

A horizontal standard for pH measurements – The influence on pH measurements of sample pretreatment, ionic composition / ionic strength of the extractant and centrifugation / filtration

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The starting point of this study was the fact that pH in soils is usually measured in suspensions of air-dry samples, using either high quality water (≤ 0.2 mS/m at 25°C; EN ISO 3696:1997), or a solution of a neutral salt (0.01 M CaCl₂ or 1 M KCl) as an extractant, all according to ISO 10390 (1995). pH in sludge according to EN 12176 (1998) or biowaste according to EN 13037 (1999) is usually measured in water extracts of fresh samples. Using the same methodology for soils as for sludge or biowaste would facilitate comparisons of these three materials. However, soil pH values measured in fresh samples after water extraction would be difficult to compare with most of the pH values previously collected in soils worldwide, particularly as these latter values are mostly based on air-dry samples and 0.01 M CaCl₂ as an extractant, although some pH measurements in H₂O extracts of air-dry samples have also been made.

In this study we compared pH values in fresh and air-dry (40° C) samples of soil, sludge and compost (biowaste). We used 10 soils, 2 types of sewage sludge and 1 compost sample. Our main aim was to test different pretreatment and extraction procedures with respect to their feasibility and their effects on the repeatability (i.e. robustness) of the measured pH values.

The reason for the choice a small number of sludge and biowaste samples compared to the number of soil samples was that the former two materials are generally strongly influenced by their high organic matter content. For instance the organic carbon content in several sewage sludge materials in southern Sweden varied between 22 and 32% on a dry weight basis (Åslund 2000), which was similar to the organic carbon content of the sludge materials used in this study (about 30%). However, pH values and buffer capacities in soils are dependent on both organic matter content, clay content, clay mineralogy and chemical interactions between organic matter and clay.

We used either high quality distilled H₂O as defined above, 0.01 M CaCl₂ or 1M KCl as an extractant. To facilitate comparisons between the different materials we consistently used a volume ratio of substrate : extractant = 1:5 according to the present standard ISO 10390 (1995) for soil pH and EN 13037 (1999) for pH in treated biowaste.

We used two different extraction procedures. In both cases samples were shaken on an end-over-end shaker and were then allowed to stand in room temperature for a maximum of 24 hours. In the first extraction procedure the samples were thereafter thoroughly shaken for a few minutes and pH was immediately measured in the suspensions. In the second procedure the samples were centrifuged and the supernatants were then filtered through a 0.45 µm Millipore filter before pH was measured. The latter alternative was used to remove substrate particles and colloids from the supernatant, and test the influence of this treatment on the measured pH values and the robustness of the measurements. All pH measurements took place at 22°C. Buffer solutions of pH 4.00 and 7.00 were used for the calibration. For each of the 10 soil samples, 2 sewage sludge samples and the compost sample, there were 12 combinations, i.e. 2 moisture regimes (fresh and air-dry) x 3 extractants x 2 modes of suspension treatment. In each of these combinations pH was measured on 6 subsamples, i.e. the total number of pH measurements was 72 per sample. In all, this amounted to totally 13 x 72 = 936 pH measurements.

The data obtained for each sample are presented as arithmetic means, pH ranges expressed as such, and ranges expressed as pH units. The latter type of data are used as estimates of the robustness. We have used the following recommendations for acceptable differences in pH

units between the highest and lowest sample pH, which are presently applied to soil samples according to ISO 10390 (1995):

Table 1. Acceptable pH difference (Diff) according to ISO 10390

<u>pH range</u>	<u>Diff</u>
< 7.00	0.15
7.00 – 7.50	0.20
7.50 – 8.00	0.30
> 8.00	0.40

Table 2. Brief description of the 10 soils

Locality and soil	Fertilizer treatment	Soil classification according to Soil Taxonomy	Clay as % dry weight of fine earth (particles < 2 mm)	Organic carbon as % dry weight of fine earth (particles < 2 mm)
1. Vreta kloster, E9	Farmyard manure	Not classified	50	2.1
2. Högåsa, E10	- ” -	- ” -	10	2.0
3. Bjertorp, R 94	- ” -	- ” -	30	2.0
4. Ekebo, M6, Plot 1	- ” -	Eutrochrept	14	2.7
5. Ekebo, M6, Plot 2	- “ -	- “ -	14	2.3
6. Fjärdingslöv, M1	Mineral fertilizer	Hapludoll	17	1.4
7. Asa, Forest floor Oe layer	Not fertilized	Haplorthod	-	
8. Asa, upper A/E horizon	- “ -	- “ -	5	
9. Asa, lower A/E horizon	- “ -	- “ -	5	
10. Asa B horizon	- “ -	- “ -	4	

Samples 1 – 6 are collected from the Ap horizon of arable soils used for long-term crop nutrition trials. Data from Carlgren & Mattson, (2001); Samples 7-10 are collected from different soil horizons in a forest stand of Norway spruce. Data from Berggren et al., (2004).

