

# Methodologically controlled variations in laboratory and field pH measurements in waterlogged soils

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## Summary

We have tested the reliability and consistency of conventional pH measurements made on water-soil mixtures with respect to sieving, drying, ratio of water to soil, and time of shaking prior to measurement. The focus is on a waterlogged soil where the preservation potential of archaeological artefacts is critical. But the study includes agricultural and forest soils for comparison. At a waterlogged site, laboratory results were compared with three different field methods: calomel pH probes inserted in the soil from pits, pH measurements of soil solution extracted from the soil, and pH profiles using a solid-state pH electrode pushed into the soil from the surface. Comparisons between *in situ* and laboratory methods revealed differences of more than 1 pH unit. The content of dissolved ions in soil solution and field observations of O<sub>2</sub> and CO<sub>2</sub> concentrations were used in the speciation model PHREEQE in order to predict gas exchange processes. Changes in pH in soil solution following equilibrium in the laboratory could be explained mainly by CO<sub>2</sub> degassing. Only soil pH measured *in situ* using either calomel or solid-state probes inserted directly into the soil was not affected by gas exchange processes. Variations on the order of 0.2–0.5 pH unit in different laboratory methods could not be explained by degassing and seem to be soil-type specific and strongly influenced by drying and shaking. Further attention should be given to standardization of pH measurements, particularly before pH measurements from different soil types are compared.

## Introduction

Soil pH is one of the most useful parameters for characterizing soil functions and processes and is therefore frequently measured in the laboratory in both soil pastes and in the solution extracted from the soil. Soil pH varies dramatically at small scales (Laslett & McBratney, 1990) as well as in large-scale tests (Madsen & Munk, 1987). The importance of accurate pH measurements has been known for a long time in relation to aluminum, cadmium and copper solubility (Lofts *et al.*, 2001; Strobel *et al.*, 2005), microbial activity, substrate availability, dissolved organic carbon leaching (Ste-Marie & Paré, 1999; Andersson & Nilsson, 2001; Imek & Cooper, 2002) and pesticide degradation (Houot *et al.*, 2000).

Several strategies for characterizing soil pH have been reported (Thomas, 1996) and the concept of pH determination is described elsewhere (e.g. Bates, 1978). A well-described and often-used method includes 10 g air-dry soil mixed with 10 ml deionized water. Variations of this methodology are numerous. Effects of the ratio of water to soil in the suspension, salt effects,

temperature and the so-called ‘suspension effect’ are well documented (Thomas, 1996). Other elements of the laboratory method are less well-documented, e.g. soil-type specific effects of drying and/or sieving samples prior to measurements, time of shaking and type of water used, despite the importance when one method is used and its results applied to map soil pH across several soil types. Several studies have reported laboratory soil pH data generated from samples collected during a soil survey operation and may even include thousands of observations for a large number of soil types, collected over a lengthy period. Examples include Walter *et al.* (1997), who reported mean values of soil pH measured in water based on 67 600 soil samples across Brittany and France, and Madsen & Munk (1987), who evaluated the spatial variability in soil pH in Denmark based on 4200 soil samples. In both cases, results were analysed statistically and summarized to characterize the spatial variation of soil acidification over a region consisting of contrasting soil types.

In order to validate pH measurements from the laboratory on an absolute scale, an accurate methodology is required in the field. Some have focused on pore water in the soil, and used either dipwells or piezometers in waterlogged environments

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(Bunning *et al.*, 2000; Hogan *et al.*, 2001; Matthiesen *et al.*, 2003), or suction samplers that allow sampling of pore water from soil above the groundwater level (Elberling & Jakobsen, 2000). Direct measurement of pH in soil has been tried at several waterlogged sites by Caple & Dungworth (1998), using electrodes installed at a selected depth for 7–10 days. More recently, Ritvo *et al.* (2003), Matthiesen (2004) and Viscarra Rossel & Walter (2004) have determined *in situ* pH values using ion sensitive field transistor (ISFET) probes.

A problem with interpreting pH measurements in soil solution is the lack of data on subsurface concentrations of O<sub>2</sub> and CO<sub>2</sub>. Dissolution of O<sub>2</sub> after sampling tends to oxidize reduced species such as Fe<sup>2+</sup>, which decrease pH. Degassing CO<sub>2</sub> (and H<sub>2</sub>S) from the sample could increase its pH, whereas loss of gaseous ammonia could decrease the pH. The magnitude of these problems will vary between different methods and sites, but carbon dioxide degassing during use of suction samplers can easily lead to pH increases of 0.5–1 pH unit (Elberling & Jakobsen, 2000). Suarez (1986) found that CO<sub>2</sub> degassing from a soil solution buffered by carbonate species could increase pH by up to one unit during soil solution sampling with soil-water extractors. Soil types most likely to be affected are those with pH above 4.5 (Zabowski & Sletten, 1991).

