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Observation on Laboratory pH Measurement in Soil by Water, Calcium Chloride and Potassium Chloride Solution for Soils under Laboratory Study

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Abstract

The experiment was conducted from April to September, 2021 at Chole District, Eastern Arsi Zone, to generate baseline information on soil pH measurements under routine laboratory analyses. The study evaluated soil pH in different electrolyte solutions and soil-to-solution ratios to establish relationships using statistical regression. A total of 55 surface soil samples (0–20 cm) collected from cultivated agricultural lands were analyzed. The relationships among pH measured in water (pH_{H2O}), 0.01 M $CaCl_2$ (pH_{CaCl2}), and 1 M KCl (pH_{KCl}) solutions were investigated following standard laboratory procedures. Soil pH is one of the most commonly measured soil properties and serves as an important indicator of soil quality, fertilizer recommendations, liming requirements, and biogeochemical processes in terrestrial ecosystems. The results showed that pH values measured in salt solutions were lower than those measured in water, with variations depending on the electrolyte solution used. The average pH $CaCl_2$ value was lower than pH H_2O by 0.85 ± 0.09 pH units, while pH KCl was lower than pH H_2O by 1.27±0.10 pH units. Linear regression analysis indicated strong relationships between pH_{H2O} and pH measured in electrolyte solutions. The correlation coefficients obtained were r=0.6355 for $CaCl_2$ and r=0.6239 for KCl solutions. The findings confirm that both $CaCl_2$ and KCl solutions are useful for soil pH determination and can provide reliable information for soil management and agricultural practices.

Keywords: Soil pH methods, pH water, pH calcium chloride

1. Introduction

Soil pH is one of the most important chemical indicators used in soil science because it controls nutrient availability, microbial activity, and soil fertility status. It indicates the degree of soil acidity or alkalinity and strongly affects the solubility of essential nutrients and toxic elements. Due to its importance in agricultural productivity and environmental management, soil pH is among the most frequently measured parameters in soil analysis laboratories worldwide. Several studies have reported that soil pH measurements are influenced by methodological factors such as soil-to-solution ratio, electrolyte concentration, and stirring conditions (Desalegn et al., 2016; Wogi et al., 2021). Generally, increasing the soil-to-solution ratio results in higher pH values, whereas increasing electrolyte concentration decreases measured pH values due to the suspension effect. Different methods are used for soil pH determination depending on the objectives of the study. According to Wang et al. (2015), Wogi et al. (2021), and Aliyu et al. (2022), standard field measurements in the United States commonly use a 1:1 soil-to-water suspension, while European laboratories often apply a 1:5 ratio. More diluted suspensions usually produce relatively higher pH values because many protons remain adsorbed on soil colloids rather than being released into the soil solution. Besides water, electrolyte solutions such as $CaCl_2$ and KCl are also widely used to soil pH measurements in research and soil classification studies. Measurements using 0.01 M $CaCl_2$ are preferred because they minimize seasonal variations caused by fluctuations in soil salt concentration (Wogi et al., 2021; Gerenfes et al., 2023; Georges et al., 2024). The use of electrolyte solutions provides additional information about soil colloidal charge characteristics. The difference between pH measured in KCl and water, commonly called delta pH (pH KCl–pH H_2O), and indicates the net surface charge of soil colloids. Negative delta pH values imply net negative charges and dominant cation exchange capacity, whereas positive values suggest net positive charges and anion exchange capacity. In addition, NaF solutions are used to detect short-range order minerals such as allophane and amorphous materials in volcanic soils (Hao et al., 2019; Wogi et al., 2021; Arthur and Okae, 2022). In Ethiopia, routine soil pH measurements are commonly conducted using the potentiometric method with a 1:2.5 soil-to-water ratio, while the International Standard NF ISO 10390 (1994) recommends a 1:5 soil-to-water ratio. The 1:2.5 ratio is more widely adopted because it is considered suitable for evaluating soil fertility constraints, nutrient availability, and fertilizer recommendations. However, variability among methods creates challenges when comparing soil databases generated by different laboratories. According to Seybold and Libohova (2017) and Libohova et al. (2014) emphasized that harmonization of soil pH measurements is essential for developing reliable soil databases, digital soil mapping, and pedotransfer functions. Soil pH has also become increasingly important in studies addressing soil degradation and acidity problems in Ethiopian highlands (Achalu, 2023; Tadesse et al., 2025). Recent findings from Ethiopian soils confirmed that land use type, soil depth, and management practices significantly influence soil pH variability and nutrient dynamics. Because soil pH influences many physical, chemical, and biological processes, accurate and comparable measurements are necessary for sustainable soil management. Therefore, understanding the relationships among different soil pH measurement methods is important for laboratory standardization and interpretation of soil fertility data. However, information regarding the relationships among pH measurement methods for soils of Eastern Arsi Zone remains limited. The study specifically evaluates soil pH measured under different soil-to-solution ratios and electrolyte solutions using regression analysis. The findings are expected to support routine laboratory analyses and contribute to the development of soil databases at the Kulumsa Agricultural Research Center soil and plant analysis laboratory.

