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Running title: Soil aeration

Summary

The soil water content affects rates of oxygen diffusion and redox potentials (E_H). When water-saturated soils become aerated, a switch from reducing to oxidizing conditions occurs. However, limited information is available at which air-filled pore volume (ϵ) this shift happens. To obtain values of ϵ , undisturbed soil cores were taken from a Fluvisol and a Gleysol that differed in structure and clay content. Experiments on submergence and drying following a new experimental design were performed in the laboratory. After submergence, the cores were sealed with a glass hood to exclude oxygen and to achieve reducing conditions ($E_H < -100$ mV). We then aerated the sample by removal of glass plugs in the hood and consecutive-

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/ejss.12717

ly measured E_H by platinum (Pt) electrodes and ε by matric potential readings on an hourly basis. From the drying curve we determined two characteristic values: (i) $\varepsilon_{\text{Pt reaction}}$ indicates the air-filled pore volume at which a response of the Pt-electrode from contact with oxygen occurs (i.e. E_H increase $> 5 \text{ mV hour}^{-1}$) and (ii) $\varepsilon_{\text{Pt aeration}}$ indicates when oxidizing soil conditions are present (i.e. $E_H > 300 \text{ mV}$ at pH 7). The Fluvisol was characterized by an $\varepsilon_{\text{Pt reaction}}$ value of $0.036 \pm 0.006 \text{ cm}^3 \text{ cm}^{-3}$ and an $\varepsilon_{\text{Pt aeration}}$ value of 0.047 ± 0.005 , whereas for the Gleysol these values were 0.048 ± 0.008 and $0.085 \pm 0.007 \text{ cm}^3 \text{ cm}^{-3}$, respectively. We aimed to obtain such characteristic values for different soils to estimate the aeration status of a soil when ε is known, but E_H measurements are unavailable.

Keywords: wetlands, environmental monitoring, Fluvisol, Gleysol, soil heterogeneity, reducing soil conditions, soil structure

Highlights

- We studied the relation between E_H and air-filled pore volume (ε) for two soils varying in texture.
- Two characteristic ε values are proposed: $\varepsilon_{\text{Pt reaction}}$ (E_H increases $> 5 \text{ mV hour}^{-1}$) and $\varepsilon_{\text{Pt aeration}}$ ($E_H > 300 \text{ mV}$ at pH 7).
- $\varepsilon_{\text{Pt aeration}}$ was larger for a clayey Gleysol than a sandy Fluvisol, but $\varepsilon_{\text{Pt reaction}}$ was similar.
- Small-scale heterogeneity in soil structure had no effect on the E_H - ε relation.

Introduction

The change between oxidizing (low electron availability) and reducing (high electron availability) conditions is considered to be the most important chemical change that can occur in soil (Ponnamperuma *et al.*, 1967). To quantify the intensity of reduction (or oxidation), the redox potential (E_H) scale in units of electrochemical energy (e.g. mV) can be applied (DeLaune & Reddy, 2005). The heterogeneous nature of soil makes it particularly challenging to study complex processes controlled by a combination of physical (e.g. arrangement of solid particles and pores), biological (e.g. microbial community and activity) and chemical (e.g. soil pH and mineralogical composition) properties. Nevertheless, the E_H has been used widely as a key property to characterize the environment for biogeochemical processes in soil. Examples include delineating the redox ‘window’ where the emission of greenhouse gases is minimized (Yu & Patrick, 2004), assessing the effect of flood pulses on nitrogen transformations in floodplain soils (Shrestha *et al.*, 2014), studying the stable isotope inventory of dissolved iron (Schuth *et al.*, 2015) and implementing biochemical models to assess potential mobilization of contaminants in general (Couture *et al.*, 2015).

Reducing conditions ($E_H < 300$ mV, pH 7; Reddy & DeLaune, 2008) occur in soils affected by (i) groundwater, (ii) perched water, (iii) irrigation, (iv) flooding and (v) heavy rain. Water saturation results in markedly curtailed gas exchange between soil and air (Ponnamperuma, 1972). After consumption of the remaining oxygen (O_2), reducing conditions are established. In such conditions, microbial metabolism switches from aerobic to anaerobic, and instead of O_2 other terminal electron acceptors are used. This altered metabolism has large ecological implications because, for example, the potent greenhouse gases nitrous oxide and methane are produced or contaminant behaviour is affected (see above). Reducing conditions might prevail permanently, but typically alternating cycles of reduction and oxidation occur because of drainage or water loss by evapotranspiration. Then, O_2 enters the soil environment and a shift

from reducing to oxidizing conditions occurs. Such an increase can be as large as ~540 mV within 24 hours (Dorau & Mansfeldt, 2016) constituting the largest natural short-term change in a soil's biochemical milieu.