Similar deviations are possible whenever soil or water is sampled for later analysis in the laboratory, or when water is standing in a dipwell open to the atmosphere. Theoretically, the ideal method for obtaining a momentary value of hydrogen ion activity in solution is to measure the pH *in situ* in the soil rather than taking samples (Caple, 1994). The current study investigates the feasibility of this solution.

The objectives of this work are threefold: (i) to evaluate the sensitivity of conventionally measured soil pH values in the laboratory for a range of soil types; (ii) to compare pH measurements from the laboratory with field-based measurements of soil pH using traditional pH probes and ion sensitive field effect transistor (ISFET) probes inserted in the soil, and pH measurements on extracted soil solution; and (iii) to discuss current guidelines for monitoring contrasting pH conditions in various soil types with the focus on waterlogged soils as these soils are ideal for ISFET measurements.

## Materials and methods

### Study sites and collection of soil samples

Soil samples for laboratory experiments were collected in November 2003 from a cultivated field, a beech forest and a waterlogged meadow located in close vicinity to each other in north Zealand, Denmark (55°N, 12°E). Detailed field and laboratory measurements were made at a meadow site in July 2003 at Nydam in South Jutland (55°N, 9°E).

The Zealand sites are situated on a sandy ground moraine from the Weichsel ice age. The forest and cultivated field soils have been classified as Typic Udorthents according to Soil Tax-

onomy (Soil Survey Staff, 1999), the texture is predominantly loamy sand and stones of varying sizes are present in the soil. The meadow site (Nydam) was a freshwater lake between 0 and 400 AD (Christensen, 1995), subsequently filled with gyttja (with innumerable shell fragments) and, later, with peat. Archaeological excavations in the meadow took place on several occasions from 1859 up to modern times (Jørgensen & Petersen, 2003; Rieck, 2003). In 1997, Denmark decided to preserve the remaining archaeological artefacts *in situ*. The pH measurements presented here form part of an intense monitoring scheme in the area carried out by the National Museum of Denmark (Sørensen & Gregory, 1998; Gregory *et al.*, 2001; Matthiesen *et al.*, 2003, 2004). The water level can fall to 50 cm below ground level in very dry summers, whereas in winter the area normally turns into a shallow lake. Most archaeological artefacts are found 100–150 cm below ground near the interface between the peat and the gyttja.

Samples for the laboratory experiments included one bulk sample per site as well as two bulk samples from the cultivated field site, representing two depth intervals (Table 1). Additional samples for laboratory pH measurements included one profile at the meadow site (Nydam) at depths 5, 10, 30, 50, 70, 90, 110, 130 and 150 cm below the surface. All samples were taken from pits and stored in plastic bags and kept near 7°C and in the dark until processed in the laboratory.

### Field measurements at Nydam

Equipment used in the field included an ion sensitive field effect transistor (ISFET) electrode (pH 37SS; IQ Scientific Instruments Inc., Carlsbad, CA, USA; tip diameter 3.5 mm), which is a solid-state, non-glass pH electrode based on a semiconductor technique. The ISFET electrode was mounted in a specially designed probe enabling the electrode to penetrate peat and gyttja, thus providing a vertical pH profile without the need for a soil pit or destructive sampling (Matthiesen, 2004). The electrode is pointed and very sturdy, which allows it to be cleaned with a toothbrush and water. Before use, the electrode was calibrated in certified buffers of pH 4.01, 7.00 and 10.01. ISFET-pH measurements (soil-pH<sub>ISFET</sub>) were made from the soil surface by pushing the probe step-wise into the ground. The ISFET electrode was then introduced and the tip pressed 7 cm into the undisturbed soil below the tip of the tube. pH

**Table 1** Soil characteristics from the three different sites. Results are means of three measurements ± one standard error

Land use	Horizon	Depth /cm	Organic C /%	pH <sup>a</sup>	Clay content /%
Field	Ap	0–10	3.2 ± 0.3	6.2 ± 0.2	7.2
Field	B	30–40	0.5 ± 0.1	6.2 ± 0.1	6.5
Forest	B	30–40	0.4 ± 0.1	4.6 ± 0.1	6.4
Waterlogged	H	0–20	35 ± 0.8	5.0 ± 0.2	–

<sup>a</sup>pH measured in air-dried soil in a water suspension (1:2.5) after shaking.

was measured, the electrode tip withdrawn just into the tube, and the tube was pressed down to the next measuring position. This approach protected the electrode against mechanical damage, at the same time minimizing the amount of soil entering the tube. The electrode was withdrawn and the tip cleaned between each pH measurement. The same steel probe was used for *in situ* measurements of oxygen and carbon dioxide. Oxygen measurements were made with a micro-Clark electrode protected by a hypodermic needle (Unisense OX-N, Århus, Denmark) as described in Alstrøm (2001) and Matthiesen *et al.* (2004). The O<sub>2</sub>-electrode was calibrated in air (100% saturation) and in de-aerated water (0% saturation). Carbon dioxide was measured with a MI-720 (Microelectrodes Inc., Bedford, NH, USA), which operates by measuring the pH in a thin layer of NaCO<sub>3</sub> trapped between the tip of a small pH sensor and a CO<sub>2</sub> permeable membrane (Cai & Reimers, 2000). The electrode was calibrated in a NaHCO<sub>3</sub> solution adjusted to various pH values with HCl.

