Determination of Soil pH in Dominant Soil Types in the Republic of Croatia

Darija ČAPKA
Ivica KISIĆ (✉)
Željka ZGORELEC
Milan MESIĆ
Aleksandra JURIŠIĆ

Summary

Soil pH is a basic soil parameter, since many processes in the soil depend on it, such as the growth and development of plants. Therefore, the monitoring of soil pH is very important. In this paper the values of soil pH are obtained by measurement of the samples in three media: H_2O, KCl and $CaCl_2$. The sampling was conducted at 18 locations on 11 soil types and 15 lower systematic units. The aim of this work was to establish functional connections between the pH values in all three media.

Repeatability of measurement expressed through the relative standard deviation, ranged from 0.21% to 3.87% in the H_2O suspension, from 0.19% to 7.74% in the KCl suspension and from 0.25% to 4.19% in the $CaCl_2$ suspension.

Correlation coefficients varied in the classes: strong, very strong and absolute. The correlation coefficients for all measured samples were: r=0.96 for the pH KCl/H_2O; r=0.97 for the pH KCl/$CaCl_2$ and r=0.99 for the pH H_2O/$CaCl_2$ (absolute correlation). The correlation coefficients determined in the acid soils were: r=0.97 for the pH KCl/$CaCl_2$ and pH H_2O/$CaCl_2$; r= 0.91 for the pH KCl/H_2O (absolute correlation). In the neutral soils, the correlation coefficient for the pH KCl/$CaCl_2$ was r=0.69 (strong correlation), correlation coefficient for the pH KCl/H_2O was r=0.80 (very strong correlation) and the correlation coefficient for the pH H_2O/$CaCl_2$ was r=0.92 (absolute correlation). In the alkaline soils, the correlation coefficient for the pH KCl/$CaCl_2$ and pH KCl/H_2O was r=0.66 (strong correlation), and correlation coefficient for the pH H_2O/$CaCl_2$ was r=0.88 (very strong correlation).

The existence of alleged functional connections through this work has been proven with very high significance.

Key words

soil pH, soil type, Croatia

University of Zagreb, Faculty of Agriculture, Department of General Agronomy, Svetošimunska 25, 10000 Zagreb, Croatia
✉ e-mail: ikisic@agr.hr

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Introduction

Soil pH is a very important soil characteristic. All formation factors of the soil (parent material, climate, relief, pedogenetic and organisms) have influence on the soil pH, although the largest changes in a very short period, either positive or negative, can be caused by human activities. Most soil processes depends on the value of soil pH, and this reflects also to all pedoecological characteristics. Especially important is the activity of nitrifiers and nitrogen fixators. Its activity depends on the soil pH, as well as the growth and development conditions of all organisms. Formation of humus, cation exchange capacity, oxide-reduction processes, the dynamics of plant nutrients, the range and the optimum of plant nutrients receiving are also connected with the soil pH. Therefore, the pH value is an important factor of plants growth and development. Due to the great coherence with the pedogenetic (soil forming processes) and pedoecological characteristics, the soil pH is an irreplaceable information in the interpretation of the various aspects of soil treating. Determination of soil pH belongs to the basic soil information and therefore it is obligated and the first method in soil analysis. It would be the best to measure the pH value in natural conditions, but it is unsuccessful even at the moisture of a field capacity due to the insufficient contact of electrodes and suspensions. Therefore, the determination of soil pH is usually conducted in a suspension or filtrate, by colorimetric or electrometric method. Determination in a suspension can be conducted in three media: H_2O suspension - for pedogenetic and pedodinamic conclusions, and in the KCl or $CaCl_2$ suspension, for the ecological purposes. The samples were presenting the types of soil that are most common in the Republic of Croatia (Husnjak et al., 2005; Čapka, 2007), and they are divided by their evolution-genetic horizons. Statistical analysis was conducted for the whole range and for the three groups of soil according to their acidity determined in KCl: acid, neutral and alkaline soils (Škorić, 1990; 1991; Martinović, 2000).

