Bangladesh J. Soil Sci. 2024, 40 (2): 111-124

VARIATIONS IN pH VALUES OF CALCAREOUS SOIL ON ACCOUNT OF VARIOUS MEASURING TECHNIQUES

M.M.H. Sarker*, M.I. Hossain, M.S. Hossain, K.S. Begum and M.F.M. Olik

Department of Soil Science, Sylhet Agricultural University, Sylhet-3100, Bangladesh

**Corresponding author: mosharaf_soil@sau.ac.bd*

Abstract

Soil pH is an important parameter in soil chemistry which varies under different determination techniques. Therefore, an experiment was conducted to observe the effects of different matrices, their mixing ratios and time of reading on pH of calcareous soil, and also to observe the relationship of different soil properties with pH. The experiment comprised two factors viz., three mixing ratios of soil and matrices (1:1.0, 1:2.5 and 1:5.0), and three times of reading after mixing of soil and matrix (reading after 30 minutes of mixing, RA30MM; reading after 90 minutes of mixing, RA90MM; and reading after 150 minutes of mixing, RA150MM). Six soil samples from six different locations were treated as six replications. A total of 12 soil samples were analyzed for pH by using three matrices (distilled water, $CaCl_2$ and KCl). The mean pH values measured in distilled water, 0.01M $CaCl_2$ and 1M KCl showed a distinct declining trend from high to low following the order $pH_w>pH_{Ca}>pH_K$, respectively. The increase in dilution of the soil and matrix ratio showed a tendency to increase the soil pH value which can be expressed as $pH_{1:1.0}<pH_{1:2.5}<pH_{1:5.0}$. Time after mixing of the soil and matrix affected pH values which is in the order of RA90MM>RA30MM>RA150MM. Interaction between soil-matrix ratio and duration also significantly affected soil pH. Variations in relationship of soil pH and other soil parameters were very strong in calcareous soils.

Keywords: Calcareous soils, $CaCl_2$, KCl, Soil pH, Soil-matrix ratio

1. Introduction

Soil pH is an important parameter in soil chemistry and proof for many soil chemical reactions as well as biological reactions (Moore and Leoppert, 1987). It determines the nutrient availability, microbial diversity and transformation of nutrients and compounds in soils. It has effect on the solubility, bioavailability and translocation of micro-nutrients in plants (Forstner, 1995). As microbial activity in soil depends on soil pH (Miller and Kissel, 2010) the decomposition of soil organic matter also affected by it and contributed in plant nutrient releases (Jones and Benton, 2012). In accordance with biochemical changes, physico-chemical processes like dissolution, precipitation and volatilization also influenced by soil pH (Kulikowska and Klimiuk, 2008). For the purpose of determining acid-base balance, including carbon dioxide and carbonate equilibrium, accurate soil pH measurement is necessary (Suarez, 1977; Stumm and Morgan, 1996). The pH determination of soil is exclusively method dependent. In most cases, soil pH is determined using water or another aqueous medium, such as a diluted salt solution. A significant challenge to determining soil pH is the effect of soil-water suspension (Reuter *et al.* 1999). Some factors need to be considered to reduce variability in pH determination. These include the ratio of soil to the solution, the cation concentration in the soil solution, the type of electrode used in the pH meter, the depth at which the electrode is submerged in the soil suspension, and the duration of time the suspension has been stirred. The soil-water ratio used in the suspension effects greatly in pH measurement where pH increa with a decrease in the soil-water ratio. An increase of 0.4 was found for a decrease of soil-water ratio from 10:1 to 1:10 (Keaton, 1938; Davis, 1943). McLean (1982) described suspension effect as the difference in the measured pH in the sediment and in the supernatant. According to Foth and Ellis (1988), the clay and humus particles which encounter the electrode and the equilibrium of soil CO_2 with its atmospheric concentration govern the suspension effect. Use of dilute calcium chloride (0.01M) and KCl (1M) as matrix is an easy solution of minimizing suspension effect (Sumner, 1994). The soil suspension pH affected greatly by the variations in salt concentration of soil solution when the levels of salt in soil solution was very low. Increase in soil pH due to soluble salt leaching was noticed by Puri and Asghar (1938). Studies regarding the role of electrolyte on soil pH determination in calcareous soil are scanty, and a comprehensive study is needed to learn the magnitude of the operational effects on the pH measurements. With this in mind, we examined the impacts of different matrices, their mixing ratios, and the mixing time on the measured pH of surface and sub-surface calcic soil as well as to observe the interaction of various soil parameters with pH.