For the upper 20 cm at the same sites, repeated pH measurements were made in detail with a handheld ISFET electrode (without the steel rod). To avoid carry-over (i.e. the transport of soil particles from one measuring point to the next) the entire electrode was cleaned thoroughly between each measurement. For every 5–10 measurements, the electrode was checked in a buffer, and if pH had changed more than 0.1 pH unit, the electrode was recalibrated.

Additional soil pH measurements were made using a standard glass electrode/calomel electrode system (pH meter Knick Porta test 655 and a pH electrode Metrohm 6.0233.100 after calibration in certified buffers of pH 4.01, 7.00 and 10.01). These soil-pH measurements (soil-pH<sub>standard</sub>) were made by pushing the electrode 2–3 cm directly into soil blocks cut from a soil profile (20 × 20 cm to a depth of 30 cm). The same blocks were used to obtain detailed CO<sub>2</sub> profiles with the MI-720 electrode. After measuring the ISFET pH profiles, soil samples were taken from the different soil layers for pH measurements in the laboratory (5, 10, 30, 50, 70, 90, 110, 130 and 150 cm).

The third method to characterize the pH was based on soil solutions collected by PRENART SUPER QUARTZ<sup>®</sup> suction probes installed 2, 10, 30 and 50 cm below the surface in one profile. The suction probes consist of PTFE mixed with silica flour, having a pore radius of 2 micrometres and a hydraulic conductivity of  $3.31 \times 10^{-7}$  cm s<sup>-1</sup>. The suction probes were connected by Teflon<sup>®</sup> tubes to 250-ml sampling bottles placed on the soil surface. To ensure high spatial and temporal resolution of the sampling (Grossmann & Udluft, 1991), small volumes (between 50 and 100 ml) were sampled over short intervals (typically 1–2 hours), with low suction in the probes (approximately 15 kPa). Conductivity and pH of the recovered water (solution – pH) were determined immediately, and alkalinity was determined by titrating with HCl within an hour. The rest of the water was stored in a cool and dark place until analysed in the laboratory at the University of Copenhagen in Denmark.

### Laboratory measurements

All pH measurements were made with a Metrohm 691-pH meter at 21–22°C and after at least daily calibration using certified buffers of pH 4.01 and 7.00. Measurements of soil pH were made on 10 g air-dried samples mixed with 25 ml double-deionized water. The suspension was shaken (using a shaking machine, 120 r.p.m.) in a 50-ml beaker for 50 minutes and left for 10 minutes before pH was measured in the solution above the sediment. Readings were taken when pH values changed by less than 0.1 within 30 s or after 30 s if pH values changed less than 0.02 pH within 5 s. Measurements were made in two replicates and repeated if the difference in pH was larger than 0.02 units. Total soil organic carbon (TOC) was measured after acidification (to remove inorganic C) using a dry combustion method at 1250°C (Eltra SC-500 analyser; ELTRA GmbH, Neuss, Germany) with an accuracy of ± 0.2%.

Similar measurements of pH were made directly in extracted soil solutions collected in the field. Acidified subsamples of extracted soil solution were analysed for dissolved Fe, Mn, Mg, Ca, K and Na by atomic absorption spectroscopy, and non-acidified subsamples were analysed for Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> by ion chromatography.

### Laboratory experiments

The sensitivity of the above protocol for pH measurements was investigated by changing one parameter at a time. Air-dried samples (10 g) were mixed with 10, 20, 25, 30, 50 and 100 ml double-deionised water. Air-dried samples (10 g) mixed with 25-ml double-deionised water were shaken for 10, 30, 50, 120, 240 and 1440 minutes. Samples without drying were mixed with double-deionised water to reach a ratio of 1 soil to 2.5 water (taking the initial water content into account), and air-dried samples were sieved at 2 mm prior to mixing with 25-ml double-deionised water. All experiments were made in triplicate.

### Model simulation

The solution of a CO<sub>2</sub> equilibrium problem with a computer program requires a routine to calculate ion activities from concentrations and mass balance equations. In order to simulate pH of the soil solution at steady state, input is required for CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) and inorganic C measured as alkalinity. The computer program PHREEQE for geochemical equilibrium calculations was used (Parkhurst *et al.*, 1980). The speciation program is based on thermodynamic data given for temperatures between 1 and 100 °C. Inputs for simulations include concentrations of dissolved chemicals, CO<sub>2</sub> partial pressure and temperature. For modelling the pH of the soil solution from the field site, the actual measured concentrations of Fe, Al, Mn, Mg, Ca, K, Na, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, as well as the observed soil and atmospheric contents of CO<sub>2</sub>, were used for the input file.

