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Original Research

Conversion of Soil pH 1:2.5 KCl and 1:2.5 H_2O to 1:5 H_2O: Conclusions for Soil Management, Environmental Monitoring, and International Soil Databases

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Abstract

Both the international ISO standard and modern soil classifications and databases require soil pH measurement at a 1:5 soil:solution ratio, while the ratio 1:2.5 is still the most commonly used in Poland and other European countries. The transformation of laboratory practices is necessary, but it is also necessary to establish and validate a reliable procedure for converting soil pH at soil:solution ratios of 1:5 and 1:2.5. Based on 200 soil samples representing typical soil types and soil properties of southwest Poland (including arable and forested areas, both in the lowlands and mountains), a general conclusion was derived that pH values measured at soil:solution ratios 1:2.5 and 1:5 in distilled water and KCl solution, respectively, have nearly identical values and do not require conversion in most practical applications. If precise conversion of $pH_{1:2.5}$ to $pH_{1:5}$ is necessary, e.g., for soil database construction or long-term soil quality monitoring, the following equations are suggested: $pH_{H2O\ 1:5} = 0.14 + 0.99*pH_{H2O\ 1:2.5}$ and $pH_{KCl\ 1:5} = 0.09 + 1.00*pH_{KCl\ 1:2.5}$, respectively. When the direct conversion of $pH_{KCl\ 1:2.5}$ to $pH_{H2O\ 1:5}$ is required, a simple logarithmic model offer precise and reliable transformation: $pH_{H2O\ 1:5} = -1.95 + 11.58*\log_{10}(pH_{KCl\ 1:2.5})$. This model makes the archival records still useful, both for international soil classifications, background data in the long-term measurement series, and as input data for modern international soil databases.

Keywords: soil pH, soil reaction, pH in water, pH in KCl, soil monitoring, soil databases

Introduction

Soil reaction may directly influence plant growth and yield quality [1, 2], or indirectly – by regulation of soil sorption [3] – solubility, and availability of nutrients [4-6] and toxic substances [7-10]. Moreover, soil reaction influences soil biological activity [11], soil structure [12], direction and intensity of soil-forming processes [13], rate of mineral weathering [14], organic matter decomposition [15], and nutrient cycling [16]. Thus, soil reaction is considered a crucial soil characteristic, important for

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food production, forestry, water management, waste and wastewater disposal, biodiversity protection, etc. [17-20]. Changes in soil pH are considered a sensitive indicator of human impacts (from agriculture, industry, urbanization, and others), both as acidification [21-23] and alkalization [24-30]. Soil pH is therefore involved in all soil-oriented studies, inventories, and databases [31-34], as well as in most environmental monitoring programs [35-39].

Unfortunately, there are several measures of soil reaction used worldwide. The most common eluents are distilled water (H_2O), 1 mol L^{-1} KCl (KCl), and 0.01 mol L^{-1} $CaCl_2$ ($CaCl_2$), and the most common soil-eluent ratios are 1:1, 1:2.5, and 1:5 [40]. Regional or national popularity of a particular eluent and soil:eluent ratio is firmly rooted in the local scientific tradition, but it is also justified by local soil properties, climate conditions, or management practices [41]. Different measurement methods lead, however, to incompatibility of data from various countries and disturb data integration in the international soil databases [33]. The most widespread eluent for soil pH measurement in Poland and also common in other countries has been KCl at a soil:solution ratio 1:2.5, used for evaluating soil fertility, liming needs, and soil contamination [42-44]. Recent international standards for soil pH measurement, ISO 10390:2005, has unified the pH analysis at a soil:solution ratio of 1:5. All legal laboratory certification (accreditation) procedures based on the ISO standard and the older protocols related to the ratio 1:2.5 are no longer accepted. Finally, several European and worldwide initiatives [33], including the GlobalSoilMap [31], and the international soil classification [45] have unified the pH measurement (soil:distilled water at the ratio of 1:5). Therefore, there is urgent need to determine whether the archival soil pH data are fully comparable to the results of recent measurements or require recalculation. The answer is important for each farmer as it is related to the continuity of information about the soil state (e.g., fertility and acidity) and the results of management (e.g., liming). Also, it is important for all long-term monitoring series and remediation projects initiated under the previous standard and continued/finished under the new one [24, 26, 35].