2. Materials and Methods

2.1. Description of the study area

In this study, the study was conducted in Chole Wored and its surrounding, Arsi zone of Oromia regional state, southern east Ethiopia from March, 2020 to April, 2021. Chole is one of the Arsi Zone wored with the geographical location of 8°10'N and 39°50'E east to Asella town. The climatic condition of the wored is divided into highland, midland, lowland and werch respectively. The topography of this area includes plates, mountains, hill, and its total land area is estimated to be 68200 hectares. The woreda has a huge livestock population such as cattles, sheep, Goat, Horse, Donkeys, Mules, and poultry. The human population of the woreda is estimated to be 88,190 both in urban and rural areas (Hussien et al*.,* 2017). The agricultural system and husbandry practice of the communities specially the farmers is mainly mixed farming system and an extensive management system respectively. The soil type of Chole Woreda is silt and sandy soil. The main rainy season in the district is from April to September, 2021. Some major crops grown in the district include: Coffee, Maize, Sorghum, Teff, and Groundnut.

2.2. Soil sample collection and preparation

In this study, fifty-five soil samples were collected from the surface (0–20 cm) horizons of cultivated farmlands in different locations using the soil auger systematic sampling technique from different locations of Chole Districts. Soil samples taken from areas were separately labeled and transferred into airtight polythene bags and brought to the Kulumsa Research Center for laboratory analysis. Before it's transported to the research laboratory, care was taken, to the extent possible, to ensure that there were no other sources of contamination at the site of investigation. The collected soil samples were air dried, crushed with a mortar and pestle, passed through a 2-mm mesh sieve to remove coarse particles, and stored at ambient temperature prior to analysis. The composite soil sample was divided into storage soil sample materials such as plastic bags, plastic bags with cartons, and polyethylene bottles with three replications.

2.3. Soil pH (Potentiometric method)

According to Nair et al. (2021), the pH, which stands for "potential of hydrogen," refers to the hydrogen ion (H+) concentration of a solution or soil. With reference to soils, it is alternatively known as soil reaction. It is the measure of the acidity or basicity of a solution, or of soil, and is expressed or defined as the negative logarithm of hydrogen ion concentration. It is written as; pH=−(H+). When the concentration of hydrogen ions is high, the soil is said to be acidic, and when the concentration of hydrogen ions is low, the soil is alkaline. We consider that a soil is acidic when there is an abundance of acidic cations like hydrogen (H+) and aluminum (Al3+) present compared to the alkaline cations like calcium (Ca2+), magnesium (Mg2+), potassium (K+), and sodium (Na+).

2.4. Laboratory analysis

Soil pH of the <2 mm fraction was measured in distilled deionized water, 1 M KCl, and 0.01 M $CaCl_2$ in soil-solution ratios of 1:2.5, 1:2.5 and 1:5 at the soil and plant laboratory of Kulumsa Agricultural Research Center following standard procedures for soil pH determination as described by Seybold et al., 2017 and Minansy et al., 2011, using digital pH meter (Thomas, 1996; Wogi et al., 2021) (HI9017, HANNA) bearing a glass electrode and a reference electrode, which had previously been calibrated with buffer solutions of pH 4 and 7. The 1 M KCl solution was prepared by dissolving 7.456 g of KCl in 1 L of distilled water, while the 0.01 M $CaCl_2$ solution was prepared by dissolving 1.47 g of $CaCl_2 \cdot 2H_2O$ in 1 l of distilled water. All reagents (KCl and $CaCl_2 \cdot 2H_2O$) used were of analytical grade. All measurements were carried out at room temperature (varying between 18.8 and 23.4°C). In order to minimize the influence of contact time between solution and soil on soil pH readings, all measurements were done after 30min of agitation following recommendations made by (Wang et al., 2015; Merl et al., 2022; Gerenfes et al., 2023;

Butnan et al., 2024). For all pH measurements, soil samples of 10 g were used to effectively cover the junction of the combination electrode by the supernatant liquid, especially for 1:1 soil-to-solution ratios

2.5. Data analysis

The analyzed soil data were subjected to analysis of variance using the SAS computer software package version 9.0 (SAS Institute, Inc., Cary, NC). A mean comparison was performed using the least significant difference test at 5% probability level and conducted using the SAS statistical package to assess the relationship between soil pH data in different electrolytes and soil-to-solution ratios. Variability in soil pH was analyzed using the coefficient of variation.