## Results and discussion

### Laboratory experiment

The effects of the dry soil to water ratio (varying from 1:1 to 1:10), total time of shaking (up to 24 hours) and pre-treatment of soil (drying and sieving) appear in Figure 1. Measurements of pH in the laboratory vary significantly with respect to both the protocol used and soil type. Consistent with Thomas (1996), the ratio of water to soil in the suspension has a significant effect of increasing pH as the ratio increases. However, in all cases the effect is less than expected due to a straightforward dilution of  $H^+$  concentration. This is probably a result of dissociation of  $H^+$ ,  $Al^{3+}$  and other cations from the soil surface as discussed by Thomas (1996). Exchangeable hydrogen is only of concern at pH less than 4, while exchangeable Al occurs at soil pH values less than approximately 5.5 (Bohn *et al.*, 2001). The most significant increase in pH due to dilution was found for the well-decomposed humus H horizon at the waterlogged site, while almost no effects on soil pH could be noted for the mineral B horizon at the field or forest sites. That means that the effect of exchangeable Al was most pronounced for the two latter soil samples.

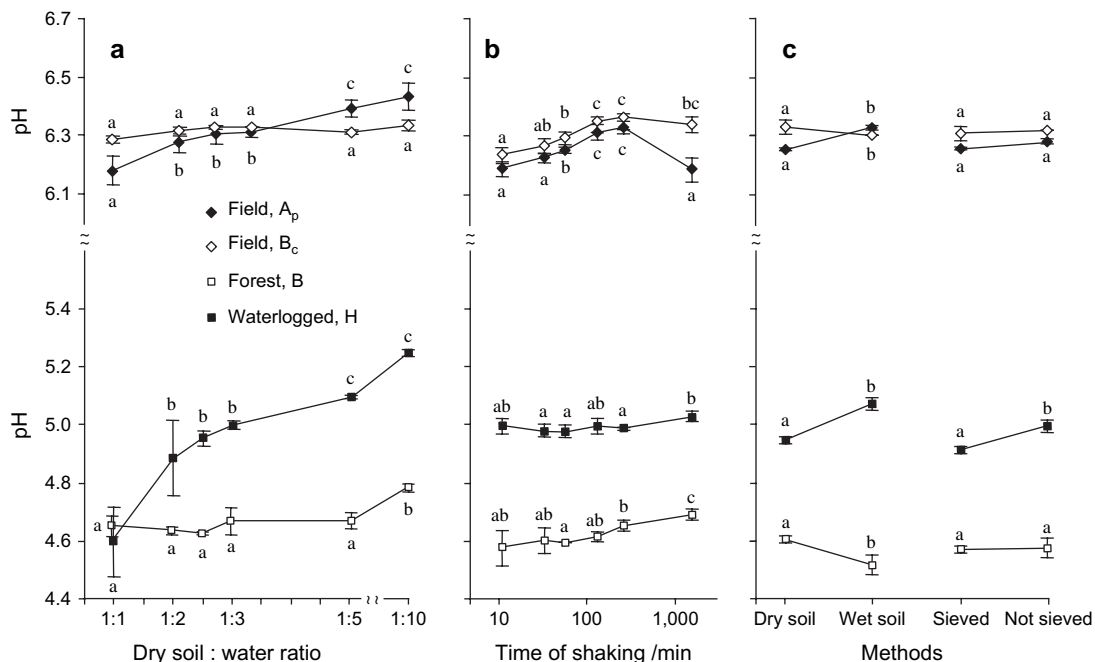
Effects of total shaking time are significant as well, and pH values increase with time. This suggests that the system approaches equilibrium conditions during shaking. However, for the two soils from the field site, the final pH readings after 24 hours decrease again in both cases. Significant effects of dry-

ing are evident for all four soils, but the most important issue is that the effects are inconsistent for the different soil types. The two mineral B horizons have both small organic carbon contents (Table 1) and greater pH values in air-dried samples compared with non-air-dried samples. The opposite was seen for near-surface samples from the field and the meadow. Effects of sieving are generally limited and only the waterlogged site reveals significant effects on pH following sieving.

