

Time-resolved *in-situ* pH measurement in differently treated, saturated and unsaturated soils

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Abstract

The pH-value is of utmost relevance for soil properties and functioning. Hence, a time-resolved *in-situ* measurement is mandatory but lacking. As an alternative, a two-probe pH electrode with gel-covered reference electrode was newly constructed and tested for a continuous, *in-situ* pH recording in saturated and unsaturated soil. This was done using samples from a set of 14 soils with different composition and $\text{pH}_{\text{CaCl}_2}$ ranging from 3.5 to 7.5 in batch and repacked soil column experiments. In the latter, changes in pH and redox potential were monitored upon transport of citrate-phosphate buffer and pig slurry through the soil columns. The pH measurements were largely stable even upon substantial shifts in soil moisture content down to air-dry conditions. The results of the pH measurements agreed with standard methods using settled soil suspensions in electrolyte solutions and the conventional combination (single-probe) pH electrode. Testing the suspension effect, it was found that measuring pH directly in the soil is recommended. The pH measured *in-situ* was closest to pH values determined in 0.01 M CaCl_2 suspensions according to DIN ISO 10390 (DIN, 2005). The transport of citrate buffer and pig slurry as pH active substances through soil induced strong effects on the pH and in part on the redox potential; the reversible effects lasted over days, which may affect the mobility and speciation of nutrients and pollutants as well as microbial processes.

Key words: real-time pH analysis / pH online measuring system / two-probe pH electrode / soil column experiment / redox potential

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1 Introduction

The pH-value is a key parameter among the physico-chemical properties of soil as it governs soil chemical as well as biological processes and functions. This encompasses for example the influence on surface charge and sorption of ions and polar chemicals, metal speciation, organic matter complexation and release (Bolan et al., 2004; Grybos et al., 2007; Blume et al., 2010; Tan, 2011). The pH is closely linked to the redox potential since H^+ ions are involved in the majority of redox reactions in soil (Blume et al., 2010); the relation between H^+ activity and the redox potential is described in the Nernst equation (Tan, 2011). The abundance of soil biota and their functions and activity, e.g., in biogeochemical cycling of nutrients, is strongly affected by soil pH (Paul, 2007). *Vice versa*, pH is influenced by these parameters and processes, and thus varies within a soil profile and time.

Hence, a soil depth- and time-resolved determination of pH and redox potential is necessary to monitor biological and chemical conditions and processes in soil. This is of particular relevance for structured and unsaturated soil, for example to determine the influence of pH and redox potential on the mobility and transport of nutrients and pollutants. In contrast to

the measurement of the redox potential (Mansfeldt, 2003), however, until now no method is available for the continuous determination of pH *in-situ* and in unsaturated soils (Blume et al., 2011).

This is due to substantial problems combined with the electro-metric measurement of pH. Technical problems may arise with the use of electrometric glass electrodes due to losses of the inner aqueous electrolyte solution to the unsaturated soil and drying of the glass membrane (Schaller and Fischer, 1981) as well as possible frost damage to the electrode under field conditions. Even more, the suspension effect may unpredictably alter the pH reading (Pallmann, 1930; Oman, 2000a; Oman, 2000b; Al-Busaidi et al., 2005). The suspension effect results in different pH readings, when pH is measured in the soil (sediment) compared to the equilibrium solution (supernatant) of a settled soil suspension (Overbeek, 1953; Oman et al., 2007).

The problems outlined are operationally solved by convention measuring pH in the supernatant of a settled soil suspension (soil-to-solution ratio 1:2.5) using either deionized H_2O , 1 M KCl or, following DIN ISO 10390 (DIN, 2005), 0.01 M CaCl_2 (Blume et al., 2011; Tan, 2011). However, all these methods



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only allow short-term measurements and are not suitable for longer-term monitoring. They require the disturbance of the soil structure, as well as the complete modification of the actual moisture status (Ritvo et al., 2003) and soil solution as well as gas phase composition. Yet, especially the Ca^{2+} activity and the CO_2 partial pressure influence the actual pH (Blume et al., 2011).

Consequently, alternative methods for pH measurement are needed and have been proposed to enable *in-situ* monitoring of pH in environmental samples. Instead of the glass electrodes with Ag/AgCl system, Sb electrodes (Schaller and Fischer, 1981), SnO_2 transparent electrodes (Tamogami et al., 2009), optical methods using polymer optical fibers (Motellier et al., 1995; Blossfeld and Gansert, 2007), luminescent planar optodes (Stahl et al., 2006; Schröder et al., 2007), and fluorescence alterations of pH-sensitive fluorophores (Boldt et al., 2004) have been used for real-time and *in-situ* pH measurement for example of bacterial consortia and rhizospheres. However, none of these systems has made it to routine and several of them are restricted to measurements on the sample's surface (Boldt et al., 2004; Stahl et al., 2006; Blossfeld and Gansert, 2007), e.g., the rhizoplane (Schreiber et al., 2012).