Various efforts have been made to measure and discuss E_H changes under laboratory and field conditions in relation to the water table (WT) depth (Callebaut *et al.*, 1982; Mansfeldt, 2003), soil gas composition (Callebaut *et al.*, 1982; Shrestha *et al.*, 2014), rates of O_2 diffusion (Devitt *et al.*, 1989; Zausig *et al.*, 1993) and dissolved O_2 concentrations (Bezbaruah & Zhang, 2004; Rickelt *et al.*, 2013). In general, as the air-filled pore volume (ε) increases, the volume of anaerobic soil decreases (Reddy & DeLaune, 2008) facilitating oxidizing soil conditions. However, there is uncertainty at which air-filled pore volume a shift from reducing to oxidizing conditions takes place. Uteau *et al.* (2013) reported an increase in O_2 diffusion at 0.09 to 0.12 $cm^3\ cm^{-3}$ air-filled pore volume that accompanied an increase in E_H . However, their results were derived from homogenized and repacked soil columns that do not necessarily match any internal structure that occurs under natural conditions.

Despite its potential ecological importance, the relation between E_H and ε of undisturbed soil samples as a means to characterize at which air-filled pore volume a shift from reducing to oxidizing conditions occurs, has not been assessed systematically to date. This relation would be useful when, for example, matric potential or soil water content measurements are available but those of E_H are not. The aim of this prototype study was to (i) characterize the relation between E_H and ε for two contrasting soils differing in texture and (ii) to assess the variation in E_H development during multiple rewetting–drainage cycles. To achieve our objectives, we performed artificial submergence–drying experiments in the laboratory on undisturbed soil cores from two study sites. Determination of the water retention characteristics was performed by a new experimental design which enabled us to measure changes in air-filled pore volume close to water saturation accurately (± 1.5 hPa) in conjunction with high measurement resolu-

tion (0.01 hPa) that has not been investigated thus far. Concomitantly with E_H measurements, we shed more light on the anaerobic–aerobic transition during the aeration process in real time because our hourly measurement interval was another unique feature. The final goal was to use the relations between measured E_H and ε to derive soil specific characteristic values of air-filled pore volume that parameterize the tipping range from anoxic to oxic conditions.

Materials and methods

Study sites

Two soil samples were chosen that differ in their structural and textural composition, but can both be temporarily affected by reducing conditions as revealed by field E_H measurements (Dorau & Mansfeldt, 2016; Shrestha *et al.*, 2014). Therefore, at both sites microorganisms are adapted to a temporary lack of O_2 . The first sample set was obtained at a site that is influenced by episodic water saturation because of high-intensity summer flash floods (Shrestha *et al.*, 2014). It is on a floodplain along the River Thur in northeast Switzerland (8°77'12" E; 47°59'10" N). The soil is a Haplic Fluvisol (Calcaric) IUSS Working Group WRB, 2014). The second site is at Polder Speicherkoog in north Germany (54°8'1" N; 8°58'28" E) and characterized by strong short-term and seasonal fluctuations of the near-surface groundwater table (Dorau & Mansfeldt, 2016). The soil developed from calcareous marine sediments and is a Calcaric Gleysol (Eutric) (IUSS Working Group WRB, 2014).

Sampling

At each site, a small soil pit was excavated to a depth of 30 cm to obtain 7 undisturbed soil cores using 250 cm³ stainless steel cylinders (50 mm in height and 80 mm diameter). The cylinders were driven horizontally into the topsoil from 2 to 10 cm below ground. Afterwards, the cylinders were carefully removed from the soil with a saw knife, sealed from both sides with a plastic protection cap and transferred to polyethylene foam boxes to avoid collapse of the pore network during transport. The steel cylinders were stored at 5 °C in the laboratory to slow down microbial activity and prevent the formation of mould until they were used for the experiments. Three steel cylinders from each site were used for determination of the water retention curve, three for determination of the relation between E_H and ε in the single aeration experiment, and one cylinder in the multiple aeration experiment.