Material and methods

Research locations and sampling

Sampling was conducted at 18 locations with the dominant types of soil by their evolution-genetic horizons: in the vicinity of Zalesina (Podzol[1] – Haplic Podzols[2]); Fužine (Calcocambisol[1] – Calcic Cambisols[2]); Delnice (Rendzina, leached[1] – Rendzic Leptosols[2]); Vodnjan (Calcocambisol[1] - Calcic Cambisols[2]); Tinjan near Poreč (TerraRossa[1] –Rhodic Cambisols[2]); Ripenda near Plomin (Rendzina, brownish[1] - Rendzic Leptosols[2]); Stružec near Popovača (Pseudogley[1] – Stagnic Gleysols[2]); Gospić - Veliki Žitnik (Brown dystric[1] - Dystric Cambisols[2]); Kneževo in Baranja (Chernozem[1] - Kastenozems[2]); Bilje near Osijek (Semigley, calcareous[1] – Gleyic Fluvisols[2]); Ivanovec near Osijek (hydromorphous Black soil, calcareous[1] – Humic Gleysols[2]); Đakovo (Brown eutric[1] – Eutric Cambisols[2]); Županja (Epigley non-calcareous[1] - Gleysols[2]); Zagreb, in floodplain of the Sava River, near the Cvjetno settlement – (Alluvial soil[1] - Calcaric Fluvisols[2]) and in surroundings of the gas wells Molve 10 (Semigley, non-calcareous[1] - Gleyic Fluvisols[2]); Molve 11 (Epigley[1] - Gleysols[2]), Molve 12 (Eugley, amfigley, vertic[1] – Haplic Gleysols[2]) and Molve 14 (Sirozem-regosol[1] –Haplic Regosols[2]) (Husnjak et al., 2005). Sampling, transport and preservation of samples were conducted in a compliance with the protocol ISO 10381 from 1 - 8 (1993-2006) and Mesić et al., 2006.

Preparation of samples and analysis of pH

Preparation of samples was conducted in a compliance with the protocol HRN ISO 11464:2004. Analysis of pH values was conducted in a compliance with the protocol HRN ISO 10390:2005 in the laboratory of the Department of General Agronomy, Faculty of Agriculture, University of Zagreb. The soil pH was measured using the electrometric method with the Beckman pH-meter Φ 72, in three different suspensions: H_2O, KCl and $CaCl_2$.

Results and discussion

Statistical analysis was performed for the whole range of samples and for the three groups of soil samples according to their acidity determined in KCl: acid, neutral and alkaline soils. The basic statistical parameters: minimum, maximum, arithmetic mean and relative standard deviation were calculated. The functional dependence of pH values in H_2O, KCl and $CaCl_2$ was calculated by method of linear regression, also as the correlation of pH value in different suspensions.

Results of soil pH (minimum - min, maximum - max, arithmetic mean - mean, relative standard deviation - RSD,%) measured in the suspensions of H_2O, KCl and $CaCl_2$ are shown in Table 1 for the acid soils, in Table 2 for the neutral soils and in Table 3 for the alkaline soils.

pH values of samples belonging to the acid soils

The group of the acid soils includes 10 soil types or 33 horizons (pH ≤ 6.5). The lowest values were recorded in H_2O (4.10) and in $CaCl_2$ (3.27) at the Zalesina location (A horizon) and in KCl (3.03) at the Zalesina location (E horizon). The highest values were recorded in H_2O (7.59) and $CaCl_2$ (6.87) at the Đakovo location [horizon B(v)] and in KCl (6.35) at the Fužine location [horizon B(v)].

pH values of samples belonging to the neutral soils

The group of the neutral soils includes 5 soil types or 7 horizons (pH = 6.5-7.2). The lowest values were measured in all three media at the Kneževo location (Amo horizon) and the range was from 6.69 to 7.54. The highest values were measured in all three media at the different locations: in H_2O (8.16) at the Županja location (Gr/so horizon), in $CaCl_2$ (7.24) at the Ivanovac location (Aa horizon) and in KCl (7.19) at the Ripenda location in Istria County (Ap horizon).

pH values of samples belonging to the alkaline soils

The group of the alkaline soils includes 6 soil types or 11 horizons (pH ≥ 7.2). The lowest values were measured in all three media at the different locations: in H_2O (7.99) at the lo-

[1] Croatian classification according to Škorić, 1985.
[2] Classification according to World reference base for soil resources, 2006.