As an alternative, a two-probe pH electrode with gel-covered reference electrode was newly constructed for the study presented, and tested for a continuous, *in-situ* pH recording in saturated and unsaturated soil. In detail, the aims of this study were to investigate in consecutive experiments (1) whether the two-probe electrode yields the same pH data as regular single-probe electrodes, (2) in how far the pH measurement directly in the soil is affected by the suspension effect, and (3) whether long-term pH measurement in unsaturated soil is possible and/or affected by a changing water content. Finally, (4) combined effects on pH and redox potential were investigated by following the transport of citrate-phosphate buffer and pig slurry, respectively, as pH-active substrates through soil. These experiments were done with samples from a set of 14 soils with different composition and $\text{pH}_{\text{CaCl}_2}$ ranging from 3.5 to 7.5, using batch and repacked soil column experiments.

2 Material and methods

2.1 pH and redox electrodes and measurement

For our measurements we used a two-probe pH electrode, which has newly been re-designed especially for the permanent installation in soils [registered utility patent; Art.no. 465 (single pH electrode), ecoTech GmbH, Bonn, Germany]. The system basically consists of a single reference electrode, acting as the negative pole in the electrical circuit, and a glass measuring electrode, acting as the positive pole. The reference probe is a classical Ag/AgCl-electrode, but it is additionally embedded into a 'salt bridge', a tube filled with 3 M KCl (with an additive of AgCl), stabilized by Agar gel in order to slow down the leaching process of KCl solution through the ceramic diaphragm at the tip of the reference probe. The glass electrode has got small dimensions (diameter 6 mm) and is manufactured from three different glass types to (1)

achieve a long lifetime and (2) to prevent damages by installation, freezing, etc. It has got a reinforced glass measuring membrane with a cylinder shape to avoid hairline cracks at the junction to the glass shaft. Additionally, it has got a transition glass section with an expansion coefficient lying between the coefficients of the membrane glass and the shaft glass to prevent damage by strong temperature changes. The electrode is filled with a gel electrolyte of 3 M KCl for being able to be installed in any direction. With its small diameter it is suitable for column and pot experiments in the laboratory, and it can be equipped with a protective shaft for long-term field use also. Within our experiments, we worked with one reference electrode and three single glass electrodes, and we compared the readings with the combination (single-probe) pH electrode 'SenTix 41' (WTW, Weilheim, Germany).

Redox potential was measured using three redox electrodes according to Mansfeldt (2003). These probes were designed for continuous redox determination in soils, and are basically made of hard-drawn platinum rods (99.95% Pt) of 5 mm length and a diameter of 1 mm, molded in a shaft from carbon fiber (diameter 6 mm). Both pH and redox electrodes were simultaneously connected to the same reference electrode. Data conversion to the standard hydrogen electrode (Eh) and temperature compensation for 20°C was done according to Kölling (2000).

For time-resolved measurements, electrodes were connected to a WTW pH340i (WTW, Weilheim, Germany) pH/Eh instrument in automatic mode, and measured data were continuously transferred to a standard notebook connected via RS232 interface. The contact between the reference electrode and each measuring electrode was realized by a switching relay. The latter enabled the recording of outgoing signals from each measuring electrode over 1 min before switching to the next electrode, so that one measuring cycle for three pH and three redox measuring electrodes was completed within 6 min.

2.2 Soil samples, chemicals, and experiments

Experiments were done with samples taken from a set of 14 agricultural, grassland, and forest soils in Germany (topsoils and one C-horizon sample), covering a $\text{pH}_{\text{CaCl}_2}$ range from 3.5 to 7.5. General soil properties are listed in Table 1. All soil samples were sieved ≤ 2 mm, homogenized and air-dried prior to the experiments. The pH standard solutions of pH 2, 4, and 7 were obtained from WTW (Weilheim, Germany) and all other chemicals used were of analytical grade and obtained from Merck (Darmstadt, Germany) and Roth (Karlsruhe, Germany), respectively. Redox electrodes were calibrated in a redox buffer according to Funk and Schär (1996).

The performance of the two-probe pH electrode versus the conventional single-probe electrode was tested in soil suspensions using deionized H_2O , 0.01 M CaCl_2 , and 1 M KCl, respectively, at a soil-to-solution ratio of 1:2.5.

The *in-situ* pH measurement with the pH electrodes directly inserted into the soil was first investigated in saturated soil using three 200-g soil samples (samples 5, 12, and 13; Table 1).