Water retention curve and air-filled pore volume

Determination of the water retention curve was based on the evaporation method (Schindler *et al.*, 2010; UMS, 2015) using the HYPROP device (UMS, Munich, Germany). Therefore, the steel cylinders were transferred to a water bath containing a 0.01 M CaCl₂ solution and saturated slowly with water by capillary force. After seven days, the HYPROP sensor unit was cautiously set upside down on to the soil sample in the steel cylinder and the whole test assembly was turned again afterwards. This sensor unit was placed on to a balance (accuracy ± 0.01 g) to record the loss of water during the evaporation process. It contained two micro tensiometers to record the matric potential during the experiment. The positions of the tensiometers (both 5 mm diameter) were at 12.5 (‘upper’ tensiometer, 56-mm length) and 37.5 mm (‘lower’ tensiometer, 31-mm length) below the sample surface, respectively (Figure 1). Matric potential readings and the decrease in weight from evaporation were measured hourly. This procedure has fundamental advantages because the water retention function, a key property to convert the air-filled pore volume, was measured at higher temporal resolution and with greater precision rather than it can be estimated by pedotransfer functions. For a mathematical description of the water retention curve we used the Durner equation based on a van Genuchten-Mualem type function as

$$S_e = w_1(1 + (a_1 h)^{n_1})^{-m_1} + w_2(1 + (a_2 h)^{n_2})^{-m_2} \quad (1)$$

where S_e is the effective water content, w_1 and w_2 are weighting factors for two overlapping regions, and a_1 , a_2 , n_1 , n_2 , m_1 and m_2 are empirical parameters for the hydraulic function (Durner, 1994). This equation resulted in the smallest root mean square error (RMSE) for our retention data obtained by the HYPROP device ($\theta_{\text{RMSE}} < 0.01$). It is suitable, therefore, to convert matric potential measurements to volumetric water contents by the formula

$$\varepsilon = \theta_s - \theta, \quad (2)$$

where ε is the air-filled pore volume ($\text{cm}^3 \text{ cm}^{-3}$), θ_s is the volumetric water content at saturation ($\text{cm}^3 \text{ cm}^{-3}$) and θ is the calculated volumetric water content in the sample ($\text{cm}^3 \text{ cm}^{-3}$). Because of hysteresis effects, this assumption is certainly true for the drying curve because the retention data and fitting procedure are based on the evaporation method, but it is unreliable for the wetting curve. The aim of the study was, however, to determine the tipping range when aeration occurs in terms of an increase in E_H , therefore, this methodological restriction can be disregarded.

Air-filled pore volume and redox potential in the single aeration experiment

The experimental setup to determine the water retention curve was extended by placing a self-manufactured glass hood on top of the steel cylinder to create a reducing soil milieu within the soil sample (Figure 1). To guarantee an O_2 -free atmosphere, the interface between glass and steel was sealed by silicone gel and the four ventilation ports at the side were sealed by glass plugs. We decided to aerate the sample by removing the glass plugs as soon as a steady-state of -100 mV was reached, which was determined by E_H readings. The glass hood had three entry slots for platinum (Pt) electrodes to measure the E_H at depths of 10, 25 and 40 mm below the surface of the soil core. One entry slot remained for the silver–silver chloride (Ag–AgCl, 3 M KCl internal electrolyte) reference electrode (SE 23, Sensortechnik Meinsberg, Meinsberg, Germany). The Pt electrodes (ecoTech, Bonn, Germany) were enclosed in a carbon fibre body (6-mm diameter) with the small-sized Pt tip (5-mm length and 1-mm diameter). The carbon fibre body was sealed on top by a rubber plug to prevent O_2 from entering the glass hood (Figure 1). Simultaneously to matric potential readings, the voltage was recorded every hour and converted to the standard hydrogen electrode by adding 207 mV (reference temperature at 25°C ; the temperature during the experiments ranged from 19.9 to 20.9°C , but the voltage difference of $< 4 \text{ mV}$ can be disregarded). Because we expected the topsoil at both study sites to be neutral (Mansfeldt, 2003; Shrestha *et al.*, 2014), we did not correct the

E_H values to pH 7 as is done sometimes for comparability (Bohn, 1971). To test for significant differences between the samples we used a one-way analysis of variance (ANOVA) by XLSTAT-Pro (Addinsoft V.2014.1.05.).