Table 1. The soil pH of the acid soil samples in the suspension of H_2O, KCl and $CaCl_2$ (n=5)

Mark	Location	Horizon, depth (cm)	pH/H_2O				pH/KCl				pH/$CaCl_2$			
			min	max	mean	RSD,%	min	max	mean	RSD,%	min	max	mean	RSD,%
1	Zalesina	A (0-12)	4.06	4.19	4.10	1.32	2.99	3.10	3.05	1.34	3.19	3.31	3.27	1.51
2		E (12-20)	4.09	4.30	4.15	2.02	2.94	3.08	3.03	1.91	3.31	3.39	3.35	1.22
3		Bh (20-50)	4.51	4.70	4.60	1.67	3.80	3.86	3.83	0.68	3.83	4.03	3.92	1.96
4	Fužine	Aoh (0-5)	6.84	6.96	6.90	0.66	6.17	6.30	6.25	0.85	6.21	6.37	6.31	1.01
5		(B)v(5-30)	7.23	7.33	7.29	0.55	6.28	6.44	6.35	0.97	6.40	6.52	6.48	0.74
6	Delnice	A (0-5)	6.70	6.90	6.81	1.06	5.93	6.01	5.97	0.59	6.04	6.25	6.16	1.35
7		C (5-30)	6.97	7.19	7.06	1.22	5.18	5.27	5.24	0.70	5.81	5.90	5.85	0.55
10	Tinjan	A (0-40)	6.79	7.12	6.97	1.70	4.87	4.98	4.93	0.90	5.55	5.69	5.62	1.00
11		I-C(40-120)	6.88	7.06	6.97	0.95	5.15	5.72	5.29	4.60	5.78	5.92	5.86	1.21
14	Stružec	P (0-30)	7.24	7.54	7.39	1.48	5.85	6.23	6.03	2.78	6.46	6.65	6.56	1.07
15		E/Bt (30-58)	6.16	6.53	6.27	2.35	4.30	4.61	4.49	2.73	5.23	5.46	5.29	1.80
16		Btg (58-80)	5.97	6.12	6.06	0.97	3.99	4.20	4.11	2.07	4.78	4.95	4.87	1.34
17	Veliki	P (0-22)	5.25	5.37	5.28	0.93	4.00	4.11	4.06	1.20	4.16	4.27	4.24	1.11
18	Žitnik,	(B) (22-55)	5.26	5.36	5.31	0.81	4.16	4.23	4.21	0.64	4.22	4.35	4.30	1.16
19	Gospić	C (55-90)	5.41	5.59	5.51	1.55	3.86	3.98	3.93	1.13	4.06	4.27	4.17	2.30
30	Đakovo	(B)v(25-45)	7.49	7.68	7.59	1.06	5.78	6.69	6.13	5.51	6.76	6.98	6.87	1.23
31		C (45-70)	7.46	7.54	7.50	0.44	5.51	6.67	5.88	7.74	6.59	6.89	6.72	1.81
32	Županja	A (0-25)	6.41	6.63	6.53	1.41	4.88	5.06	4.97	1.63	5.56	5.69	5.63	0.83
33		Gso/r (25-50)	6.82	6.89	6.85	0.41	5.13	5.35	5.23	1.76	5.92	6.14	6.00	1.44
35	Molve	P (0-20)	6.00	6.23	6.08	1.49	4.29	4.40	4.35	1.24	4.79	4.94	4.85	1.12
36	14/40	P/C (20-40)	5.99	6.15	6.06	1.02	4.34	4.52	4.41	1.59	4.80	4.97	4.89	1.64
37		C(>40)	6.36	6.41	6.38	0.30	4.42	4.67	4.56	2.07	4.91	5.18	5.07	2.14
38	Molve 10	A (0-12)	6.03	6.66	6.25	3.87	4.65	4.73	4.70	0.76	4.89	5.15	5.00	2.08
39		Gso (12-28)	6.03	6.37	6.22	2.14	4.42	4.83	4.64	3.99	4.70	5.24	5.00	4.19
40		Gso/r (28-63)	6.23	6.51	6.38	1.59	4.17	4.29	4.23	1.09	4.77	4.98	4.86	1.99
41	Molve 11	A (0-11)	6.13	6.36	6.25	1.45	4.70	4.86	4.76	1.37	5.14	5.24	5.20	0.83
42		Gso (11-32)	5.95	6.34	6.22	2.69	4.34	4.50	4.41	1.38	4.94	5.10	5.03	1.33
43		Gso/r (32-67)	6.46	6.79	6.64	2.05	4.69	4.81	4.74	0.98	5.48	5.71	5.55	1.69
44		Gr/so (67-110)	6.93	7.12	7.00	1.06	5.18	5.23	5.22	0.42	5.87	6.02	5.95	0.90
45	Molve 12	Aa (0-13)	6.41	6.57	6.48	1.26	5.03	5.12	5.08	0.79	5.59	5.68	5.65	0.67
46		Gr_1 (13-47)	6.81	6.97	6.88	1.16	5.24	5.32	5.28	0.55	5.96	6.10	6.01	1.00
47		Gso (47-71)	6.91	7.32	7.17	2.17	5.58	5.69	5.64	0.70	6.32	6.43	6.38	0.79
48		Gr_2 (71-94)	7.22	7.52	7.37	1.48	5.80	5.86	5.83	0.41	6.49	6.58	6.52	0.56