Table 1: Selected characteristics of the tested soil samples and pH-values measured in 0.01 M CaCl₂ with a single-probe electrode; standard deviation in parentheses (*n* = 3). IC = inorganic C; OC = organic C; ECEC = effective cation exchange capacity.

#	Major soil group	Location in Germany	Horizon	Texture	IC	OC	ECEC	pH _{CaCl₂}
	(WRB, 2014) ^a			(WRB, 2014) ^a	/ %	/ %	/ cmol _c kg ⁻¹	single-probe
1	Dystric Cambisol	Trier	Ah	silt loam	– ^b	8.19	7.55	3.5 (0.06)
2	Plaggic Anthrosol	Vechta	Ap	sand	–	3.39	5.42	4.5 (0.09)
3	Haplic Phaeozem	Halle	Ap	sandy loam	–	1.01	6.43	5.3 (0.10)
4	Podzolic Cambisol	Ferschweiler	Ap	sandy loam	–	1.72	8.51	5.5 (0.12)
5	St-Gl Cambisol ^c	Königswinter	Ah	clay loam	–	1.10	19.20	5.8 (0.00)
6	Stagnic Cambisol	Groß Lüsewitz	Ap	sandy loam	–	1.02	10.22	6.1 (0.06)
7	Eutric Fluvisol	Kenn	Ap	sandy clay loam	–	1.59	12.99	6.3 (0.04)
8	Stagnic Cambisol	Kenn	Ap	loamy sand	–	1.65	9.67	6.6 (0.12)
9	Haplic Retisol	Rostock	Ah	sandy loam	1.28	1.56	12.16	6.7 (0.11)
10	Fluvisol Arenosol	Sylt	C	coarse sand	0.09	– ^b	1.41	6.7 (0.13)
11	Eutric Cambisol	Rostock	Ah	sand	0.65	0.79	5.33	6.8 (0.04)
12	Eutric Cambisol	Troisdorf	Ah	sandy loam	0.11	2.00	8.75	6.9 (0.06)
13	Eutric Cambisol	Bonn	Ah	sandy clay loam	0.88	1.00	13.43	7.3 (0.06)
14	Hortic Anthrosol	Zemmer	Ah	loam	2.23	3.36	18.62	7.5 (0.11)

^aIUSS Working Group WRB (2014);^bbelow detection limit;^cStagnic-Gleyic Cambisol.

The soil samples were repacked, each in one of three vertical sections of a 7.5 cm × 15 cm polypropylene box (soil depth 4.5 cm), so that the soils were adjacent and in direct contact to each other. Soils were remoistened with deionized H₂O until saturated. Measurement electrodes were placed in all three soils, while the reference electrode was placed in soil sample 5. All electrodes remained over four consecutive days and the pH was read every 24 h.

In a second *in-situ* pH measurement, the influence of varying soil moisture in unsaturated soil on the pH reading was determined using soil material from the Ap horizon of a Podzolic Cambisol (sample 4; Table 1). For this purpose, 600 g of air-dry soil were filled into a polypropylene box (see above), allowing the water to freely evaporate. The pH electrodes were inserted into the soil and pH was continuously recorded (see 2.1). For the duration of the experiment the soil was stored at 20°C ± 2°C. The water content was regularly controlled gravimetrically and five times readjusted by adding deionized H₂O.

The influence of pH-active substances on pH during their transport through the soil was investigated using a repacked soil column experiment. A polypropylene tube with 10 cm inner diameter and 40 cm height was equipped with a sprinkling head system consisting of nine cannulas to evenly irrigate the soil surface with deionized H₂O at 11 mm h⁻¹, delivered by a peristaltic pump. Washed quartz sand was used as lower boundary condition, and seepage water was withdrawn at a constant vacuum of 500 hPa.

The column was filled up to a height of 30 cm with 23.1 kg dry soil equivalent of topsoil (Ap) material from a loamy sand Stagnic Cambisol (sample 8, Table 1) reaching a final density of 1.1 g cm⁻³. The pH and redox electrodes were inserted in the soil column at 5, 15, and 25 cm from the top. The redox potential and the pH values were continuously recorded as described in section 2.1. The soil profile was conditioned by precipitation with 0.01 M CaCl₂ for one week before application of pH active substrates. As pH-active substances either citrate-phosphate buffer, pH 5.0 (0.1 pore volume), or pig slurry was used. The pig slurry had a dry matter content of 12%, a total C content of 40% and a pH of 8.6 (Arenz-Leufen, 2012), and was obtained from a conventional pig fattening farm in Luxembourg. The amount of 245 g liquid manure that was applied to the soil surface was equivalent to 35 t ha⁻¹, which is typical for agricultural practice.