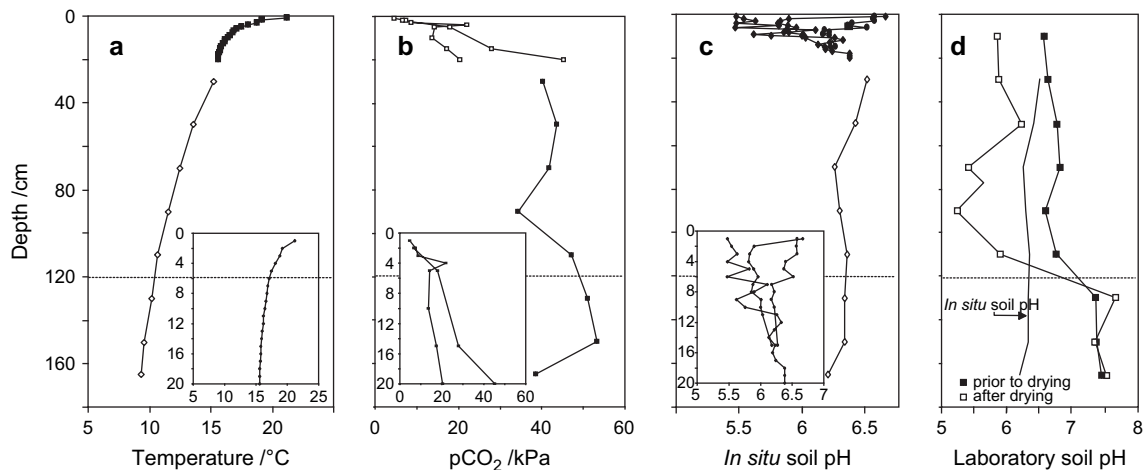
The main conclusions are that pH readings are sensitive to the methodology used, observed changes can be up to 0.6 in pH and that the absolute pH value is not important for the effect while the type of soil can be critical.

### Field versus laboratory pH measurements

Detailed soil profiles were made at Nydam and represent combined results on soil temperature,  $CO_2$  and  $O_2$  partial pressures and  $pH_{ISFET}$  (Figure 2). Oxygen profiles are not shown as the penetration depths of oxygen were consistently 3–5 cm. Over time, the depth of oxygen penetration probably varies with the water table. Repeated pH profiles at depths below 20 cm were very similar, while larger variations were noted for the upper 20 cm (Figure 2c). It is worth noting a fairly stable  $pH_{ISFET}$  level below 50 cm (approximately a pH value of 6.3) despite the change in soil composition from peat to gytja at approximately 120-cm depth. Comparisons between soil  $pH_{standard}$  and soil  $pH_{ISFET}$  measurements in blocks of soil measured in



**Figure 1** Results of pH measurements in the laboratory for (a) soils mixed with various amounts of water, (b) time of shaking prior to measurements, and (c) soil with and without drying and sieving prior to measurements. Standard errors are based on three replicates. If the vertical bars are not visible, the standard error is less than the symbol. Soil characteristics from the sites are presented in Table 1. Different letters represent significant effects of differences ( $P < 0.05$ ) tested by one-way ANOVA.



**Figure 2** Soil profiles in Nydam showing (a) temperature, (b) CO<sub>2</sub> partial pressure, (c) ISFET-pH measurements, and (d) laboratory pH values on depth-specific soil samples. In (d) the ISFET profile is included. Inserts in (a), (b) and (c) represent replicate profiles within the upper 20 cm of the soil profile. The dashed line indicates the lower boundary of peat covering the gytja.

the field reveal a high correlation ( $r = 0.94$ ) for the soil pH range present at Nydam (5.5–6.5).

For comparison, results from laboratory soil pH measurements are included (Figure 2d). Within the upper soil profile consisting of peat, soil pH values measured in 1:2.5 soil:water suspension with undried soil are consistently greater than soil pH measured *in situ*, while soil pH values measured in 1:2.5 soil:water suspension with the air-dried soil are consistently less. Below the peat and within the gytja both laboratory measurements are greater than soil pH measured *in situ*. The initial increase in soil pH measured in the laboratory (without soil drying) is in line with a smaller CO<sub>2</sub> partial pressure in the laboratory compared with the field values. Figure 2(d) reveals a deviation between field and laboratory measurements at the order of one pH unit and even greater between laboratory measurements. Assuming that  $pH_{ISFET}$  and soil  $pH_{standard}$  values represent the most accurate measure of soil acidity (in this case about 6.3), our results suggest that laboratory measurements may vary from 5.6 to 7.5. In other words, laboratory measurements may give different results for soil acidity, and results are not only biased by predictable degassing effects but also by soil-type specific effects, which in this case were not fully understood.