2. Materials and Methods

The experiment was carried out at the Soil Science Lab, Sylhet Agricultural University, Sylhet, and the Soil Resource Development Institute (SRDI), Sylhet, during November 2020 to February 2021. Soil samples were collected from different respective sampling sites. The soil samples were collected just prior to the land preparation for *rabi* crop planting. Six sites were selected, and from each site two samples were collected at two soil depths (0-15 cm and 15-30 cm). GPS reading was recorded for each site (Table 1). The collected soil samples were spread on a brown paper in the laboratory for air-drying. After removing the plant roots and other debris the air-dried soil was ground and passed through a 2-mm sieve to remove debris, pebbles and gravels. The processed samples were kept in polyethylene bags and then analyzed for basic soil properties (pH, organic carbon, electric conductivity) and some other cations (potassium, calcium, magnesium, zinc, copper, iron and manganese) following standard methodology as described in Table 2.

2.1 Determination of Soil pH

Soil pH was measured in distilled water (pH_W), 0.01M $CaCl_2$ (pH_{Ca}), and 1M KCl (pH_K) for all the soil samples. The soil matrix ratios of 1:1.0, 1:2.5 and 1:5.0 (w/v) were used for each of the electrolytes. In each case, the amount of soil was 10 g. After mixing the soil and respective matrix/electrolyte, the suspension was stirred manually with the help of a glass rod for 10 minutes. The reading was taken after 30, 90 and 150 minutes after mixing the soil suspension. All pH measurements were performed at room temperature (27±2°C) using AD1030 pH/mV & Temperature Meter and AD1131B pH electrode, which had previously been calibrated at pH 4.1, 7.0 and 10.0. The meter was recalibrated, when necessary, to ensure accuracy (Al-Busaidi et al. 2003). Duplicate quality control samples were evaluated in each batch.

Table 1. Locations of soil sample collection

SL. No.	Location	AEZ	GPS reading
01	BSRI farm, Ishwordy, Pabna	AEZ-11	24^{0}7′ 24.3″; 89^{0}4′52.72″
02	BSRI farm. Ishwordy,Pabna.	AEZ-11	24^{0}6′43.6″; 89^{0}4′43.85″
03	Village: Sara Jhaudia, PO: Ishwordy, Pabna	AEZ-11	24^{0}7′23.7″; 89^{0}4′51.15″
04	BINA Sub-station Farm, Ishwordy, Pabna	AEZ-11	24^{0}6′47.7″; 89^{0}2′5.34″
05	BINA Sub-station Farm, Ishwordy,Pabna	AEZ-11	24^{0}6′54.4″; 89^{0}5′21.04″
06	BSRI Farm, Ishwordy, Pabna	AEZ-11	24^{0}6′47.6″; 89^{0}5′6.31″

Table 2. Methods for analysis of soil properties

Soil properties	Analytical methods
Organic carbon	The soil organic matter was oxidized using 1N potassium dichromate according to the wet oxidation method (Nelson and Sommers, 1996), and the amount of organic carbon in the aliquot was measured by titration against 0.5 N ferrous sulphate hepta-hydrate solutions. The percentage of organic carbon was multiplied by the van Bemmelen factor of 1.73 to get the amount of organic matter (Piper, 1950).
Exchangeable Ca, Mg, and K	The extractable amount for Ca, Mg, and K were determined using atomic absorption spectrometer after these elements were extracted from soil using 1M CH_3COONH_4 at a ratio of 1:1.0 soil-extractor. (Knudsen *et al.* 1982)
Available Zn, Cu, Mn, and Fe	By using a 0.05M DTPA solution (pH 7.3) and a 1:2 soil-extractant ratio, these micronutrients were extracted. Using atomic absorption spectrometer, the extracted level was quantified (Lindsay and Norvell, 1978).