2.3 Data analysis

For calculating means of pH values, the data were delogarithmized, then averaged and logarithmized again. For statistical analysis by one-way ANOVA and correlation, and for data smoothing by adjacent averaging of five data points, the Origin 7.5 software (Northampton, MA, USA) was used.

Since the pH is defined as the negative decadic logarithm of the H⁺ ion activity, changes in pH, even when they are based on the same change in H⁺ ion activity, appear as smaller dif-

ferences when the pH declines, while differences appear to be much larger for increases in pH. To overcome this distortion of the data, the changes in H^+ ion activity ($\Delta[H^+]$) between the initial pH at the start of the experiment (t_0) and the pH at time t_1 were calculated:

$$\Delta[H^+] = 10^{-pH_{t_0}} - 10^{-pH_{t_1}} \quad (1)$$

The $\Delta[H^+]$ is displayed in Figs. 4 and 5 instead of the pH.

3 Results and discussion

The applicability of the two-probe electrode system was checked by comparative pH measurement using a customary single-probe electrode as reference. Soil acidity was measured as recommended in the supernatant of a settled soil suspension using 0.01 M $CaCl_2$ following DIN ISO 10390 (DIN, 2005). The results of both measurements very much agreed ($R^2 = 0.99$) and almost followed the 1:1 line (Fig. 1). With one-way ANOVA it was determined that the pH measurements of both electrode systems were not significantly different ($F = 0.088$; $p = 0.770$). Hence, it is assumed that this proved the usability and accuracy of the two-probe electrode system under standard pH measurement conditions.

The suspension effect was measured by inserting the reference and/or the measuring electrode of the two-probe electrode system in the settled soil and/or in the supernatant using the method according to DIN ISO 10390 (DIN, 2005). Previous, repeated stirring and settling of the suspension over 3 h ensured that H^+ exchange reached equilibrium conditions. The results in Table 2 show that the position of the measuring electrode governed the pH reading, while that of the reference electrode was negligible; differences between variants A and B as well as between variants C and D were not significant (not shown). Instead, the measured pH values were lower and for most samples tested significantly lower, when the measuring electrode was in direct contact to soil, as it has been previously reported (Al-Busaidi et al., 2005; Tan, 2011).

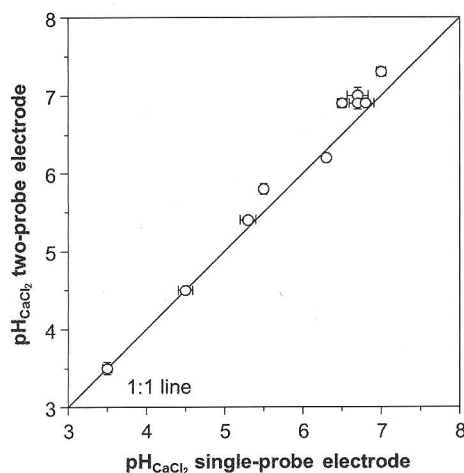


Figure 1: The pH_{CaCl_2} values of 10 soil samples measured either using a single-probe electrode or a two-probe electrode system. Error bars indicate standard deviations of triplicate measurements; error bars not shown are smaller than symbols.

The difference in pH readings in solution *versus* in soil was largest for the Hortic Anthrosol Ah (soil 14, Table 1) with the highest pH of 7.5 and tended to decline and to become less or even not significant with increasing soil acidity. Furthermore, most of the differences vanished, when the measured pH values were rounded to one decimal place, as it is usually done for routine analysis. The difference in H^+ ion activity ($\Delta[H^+]$) tended to increase and was negatively correlated ($r = -0.81$, $p = 0.1$) with the soil pH measured according to DIN ISO 10390 (DIN, 2005). Using a similar set-up of separate pH measuring and reference electrodes, Oman (2000b) found a similarly reduced soil pH when the measurement electrode was placed in the soil compared to the solution. In accordance with this study, the difference in pH was smallest for the acidic soil samples, while deviations of up to 0.5 pH unit were reported for alkaline soils (Oman, 2000b). Consequently, the conclusion of Tan (2011) that the position of the

Table 2: Test for the soil suspension effect, when electrodes of the two-probe system are immersed in the supernatant or the settled soil of suspensions prepared in 0.01 M $CaCl_2$ according to DIN ISO 10390:2005-12 (DIN, 2005). Sample numbers refer to Table 1.