It is well known that the relationship between soil pH measured in the salt solution and distilled water is nonlinear [41, 46, 47]. Thus, several conversion equations were developed (e.g., for H_2O / 0.01 mol L^{-1} $CaCl_2$), including linear, curvilinear, exponential, smoothing spline, and second/third order polynomial models [48]. The conversion models for KCl and H_2O are less common or completely lacking for some soil:solution ratios [49].

The aim of this study was: 1) to compare the soil pH measured in KCl and H_2O at the previously most commonly used ratio 1:2.5 and presently desired 1:5 ratio, and 2) to develop a simple and accurate model for converting the archival pH_{KCl} data into the format consistent with ISO standard and requirements of international databases and classifications.

Material and Methods

A set of 200 soil samples were collected in SW Poland for this experiment, representing soils from the Silesian Lowland and the Sudeten Mountains. Sixty percent of soils were from arable fields and 40% from forested sites. Soils were sampled at various depths, from all genetic horizons of Arenosol, Cambisol, Gleysol, Luvisol, Chernozem, Phaeozem, Planosol, and Stagnosol profiles [45] to be representative of various parent materials, weathering stages, soil-forming processes, and biological activity. Also, all soil texture classes were represented, with the clay and silt fractions ranging between 1 and 73%, and 1 and

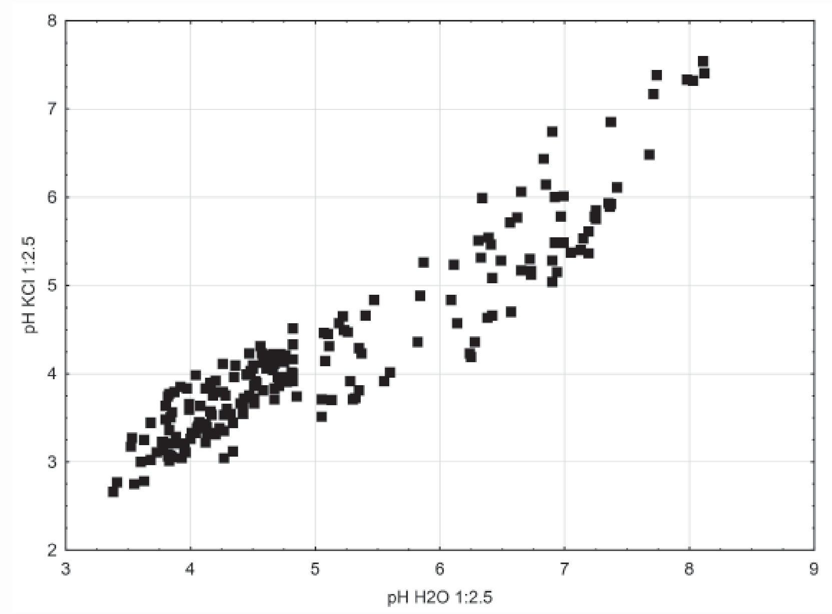

Fig. 1. Relationship between $pH_{KCl\ 1:2.5}$ and $pH_{H2O\ 1:2.5}$ in soil samples under study.

Table 1. Summary statistics for basic properties of soils used in the experiment.

Variable	N	Min.	Max.	Mean	Median	St. dev.
sand, %	164	6	99	58.2	72.0	31.1
silt, %	164	1	75	31.3	22.0	24.0
clay, %	164	1	73	10.4	4.0	11.8
TOC, %	200	0.03	47.8	8.82	0.99	14.7
soil acidity, cmol(+) kg^{-1}	200	0.00	13.4	2.50	1.55	2.8
base cations (BC), cmol(+) kg^{-1}	200	1.31	82.4	7.55	3.85	10.8
base saturation (BS), %	200	15.5	100	67.5	79.2	30.8
$pH_{H2O\ 1:2.5}$	200	3.39	8.13	5.12	4.67	1.25
$pH_{KCl\ 1:2.5}$	200	2.65	7.53	4.27	3.97	1.07
$pH_{H2O\ 1:5}$	200	3.47	8.21	5.22	4.77	1.22
$pH_{KCl\ 1:5}$	200	2.75	7.73	4.37	4.07	1.09

75%, respectively (Table 1). Little overrepresentation of coarse-textured soils (sand and loamy sand) is justified by the prevalence of these texture classes in Central European post-glacial landscapes. Samples are characterized by wide ranges of organic carbon content (0.03-47.8%), KCl-extractable acidity (0.0-13.4 cmol (+) kg^{-1}), sum of base cations (1.3-82.4 cmol (+) kg^{-1}), and base saturation (15.5-100%).