3. Results and Discussion

3.1. Description of pH measurements

For the samples considered in the study, the range of pH_{H2O} variation is not so large: from a minimum pH value of 4.68 to a maximum pH value of 6.70, the dominant soil reaction being neutral to strong acid. For the three series of pH measurement methods in the samples, the soil reaction is characterized by the pH of water (average pH=5.56), pH of $CaCl_2$ (average pH=4.71), and a potassium chloride reaction (average pH=4.29), respectively.

When electrolytic salts such as KCl and $CaCl_2$ are added to soil for pH measurement, the pH decreases due to the displacement and release of protons compared to when distilled water is used. Another explanation of the difference between pH $CaCl_2$ (or KCl) and pH H_2O is that the addition of 0.01 M $CaCl_2$ (or 1 M KCl) helps to suppress what has been termed the "salt effect" or "suspension effect or junction potential effect" (Wang et al., 2015; Bationo et al., 2018; Georges et al., 2024), which results due to the exchange of excess Ca2+ (or K+) with H+ (and Al3+ when pH<5.5) on the surface of soil colloids. Thus, these excess cations in the soil solution lower the tendency for K+ from the salt bridge to diffuse to the exchange sites of soil particles. Variation in soil pH within a landscape is generally attributed to factors such as topography (slope), altitude, soil management type, soil microbial activity and organic matter content, and quality, among others. However, all samples used in this study originated from the same type of parent material, though factors influencing the spatial variability of soil pH were not determined. Probably, the high organic matter content of these soils (Liu et al., 2020; Gerenfes et al., 2023) could provide a large pH buffering capacity due to the presence of multiple acidic functional groups (Wang et al., 2015; Merl et al., 2022).

Based on the statistical description of the soil pH measurements in three methods are indicated in Table 1 below. There are a lot of factors that influence the variability of soil *p*H measurements: soil-solution ratio, the nature and concentration of electrolyte in the solution, the procedure used for determinations, the soil properties, the stirred/non-stirred conditions, etc. (Tekalign et al., 1991; Minasny et al., 2011; Wogi et al., 2021).

Table 1: Statistical description of the pH measurement methods

Statistical description	pHw	$pHcacl_2$	PHkcl	PHw-PHkcl	$PHw-PHcacl_2$
Mean	5.56	4.71	4.29	1.27	0.85
Sdev	0.48	0.39	0.38	0.10	0.09
variance	0.23	0.15	0.15	0.09	0.08
max	6.70	5.86	5.34	1.36	0.84
min	4.68	3.97	3.61	1.07	0.71
mode	5.41	4.41	4.18	1.23	1.00
median	5.55	4.71	4.19	1.36	0.84
kurtosis	-0.34	0.79	0.29	-0.63	-1.13
Skewness	0.25	0.56	0.62	-0.37	-0.31

pHw: pHwater; $pHcacl_2$: pH calcium chloride; pHkcl: pH potassium chloride

For the data presented in the paper we can discuss about a period of time between the sampling and the measurement moments of soil *p*H. The differences are in the range of experimental errors and should not be ignored for precious measurements of soil *p*H. As indicated in Table 1 above, the pH difference $pHw-pHcacl_2$ and pHw-pHkcl is 0.85, 1.27 units, respectively. This shows that the result of soil $pHw>pHcacl_2$ >pHkcl. Thus, the *p*H measurement in water is a routine method and could be used *in-situ* while the method in $CaCl_2$ solution is more precise and gives us the possibility to avoid high variation of the results during some period (Liu et al., 2020; Sadiq et al., 2021; Merl et al., 2022). The equation of linear regression is given in Figure 1 and 2, could be used to recalculate the pH values. Linear relationship with slope close to unity and intercept different from zero had been obtained and this involves a difference between these two variables over the pH range of interest. A slope less than unity indicates that the difference between pH_{H2O} and pH_{CaCl2} decreases with the decreasing of pH values.