Air-filled pore volume and redox potential in the multiple aeration experiment

One steel cylinder from each study site was used, as described in the experimental set-up, for a multiple aeration experiment with several drying–rewetting cycles. After evaporation of water from the steel cylinder, an aqueous 0.01 M CaCl_2 solution was refilled repeatedly through the ventilation ports until ponding conditions of 5 mm above the sample surface occurred. We decided to irrigate the sample when oxidizing soil conditions ($E_H > 300$ mV) occurred for all Pt electrodes. In total, five wetting and drainage cycles were performed for 220 days to assess whether the development of E_H and the response to aeration was altered by individual cycles. To assess the relation between E_H and ε we tested for normality by the Shapiro–Wilk test, and because the data were not normally distributed we calculated Spearman’s rank correlation coefficient by XLSTAT-Pro (Addinsoft V.2014.1.05.).

Soil properties

We determined soil properties from the steel cylinders used in the single aeration experiment. Soil was removed from the cylinders, oven dried at 40 °C and sieved < 2 mm. The soil from each cylinder was analysed separately. Soil pH was measured potentiometrically with a glass electrode in a 0.01 mol l⁻¹ CaCl_2 solution mixed 5:1 with soil (v/v). The particle-size distribution was measured by the sieve and settling method. Total carbon (TC) and nitrogen (N) were determined by dry combustion with a CNS analyser (Vario EL cube, Elementar, Hanau, Germany) and organic carbon (OC) by dry combustion after removing inorganic carbon by treatment with hydrochloric acid (10% HCl). Inorganic carbon (IC) was calculated from the difference between TC and OC. Because $\text{Mn}^{\text{III,IV}}$ and Fe^{III} oxides act as redox buffering compounds that affect E_H development, a dithionite-citrate-bicarbonate (DCB) extraction was

performed to quantify their amounts (Mehra & Jackson, 1960). The extracts were analysed by flame atomic absorption spectrometry (iCE 3000 series, Thermo Scientific, Waltham, MA, USA). All analytical measurements were made in duplicate and the data are presented per study site as mean with the standard error ($n = 3$).

Results and discussion

Soil properties

Major differences were evident between the sample sets with respect to their water retention characteristics. In particular, they differed strongly in air capacity (coarse pore with radii $> 50 \mu\text{m}$) of $0.303 \pm 0.013 \text{ cm}^3 \text{ cm}^{-3}$ for the Fluvisol from River Thur and $0.090 \pm 0.002 \text{ cm}^3 \text{ cm}^{-3}$ for the Gleysol from Polder Speicherkoog (Figure 2). The volume of coarse pores and fissures between aggregates reflects air capacity and, as was the case in this study, was large in loose structureless sands (Thomasson, 1978). The structure of the topsoil from River Thur was single grain in contrast to a subangular blocky structure at Polder Speicherkoog, which was assessed by the visual appearance of aggregates. The bulk density was slightly larger for samples from River Thur with $1.18 \pm 0.06 \text{ g cm}^{-3}$ compared with $1.07 \pm 0.01 \text{ g cm}^{-3}$ for Polder Speicherkoog. A large sand content of 880 g kg^{-1} characterized the textural class of samples from the River Thur as sand, whereas samples from Polder Speicherkoog were silt loam (IUSS Working Group WRB, 2014) (Table 1). Soil reaction of the samples was at circumneutral pH (Table 1). Nitrogen and OC contents were larger for samples from Polder Speicherkoog than for samples taken from the River Thur, but they had a narrow C:N ratio in common of between 9 and 12. Inorganic carbon was considerably larger for the Thur samples, but extractable Fe^{III} and $\text{Mn}^{\text{III,IV}}$ oxide contents were 3.8 and 16.4 times smaller, respectively, than in samples from Polder Speicherkoog (Table 1). These findings can be related to larger clay contents in soil samples of Polder Speicherkoog; clay-sized particles are known to sequester organic nitrogen and OC preferentially (Kögel-Knabner *et al.*, 2008), and the clay content is positively correlated with the Fe^{III} and $\text{Mn}^{\text{III,IV}}$ oxide fractions of a soil (Cornell & Schwertmann, 2003).