Samples were collected and analyzed within three research projects (as indicated in Acknowledgements). For this study, soil pH was measured once again in all selected samples to avoid possible differences between series, related to laboratory practices or conditions. The pH of each soil sample was measured in distilled water (pH_{H2O}) and 1 mol L^{-1} KCl solution (pH_{KCl}) at two ratios of 1:2.5 and 1:5 (volume:volume). 10 mL portions of soil, previously dried, ground, sieved (ø 2 mm sieve), and thoroughly mixed, were placed using the plastic calibrated spoon in 50-100 ml (respectively) beakers, and the 25 ml or 50 ml portions or distilled water or 1 mol L^{-1} KCl were added, respectively. Each combination was prepared in triplicate. After hand mixing, the suspensions were left overnight. The next day suspensions were mixed twice before pH measurement. The measurement was conducted potentiometrically, using the combined glass electrode (Mettler Toledo SevenCompact S-220), after calibration based on standard solutions in a pH range of 4.01-7.01-10.01 (Hanna Instruments).

Statistical analysis and graphical representation were executed using the Statistica 10 package (StatSoft Inc.).

Results and Discussion

The soils used for the experiment represent a full range of soil reactions expected in Central European soils, from strongly acid to alkaline, exemplified by $pH_{H2O\ 1:2.5}$ in a range 3.39-8.13, mean 5.12 (Table 1). Mean value of $pH_{KCl\ 1:2.5}$ was lower than mean $pH_{H2O\ 1:2.5}$ by 0.85 units (mean value of 4.27), due to K^+/H^+ exchange in the salt:soil suspension and the release of H^+ ions to the solution [39]. The values of $pH_{KCl\ 1:2.5}$ and $pH_{H2O\ 1:2.5}$ are highly correlated ($R^2 = 0.86$, $p<0.001$); however, their relationship is non-linear (Fig. 1).

Mean pH_{H2O} measured at soil:solution ratio 1:5 was 5.22 and was higher than mean $pH_{H2O\ 1:2.5}$ by ca. 0.1 pH unit (Table 1), and the difference was statistically insignificant (checked by t-Student test). Soil pH at these two soil:solution ratios was very highly correlated ($R^2 = 0.996$, $p<0.001$) and the relationship was strictly linear (Fig. 2a), described by a simple linear regression equation:

$$pH_{H2O\ 1:5}=0.14 + 0.99*pH_{H2O\ 1:2.5} \qquad (1)$$

Similarly, the mean pH_{KCl} at soil:solution ratio 1:5 was higher than mean $pH_{KCl\ 1:2.5}$ by 0.1 pH units (Table 1), and this difference was statistically insignificant. Soil pH_{KCl} at two soil:solution ratios was very highly correlated ($R^2 = 0.998$, $p<0.001$) and the relationship was strictly linear (Fig. 2b), described by a simple linear regression equation:

$$pH_{KCl\ 1:5}=0.09 + 1.00*pH_{KCl\ 1:2.5} \qquad (2)$$

The linear correlations between soil pH measured at soil:solution ratios 1:2.5 and 1:5 existed in all pH classes, from acid to neutral (Fig. 2a), and both in arable and forested soils.