3.2. Comparison of pH_{H2O} vs pH_{CaCl2}

Summary of the data used in this study is shown in Table 1 and the frequency distribution plots are shown in Figure 1. pH values were highest in water, followed by $CaCl_2$ and lastly in KCl. In general, pH values measured in water and in KCl increased with increase in solution volume, this as a result of the dilution effect. Thomas (1996) and Wogi et al., (20121) observed that increase in soil pH with increasing soil-to-solution ratio was due to a reduction in proton (H+) dissociation from soil surfaces and less hydrolysis of Al that could be present. The importance of electrolyte solution in routine *p*H measurements is emphasized in many papers and Schofield and Taylor (1955) found that 0.01M $CaCl_2$ solution is the most satisfactory solution for use in nonsaline soils. The obtained results show that soil pH in water (pPH_2O) was significantly higher than in $CaCl_2$ solution ($pHCaCl_2$). As can be seen (Figure 1 and 2) there is a good R-squared value between these two series of measurements (R^2=0.6355). The *p*H in the $CaCl_2$ solution is lower with 0.85±0.09 *p*H units (average value) than in water and the min-max differences were 0.71–0.84 *p*H units for all analyzed samples.

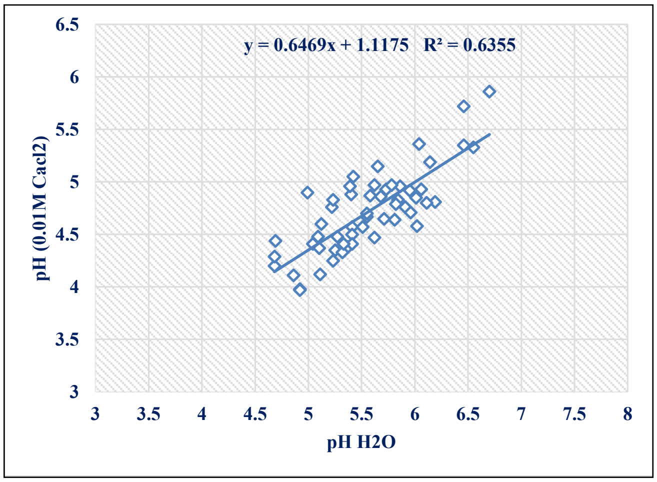

Figure 1: Comparison between soil pH in water and KCl in 0.01 M $CaCl_2$ solution (average samples) difference of 0.604 pH units, for 55 samples)

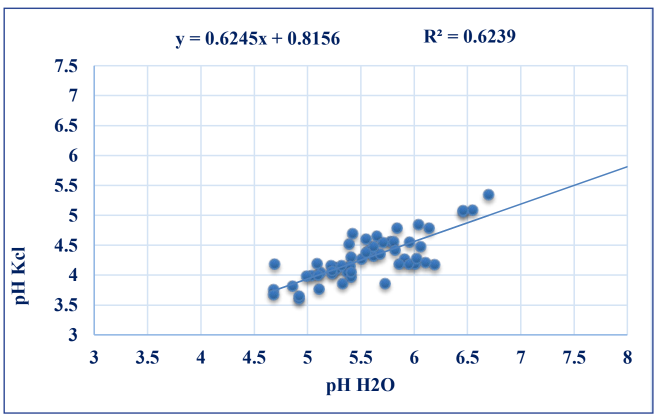

Figure 2. Comparison between soil pH in water and in 1 M solution (average difference of 0.895 pH units, for 55)

While the relationship between these two variables is described by linear regression which gave a good representation of the data, this means that the soils considered here present variable charge characteristics. This slight improvement in the coefficient of determination indicates that the relationship could be curvilinear and a different mechanism governs the differences between *p*HH_2O and *p*H$CaCl_2$. The shape of the curve is very close to the linear one for these two variables and describes the data better than the linear fit only for the high *p*H values (*p*HH_2O≥5), where there are more sample points. The estimated correlation coefficient between these two series of measurements is very high and significant for all soil types considered in the experiment (Figure 1). Similar studies used linear regression to relate pH H_2O to pH $CaCl_2$. For most researchers, the data have permitted the examination of the relationship between these two kinds of measurements across a wide range of soil types, through linear regression.

According to Wogi et al. (2021) the values of *p*HH_2O for a large number of samples and they have been compared the data for *p*H above 8.0 have been compared with those below 5.0. They found a curvilinear relationship for 91 acidic soils samples between *p*H in water and in $CaCl_2$ solution, in a 1:5 soil: solution ratio. The authors have attributed this relationship to the acidic *p*H soil, very close to the point of zero salt effect, with small differences between these two measurements. For non-acidic soils, they found a higher difference between *p*H in water and in calcium chloride solution. Other authors (Liu et al., 2020; Butnan et al., 2024) have worked with the same electrolytes ($CaCl_2$ and KCl) and in different dilution ratios and they found a good correlation over a wide range of soil pH. They also found the regression equation between pH H_2O and pH $CaCl_2$, which was valid only for non-saline, net negatively soils samples. The deviation from linearity of the sigmoidal curve was due to the buffering effect of Al at low *p*H and to the presence of carbonate at high *p*H, because the soil of the study area has low pH values with a min-max range of 4.68 to 6.70, which indicates the acidic properties in the soil.