Measuring electrode	Reference electrode	Hortic Anthrosol Zemmer (sample 14)		Stagnic Cambisol Kenn (sample 8)		Stagnic Cambisol G. Lüsewitz (sample 6)		Plaggic Anthrosol Vechta (sample 2)		Dystric Cambisol Trier (sample 1)	
		pH	SD	pH	SD	pH	SD	pH	SD	pH	SD
A	supernatant	7.49	(0.09)	6.73	(0.04)	6.19	(0.07)	4.96	(0.03)	3.57	(0.04)
B	supernatant	7.43	(0.05)	6.79	(0.05)	6.13	(0.05)	4.73	(0.03)	3.62	(0.06)
C	soil	7.06	(0.06)	6.63	(0.04)	6.08	(0.04)	4.64	(0.01)	3.62	(0.06)
D	soil	7.09	(0.05)	6.63	(0.03)	6.03	(0.09)	4.69	(0.01)	3.64	(0.06)
ΔpH	$\bar{x}(A, B) - \bar{x}(C, D)$	0.39		0.13		0.11		0.17		-0.03	
$\Delta[H^+]^a$		0.41		0.74		0.85		0.68		1.08	
p^b		***		***		*		**		n.s.	

^aDifference in H^+ ion activity ($[H^+] = 10^{-pH}$).

^bSignificance of difference between A, B and C, D, tested by one way ANOVA. * $p = 0.05$, ** $p = 0.01$, *** $p = 0.001$, n.s. = not significantly different.

glass electrode is irrelevant at the equilibrium condition is supported by this study and *Oman* (2000b) for soils with pH ≤ 6.1 but not for neutral or alkaline soils. Consequently, it was proposed that pH electrodes should be directly placed in the soil or sediment (*Tan*, 2011).

In-situ pH measurements were conducted by introducing the two-probe electrodes (three measurement and one reference electrode) directly into three repacked and unsaturated soil samples. This was done by filling three separate sections of one polypropylene box with three different soil samples in the order (pH_{CaCl₂}) 6.9, 7.3, and 5.8. The water-saturated soils were in direct contact to each other. The pH measurement was conducted over four consecutive days (96 h) and compared with the results from conventional measurements in settled soil suspension using either deionized H₂O, 0.01 M CaCl₂ or 1 M KCl. Results are shown in Fig. 2.

As expected, a clear difference in pH measured in different electrolyte solutions was determined especially in the more acidic soil. The pH declined in the sequence H₂O > 0.01 M CaCl₂ > 1 M KCl, which sequence was previously reported (*Conyers and Davey*, 1988; *Tan*, 2011). For example, in a study by *Gascho et al.* (1996) the mean pH of 576 slightly acidic soil samples was 6.34 in H₂O, 5.62 in 0.01 M CaCl₂, and 5.21 in 1 M KCl, matching the results of the presented study. The pH readings from all three methods were highly correlated ($r \geq 0.747$, $p \leq 0.01$), confirming the findings of *Conyers and Davey* (1988) and *Gavriloaiei* (2012). Differences in pH measured in different solutions are explained by a reduction of the double layer potential of the charged soil surfaces, which is stronger in the presence of electrolytes, leading to an increased release of H⁺ to the solution (*Al-Busaidi et al.*, 2005). Secondly, the liquid junction effect has been reported as a further cause (*Al-Busaidi and Cookson*, 2002; *Al-Busaidi et al.*, 2005). This effect is assigned to an unequal diffusion of electrical charges across the junction between electrolyte and internal electrode solution and typically larger in the presence of H₂O (*Moore and Loeppert*, 1987).

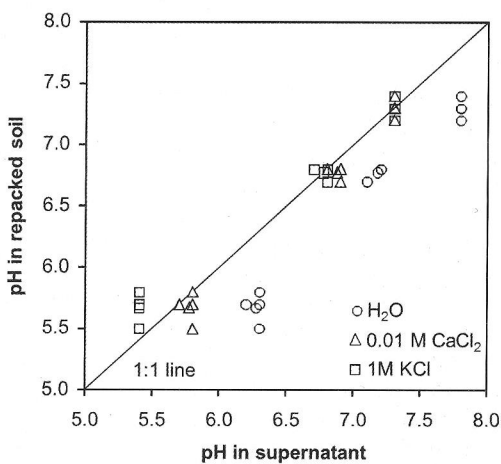


Figure 2: The pH values of three soil samples measured in triplicate in supernatants of settled soil suspensions using three different solutions (H₂O, 0.01 M CaCl₂, and 1 M KCl) compared to continuous, *in-situ* pH measurement in repacked saturated soil over four consecutive days. Data points along the Y-axis indicate pH readings after 24, 48, 72, and 96 h.

Irrespective from that, in this study, measurements in saturated soil and in the supernatant of settled soil suspensions were closely correlated ($r > 0.98$). Strongest agreement was found for the pH measured in 0.01 M CaCl₂, which followed the 1:1 line. One-way ANOVA revealed that both pH measurements were not significantly different ($F=0.050$; $p=0.825$). The pH reading in all three soils was stable over 96 h with standard deviations of 0.05 to 0.13 and did not meander with time as was suspected by *Conyers and Davey* (1988). At the end of the experiment the pH measurement was repeated by placing the reference electrode in each of the three soils. No effect on the pH reading was determined (data not shown).