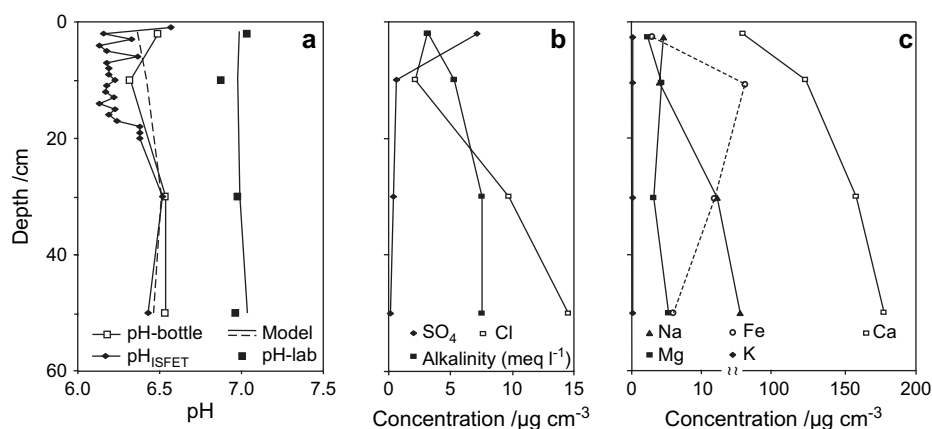
Other atmospheric gases than CO<sub>2</sub> may interact with the soil and soil solution as an aspect of laboratory handling. Oxygen dissolution in soil solutions extracted from wet soils may cause oxidation of dissolved ferrous-iron, causing acid production, and a decrease in pH as well as ferric hydroxide precipitation in the sampling bottle. This could explain the more acid pH observed in the laboratory after soil drying as compared with *in situ* measurements (Figure 2d), and is furthermore consistent with large concentrations of dissolved Fe as observed in water extracted from the soil (Figure 3c). The latter pH errors will probably also be unpredictable and controlled by site-

specific physical and chemical conditions, especially as ferrous Fe is present in solution as well as in solid phases depending on concentrations of other substances such as sulphate.

Ritvo *et al.* (2003) discussed deviations between field and laboratory soil pH measurements and suggested an empirical relationship to calculate *in situ* soil pH based on laboratory measurements. Ritvo *et al.* (2003) used waterlogged soil samples with variable amounts of carbonates, and laboratory pH measurements were made using dry re-wetted samples. The empirical relationship reported suggests that laboratory pH values are greater than *in situ* soil pH, which is in line with results from Nydam. However, results from Nydam suggest that the use of such relationships is limited, and it is unlikely that such empirical relationships represent other soil types than the one used for establishing the relationship.

#### *In situ soil pH versus pH measured on extracted water*

Water sucked from the soil solution may not ensure a representative water sample. The reason is that cation concentrations, including H<sup>+</sup> cations, are distributed in the diffuse double layer, near ionized organic groups and mineral edges, so that H<sup>+</sup> concentrations near soil colloid surfaces may be 100–1000 times greater than in the bulk solution (Bohn *et al.*, 2001). This means that the more powerfully soil water is sucked out (depending on the soil retention characteristics), the more acidic is the pH of the extracted water, everything else being equal. Figure 3(c) indicates that pH values measured in the extracted soil solution are slightly but consistently more alkaline than *in situ* soil pH values. The contrast between *in situ* soil pH values and measured pH in soil solution increases dramatically as the water is brought to the laboratory and allowed to equilibrate with the atmosphere. PHREEQE simulations reveal that the pH change in the soil solution is



**Figure 3** Chemical composition of soil solution extracted from suction probes at Nydam. (a) pH-bottle is that measured on the water solution immediately after collection in the field, while pH-lab is that measured in the laboratory after equilibration with the atmosphere. (b) Concentrations of anions and alkalinity (nitrate < 0.01 mg litre<sup>-1</sup>). (c) Major cations. pH measurements are compared with pH<sub>ISFET</sub> measurements prior to soil solution extraction. PHREEQE simulations ('Model') are included in (a) to predict the CO<sub>2</sub> degassing effect following equilibrium in the laboratory (thick solid line) as well as to predict *in situ* pH based on observed soil-pCO<sub>2</sub> (thick dashed line).

explainable by the degassing of CO<sub>2</sub> (Figure 3a). Subsequently, we used the PHREEQE model to back-calculate *in situ* pH based on measured pCO<sub>2</sub> values (Figure 2b). Results of such inverse modelling (Figure 3a) suggest that part of the deviation between *in situ* soil pH and soil solution pH is due to degassing.

### Conclusions and recommendations

Measurements of pH in the field can be made using ISFET, which seems to be non-destructive and not affected by degassing. Compared with other field-based pH measurements, the pH<sub>ISFET</sub> values are similar to pH measured by conventional electrodes inserted directly into the soil, but consistently less than pH measured in water extracted from the soil. In most soils, pH values are strongly influenced by the greater pCO<sub>2</sub> as compared with atmospheric conditions. Thus, pH measured in the laboratory on water and soil is affected by degassing and biased pH values, which are consistently greater (more alkaline) than under field conditions. Thus, soil acidification based on laboratory measurements is generally underestimated. At waterlogged sites, introduced atmospheric oxygen can initiate oxidation processes that may lead to H<sup>+</sup> cation producing processes such as Fe<sup>2+</sup> oxidation, and the net pH values obtained in the laboratory will be unpredictable.

When soil pH measured in the laboratory is compared with *in situ* measurements, deviations of more than one pH unit were observed, which indicates that conventional pH measurements using dried soil samples may give a completely different impression of the real field conditions.