Single aeration experiment

Figure 3 shows an example of one of the three replicate experiments with River Thur samples (a; Thur_3) and Polder Speicherkoog samples (b; Koog_1). The E_H had already declined at the beginning of the experiment because the soil samples were saturated with water for seven days before the Pt electrodes were installed. To equilibrate at an E_H of < -100 mV it took longer for all replicate cylinders and across all depths for samples from Polder Speicherkoog (97 to 823 hours with on average 340 ± 89 hours) than for River Thur samples (4 to 40 hours with on average 14 ± 4 hours) (Figure 3a,b, Table 2). This might be related to larger contents of $Mn^{III,IV}$ and Fe^{III} oxides in samples of Polder Speicherkoog (Table 1) because the soil E_H remains at the potential of a distinct redox couple (e.g. $Fe^{III}-Fe^{II}$) and the E_H decreases (e.g. to a couple with a smaller electrode potential such as $S^{VI}-S^{II}$) only when the oxidant (ferric Fe in Fe^{III} oxide) is depleted (Strawn *et al.*, 2015). In contrast, the steep decrease in E_H of samples from the River Thur indicate a poorly buffered soil environment where $Mn^{III,IV}$ and Fe^{III} oxides occur at small concentrations and the redox buffer capacity is small. Shrestha *et al.* (2014) also observed a strong decrease in E_H during a flood event in field experiments at the Thur site.

After removal of the glass plugs (after 170 hours), the soil water evaporated, air entered the soil and the air-filled pore volume gradually increased (Figure 3a,b). The increase in air-filled pore volume was faster for River Thur soil because of the coarser pores present in the sample than for Polder Speicherkoog soil (Figure 2). For example, the air-filled pore volume increased to $0.051 \text{ cm}^3 \text{ cm}^{-3}$ until after 270 hours of the experiment (Figure 3a), whereas the increase was only $0.018 \text{ cm}^3 \text{ cm}^{-3}$ for Polder Speicherkoog within the same period (Figure 3b).

Figure 3 shows the temporal development of E_H and ε , whereas Figure 4 includes the same data set but with E_H plotted against ε for the samples Thur_3 (Figure 4a) and Koog_1 (Figure 4b). We parameterized this aeration curve with two characteristic values. First, $\varepsilon_{Pt \text{ reaction}}$ was

defined as the air-filled pore volume where the increase in E_H was $> 5 \text{ mV hour}^{-1}$ and characterized the first change in slope along the curve. Second, $\varepsilon_{\text{Pt aeration}}$ was defined as the air-filled pore volume where E_H was 300 mV at pH 7, i.e. where the switch from reducing to oxidizing conditions occurred. The $\varepsilon_{\text{Pt reaction}}$ values were similar for Polder Speicherkoog samples of $0.048 \pm 0.008 \text{ cm}^3 \text{ cm}^{-3}$ (mean $\pm$ standard error for three replicates) and River Thur samples of $0.036 \pm 0.006 \text{ cm}^3 \text{ cm}^{-3}$ (Table 2). The $\varepsilon_{\text{Pt aeration}}$ values were $0.047 \pm 0.005 \text{ cm}^3 \text{ cm}^{-3}$ for River Thur samples, and almost twice as large for Polder Speicherkoog samples of $0.085 \pm 0.007 \text{ cm}^3 \text{ cm}^{-3}$ (Table 2). Based on a one-way analysis of variance (ANOVA), the two sample sets differed significantly for $\varepsilon_{\text{Pt aeration}}$, but not for $\varepsilon_{\text{Pt reaction}}$. This indicates that larger clay contents and greater aggregation in samples of Polder Speicherkoog require a larger air-filled pore volume to achieve oxidizing soil conditions than samples from River Thur. This concept is illustrated in the schematic drawing in Figure 5 where the coarse pore content is larger in samples of River Thur that promote the access of O_2 (Figure 5a). In contrast, large clay contents favour a pore-size distribution towards medium and fine pores that retain more water around the Pt tip, which prevents the access of O_2 (Figure 5b). This is reflected by a field capacity that was eight times greater for samples of Polder Speicherkoog than those of River Thur (Figure 2).

Aggregation and soil structure clearly had a further effect on the sequence of the increase in E_H after aeration (Figure 3). As the drying front moved downwards from the soil surface, one might expect that the increase in E_H should be in the order 10-, 25- and 40-mm depths. However, this idealized sequence was observed for the Thur_3 sample only, where an increase in E_H was measured initially at the 10-mm depth (solid line; at $\varepsilon_{\text{Pt reaction}} 0.039 \text{ cm}^3 \text{ cm}^{-3}$) followed by the 25-mm depth (dashed line; at $\varepsilon_{\text{Pt reaction}} 0.046 \text{ cm}^3 \text{ cm}^{-3}$) and finally by the 40-mm depth (dotted line; at $\varepsilon_{\text{Pt reaction}} 0.054 \text{ cm}^3 \text{ cm}^{-3}$) (Figure 3a; Table 2). For the sample Koog_1, however, the order was 25-, 10- and 40-mm depths, respectively, with corresponding values of $\varepsilon_{\text{Pt reaction}}$ of $0.040 < 0.050 < 0.055 \text{ cm}^3 \text{ cm}^{-3}$ (Figure 3b and Table 2). This order also