Table 3. Origin of sludge and compost

Sludge 1	Uppsala Waterworks
Sludge 2	Stockholm Water Waterworks;
Compost	Garden compost Uppsala

All pH data are shown in Appendix 1. As expected, the general trend was that $pH_{\text{fresh samples}} > pH_{\text{air-dry samples}}$, and that $pH_{\text{H}_2\text{O}} > pH_{\text{salt solution}}$. $pH_{1\text{M KCl}}$ was usually less than $pH_{0.01\text{M CaCl}_2}$, although exceptions were found among the samples with the highest pH values probably because already 0.01 M CaCl_2 extracted the low amount of exchangeable acidity that would be typical for these samples (cf. Andersson, Nilsson and Jennische 2003). The changes in average pH in sludge or compost caused by either air-drying or the use of neutral salt solutions instead of water amounted to approximately 0.1 – 0.6 pH units.

The most satisfying robustness for soils was obtained for air-dry soils when pH was measured directly in soil suspensions. Centrifugation plus filtration yielded a less satisfactory robustness. Several of the pH differences (highest value minus lowest value) were beyond the permissible ranges shown in Table 1 when the latter procedure was used.

Concerning the two sludge materials and the compost material the robustness was slightly better in air-dry samples compared to fresh samples. There was a rather small difference in robustness between measurements in suspensions and measurements after centrifugation + filtration.

Recommendations for a horizontal standard

The new standard should be based on ISO 10390 (present standard for soils), EN 12176 (present standard for sewage sludge) and EN 13037 (present standard for biowaste).

For practical reasons, for instance the need to facilitate relevant comparisons with previous measurements, soils should generally be air-dried, even if fresh samples would represent the conditions in the field in a better way (Andersson, Nilsson & Jennische 2003). Air-drying can be used for all soils with one important exception: *pH in soils which contain sulphidic material should be measured on fresh samples* to avoid sulphide oxidation resulting in the formation of sulphuric acid. Whenever sulphidic soils are to be compared with other soils the comparison should preferably be based on fresh soil samples.

High-quality distilled H_2O (≤ 0.2 mS/m at 25°C) and 0.01 M CaCl_2 should be used as extractants. We see no obvious advantage of using 1 M KCl as an extractant for routine measurements of pH, although it is recommended for *quantitative* determinations by titration, of exchangeable acidity. The ionic strength of the KCl solution (1 M) seems rather unrealistic for pH measurements in soil. 0.01 M CaCl_2 (ionic strength 0.03 M) would be closer to the expected ionic strength in soil solutions and is therefore the most reasonable choice of a neutral salt extractant. We recommend that extractions with H_2O and 0.01 M CaCl_2 should as far as possible be made on the same sample, to allow pH comparisons to be made between extractants and to some extent also between different materials (soil versus sludge or biowaste).

Concerning sludge and biowaste, fresh samples should be preferred and H_2O should be used as an extractant, in order to facilitate comparisons with previous measurements. It should be noted that according to our measurements air-drying seems to give a slightly better robustness than is obtained for fresh samples, but air-drying might also introduce artifacts due to stimulation of oxidation processes and should therefore be avoided.

Literature references:

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Appendix 1

Measured average pH values. The pH range for each sample and procedure is shown within brackets. Δ expresses the range in pH units and is an estimate of the repeatability (robustness). Non-acceptable pH differences according to Table 1 are marked with figures written in **bold**. 'Susp' indicates direct measurements in the suspensions. 'Centr' indicates that measurements are preceded by centrifugation plus filtration of the suspensions.

