authors have reduced it to 3 min (*Bhandral* et al., 2010) or to 2.5 min (*Logsdon*, 2003). Systematic correction may be necessary when comparing the results with those from studies using longer polarization times. Moreover, the here determined ODR bias of 11% may be valid for this soil type only. The soil properties influencing a potential residual negative slope of the decay curve between 2.5 and 5 min (Fig. S5) are not known, and the assumed steady state of oxygen diffusion at the time point when the ODR current is read is only a quasi-steady state. The soil pore system may be one of the factors influencing this residual slope, and we therefore recommend using undisturbed soil samples for calibration under variable saturation conditions to provoke a range of different ODR. Thus, site-specific calibration may be necessary if inter-experimental comparison of small differences are targeted. However, the spatial and temporal variability in ODR in field soils is generally large and therefore the 11% overestimation is normally of minor relevance.

Electrode poisoning has been discussed as cause for electrode malfunction for ODR (*Rickman* et al., 1968; *Gliński* and *Stępniewski*, 1985b; *Devitt* et al., 1989) as well as E_H (*Fiedler* et al., 2007) long-term measurements when the electrodes are left in soil for a long time. For example, *Rickman* et al. (1968) found ODR readings 50% reduced at electrodes left in place in a loamy sand after two months of periodic readings compared to readings from reinserted electrodes in the same soil. However, ODR readings remained comparable when the electrodes were left in place in a clay soil. *Rickman* et al. (1968) reported that the platinum surface of the electrodes in the loamy sand were coated with an indurated mixture of clay and silt particles and calcium bicarbonate, whereas less coating had formed on the electrodes in the clay soil. The coating was identified as the cause of the reduced ODR readings. Similarly, *Devitt* et al. (1989) found declining ODR readings after 14 to 22 weeks from electrodes left in place at a depth of 15 cm in a lysimeter packed with a sandy loam soil leached with a high salinity solution of calcium and sodium chloride (2:1 Ca:Na equivalent on a weight bases in tap water). However, ODR readings did not decline when the leaching solution was of low salinity. Percentage of electrodes showing coatings depended on salinity, leaching fraction and soil depth. Chemical analyses of the coating crusts suggested that coating formation is directly linked to the soil solution chemistry. The authors concluded that little can be done to prevent coating formation except considering that the probability of electrode poisoning increases with time, salinity, depth and decreased leaching fraction. Leaving electrodes in place has considerable advantages since removal and cleaning may interrupt the continuous record of data because reinserting the platinum tip into exactly the same microsite of the soil is difficult, especially *in situ*. Moreover, removal and reinsertion may alter the soil conditions around the platinum tip. However, attention should be paid to decreasing ODR values and changing E_H values if they are not associated with changes in the soil-water-aeration status. In such cases, we recommend removing and cleaning the electrodes, preferably by applying the polishing procedure described in section 2.1. Calcium in the soil solution may be one of the driving forces for the formation of coatings on the electrode surface. Thus, the absence of calcium in our soil along with the climatic conditions may explain the absence of electrode poisoning.

5 Conclusions

Combined measurement of ODR and E_H in soil can be achieved with a single recording system. Our system for combined quasi-continuous recording of ODR and E_H uses the same platinum probe for both measurements, revealing the interrelations between oxygen availability and changes in E_H. As the causal relationship is mediated by soil biology and redox-active soil constituents, this technique can provide insights into biological activity and redox-buffering capacity at microsites and at field scale. Continuous recording of ODR and E_H provides useful information on soil aeration and on changes in aeration at seasonal and annual time scales. The fully automated system allows for full-time series of replicate measurements in multifactorial field studies with reasonable labor requirements. It may be particularly suitable for studies examining the effects of soil tillage, compaction, and irrigation, where structure-related soil properties such as porosity, gas permeability, and soil aeration play a dominant role. However, there are some limitations with the system. The temporal resolution of the recorded ODR- E_H data pairs is restricted to 8 hours and thus short-term changes of the redox conditions and soil aeration on an hourly basis cannot be captured. Furthermore, the ODR values are slightly higher than values obtained using the conventional method. Systematic soil-specific calibration may be necessary when comparing small differences in results with those from studies using longer polarization times.

Supplementary information

The supplementary information provides descriptions and results of two laboratory experiments conducted in order to secure accurate E_H readings after electrode polarization for ODR and to maximize the temporal resolution of E_H-ODR data pairs. In experiment 1, the recovery of biased E_H readings after ODR measurement was investigated in a soil sample under oxidizing and reducing conditions. In experiment 2, the effect of the holding time shortened from 5 min to 2.5 min on the ODR accuracy was investigated using an undisturbed soil sample.

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