As suggested by others, measurements of pH should, if possible, be made immediately in the field with as minimal an interaction with the atmosphere as possible. Field evaluation of pH

and soil acidification in saturated or near-saturated soils can be made using ISFET probes. For other soil types, soils should be brought to the laboratory after measuring depth-specific CO<sub>2</sub> concentrations. Samples should be handled as little as possible prior to pH measurements. No sieving or drying is necessary or desirable, and at least three replicate soil samples should be used to determine soil variability. The amount of water used to make a paste should be minimized, and soil-type specific effects should be kept in mind. If the soil pH is measured in order to characterize the soil environment, e.g. biological degradation, weathering or adsorption characteristics, only water sufficient to make a paste is needed, and the probe should be inserted into the paste. If soil pH measurements are taken in order to characterize infiltration water, more water is needed to produce the paste to ensure a pH reading in the water above the suspension. Due to the significant soil-type specific effects of the soil to water ratio, attempts to extrapolate dilution effects from one soil type to another should be avoided.

The complexity of pH and soil acidity requires future attention on the sensitivity of soil pH and future use of speciation models to calculate equilibrium conditions within the soil environment as most pH readings are taken between equilibrium conditions, consequently being of little use in predicting other soil processes. Knowing the *in situ* soil pCO<sub>2</sub> and pH measured in water in equilibrium with the atmosphere, the *in situ* soil pH values can be predicted successfully.

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## References

- Alström, T. 2001. The use of micro sensors for measurements of environmental parameters in wetland areas. In: *Proceedings of the 8th ICOM Group on Wet Organic Archaeological Materials Conference, Stockholm, 11–15 June 2001* (eds P. Hoffmann, J.A. Spriggs, T. Grant, C. Cook & A. Recht), pp. 225–229. International Council of Museums (ICOM), Committee for Conservation Working Group on Wet Organic Archaeological Materials, Bremerhaven, Germany.
- Andersson, S. & Nilsson, S.I. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. *Soil Biology and Biochemistry*, **33**, 1181–1191.
- Bates, R.G. 1978. Concept and determination of pH. In: *Treatise on Analytical Chemistry. Part 1, Volume 1* (eds I.M. Kolthoff & P.J. Elving), p. 821. Wiley-Interscience, New York.
- Bohn, H.L., McNeal, B.L. & O'Connor, G. 2001. *Soil Chemistry*, 3rd edn. John Wiley & Sons, New York.
- Brunning, R., Hogan, D., Jones, J., Jones, M., Maltby, E., Robinson, M. et al. 2000. Saving the Sweet Track. The *in situ* preservation of a neolithic wooden trackway, Somerset, UK. *Conservation and Management of Archaeological Sites*, **4**, 3–20.
- Cai, W.-J. & Reimers, C.E. 2000. Sensors for *in situ* pH and pCO<sub>2</sub> measurements in seawater and at the sediment–water interface. In: *In Situ Monitoring of Aquatic Systems. Chemical Analysis and Speciation* (eds J. Buffle & G. Horvai), pp. 75–119. Wiley-Interscience, New York.
- Caple, C. 1994. Defining a reburial environment: research problems characterising waterlogged anoxic environments. In: *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference* (ed. P. Hoffmann), pp. 407–421. International Council of Museums (ICOM), Committee for Conservation Working Group on Wet Organic Archaeological Materials, Bremerhaven, Germany.
- Caple, C. & Dungworth, D. 1998. *Waterlogged Anoxic Archaeological Burial Environments*. Report 22/98. English Heritage. Ancient Monuments Laboratory, London.
- Christensen, C. 1995. *Nydam Mose: Bassinets geologiske udvikling i relation til offerfundene*. National Museum of Environmental Archaeology (Nationalmuseets Naturvidenskabelige Undersøgelser) Report 11. National Museum of Denmark, Copenhagen (in Danish).
- Elberling, B. & Jakobsen, B.H. 2000. Soil solution pH measurements using in-line chambers with tension lysimeters. *Canadian Journal of Soil Science*, **80**, 283–288.
- Gregory, D., Matthiesen, H. & Björndal, C. 2001. *In situ* preservation of artefacts in Nydam Mose: studies into environment monitoring and the deterioration of wooden artefacts. In: *Proceedings of the 8th ICOM Group on Wet Organic Archaeological Materials. Conference* (eds P. Hoffmann, J.A. Spriggs, T. Grant, C. Cook & A. Recht), pp. 213–223. International Council of Museums (ICOM), Committee for Conservation Working Group on Wet Organic Archaeological Materials, Bremerhaven, Germany.
- Grossmann, J. & Udluft, P. 1991. The extraction of soil water by suction-cup method: a review. *Journal of Soil Science*, **42**, 83–93.
- Hogan, D.V., Simpson, P., Jones, A.M. & Maltby, D. 2001. Development of a protocol for the reburial of organic archaeological remains. In: *Proceedings of the 8th ICOM Group on Wet Organic Archaeological Materials Conference* (eds P. Hoffmann, J.A. Spriggs, T. Grant, C. Cook & A. Recht), pp. 187–212. International Council of Museums (ICOM), Committee for Conservation Working Group on Wet Organic Archaeological Materials, Bremerhaven, Germany.
- Houot, S., Topp, E., Yassir, A. & Soulas, G. 2000. Dependence of accelerated degradation of atrazine on soil pH in French and Canadian soils. *Soil Biology and Biochemistry*, **32**, 615–625.
- Imek, M. & Cooper, J.E. 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science*, **53**, 345–354.
- Jørgensen, E. & Petersen, P.V. 2003. Nydam bog – new finds and observations. In: *The Spoils of Victory – the North in the Shadow of the Roman Empire* (eds L. Jørgensen, B. Storgaard & L.G. Thomsen), pp. 258–285. National Museum, Copenhagen, Denmark.
- Laslett, G.M. & McBratney, A.B. 1990. Estimating and implications of instrumental drift, random measurements error and nuggets variance of soil attributes – a case study for soil pH. *Journal of Soil Science*, **41**, 451–471.
- Lofts, S., Woof, C., Tipping, E., Clarke, N. & Mulder, J. 2001. Modelling pH buffering and aluminium solubility in European forest soils. *European Journal of Soil Science*, **52**, 189–204.
- Madsen, H.-B. & Munk, I. 1987. The influence of texture, soil depth and geology on pH in farmland soils. *Acta Agricultural Scandinavica*, **37**, 407–418.
- Matthiesen, H. 2004. *In situ* measurement of soil pH. *Journal of Archaeological Sciences*, **31**, 1373–1381.
- Matthiesen, H., Gregory, D., Jensen, P. & Sørensen, B. 2004. Environmental monitoring at Nydam, a waterlogged site with weapon sacrifices from the Danish iron age. I. A comparison of methods used and results from undisturbed conditions. *Journal of Wetland Archaeology*, **4**, 55–74.
- Matthiesen, H., Hilbert, L.R. & Gregory, D. 2003. Siderite as a corrosion product on archaeological iron from a waterlogged environment. *Studies in Conservation*, **48**, 183–194.
- Parkhurst, D.L., Thorstenson, D.C. & Plummer, L.N. 1980. *PHREEQE – A Computer Program for Geochemical Calculations*. U.S. Geological Survey. Water Resources Investigation 80–96. USGS, Reston.
- Rieck, F. 2003. The ships from Nydam bog. In: *The Spoils of Victory – the North in the Shadow of the Roman Empire* (eds L. Jørgensen, B. Storgaard & L.G. Thomsen), pp. 296–309. National Museum, Copenhagen.
- Ritvo, G., Avnimelech, Y. & Kochba, M. 2003. Empirical relationship between conventionally determined pH and *in situ* values in waterlogged soils. *Aquacultural Engineering*, **27**, 1–8.
- Soil Survey Staff 1999. *A Basic System of Soil Classification for Making and Interpreting Soil Surveys*, 2nd edn. United States Department of Agriculture Handbook. Natural Resources Conservation Service Number 436. United States Department of Agriculture, Washington, DC.