Table 2. The soil pH of the neutral soil samples in the suspension of H_2O, KCl and $CaCl_2$ (n=5)

Mark	Location	Horizon, depth (cm)	pH/H_2O				pH/KCl				pH/$CaCl_2$			
			min	max	mean	RSD,%	min	max	mean	RSD,%	min	max	mean	RSD,%
8	Vodnjan	A (0-7)	7.80	7.95	7.86	0.73	7.01	7.06	7.04	0.29	6.90	7.02	6.96	0.66
9		Brz (7-32)	7.90	8.04	7.97	0.72	6.77	6.90	6.84	0.93	6.98	7.05	7.02	0.38
12	Ripenda	Ap (0-22)	8.04	8.30	8.14	1.18	7.17	7.22	7.19	0.27	7.11	7.25	7.16	0.73
20	Kneževo	Amo(0-30)	7.52	7.56	7.54	0.21	6.65	6.81	6.71	0.95	6.59	6.79	6.69	1.09
21		AC (30-45)	7.90	8.17	8.01	1.39	7.02	7.15	7.11	0.75	6.88	7.10	6.97	1.14
26	Ivanovec	Aa (0-30)	8.00	8.08	8.03	0.45	6.88	7.30	7.03	2.30	7.07	7.39	7.24	1.58
34	Županja	Gr/so (50-70)	8.12	8.24	8.16	0.58	6.99	7.11	7.04	0.67	7.05	7.24	7.19	1.08

cation near Đakovo (A horizon), in KCl (7.25) at the Bilje location (G horizon) and in $CaCl_2$ (7.02) in Zagreb, in floodplain of the Sava River, near the Cvjetno settlement (I horizon). The highest values were measured at the same location, in Ivanovec (Gso horizon), and the range was from 7.90 to 8.99.

pH values in acid, neutral and alkaline soils measured in the suspensions of H_2O, KCl and $CaCl_2$

For the whole range in all three media, the greatest range of soil pH value (the difference between the maximum and minimum mean value) was at the pH values measured in KCl suspension - 5.19 pH units, then follows the pH values measured in H_2O suspension - 4.89 pH units, while the lowest range of pH values was measured in a $CaCl_2$ suspension - 4.62 pH units.

Average soil pH values measured in three media on 51 horizon/layer are shown at Figure 1.