2.2 Experimental design

Effects of different matrices, their mixing ratios and reading time after soil suspension mixing on the pH measurement were studied using factorial complete randomized design with six replications. The experiment comprises with two factors viz., three mixing ratios of soil and matrices (1:1.0, 1:2.5 and 1:5.0), and three times of reading after mixing of soil and matrix (reading after 30 minutes of mixing, RA30MM; reading after 90 minutes of mixing, RA90MM; and reading after 150 minutes of mixing, RA150MM). Thus, nine treatment combinations were tested.

2.3 Statistical analysis

Data collected on different parameters were subjected to statistical analysis using a computer based statistical program R following the basic principles, as outlined by Gomez and Gomez (1984). Significant effects of different treatments were determined by analysis of variance and treatment means were compared using Duncan's Multiple Range Test. The relationship between measured pH value and other soil characteristics were examined by SPSS.

3. Results

3.1 Effects of different matrices, mixing ratios and time after soil suspension mixing on the pH measurement

3.1.1 Surface soil pH using distilled water as matrix

Surface soil pH was affected significantly by the ratio of soil and water, time duration and their interaction (Table 3). Among the mixing ratio, the highest and lowest pH value was recorded for 1:5.0 and 1:1.0 ratios, respectively. In case of time duration, the highest pH value was found in 90 minutes after soil and matrix mixing. The lowest pH value was recorded for reading after 150 minutes of mixing soil and matrix (RA150MM). In terms of interactions, the highest pH value was observed from the interaction between1:5.0-ratio reading after 90 minutes of mixing soil and matrix while the lowest pH value was found from the interaction between 1:1.0 ratio reading after 150 minutes of mixing soil and water.

3.1.2 Sub-surface soil pH using distilled water as matrix

The ratio of soil to water, the duration of time, and their interaction all had significant effects on the pH of subsurface soil (Table 3). In terms of mixing ratios, the 1:5.0 ratio had the greatest pH value while the 1:1.0 ratio had the lowest pH value. Following 90 minutes of soil and matrix mixing and 150 minutes of soil and matrix mixing, respectively, the readings with the highest and lowest pH values were found. The interaction of 1:5.0 ratio –reading after 90 minutes of mixing (RA90MM) generated the highest pH value (8.69). On the contrary, the lowest pH value (8.31) was recorded from the interaction of 1:1.0 – reading after 150 minutes of mixing of soil and matrix (water).

3.1.3 Surface soil pH using KCl as matrix

The mixing ratio of soil and matrix (KCl), time duration and their interaction had significant role in pH determination of calcareous surface soil (Table 4). The highest surface soil pH value among the three mixing ratios was recorded for the 1:5.0 ratio, while the lowest surface soil pH value was for the 1:1.0 ratio. The reading of the soil pH value after 30 minutes of soil and KCl (matrix) mixing yielded the greatest value, and the reading after 150 minutes of soil and matrix mixing yielded the lowest value (RA150MM). Accordingly, the highest pH was observed from the interaction of 1:5.0 - reading after 30 minutes of mixing (RA30MM) followed by 1:5.0 - reading after 90 minutes of mixing soil and matrix and 1:1.0 - reading after 150 minutes of mixing (RA150MM) interaction gave the lowest pH value.

Table 3. Effects of distilled water as matrix, mixing ratios and time after soil suspension mixing on pH