occurred for other samples of the Thur and Speicherkoog sites (Table 2). These observations reflect the heterogeneous soil structure. The Pt tip might be located either along a macro pore enabling enhanced O_2 diffusion or embedded within a fine-textured soil matrix retarding the entrance of O_2 to increase E_H . This concept of ‘nonaerated’ and ‘aerated’ soil volume was discussed by Flühler *et al.* (1976) with suggestions to use a binomial function to approximate real soil conditions rather than a simple dual differentiation. Overall, even though $\varepsilon_{Pt \text{ aeration}}$ might exceed a certain threshold, it must be expected that microsites of anoxia are still present.

Multiple aeration experiment

Figure 6 (a,b) shows five consecutive drainage and rewetting cycles during the course of eight months of incubation. At water saturation, E_H was small, whereas an increase in air-filled pore volume was associated with large E_H values for River Thur (Figure 6a) and Polder Speicherkoog (Figure 6b). Mansfeldt (2003) reported a strongly negative Spearman rank correlation coefficient ($r_s = -0.971$, $P < 0.01$, $n = 20$) between the duration of water saturation determined by WT depth and E_H during a 4-year study at Polder Speicherkoog. The WT was the master variable in explaining the temporal and spatial patterns in E_H with reducing conditions in the winter time (shallow groundwater) and oxidizing soil conditions in the summer time (deep WT). The relation between air-filled pore volume and E_H was strongly positively correlated for the single aeration experiment of River Thur ($r_s = 0.841$, $P < 0.001$, $n = 285$; Figure 4a) and Polder Speicherkoog ($r_s = 0.958$, $P < 0.001$, $n = 285$; Figure 4b). In the multiple aeration experiment, the variables were also strongly positively correlated for Polder Speicherkoog ($r_s = 0.917$, $P < 0.001$, $n = 1555$; Figure 7b), but only moderately correlated for River Thur ($r_s = 0.694$, $P < 0.001$, $n = 2407$; Figure 7a). The discrepancy between the first aeration cycle (top curve) and the subsequent four aeration cycles (lower curves) becomes apparent (Figure 7a). We assumed that erosion of soil particles along the Pt-tipped electrode occurred because we

watered the soil sample from the top. Therefore, presumably the Pt surface did contact the soil matrix facilitating an increase in E_H at very small air-filled pore volumes of $< 0.005 \text{ cm}^3 \text{ cm}^{-3}$ (Figure 7a). To account for these operational failures, $\varepsilon_{\text{Pt reaction}}$ and $\varepsilon_{\text{Pt aeration}}$ values should be determined in triplicate at least. Despite this shortcoming, the shape of the ‘aeration curves’ together with $\varepsilon_{\text{Pt reaction}}$ and $\varepsilon_{\text{Pt aeration}}$ values were similar between the single and multiple aeration experiments for samples from Polder Speicherkoog (Figure 4b and Figure 7b). The $\varepsilon_{\text{Pt reaction}}$ values from multiple submergence–drying cycles of a single sample were slightly larger and ranged between 0.052 and 0.061 than that averaged from three replicates of $0.048 \pm 0.008 \text{ cm}^3 \text{ cm}^{-3}$, whereas $\varepsilon_{\text{Pt aeration}}$ was identical with values between 0.081 and 0.086 and on average $0.085 \pm 0.007 \text{ cm}^3 \text{ cm}^{-3}$, respectively. The aeration cycles from Polder Speicherkoog indicate that in well-structured soils, the process of aeration is similar during repeated wetting–drying cycles.

Limitations of the characteristic air-filled pore volume values

The characteristic air-filled pore volume values were determined in the laboratory under controlled conditions (e.g. fixed soil temperature and no plant growth) and with Pt electrodes at specified depths close to the soil surface. However, it is likely that variation occurs under field conditions.