The difference in resulting values of soil pH measured in H_2O and KCl suspension approximately amounted 1.51 pH unit in acid soils, 0.96 pH unit in neutral soils and 0.87 pH unit in alkaline soils. The difference in resulting values of soil pH measured in H_2O and $CaCl_2$ suspension approximately amounted 1 pH unit in acid soils, 0.93 pH units in neutral

Table 3. The soil pH of the alkaline soil samples in the suspension of H_2O, KCl and $CaCl_2$ (n=5)

Mark	Location	Horizon, depth (cm)	pH/H_2O				pH/KCl				pH/$CaCl_2$			
			min	max	mean	RSD,%	min	max	mean	RSD,%	min	max	mean	RSD,%
13	Ripenda	C (22-60)	8.40	8.56	8.47	0.74	7.23	7.29	7.26	0.37	7.40	7.48	7.44	0.48
22	Kneževo	C (50-80)	8.30	8.42	8.37	0.64	7.44	7.55	7.48	0.55	7.17	7.38	7.25	1.21
23	Bilje	A (0-30)	8.21	8.38	8.31	0.76	7.39	7.46	7.43	0.35	7.27	7.46	7.36	0.92
24		C (30-50)	8.38	8.45	8.42	0.34	7.47	7.54	7.51	0.39	7.40	7.58	7.47	0.94
25		G (50-70)	8.43	8.51	8.47	0.38	7.21	7.31	7.25	0.61	7.41	7.59	7.49	0.90
27	Ivanovec	Amo (30-50)	8.65	8.74	8.69	0.47	7.82	7.88	7.85	0.30	7.62	7.83	7.69	1.05
28		Gso(50-70)	8.95	9.02	8.99	0.37	8.20	8.25	8.22	0.23	7.82	8.02	7.90	1.02
29	Đakovo	A (0-25)	7.91	8.08	7.99	0.83	7.27	7.38	7.31	0.58	7.35	7.45	7.38	0.65
49	Zagreb,	A/I (0-20)	7.91	8.16	8.00	1.21	7.45	7.53	7.48	0.42	6.97	7.06	7.02	0.48
50	Cvjetno	II (20-40)	8.18	8.38	8.27	0.88	7.46	7.56	7.51	0.51	7.16	7.21	7.19	0.25
51	settlement	III (40-60)	8.17	8.34	8.24	0.82	7.38	7.42	7.40	0.19	7.22	7.32	7.26	0.59