SOILS

Air -dry samples

No	H ₂ O/susp	CaCl ₂ /susp	KCl/susp
1	6.62 (6.56 -6.65)	6.17 (6.15-6.19)	5.52 (5.49-5.54)
	Δ 0.09	0.04	0.05
2	6.21 (6.18-6.23)	5.73 (5.72-5.74)	5.58 (5.56-5.61)
	Δ 0.05	0.02	0.05
3	6.34 (6.33-6.37)	5.88 (5.86-5.90)	5.49 (5.48-5.51)
	Δ 0.04	0.04	0.03
4	5.52 (5.51-5.55)	5.10 (5.08-5.11)	4.80 (4.79-4.81)
	Δ 0.04	0.03	0.02
5	5.87 (5.83-5.91)	5.47 (5.46-4.48)	5.18 (5.17-5.19)
	Δ 0.08	0.02	0.02
6	6.61 (6.59-6.65)	6.29 (6.26-6.34)	5.83 (5.81-5.85)
	Δ 0.06	0.08	0.04
7	4.53 (4.47-4.56)	3.44 (3.42-3.45)	3.23 (3.22-3.24)
	Δ 0.09	0.03	0.02
8	4.14 (4.13-4.16)	3.41 (3.40-3.42)	3.45 (3.44-3.46)
	Δ 0.03	0.02	0.02
9	4.54 (4.53-4.55)	3.90 (3.89-3.91)	3.95 (3.95-3.96)
	Δ 0.02	0.02	0.01
10	4.88 (4.87 -4.89)	4.28 (4.27-4.29)	4.28 (4.27-4.29)
	Δ 0.02	0.02	0.02

SOILS

Air -dry samples

No	H ₂ O/centr	CaCl ₂ /centr	KCl/centr
1	6.80 (6.77-6.83)	6.40 (6.34-6.44)	5.77 (5.69-5.84)
	Δ 0.06	0.10	0.15
2	6.40 (6.37-6.42)	5.99 (5.93-6.12)	5.76 (5.68-5.80)
	Δ 0.05	0.19	0.12
3	6.63 (6.58-6.66)	6.19 (6.05-6.25)	5.70 (5.65-5.77)
	Δ 0.08	0.20	0.12
4	5.66 (5.64 -5.67)	5.24 (5.22-5.27)	4.85 (4.82-4.90)
	Δ 0.03	0.05	0.08
5	6.09 (6.05-6.14)	5.70 (5.67-5.76)	5.27 (5.21-5.29)
	Δ 0.09	0.09	0.08
6	6.78 (6.77-6.80)	6.21 (5.64-6.39)	6.03 (6.03-6.04)
	Δ 0.03	0.75	0.01

7	4.61 (4.52-4.66)	3.52 (3.51-3.57)	3.29 (3.26-3.37)
Δ	0.14	0.06	0.11
8	4.13 (4.12-4.14)	3.47 (3.46-3.48)	3.46 (3.44-3.48)
Δ	0.02	0.02	0.04
9	4.56 (4.55-4.58)	3.96 (3.95-3.96)	3.98 (3.95-4.06)
Δ	0.03	0.01	0.11
10	4.90 (4.88-4.92)	4.32 (4.32-4.34)	4.27 (4.25-4.28)
Δ	0.04	0.02	0.03

SOILS

Fresh samples

No	H ₂ O/susp	CaCl ₂ /susp	KCl/susp
1	6.69 (6.64 -6.75)	6.10 (6.01-6.25)	5.56 (5.33-5.94)
Δ	0.11	0.0	0.61
2	6.36 (6.31-6.44)	5.73 (5.68-5.76)	5.60 (5.57-5.68)
Δ	0.13	0.08	0.11
3	6.30 (6.24-6.34)	5.78 (5.76-5.80)	5.39 (5.36-5.42)
Δ	0.10	0.04	0.06
4	5.51 (5.49-5.52)	5.05 (5.03-5.08)	4.75 (4.72-4.77)
Δ	0.03	0.05	0.05
5	5.94 (5.90 -6.03)	5.41 (5.40-5.43)	5.22 (5.18-5.28)
Δ	0.13	0.03	0.10
6	6.66 (6.63-6.68)	6.07 (6.06-6.08)	5.78 (5.76-5.81)
Δ	0.05	0.02	0.05
7	4.76 (4.66-4.81)	3.55 (3.54-3.58)	3.44 (3.43-3.45)
Δ	0.15	0.04	0.02
8	4.25 (4.23-4.26)	3.47 (3.47-3.49)	3.53 (3.52-3.55)
Δ	0.03	0.02	0.03
9	4.57 (4.55-4.59)	3.94 (3.92-3.95)	4.02 (4.01-4.03)
Δ	0.04	0.03	0.02
10	4.83 (4.81 -4.86)	4.32 (4.30-4.33)	4.33 (4.32-4.35)
Δ	0.05	0.03	0.03