First, microbial activity and root respiration are sensitive to soil temperature and modify the rate of O_2 consumption (Reddy & DeLaune, 2008). Moreover, rates of root respiration are variable for different plant species with, for example, $16.2 \text{ nmol O}_2 (\text{g DW})^{-1} \text{ s}^{-1}$ for barley (*Hordeum vulgare* L.) (Bloom *et al.*, 1992) to $64.0 \text{ nmol O}_2 (\text{g DW})^{-1} \text{ s}^{-1}$ for wheat (*Triticum aestivum* L.) (Kurimoto *et al.*, 2004). Therefore, at large microbial activity and root respiration the O_2 pool might be already exhausted on the way from the soil surface to the reference depth defined by the position of the Pt electrode. On the other hand, plants that have roots

with aerenchyma could increase aeration in the rhizosphere at air-filled pore volumes smaller than $\varepsilon_{\text{Pt aeration}}$ (e.g. Philippot *et al.*, 2009).

Second, *sensu stricto*, the characteristic air-filled pore volumes are valid for the soil depths defined by Pt electrode positions, i.e. for diffusion of O_2 from a free-air reservoir with a partial O_2 pressure of $0.21 \text{ cm}^3 \text{ cm}^{-3}$ in installation distance from the electrodes. For lower depths, it has to be considered that the partial pressure of O_2 at the same distance above a hypothetical Pt electrode is likely to be already reduced, either by incomplete aeration at that depth or by biological respiration as described above (Glinski & Stepniewski, 1985).

Conclusions

We compared different soils with respect to aeration by determining drying curves for undisturbed soil cores instrumented with Pt electrodes and tensiometers at specified depths, and we parameterized these curves by two characteristic values of air-filled pore volume, $\varepsilon_{\text{Pt reaction}}$ (E_{H} increase of $> 5 \text{ mV hour}^{-1}$) and $\varepsilon_{\text{Pt aeration}}$ ($E_{\text{H}} > 300 \text{ mV}$ at pH 7). In the present prototypical study, these characteristic values differed plausibly between soils with contrasting texture and related structure. The application of $\varepsilon_{\text{Pt aeration}}$ enabled the aeration status of a soil to be assessed in terms of O_2 availability, whereas $\varepsilon_{\text{Pt reaction}}$ indicated an initial diffusion of O_2 to which the Pt surface reacts. The gap between $\varepsilon_{\text{Pt reaction}}$ and $\varepsilon_{\text{Pt aeration}}$ became wider the larger was the clay content and the more structured the soil sample. However, the small degree of variation in these values among spatial replicates, in particular for the well-structured silt-loam, suggested that small-scale structural heterogeneity had a small effect. Although these values can be altered by biological processes, and, in absolute terms, are valid only for topsoil horizons, they should prove useful for comparing soils of different texture and structure under identical conditions.

The determination of such values should be complemented by applying recently developed techniques that provide better insight into the spatio-temporal variation of redox conditions in

soils, such as small-sized sensors to measure O₂ contents *in situ* (e.g. fibrous O₂ optodes) or visualization of the air-filled pore volume by real-time tomographic measurements without disturbance of the pore network (e.g. by X-ray microtomography).

Acknowledgements

The authors thank Dr. Regine Spohner for illustration of the experimental setup. Karin Greef, Marius Gurk and Max Lösse are thanked for support during laboratory analysis. We greatly appreciate the support of Thomas Klinger who manufactured the glass dome (all University of Cologne). The second author acknowledges the financial support by the Competence Center Environment and Sustainability (CCES) of the ETH domain within the framework of the RECORD Catchment project. We also thank two anonymous reviewers for helpful comments that improved the manuscript.

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Figure captions

Figure 1 Experimental setup to determine the relation between redox potential and air-filled pore volume in undisturbed soil samples.

Figure 2 Water retention curves of samples used for the incubation experiments taken from a floodplain soil at the River Thur in Switzerland (triangle) and from a dyked marsh soil at Polder Speicherkoog in Germany (square). Shown are mean $\pm$ standard error ($n = 3$). Water content at saturation (θ_0) was 0.451 ± 0.009 and 0.535 ± 0.004 , air-capacity ($\theta_{0-1.8}$) 0.303 ± 0.013 and 0.090 ± 0.002 , and field-capacity ($\theta_{2.5-4.2}$) 0.028 ± 0.010 and $0.213 \pm 0.042 \text{ cm}^3 \text{ cm}^{-3}$ for the sample set from the River Thur and Polder Speicherkoog, respectively.

Figure 3 Development of soil redox potential (E_H) and air-filled pore volume (ε) in soil cores from (a) the River Thur and from (b) Polder Speicherkoog. Platinum electrodes for recording E_H were installed at depths of 10 (solid line), 25 (dashed line), and 40 mm (dotted line) below the sample surface. Note the different scaling of the x-axis. An arrow shows the time point of removing the glass plug to aerate the sample.