3.3. Comparison of pH_{H2O} vs pH_{KCl}

The use of high ionic-strength media, like KCl solution, in measurements of soil pH has been limited primarily to acid soils. Some authors (Liu et al., 2020; Aliyu et al., 2022) have worked with a 1 M KCl solution for calcareous soils and *p*HKCl is inversely related to the potassium concentration of the KCl extract and also to the cation exchange capacity of the samples. They concluded that the KCl solution may provide important information concerning the chemical properties of the soils. The presence of soluble salts in a soil sample may influence the *p*H value and some analysts prefer to measure it in a mixture with other chlorides to mask the differences between these two variables. The values of pH for the analyzed samples measured in 1 M KCl solution are lower than the values measured in water, due to the higher concentration of H+ in solution. As can be seen (Figure 2), there is a good R-squared value between these two series of measurements (R^2=0.6239). The pH in KCl solution is lower by 1.27±0.10 *p*H units (average value) than the values measured in water, very close to the value for the differences in $CaCl_2$ solution. The min-max differences between pH in water and in KCl-like electrolyte were 1.73–2.02 *p*H units, higher than in the case of a $CaCl_2$ solution like electrolyte.

For all soil samples, the estimated correlation coefficient between the measurements is medium and lower than the value obtained for the $CaCl_2$ solution (Table 2), which is why it can be said that $CaCl_2$ is also a good electrolyte for soil *p*H measurements. Although the relationships between pH_{H2O} and pH measured in the other electrolytes could be described by linear regression, the fitting of other equations improved

Table 2: Linear and polynomial equations for pH in water, in 0.01m $Cacl_2$, and 1 M KCl solution

Electrolyte solution	Linear equation	Correlation coefficient
0.01 M $CaCl_2$	$pHCaCl_2=0.6469pH_{H2O}+1.1175$	$R_2=0.6355$
1 M KCl	$pHCaCl_2=0.6245\ pH_{H2O}+0.8156$	$R_2=0.6239$

the coefficients of determination, which indicate that the relationships could be curvilinear.

The equation of linear regression is given in Table 2 and shows a very good slope of the straight line (close to unity), and this involves a constant difference between these two variables. A slope more than unity indicates that the difference between pH_{H2O} and *p*HKCl decreases with the increasing of *p*H values. The shape of the curve is also very close to the linear one and is an improvement over the linear regression line for high *p*H values ($pHH_2O \geq 5.5$), where there are more sample points, as it describes the data better than a linear fit. Although the linear regressions give a good correlation between the variables.

Similar studies used linear regression to relate these two parameters, but the data about the use of KCl solution like electrolyte solution in measurements of soil *p*H are less consistent. It has been shown in the literature that the deviation from linearity is due to the buffering effect of Al at low *p*H and to the presence of carbonate at high *p*H, while others have shown that ionic strength, exchangeable cations (Na, K, Ca, Mg and Al) and Al and Mn extracted could influence the measurements of soil *p*H (Desalegn et al., 2016, Wogi et al., 2021; Achalu, 2023). Some bigger differences for *p*H H_2O and pH KCl were obtained for acidic to slightly acidic samples. Other authors have used some electrolytes ($CaCl_2$, KCl, and $BaCl_2$) and different dilution ratios in determinations of soil pH and they show that the measurements were less influenced by the suspension, with and without stirring (Georges et al., 2018; Kome et al., 2018).

Addition of CaCl2 solution to the mixture has a smaller effect on the solution's ionic strength than KCl (or other salt) solution has and ionic strength has an inverse relationship with soil *p*H (Enang et al., 2017; Kome et al., 2016; Liu et al., 2020). The use of electrolyte solutions has the advantage of decreasing the variability in content of soluble salts between soils and the *p*H values obtained are less dependent on the soil solution ratio. In addition, the $CaCl_2$ solution can stabilize the dissolution of soil minerals, because of the common ion effect, more than in the case of the KCl solution.

4. Conclusion

Soil pH is influenced by ionic strength, and electrolyte solutions used during measurement. This study evaluated soil pH in water, 0.01 M CaCl, and 1 M KCl using 55 soil samples from Chole District. Results showed that pH measured in $CaCl_2$ and KCl was lower than in water by 0.85 and 1.27 units, respectively. Strong correlations existed among methods, with linear regression indicating reliable conversion relationships. Both $CaCl_2$ and KCl were found to be suitable for accurate soil pH determination.

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