- Sorensen, B. & Gregory, D. 1998. *In situ* preservation of artifacts in Nydam Mose. In: *Metal 98. Proceedings of the International Conference of Metals Conservation* (eds W. Mourey & L. Robbiola), pp. 94–98. James & James, London.
- Ste-Marie, C. & Paré, D. 1999. Soil, pH and N availability effects on net nitrification in the forest floors of a range of boreal forest stands. *Soil Biology and Biochemistry*, **31**, 1579–1589.
- Strobel, B.W., Borggaard, O.K., Hansen, H.C.B., Andersen, M.K. & Raulund-Rasmussen, K. 2005. Dissolved organic carbon and decreasing pH mobilize cadmium and copper in soil. *European Journal of Soil Science*, **56**, 189–196.
- Suarez, D.L. 1986. A soil water extractor that minimizes CO<sub>2</sub> degassing and pH errors. *Water Resources Research*, **22**, 876–880.
- Thomas, G.W. 1996. Soil pH and soil acidity. In: *Methods of Soil Analysis, Part 3, Chemical Methods* (ed. J.M. Bartels), pp. 475–490. Soil Science Society of America Book Series No 5. Soil Science Society of America, Madison, WI.
- Viscarra Rossel, R.A. & Walter, C. 2004. Rapid, quantitative and spatial field measurements of soil pH using an Ion Sensitive Field Effect Transistor. *Geoderma*, **119**, 9–20.
- Walter, C., Schwartz, C., Claudot, B., Bouedo, Th & Aourousseau, P. 1997. Synthèse nationale des analyses de terre réalisées entre 1990 et 1994. *Etude et Gestion Des Sols*, **4**, 205–220.
- Zabowski, D. & Sletten, R.S. 1991. Carbon dioxide degassing effects on the pH of spodosol soil solution. *Soil Science Society of America Journal*, **55**, 1456–1461.