Soil:Matrix/Time/Interactions	pH in surface soil	pH in sub-surface soil
Ratio		
1:1.0	8.15 ± 0.047b	8.39 ± 020c
1:2.5	8.20 ± 0.060b	8.56 ± 0.019b
1:1.5.0	8.50 ± 0.027a	8.62 ± 0.028a
Significance level	***P<0.001	***P<0.001
Time duration		
RA30MM	8.29 ± 0.059b	8.53 ± 0.027a
RA90MM	8.42 ± 0.047a	8.55 ± 0.033a
RA150MM	8.14 ± 0.054c	8.48 ± 0.036b
Significance level	***P<0.001	*P<0.05
Ratio × Time duration		
(1:1.0)-(RA30MM)	8.20 ± 0.087c	8.46 ± 0.022e
(1:1.0)-(RA90MM)	8.22 ± 0.063c	8.39 ± 0.027f
(1:1.0)-(RA150MM)	8.05 ± 0.087de	8.31 ± 0.028g
(1:2.5)-(RA30MM)	8.16 ± 0.110cd	8.62 ± 0.025bc
(1:2.5)-(RA90MM)	8.44 ± 0.052b	8.58 ± 0.028cd
(1:2.5)-(RA150MM)	7.99 ± 0.045e	8.50 ± 0.027e
(1:5.0)-(RA30MM)	8.51 ± 0.037ab	8.51 ± 0.062de
(1:5.0)-(RA90MM)	8.61 ± 0.016a	8.69 ± 0.014a
(1:5.0)-(RA150MM)	8.39 ± 0.035b	8.65 ± 0.022ab
Significance level	*P<0.05	***P<0.001
CV (%)	1.27	0.63

Means followed by same letter in a column are not significantly different at 5% level by DMRT, CV = Co-efficient of variation, 1:1.0, 1:2.5 and1:5.0 denote for the ratio of soil and matrix, RA30MM = Reading after30minutesofmixing, RA90MM = Reading after 90 minutes of mixing, RA150MM = Reading after 150 minutes of mixing.

3.1.4 Sub-surface soil pH using KCl as matrix

Similar to surface soil, sub-surface calcareous soil's pH was strongly influenced by the ratio of soil to matrix, the duration of time, and the interaction between ratio and passage of time (Table 4). The highest soil pH was obtained at a mixing ratio of 1:5.0, and the lowest pH value was at a ratio of 1:1.0. The reading with the greatest pH value was taken 30 minutes after the soil and KCl had been mixed (RA30MM). Interaction of 1:5.0 and reading after 30 minutes of mixing (RA30MM) had the highest pH value followed by 1:5.0-reading after 90 minutes of mixing (RA90MM). The lowest pH value was found from the interaction of 1:1.0-reading after150 minutes of mixing (RA150MM) soil and KCl.

3.1.5 Surface soil pH using $CaCl_2$ as matrix

Determination of pH of surface soil by using $CaCl_2$ as matrix had significantly affected by the ratio of soil and matrix ($CaCl_2$), time duration of mixing soil and $CaCl_2$ and their interactions (Table 5). In case of ratios of soil and matrix, the highest pH was found for 1:5.0 ratio while the lowest pH value was in 1:1.0 soil-matrix ratio. In terms of time, the highest pH of surface soil was found for reading after 90 minutes of mixing soil and $CaCl_2$ (RA1590MM). The lowest pH ofsurface soil was recorded for reading after30 minutes of mixing. Accordingly, interaction of 1:5.0-reading after 90 minutes of mixing soil and matrix ($CaCl_2$) had the highest pH value. The lowest pH value was found for the interaction of 1:1.0-reading after 30 minutes of mixing of soil and $CaCl_2$ matrix.

Table 4. Effects of KCl as matrix, their mixing ratios with soil and time after soil suspension mixing on pH

Soil:Matrix/Time/Interactions	pH in surface soil	pH in sub-surface soil
Ratio		
1:1.0	7.26 ± 0.024c	7.25 ± 0.015c
1:2.5	7.47 ± 0.025b	7.44 ± 0.024b
1:1.5.0	7.81 ± 0.030a	7.49 ± 0.025a
Significance level	***P<0.001	***P<0.001
Time duration		
RA30MM	7.54 ± 0.070a	7.56 ± 0.065a
RA90MM	7.53 ± 0.052a	7.50 ± 0.049b
RA150MM	7.46 ± 0.059b	7.23 ± 0.055c
Significance level	***P<0.001	***P<0.001
Ratio × Time duration		
(1:1.0)-(RA30MM)	7.26 ± 0.036d	7.27 ± 0.021e
(1:1.0)-(RA90MM)	7.31 ± 0.045d	7.28 ± 0.029e
(1:1.0)-(RA150MM)	7.20 ± 0.038e	7.21 ± 0.019f
(1:2.5)-(RA30MM)	7.45 ± 0.059c	7.51 ± 0.041c
(1:2.5)-(RA90MM)	7.50 ± 0.036c	7.47 ± 0.031c
(1:2.5)-(RA150MM)	7.45 ± 0.037c	7.35 ± 0.025d
(1:5.0)-(RA30MM)	7.91 ± 0.042a	7.89 ± 0.040a
(1:5.0)-(RA90MM)	7.79 ± 0.035b	7.75 ± 0.024b
(1:5.0)-(RA150MM)	7.74 ± 0.057b	7.73 ± 0.027b
Significance level	***P<0.001	***P<0.001
CV (%)	0.60	0.42