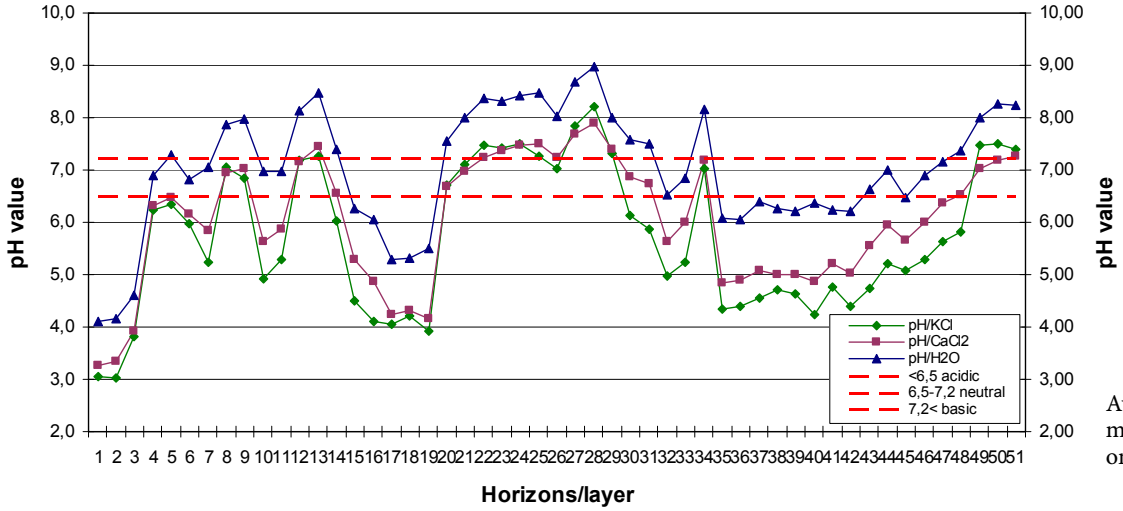

Figure 1.
Average soil pH values measured in three media on 51 horizon/layer

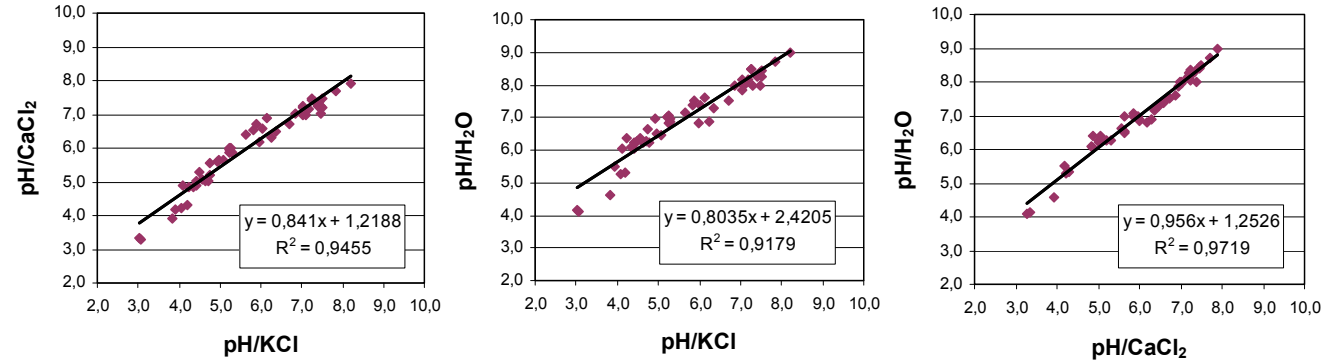

Figure 2.
Functional dependence of pH KCl/H_2O, pH KCl/$CaCl_2$ and pH $CaCl_2$/H_2O (y) and determination coefficient (R^2) for all range (n=51)

soils and 0.98 pH units in alkaline soils. The difference in resulting values of soil pH measured in $CaCl_2$ and KCl suspension approximately amounted 0.5 pH units in acid soils, 0.12 pH units in neutral soils and 0.20 pH units in alkaline soils.

Linear regression analysis

Linear regression analysis was applied to establish the correlation between the values of the soil pH in three different media. Correlation coefficient (Vasilj, 2000) presents the intensity and direction of indicators coherence, and from its value the strength of the correlation can be determined. The Roemer-Orphal scale was used in this paper.

The relations between: pH $CaCl_2$/KCl; pH H_2O/KCl and pH H_2O/$CaCl_2$ were observed and graphically presented for the whole range (Figure 2), and, due to their acidity determined in KCl suspension for the acid (Figure 3), neutral (Figure 4) and alkaline (Figure 5) soils.

According to other authors, for the most common soils in Slovakia (Makovnikova and Kanianska, 2001) the corre-

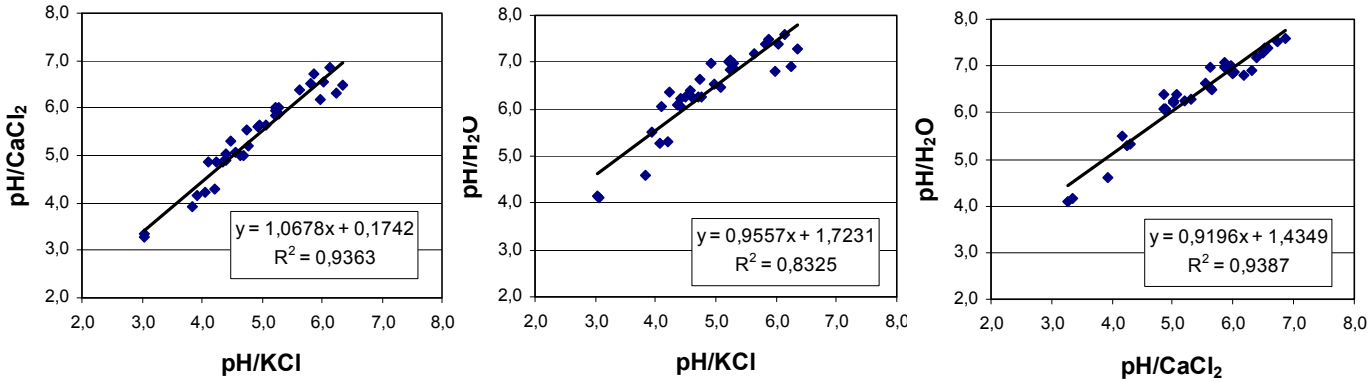

Figure 3. Functional dependence of pH KCl/H_2O, pH KCl/$CaCl_2$ and pH $CaCl_2$/H_2O (y) and determination coefficient (R^2) for the acid soils (n=33)

