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Soil pH

Background

pH determination in a soil suspension provides an estimate of the acidity of a solution in equilibrium with the soil. In the case of measurement in water, the measured pH may approach that of the soil solution.

In the methods below, the acidity is measured in a soil suspension using a combined electrode pH-meter. The soil:solution ratio will influence the results of soil pH measured in water; it is thus important to use a constant ratio and report it alongside the results. Soil pH measured in a salt solution is almost independent of variations in the soil:solution ratio (Conyers and Davey, 1988).

When measuring the pH of colloidal suspensions, the attraction of K^+ in the electrode solution for the negatively charged particles can produce a significant junction potential and an apparent pH decrease. Errors due to the liquid junction potential are minimized in flocculated suspensions and can be virtually suppressed by measuring pH in a dilute salt solution. The use of a dilute salt also eliminates the effects of small differences in electrolyte concentration without displacing a large fraction of the H^+ or Al^{3+} ions. For this reason, pH is commonly measured in (1) deionized water and (2) 0.01 M $CaCl_2$. In acidic soils, the pH of dilute $CaCl_2$ suspensions are usually about 0.2 to 0.5 units lower than pH_{water} (Schofield and Taylor, 1955).

pH is also routinely measured in 1 M KCl. pH_{KCl} is thought to represent a measure of exchangeable acidity since the concentrated KCl solution readily displaces Al from the exchange complex. As long as the cation exchange capacity exceeds the anion exchange capacity, ΔpH ($pH_{water} - pH_{KCl}$) should be positive and may be as high as 1 pH unit (Pansu and Gautheyrou, 2006).

pH should be measured as soon as possible after sampling on field-moist samples. Store samples in air-tight containers in the fridge prior to measurement.

Acid description	**pH**
Extremely acid	< 4.5
Strongly acid	4.5-5.5
Medium acid	5.6-6.0
Slightly acid	6.1-6.5
Neutral	6.6-7.3
Mildly alkaline	7.4-7.8
Medium alkaline	7.9-8.4
Strongly alkaline	8.5-9.0
Extremely alkaline	> 9.1

Safety/ Protective equipment

** This procedure involves handling of pH4 (acid) and 10 (caustic) buffer solutions.*

Labware/ Reagents

pH meter	Deionized water
Volumetric flask 1L	0.01 M $CaCl_2$ *(Dissolve 1.1 g of $CaCl_2$ (1.5 g $CaCl_2 \cdot 2H_2O$) in deionized water. Adjust volume to 1L in a volumetric flask)*
Spatula	1 M KCl *(Dissolve 74.6 g of KCl in in deionized water. Adjust volume to 1 L in a volumetric flask)*
50 mL centrifuge tubes	pH 4, 7, +/- 10 buffer solutions

pH meter calibration

- Using the correct technique to avoid exposure to atmospheric air, pour a small amount of pH 4, 7 and 10 buffer solution in the corresponding 20 mL bottle. Contact with air can alter the pH of the buffer solution over time. Replace the contents of the 20 mL bottles every 2 weeks.
- Rinse the pH electrode with deionized water. Blot dry using a Kimwipe. Do not rub or wipe as this creates static electricity that interferes with measurement.
- Turn on the pH meter.
- Follow the instrument-specific calibration protocol.
- Rinse the electrode and blot dry.

pH measurement in water

1. *Setup*

- Work in batches of 4-6 samples.
- Line up and number centrifuge tubes.
- Using a spatula, weigh 6 +/- 0.1 g of soil sample into the tubes.
- Add 15 mL of water to each tube using a graduated cylinder (1:2.5 soil:solution ratio; see AFNOR standard NF X-31-103, 1998).
- Close the tubes and set on the agitation table at low speed for 30 min (e.g., 200 rpm; see Qiu and Zhu, 1986).
- Take the tubes off the table and set upright. Allow the suspension to decant for 30 min.

Notes:

- ✓ Don't forget to include a batch of analytical replicates every 5-10 batches (10-20% replicates)
- ✓ Organic samples tend to form a thick slurry at a soil:solution ratio of 1:2.5. A lower ratio must then be accepted (e.g. 1:5).

2. *pH measurement*

- Measure pH by inserting the tip of the electrode into the supernatant. The tip of the electrode should be submerged, but should not come in contact with the slurry at the bottom of the tube.
- Wait for a stable reading.
- Record the sample number, solution type and pH reading to one decimal place.
- Rinse the electrode with deionized water and gently blot dry with a Kimwipe.
- Repeat for other samples.
- At the end of each batch, check the pH of the first sample to ensure that there was no drift.
- At the end of the analysis, clean, dry and store the electrode back in the appropriate junction solution. The electrode should never be allowed to dry. Close the filling opening (small hole on the electrode body).

3. *Cleanup*

- Re-suspend soil and discard the slurry into the soil waste bucket.
- Rinse centrifuge tubes with tap water until all traces of soil are gone.
- Rinse 3 times with deionized water.
- The tubes can then be re-used for the next batch of samples **of identical matrix** (*e.g.*, pH_{water}, pH_{CaCl2}, etc.)

pH measurement in 0.01 M CaCl2 and 1 M KCl

Repeat the measurements in 1:2.5 soil: $CaCl_2$ or soil: KCl suspensions.

pH measurement in NaF

This measurement is used to identify the presence of substances with short-range order, particularly reactive Al forms. The principle of the measurement is a consequence of the reactions:

$$Al(OH)_3 + 6\ NaF \rightarrow Na_3AlF_6 + 3\ NaOH$$
$$Al_2SiO_3(OH)_4 + 12\ NaF + 3\ H_2O \rightarrow 2\ AlF_6^{3-} + 6\ OH^- + 12\ Na^+ + H_4SiO_4$$

The release of OH^- ions causes an increase in pH. A pH of more than 9.5 indicates an abundant presence of reactive Al forms. The test is indicative for most andic horizons, except for those very rich in organic matter. See Pansu and Gautheyrou (2006) for the procedure.

References

Conyers MK and Davey BG (1988) Observation on some routine methods for soil pH determination. *Soil Sci* 145:29-36.

Pansu M and Gautheyrou J (2006) *Handbook of soil analysis*. Springer-Verlag: Berlin.

Qiu X-C and Zhu Y-Q (1986) Spectrophotometric determinations of pH value, buffer capacity and rate of lime need in acidic soil, using chrysoidine as a chromogenic agent. *Soil Sci* 142:275-278.

Schofield RK and Taylor AW (1955) The measurement of soil pH. *Soil Sci Soc Am Proc* 19:164-167.