The influence of the water content on soil pH was measured in an unsaturated Podzolic Cambisol over 18 d of which the first 10.2 d are displayed in Fig. 3. Upon continuous drying and instant remoistening the gravimetric soil water content varied from 2% (air-dry) to 26.9% (50% of water holding capacity). The pH reading of all three measurement electrodes was very similar ranging over 0.37 pH units between pH 5.60 and 5.97 (average pH 5.71). Nevertheless, one electrode showed a continuously increasing pH within a small range of ≤ 0.31 pH units, the reason being unclear yet. Some interim increases in pH are seen in Fig. 3 that are suggested to be related to the partly drastic changes in the soil water content, since the increasing pH values occurred during phases of (almost) air-dryness of the soil. The gravimetric water content and the soil pH were not correlated, though, and the observed increases in pH during extreme drying periods did not obey the theory.

Usually, observed pH values increase with increasing water volume due to a dilution of H⁺ (*Tan*, 2011) and the dissociation of adsorbed ions (*Yu and Ji*, 1993). Changing the soil-to-water ratio from 1:1 to 1:2.5 increases the pH of suspensions from alkaline soils by 0.29 units in the presence of water and by 0.16 units in the presence of CaCl₂ (*Al-Busaidi et al.*, 2005). On the other hand, the [H⁺]:[Ca²⁺] ratio, largely govern-

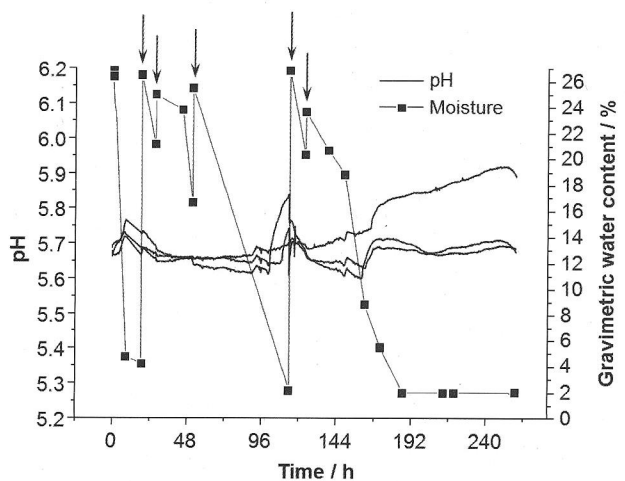


Figure 3: Changes in soil moisture of a Podzolic Cambisol topsoil upon drying and repeated rewetting (arrows) and related changes in pH over 10.2 d (244.5 h). Measurement using the two-probe electrode system with one reference and three measurement electrodes inserted into the soil.

ing soil pH, is constant over a wide concentration range, and thus independent from the soil-to-solution ratio (Blume et al., 2011).

In any case, the results of this study show that strong changes in soil moisture and strong soil dryness did not affect the pH values measured *in-situ* with the two-probe electrode system in a way that the measurement was improperly impaired. Only after a soil moisture of 2% persisted for > 90 h, the electrodes were disturbed. Extremely fluctuating and obviously erratic pH readings occurred, likely due to a loss of the electric contact *via* corresponding water films. This disturbance was reversible, and the correct measurement was reconstituted when the soil was remoistened (data not shown).

In two experiments either citrate-phosphate buffer (pH 5.0) or pig slurry (pH 8.6) was applied to the surface of a repacked soil column (Stagnic Cambisol Ap, pH_{CaCl_2} 6.6, sample 8 in Table 1). Due to the subsequent permanent irrigation with deionized H_2O at 11 mm h^{-1} , the applied substances were transported through the soil leading to staggered pH changes in different soil depths. The continuous *in-situ* pH recording clearly showed that the pH decreased upon passage of the buffer, which resulted in an increase in H^+ ion activity $[H^+]$ and a negative $\Delta[H^+]$ (Fig. 4). This effect on pH occurred consecutively and with a time delay (12, 21, 26 h) in all three soil depths (5, 15, 25 cm) as was expected from the progressing water transport in soil. After the buffer had passed through, pH in all depths recovered to the initial value. However, a strong tailing of the $\Delta[H^+]$ was determined for the soil depth of 5 cm, which was attributed to retardation and competitive exchange of the buffer components with the soil exchange sites (Mikutta et al., 2006). The exchange processes between the more acidic buffer solution and the soil matrix with higher pH proceeded after the breakthrough of the buffer through the 5 cm soil depth, leading to an overshoot of the pH ($\Delta[H^+]$), which lasted for 16 h until the initial pH ($\Delta[H^+]$) was almost re-established after 42 h (Fig. 4). This effect was much less pro-