SOILS

Fresh samples

No	H ₂ O/centr	CaCl ₂ /centr	KCl/centr
1	7.07 (6.83-7.34)	6.31 (6.21-6.55)	5.74 (5.47-6.32)
Δ	0.51	0.34	0.85
2	6.54 (6.50-6.62)	5.82 (5.77-5.87)	5.72 (5.65-5.84)
Δ	0.12	0.10	0.19
3	6.55 (6.49-6.59)	5.89 (5.82-5.94)	5.52 (5.48-5.56)
Δ	0.10	0.12	0.08
4	5.56 (5.55-5.58)	5.09 (5.06-5.15)	4.76 (4.72-4.78)
Δ	0.03	0.09	0.06
5	6.03 (5.98-6.10)	5.50 (5.48-5.54)	5.27 (5.21-5.35)
Δ	0.12	0.06	0.14

6	6.67 (6.65-6.70)	6.12 (6.10-6.16)	5.85 (5.83-5.89)
Δ 0.05	0.06	0.06	
7	4.74 (4.63-4.89)	3.55 (3.55-3.57)	3.46 (3.45-3.47)
Δ	0.26	0.02	0.02
8	4.24 (4.23 -4.25)	3.46 (3.45-3.48)	3.53 (3.51-3.56)
Δ 0.02	0.03	0.05	
9	4.57 (4.56-4.58)	3.94 (3.93-3.95)	4.03 (4.02-4.05)
Δ 0.02	0.02	0.03	
10	4.87 (4.83-4.92)	4.30 (4.28-4.32)	4.34 (4.33-4.35)
Δ 0.09	0.04	0.02	

SLUDGE AND COMPOST

Fresh samples

No	H ₂ O/susp	CaCl ₂ /susp	KCl/susp
Sludge 1	7.79 (7.74 -7.83)	7.51 (7.37-7.58)	7.49 (7.44-7.59)
Δ 0.09		0.21	0.15
Sludge 2	7.42 (7.41-7.43)	7.07 (7.04-7.11)	7.21 (7.18-7.25)
Δ 0.02	0.07	0.07	
Compost	8.82 (8.79-8.86)	8.18 (8.06-8.35)	8.04 (7.92-8.15)
Δ 0.07	0.29	0.23	

Fresh samples

No	H ₂ O/centr.	CaCl ₂ /centr.	KCl/centr.
Sludge 1	7.85 (7.82-7.92)	7.61 (7.57-7.63)	7.58 (7.53-7.65)
Δ 0.10	0.06	0.12	
Sludge 2	7.60 (7.59-7.61)	7.30 (7.29-7.32)	7.36 (7.34-7.40)
Δ 0.02	0.03	0.06	
Compost	8.68 (8.64-8.72)	8.19 (8.09-8.32)	7.87 (7.10-8.10)
Δ 0.08	0.23		1.00

SLUDGE AND COMPOST

Air-dry samples

No	H ₂ O/susp	CaCl ₂ /susp	KCl/susp
Sludge 1	7.17 (7.14 -7.22)	7.03 (6.99-7.08)	7.21 (7.19-7.23)
Δ	0.08	0.09	0.04
Sludge 2	7.20 (7.15-7.23)	6.93 (6.92-6.95)	7.02 (7.01-7.04)
Δ 0.08	0.03	0.03	
Compost	8.59 (8.53-8.64)	8.15 (8.13-8.18)	8.10 (8.08-8.13)
Δ 0.11	0.05	0.05	

Air -dry samples

No	H ₂ O/centr.	CaCl ₂ /centr.	KCl/centr.
Sludge 1	7.27 (7.22 -7.33)	7.21 (7.17-7.23)	7.33 (7.31-7.35)
Δ 0.11	0.06	0.04	
Sludge 2	7.36 (7.33-7.44)	7.08 (7.07-7.11)	7.16 (7.15-7.17)
Δ 0.11	0.04	0.02	
Compost	8.59 (8.55-8.62)	8.16 (8.14-8.18)	8.05 (8.02-8.08)
Δ 0.07		0.04	0.06