Moreover, the regression equations (1) and (2) were independent of soil texture (percentages of clay, silt, and sand fraction), organic carbon content, sum of base cations, and base saturation. The above-listed findings lead to the conclusion that all archival data of soil pH at soil:solution ratio 1:2.5 can be reliably recalculated using

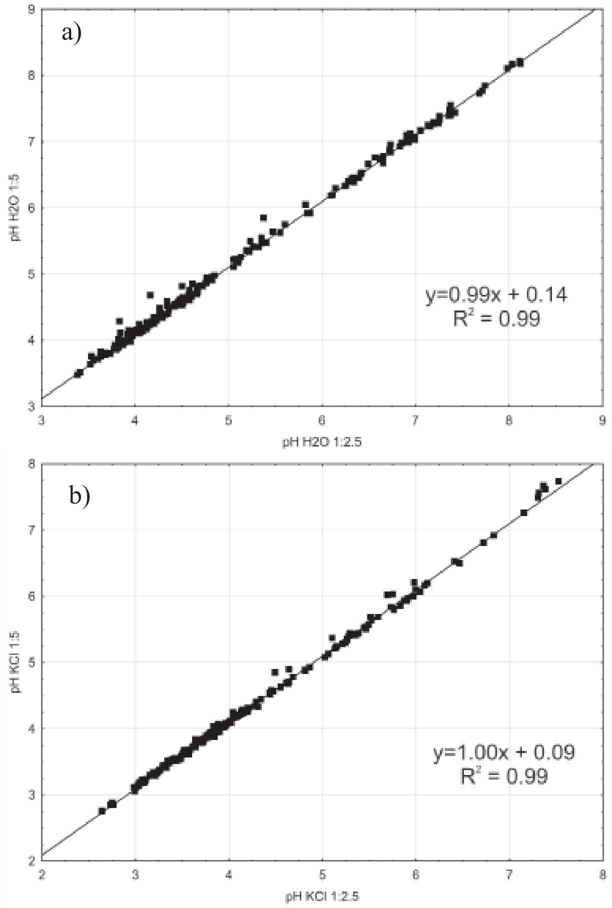

Fig. 2. Single linear regression models for predicting the pH at soil:solution ratio 1:5, based on a) $pH_{H2O\ 1:2.5}$ and b) $pH_{KCl\ 1:2.5}$.

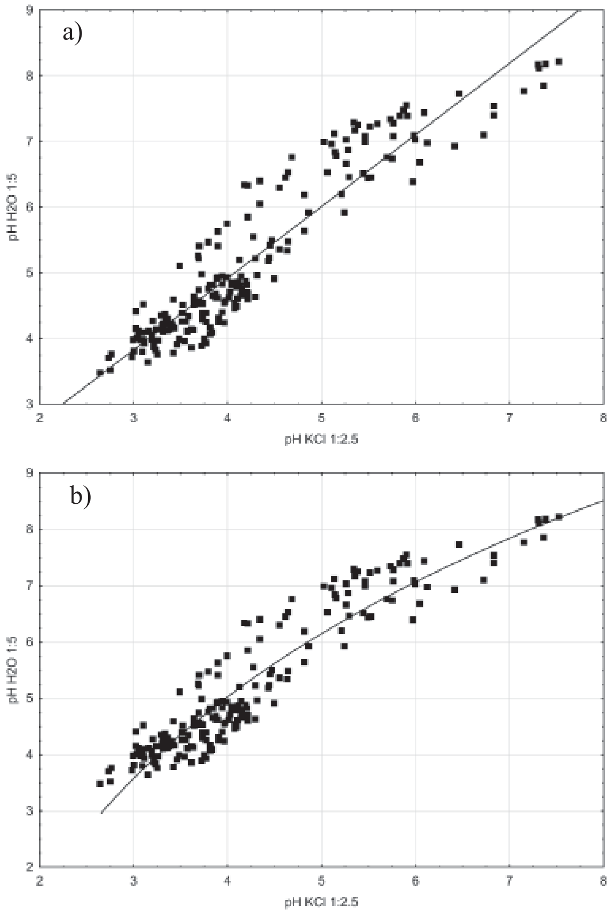

Fig. 3. Single linear a) and logarithmic b) models for conversion of $pH_{KCl\ 1:2.5}$ into $pH_{H2O\ 1:5}$.

simple linear regression equations to the desired pH values at soil:solution ratio 1:5.