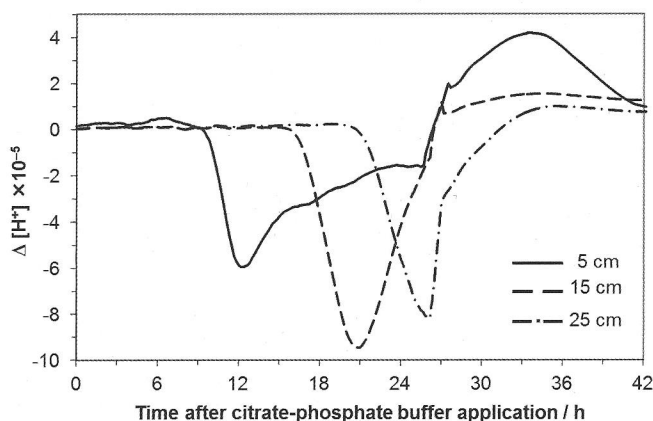


Figure 4: Changes in H^+ ion activity ($\Delta[H^+]$) at three soil depth during 42 h measured *in-situ* upon leaching of citrate phosphate buffer through a repacked topsoil material from a loamy sand Stagnic Cambisol. Use of a repacked soil column with sprinkling head and irrigation with deionized H_2O at 11 mm h^{-1} . Measurement using the two-probe electrode system with one reference and three measurement electrodes inserted into the soil at 5, 15, and 25 cm depth.

nounced in the other two soil depths. As expected, no effect of the citrate-phosphate buffer on the simultaneously recorded redox potential (Eh) was determined. The Eh varied around 550 mV ($\pm 14 \text{ mV}$) in 5 and 15 cm soil depth (data not shown) and was not correlated with pH and $\Delta[H^+]$, respectively ($r = 0.10$). At 25 cm soil depth Eh was substantially lower ($342 \pm 13 \text{ mV}$), which was likely due to insufficient water drainage at the lower boundary condition.

In contrast to the acidic citrate-phosphate buffer, the alkaline pig slurry led to an increase in pH and $\Delta[H^+]$ (Fig. 5a). Again, the pH effect occurred with a time delay (18, 44.5, 66 h) in the three soil depths (5, 15, 25 cm) indicating the transport of solutes through the soil column. Compared to the buffer solution, the migration of manure through the different soil depths was retarded due to the complex chemical and particle size composition of pig slurry. Pig slurry is a mixture of water with numerous particulate, suspended, and dissolved organic and mineral substances (Chadwick and Chen, 2002; Leenheer and Rostad, 2004). Up to 50% of the organic matter from slurry is present in the liquid phase that can be transported through soil (Japenga and Harmsen, 1990; Gigliotti et al., 2002; Aust et al., 2009), while particulate components are physically filtered out at the soil surface (McGechan, 2002). Molecular analyses of the liquid and colloidal phase from dairy manure and pig slurry showed richness in polysaccharides, N containing compounds such as proteins, phenols and lignin monomers (Deiana et al., 1990; Liang et al., 1996; Dinel et al., 1998; Aust et al., 2009) being possibly pH active substances. In the present study, this complexity resulted in a retarded transport of pH-affecting substances, and thus to a retardation and spatial dispersion of the slurry's pH effect in comparison to the citrate-phosphate buffer. The filtration and retardation of pig slurry constituents were investigated after the end of the columns experiment. The soil contents of nitrate-N and ammonium-N were determined in 5-cm layers as rough slurry indicators. Ammonium-N was increased to 10.4 and 12.8 mg kg^{-1} in 0–5 and 5–10 cm depth compared to an initial content of 1.18 mg kg^{-1} ; the content of nitrate-N was increased to 0.46 and 0.55 mg kg^{-1} in 0–5 and 5–10 cm depth compared to an initial content of 0.17 mg kg^{-1} (data not shown). After the pH increase vanished in 5 cm depth, an overshoot towards a lower pH and negative $\Delta[H^+]$ was determined that peaked at 48 h (Fig. 5a). As was discussed for the pH effect of the citrate-phosphate buffer, this may be due to delayed ion exchange processes. Additionally, in the case of manure as an easily degradable substrate, microbial processes will be activated (Kotzerke et al., 2008; Hammesfahr et al., 2011) and lead to the production of acids and temporary acidification of the soil (Aarons et al., 2004). Reflecting the effect of slurry on soil microbial processes, the redox potential in the three soil depths was significantly affected by the pig slurry (Fig. 5b). In 5 cm depth, the decline in the redox potential started at the same time (10.5 h) as the increase in pH (compare Fig. 5 a, b). The minimum was reached much later (29 h), and the effect on the redox potential lasted until the end of the experiment. Also at 15 cm depth, the effect on the redox potential lasted longer but reached the minimum earlier (40.5 h) compared to the pH effect. It is assumed that different components of the heterogeneous slurry substrate were transported with different velocity and had dissimilar effects