Means followed by same letter in a column are not significantly different at 5% level by DMRT, CV=Co-efficient of variation, 1:1.0, 1:2.5 and1:5.0 denote for the ratio of soil and matrix, RA30MM = Reading after 30 minutes of mixing, RA90MM = Reading after 90 minutes of mixing, RA150MM = Reading after 150 minutes of mixing.

3.1.6 Sub-surface soil pH using $CaCl_2$ as matrix

The effects of soil-matrix ($CaCl_2$) ratio, time duration and their interaction on pH value of calcareous sub-surface soil were significant (Table 5). The lowest pH value among the three ratios was discovered in the 1:1.0 ratio, and the highest pH value was noted for the 1:5.0 ratio. For time duration, the highest pH value and the lowest pH value were found from reading after 90 minutes and 30 minutes of mixing soil and matrix ($CaCl_2$). In case of time duration, the highest pH value was recorded for the interactionof 1:5.0-reading after 90 minutes of mixing soil and matrix ($CaCl_2$) (RA90MM) followed by1:5.0-reading after 30 minutes of mixing

(RA30MM). The lowest pH value was found from the interaction of 1:1.0-reading after 30 minutes of mixing soil and matrix ($CaCl_2$) (RA30MM).

3.2 Relationship between soil pH and other soil properties

In case of calcareous surface soil, exchangeable Ca has strong positive correlation (r=0.96**, 0.98** and 0.99**, respectively) with pH_W, pH_K and pH_{Ca} (Table 6). On the other hand, available Zn, Cu, Fe and Mn has strong negative correlation with pH_W (r = -0.86*, -0.96**, -0.97** and - 0.98**), pH_K (r = -0.80*, -0.99**, -0.99** and -1.00**) and pH_{Ca} (r= -0.78*, -0.99**, -1.00** and -1.00**), respectively.

Accordingly in case of calcareous sub-surface soil, available Ca has strong positive correlation (r=0.97**, 0.98** and 0.98**) with pH_W, pH_K, pH_{Ca} (Table 7). Like calcareous surface soil, in sub- surface soil, strong negative correlation existed between available Zn, Cu, Fe and Mn with pH_W (r=-0.92**, -0.99**, -1.00** and -1.00**), pH_K (r=-0.92**, -0.99**, -0.99** and -1.00**) and pH_{Ca} (= -0.92*, -0.99**, -1.00** and -1.00**), respectively.

Table 5. Effects of $CaCl_2$ as matrix, their mixing ratios with soil and time after soil suspension mixing on pH

Soil:Matrix/Time/Interactions	pH in surface soil	pH in sub-surface soil
Ratio		
1:1.0	7.78 ± 0.025b	7.87 ± 0.008b
1:2.5	7.79 ± 0.017b	7.88 ± 0.006b
1:1.5.0	7.83 ± 0.014a	7.91 ± 0.010a
Significance level	***P<0.001	***P<0.001
Time duration		
RA30MM	7.75 ± 0.025b	7.87 ± 0.010c
RA90MM	7.83 ± 0.012a	7.90 ± 0.008a
RA150MM	7.82 ± 0.011a	7.88 ± 0.006b
Significance level	***P<0.001	***P<0.001
Ratio × Time duration		
(1:1.0)-(RA30MM)	7.68 ± 0.053d	7.83 ± 0.007e
(1:1.0)-(RA90MM)	7.83 ±0.019ab	7.89 ± 0.010c
(1:1.0)-(RA150MM)	7.83 ± 0.017ab	7.89 ± 0.010c
(1:2.5)-(RA30MM)	7.74 ± 0.033c	7.86 ± 0.007d
(1:2.5)-(RA90MM)	7.80 ± 0.021b	7.88 ± 0.009c
(1:2.5)-(RA150MM)	7.83 ± 0.021ab	7.89 ± 0.012c
(1:5.0)-(RA30MM)	7.81 ± 0.031b	7.92 ± 0.010b
(1:5.0)-(RA90MM)	7.86 ± 0.021a	7.94 ± 0.009a
(1:5.0)-(RA150MM)	7.82 ± 0.020b	7.86 ± 0.010d
Significance level	***P<0.001	***P<0.001
CV (%)	0.43	0.16