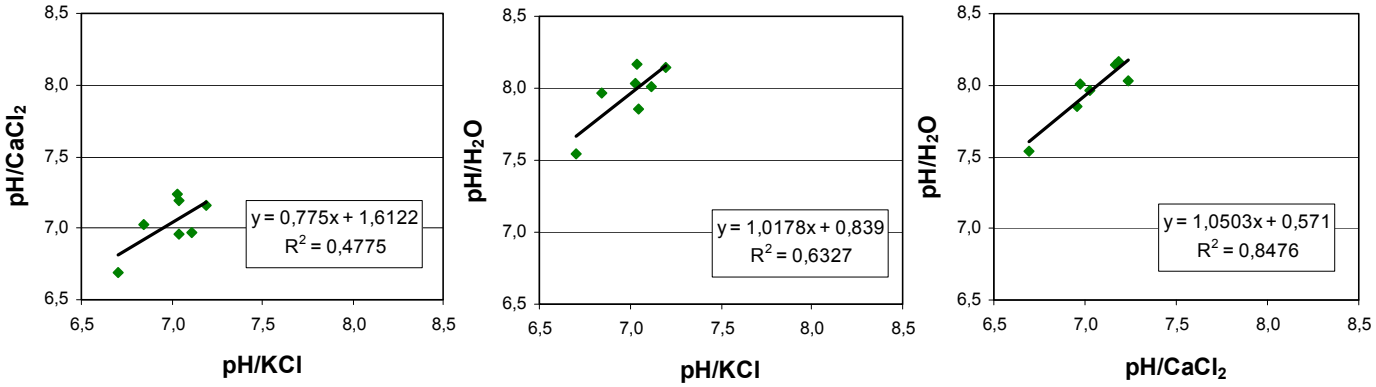

Figure 4. Functional dependence of pH KCl/H_2O, pH KCl/$CaCl_2$ and pH $CaCl_2$/H_2O (y) and determination coefficient (R^2) for the neutral soils (n=7)

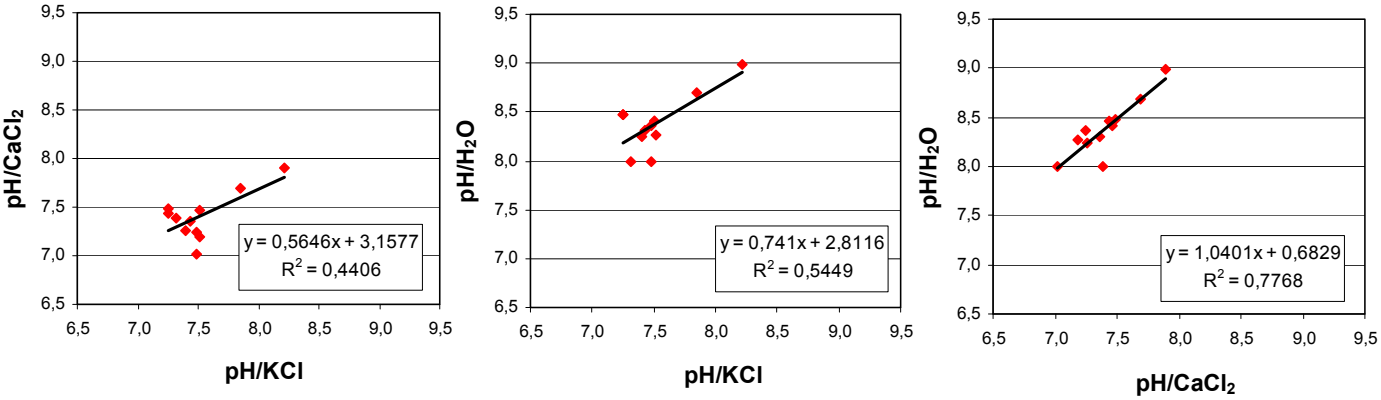

Figure 5. Functional dependence of pH KCl/H2O, pH KCl/CaCl2 and pH CaCl2/H2O (y) and determination coefficient (R2) for the alkaline soil (n=11)