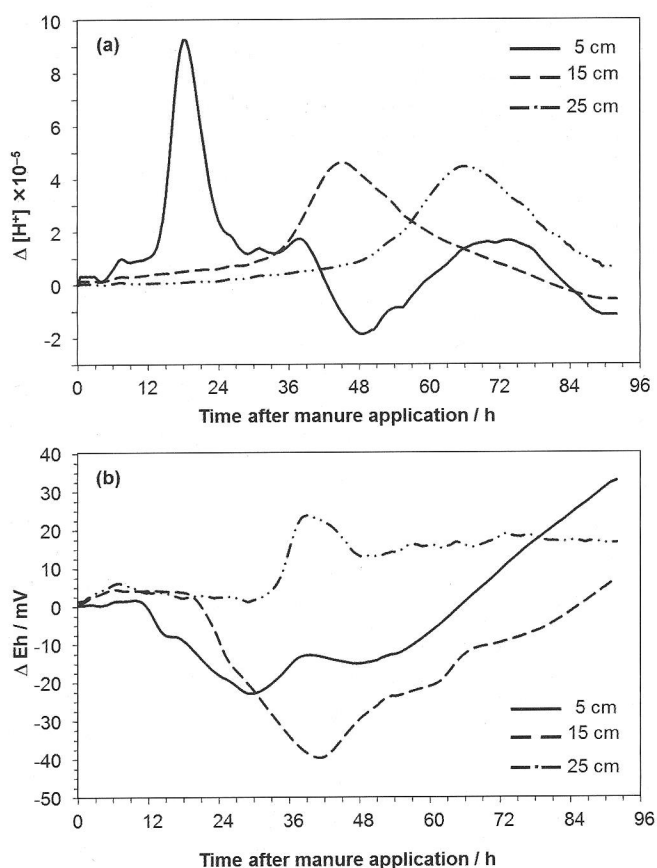


Figure 5: Changes in (a) H⁺ ion activity ($\Delta[H^+]$) and (b) redox potential (ΔEh) at three soil depth during 92 h measured in situ upon leaching of pig slurry through a repacked topsoil material from a loamy sand Stagnic Cambisol. Use of a repacked soil column with sprinkling head and irrigation with deionized H₂O at 11 mm h⁻¹. Measurement using the two-probe electrode system with one reference and three measurement electrodes for pH and three measurement electrodes for redox potential inserted into the soil at 5, 15, and 25 cm depth.

on the soil acidity and redox potential. There was no such effect on Eh at 25 cm soil depth, which was most probably due to the lower Eh in that soil depth, which has been discussed before. An interim increase in Eh was observed after 39 h (Fig. 5b), but could not be explained from the results obtained.

The correlation between pH and Eh varied between the different soil depths and was small, though significant for the 5 cm depth ($r = 0.22$, $p = 0.03$), while a strong positive correlation was found for the 15 cm depth ($r = 0.87$, $p < 0.001$) and a negative correlation for the 25 cm depth ($r = -0.62$, $p < 0.001$). This shows that pH and Eh reacted differently and were not faultily compensating each other in a way that Eh went up, when pH went down following the interaction of both parameters as it is described in the Nernst equation:

$$Eh = E^0 - 0.198 \times T \times pH, \quad (2)$$

with E^0 the standard potential and T the absolute temperature in Kelvin.

4 Conclusions

The presented two-probe electrode system with KCl gel electrolyte enables the spatially and temporally resolved monitoring of soil pH over time courses of days and weeks and presumably much longer. The applicability of this pH-electrode system even in unsaturated soil may open up new possibilities for the continuous determination of buffering reactions in soil and of respective consequences for the soil solution composition and further physico-chemical processes. To enable this also for monitoring experiments in the field, additional technical equipment has been developed parallel to this study. The electrodes are recently tested in two long-term field experiments. With the presented study it was shown that reversible effects of pH-active substrates such as pig slurry on the soil pH and redox potential last over days, which may affect the mobility and speciation of substances. Changes in pH and redox potential were not fully linked to each other and will feed back on microbial processes that may further influence pH and redox potential. Follow-up studies are now possible and on-going, investigating the effect of temperature changes on the pH, the redox potential and possible implications, e.g., for the mobility of heavy metals in soil on the laboratory and the field scale.

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