Additionally, the differences between pH values at soil:solution ratios 1:2.5 and 1:5, both in distilled water and KCl solution are under this study much smaller or even insignificant as compared to the reported pH differences related to field variability [18, 29, 36, 50, 51]. Thus, the pH values at soil:solution ratios 1:2.5 and 1:5 may be considered identical (do not require the recalculation), if 1) the natural soil variability is high, or 2) only the pH class is required (as for fertility evaluation), or 3) soil pH is the only accompanying variable (as in monitoring of soil contamination with heavy metals). The sample calculations made for selected sets of published data representing different environments [14, 19, 34, 52, 53] have confirmed, in all cases, statistically insignificant differences between soil pH at soil:solution ratios 1:2.5 and 1:5 (both in water and KCl solution).

The most common measure of soil reaction in the previous research reports in Poland is a pH_{KCl} at soil:solution ratio 1:2.5, and its direct conversion to $pH_{H2O\ 1:5}$ has crucial importance for modern application of the archival data. Relatively good correlation was found between $pH_{KCl\ 1:2.5}$ and $pH_{H2O\ 1:5}$ (Fig. 3a) as exemplified by the high value of correlation coefficient, $r = 0.93$ ($p<0.001$). A single regression equation predicting $pH_{H2O\ 1:5}$ was derived as follows:

$$pH_{H2O\ 1:5} = 0.56 + 1.09 * pH_{KCl\ 1:2.5} \quad (R^2 = 0.87,\ p<0.001) \tag{3}$$

However, the equation overestimates the predicted pH in the weak acid reaction range, while underestimating it in strongly acid and neutral/alkaline reaction ranges. Thus, multiple regression equations were derived using the stepwise regression tool of Statistica software.

Three equations were accepted with R^2 higher than R^2 of single regression model:

$$pH_{H2O\ 1:5} = 0.70 + 1.07 * pH_{KCl\ 1:2.5} - 0.006 * TOC \quad (R^2 = 0.88,\ p<0.001) \tag{4}$$

$$pH_{H2O\ 1:5} = 0.50 + 1.05 * pH_{KCl\ 1:2.5} + 0.03 * clay \quad (R^2 = 0.92,\ p<0.001) \tag{5}$$

$$pH_{H2O\ 1:5} = 0.96 + 0.79 * pH_{KCl\ 1:2.5} + 0.01 * BS \quad (R^2 = 0.92,\ p<0.001) \tag{6}$$

…where TOC is organic carbon content (%), clay is a clay fraction <0.002 mm (%), and BS is a base saturation (%).

Equations (5) and (6) give the best linear prediction of $pH_{H2O\ 1:5}$; however, required data on clay content or base saturation often are lacking in agricultural reports. Due to the same reasons, the equations are also useless for the organic soils. Equation (4) requires easily available data (pH_{KCl} and TOC); however, the prediction of $pH_{H2O\ 1:5}$ using this model is not significantly better than based on a single regression (3).

The relationship in Fig. 3a is clearly nonlinear, thus various nonlinear models were built using the least squares estimation. The best prediction of $pH_{H2O\ 1:5}$, measured as the lowest sum of residuals (differences between predicted and measured values), was found for the logarithmic model (Fig. 3b):

$$pH_{H2O\ 1:5} = -1.95 + 11.58*\log_{10}(pH_{KCl\ 1:2.5}) \qquad (7)$$

Conclusions

Analysis of 200 soil samples representing a continuum of soil types and soil properties common in SW Poland led to a general conclusion that pH measured at soil:solution ratios 1:2.5 and 1:5, in distilled water and KCl solution, respectively, has nearly identical values and does not require conversion in most practical applications. If precise conversion of $pH_{1:2.5}$ to $pH_{1:5}$ is necessary, e.g., for soil database construction or at long-term soil quality monitoring, the following equations are suggested: $pH_{H2O\ 1:5} = 0.14 + 0.99*pH_{H2O\ 1:2.5}$ and $pH_{KCl\ 1:5} = 0.09 + 1.00*pH_{KCl\ 1:2.5}$, respectively.

When direct conversion of $pH_{KCl\ 1:2.5}$ to $pH_{H2O\ 1:5}$ is required, a simple logarithmic model offers precise and reliable transformation: $pH_{H2O\ 1:5} = -1.95 + 11.58*\log_{10}(pH_{KCl\ 1:2.5})$. This model makes the archival records still useful, both for international soil classifications, background data in the long-term measurement series, and as input data for modern international soil databases.

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