Figure 4 The relation between soil redox potential (E_H) and air-filled pore volume (ε) in soil cores from (a) the River Thur and (b) from Polder Speicherkoog. The rectangles in each figure indicate the distinct moment when the E_H increase is $> 5 \text{ mV hour}^{-1}$ ($\varepsilon_{\text{Pt reaction}}$) and the circles indicate the moment when oxidizing soil conditions ($E_H > 300 \text{ mV}$ at pH 7) are achieved ($\varepsilon_{\text{Pt aeration}}$).

Figure 5 Schematic drawing of redox potential measurements by platinum (Pt) electrodes in the soil samples investigated. The close up of the Pt tip (5-mm length and 1-mm diameter) shows an idealized distribution of soil particles (grey), organic matter (green), iron and manganese oxides (brown), water-filled (blue) and air-filled (white) pores for samples from (a) the River Thur and (b) from Polder Speicherkoog.

Figure 6 Long-term development of soil redox potential (E_H) and air-filled pore volume (ε) in soil cores from (a) the River Thur and (b) from Polder Speicherkoog during multiple wetting–drying cycles. The E_H values represent the average of readings from three different depths, whereas ε values are based on measurements at two depths. Because of an electrical short-circuit of the Pt electrode installed at 10 mm below the sample surface from the River Thur, the development E_H is displayed as the mean of measurements in duplicate following the first aeration cycle.

Figure 7 The relation between soil redox potential (E_H) and air-filled pore volume (ε) in soil cores from (a) the River Thur and (bO) from Polder Speicherkoog for the multiple-aeration experiment. The rectangles in each figure indicate the distinct moment when the E_H increase is $> 5 \text{ mV hour}^{-1}$ ($\varepsilon_{\text{Pt reaction}}$) and the circles indicate the moment when oxidizing soil conditions ($E_H > 300 \text{ mV at pH 7}$) are achieved ($\varepsilon_{\text{Pt aeration}}$). The offset between the curves from multiple aeration cycles in part (a) is probably from the erosion of soil particles along the Pt tip following the first aeration cycle (top curve).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1 Soil properties from River Thur (Switzerland) and Polder Speicherkoog (Germany). Data were obtained from soil samples used for the single aeration experiment ($n = 3$) including the standard error of the mean.

	pH	IC ^a	OC ^b	N	OC/N	Fe _d ^c	Mn _d ^d	Sand	Silt	Clay
		/g kg ⁻¹			-	/g kg ⁻¹				
Thur	7.2±0.1	42.0±0.75	5.61±0.80	0.49±0.05	11.4	1.75±0.05	0.03±0.002	880±0	77±3	43±3
Koog	6.7±0.1	2.55±0.04	27.1±1.01	3.01±0.07	9.0	6.73±0.57	0.42±0.003	223±10	557±7	217±3

^a inorganic carbon

^b organic carbon

^c dithionite-citrate-bicarbonate extractable Fe

^d dithionite-citrate-bicarbonate extractable Mn

Table 2 Results of the experiment to determine the relation between soil redox potential (E_H) and air-filled pore volume (ε) for the samples investigated within the steel cylinder.

	Time to achieve a steady state ($E_H < -100$ mV)			$\varepsilon_{\text{Pt reaction}}^b$			$\varepsilon_{\text{Pt aeration}}^c$		
	E_H at 10 mm	E_H at 25 mm	E_H at 40 mm	E_H at 10 mm	E_H at 25 mm	E_H at 40 mm	E_H at 10 mm	E_H at 25 mm	E_H at 40 mm
	/hour			/cm ³ cm ⁻³					
Thur_1	5	15	4	0.038	0.008	0.044	0.046	0.021	0.058
Thur_2	6	— ^a	40	0.024	0.031	0.026	0.042	0.043	0.035
Thur_3	11	12	21	0.039	0.046	0.054	0.058	0.065	0.068
Koog_1	206	231	152	0.050	0.040	0.055	0.080	0.059	0.086
Koog_2	412	123	214	0.038	0.054	0.049	0.106	0.081	0.099
Koog_3	97	799	823	0.010	0.077	0.060	0.054	0.091	0.079

^a electrode did only reach 200 mV when aeration occurred

^b air-filled pore volume at which E_H increase is > 5 mV hour⁻¹

^c air-filled pore volume where E_H is > 300 mV at pH 7