lation coefficient was the highest among pH H_2O/$CaCl_2$ and was in the range of 0.75 to 0.99 in acid, neutral and alkaline soils. Smaller correlation coefficient was among pH KCl/H_2O and was in the range of 0.28 to 0.91.

In the acid soils in Ohio (Beery and Wilding, 1971), a high correlation (0.90-0.98) was obtained for the coherence between pH H_2O/KCl.

The difference in resulting values of soil pH measured in H_2O suspension and the KCl suspension was constant and approximately amounted one pH unit in the Netherlands (Vries de and Leeters, 2001).

In a poorly alkaline to alkaline soils in New Mexico (Carreira et al., 2005), the values of soil pH measured in H_2O suspension were from 0.5 to 1 pH unit larger than those measured in $CaCl_2$ suspension and such results were also obtained in this work.

In the Mindanao, the Philippines (Poudel and West, 1999), on average, the values of soil pH measured in KCl suspension

Table 4. The correlation coefficients and functional dependence for all measurements

Soil distribution	Horizons number (n)	Observed correlations	Linear regression	Correlation coefficient (r)	Intensity of correlation
The whole range	51	pH KCl/$H_2$0	pH/H_2O=0.80pH/KCl+2.42	r=0.96	absolute
	51	pH KCl/$CaCl_2$	pH/$CaCl_2$=0.84pH/KCl+1.22	r=0.97	absolute
	51	pH $H_2$0/$CaCl_2$	pH/$H_2$0=0.96pH/$CaCl_2$+1.25	r=0.99	absolute
Acid soils	33	pH KCl/$H_2$0	pH/H_2O=0.96pH/KCl+1.72	r=0.91	absolute
	33	pH KCl/$CaCl_2$	pH/$CaCl_2$=1.07pH/KCl+0.17	r=0.97	absolute
	33	pH $H_2$0/$CaCl_2$	pH/$H_2$0=0.92pH/$CaCl_2$+1.43	r=0.97	absolute
Neutral soils	7	pH KCl/$H_2$0	pH/H_2O=1.02pH/KCl+0.84	r=0.80	very strong
	7	pH KCl/$CaCl_2$	pH/$CaCl_2$=0.78pH/KCl+1.61	r=0.69	strong
	7	pH $H_2$0/$CaCl_2$	pH/$H_2$0=1.05pH/$CaCl_2$+0.57	r=0.92	absolute
Alkaline soils	11	pH KCl/$H_2$0	pH/H_2O=0.74pH/KCl+2.81	r=0.74	strong
	11	pH KCl/$CaCl_2$	pH/$CaCl_2$=0.56pH/KCl+3.16	r=0.66	strong
	11	pH $H_2$0/$CaCl_2$	pH/$H_2$0=1.04pH/$CaCl_2$+0.68	r=0.88	very strong

were 0.74 units lower than those in H_2O suspension, indicating a net negative charge for all horizons.

A fundamental goal of this work was to establish functional connections between all three media. The functional connections are shown in Table 4.

Since the correlation coefficients are very high, the functional connections are allowing us to calculate the expected pH value in one media if we know the pH value in another media for the certain types of soil.

Conclusions

The correlation was absolute for the whole range and for the acid soils. For the neutral soils the correlation varied from the classes strong to absolute and for the alkaline soils the correlation varied in the classes strong and very strong. These kind of results were expected and the reasons of very high correlation (absolute) in acid media, smaller correlation (strong to absolute) in neutral media and the smallest correlation (strong to very strong) in alkaline media we find in the chemical soil properties, adsorption complex, chemical structure, ion valence, ion exchange and other influencing factors.

To establish functional connections between the observed media was a fundamental goal of this work. The existence of alleged functional connections through this work has been proven with very high significance.

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