Means followed by same letter in a column are not significantly different at 5 % level by DMRT, CV = Co-efficient of variation, 1:1.0, 1:2.5 and 1:5.0 denote for the ratio of soil and matrix, RA30MM = Reading after 30 minutes of mixing, RA90MM = Reading after 90 minutes of mixing, RA150MM = Reading after 150 minutes of mixing.

Table 6. Relationship between soil $pH_{1:2.5}$ and other soil properties in calcareous surface soil

	pH_W	OC	EC	K	Ca	Mg	Zn	Cu	Fe	Mn
pH_W	1.00									
OC	0.34	1.00								
EC	-0.41	0.23	1.00							
K	-0.06	-0.58	0.00	1.00						
Ca	0.96**	0.23	-0.31	0.19	1.00					
Mg	0.16	0.24	0.10	0.30	0.30	1.00				
Zn	-0.86*	-0.52	0.52	0.38	-0.71	-0.11	1.00			
Cu	-0.96**	-0.13	0.34	-0.16	-0.98**	-0.14	0.68	1.00		
Fe	-0.97**	-0.19	0.34	-0.14	-0.99**	-0.20	0.72	1.00**	1.00	
Mn	-0.98**	-0.20	0.37	-0.12	-0.99**	-0.20	0.77*	0.99**	1.00**	1.00
pH_K	1.00									
OC	0.22	1.00								
EC	-0.40	0.23	1.00							
K	0.06	-0.58	0.00	1.00						
Ca	0.98**	0.23	-0.31	0.19	1.00					
Mg	0.16	0.24	0.10	0.30	0.30	1.00				
Zn	-0.80*	-0.52	0.52	0.38	-0.71	-0.11	1.00			
Cu	-0.99**	-0.13	0.34	-0.16	-0.98**	-0.14	0.68	1.00		
Fe	-0.99**	-0.19	0.34	-0.14	-0.99**	-0.20	0.72	1.00**	1.00	
Mn	-1.00**	-0.20	0.37	-0.12	-0.99**	-0.20	0.77*	0.99**	1.00**	1.00
pH_{Ca}	1.00									
OC	0.25	1.00								
EC	-0.36	0.23	1.00							
K	0.09	-0.58	0.00	1.00						
Ca	0.99**	0.23	-0.31	0.19	1.00					
Mg	0.21	0.24	0.10	0.30	0.30	1.00				
Zn	-0.78*	-0.52	0.52	0.38	-0.71	-0.11	1.00			
Cu	-0.99**	-0.13	0.34	-0.16	-0.98**	-0.14	0.68	1.00		
Fe	-1.00**	-0.19	0.34	-0.14	-0.99**	-0.20	0.72	1.00**	1.00	
Mn	-1.00**	-0.20	0.37	-0.12	-0.99**	-0.20	0.77*	0.99**	1.00**	1.00

**Correlation is significant at the 0.01 level (2-tailed).*Correlation is significant at the0.05 level (2-tailed)

Table 7. Relationship between soil $pH_{1:2.5}$ and other soil properties in calcareous sub-surface soil

	pH_W	OC	EC	K	Ca	Mg	Zn	Cu	Fe	Mn
pH_W	1.00									
OC	0.20	1.00								
EC	0.14	-0.07	1.00							
K	-0.04	-0.03	-0.11	1.00						
Ca	0.97**	0.26	0.24	-0.05	1.00					
Mg	0.13	0.68	0.17	0.62	0.23	1.00				
Zn	-0.92**	-0.33	0.18	-0.11	-0.87*	-0.24	1.00			
Cu	-0.99**	-0.23	-0.18	0.09	-0.98**	-0.15	0.91**	1.00		
Fe	-1.00**	-0.22	-0.16	0.05	-0.98**	-0.15	0.92**	0.99**	1.00	
Mn	-1.00**	-0.48	0.76	-0.02	0.09	-0.19	0.88*	0.33	0.10	1.00
pH_K	1.00									
OC	0.19	1.00								
EC	0.11	-0.07	1.00							
K	-0.07	-0.03	-0.11	1.00						
Ca	0.98**	0.26	0.24	-0.05	1.00					
Mg	0.10	0.68	0.17	0.62	0.23	1.00				
Zn	-0.92**	-0.33	0.18	-0.11	-0.87*	-0.24	1.00			
Cu	-0.99**	-0.23	-0.18	0.09	-0.98**	-0.15	0.91**	1.00		
Fe	-1.00**	-0.22	-0.16	0.05	-0.98**	-0.15	0.92**	0.99**	1.00	
Mn	-1.00**	-0.48	0.76	-0.02	0.09	-0.19	0.88*	0.33	0.10	1.00
pH_{Ca}	1.00									
OC	0.23	1.00								
EC	0.14	-0.07	1.00							
K	-0.04	-0.03	-0.11	1.00						
Ca	0.98**	0.26	0.24	-0.05	1.00					
Mg	0.15	0.68	0.17	0.62	0.23	1.00				
Zn	-0.92**	-0.33	0.18	-0.11	-0.87*	-0.24	1.00			
Cu	-0.99**	-0.23	-0.18	0.09	-0.98**	-0.15	0.91**	1.00		
Fe	-1.00**	-0.22	-0.16	0.05	-0.98**	-0.15	0.92**	0.99**	1.00	
Mn	-1.00**	-0.48	0.76	-0.02	0.09	-0.19	0.88*	0.33	0.10	1.00

**Correlation is significant at the 0.01 level (2-tailed).*Correlation is significant at the 0.05 level (2-tailed)

4. Discussion

4.1 Effects of different matrix on soil pH determination

The mean pH values of calcareous soil tested in distilled water, $CaCl_2$, and KCl, respectively, showed a definite decreasing trend from higher to lower (distilled water>$CaCl_2$>KCl). This variance occurred because different electrolytes (KCl and $CaCl_2$) had a stronger ability than distilled water to liberate more H^+ ions from soil colloids. Such ion exchange between cations contained in soil solution and on exchange sites in the soil results in the release of H^+ in this manner.

In particular, soils differ in their concentrations of exchangeable H^+ and Ca^{2+} ions, which an electrolyte solution can exchange more readily than pure water. It is a common observation that adding $CaCl_2$ lowers soil pH when compared to using water as a matrix (Miller and Kissel, 2010). This is thought to be because the extra Ca^{2+} displaces H^+ from soil exchange sites (Conyers and Davey, 1988). One effect of electrolyte addition to pH compared to water is likely to be, at least initially, the possibility of a double layer around a negatively charged soil surface. As a result, the number of H^+ ions released in the suspension will increase and therefore the measured pH value will decrease. Another possible factor is the effect of a liquid connection for the low pH values obtained in the electrolyte solution compared to distilled water. The fluid junction effect arises from the uneven expansion of the electric charge across the junction between the electrolyte and the internal electrode solution. The effect is usually greater when measuring pH in water than using electrolyte solutions (Moore and Leoppert, 1987). Therefore, the pH value of the soil when water is used is higher than that measured in the electrolyte solution, since the charges are carried evenly across the junction. Aitken and Moody (1990) pointed out that pHvalues in distilled water > pH in 0.01M $CaCl_2$ > pH in KCl. Similar result was also observed by Al-Busaidi *et al.* (2005). They reported that average pH in distilled water was significantly higher than the pH values in other electrolytes in calcareous soil. Kome *et al.* (2018) carried out an experiment for volcanic ash soils and found the trend in pH value which was pH in H_2O > pH in 0.01M $CaCl_2$ > pH in 1M KCl. Yusuf *et al.* (2015) obtained that the soil pH in distilled water was 7.12 and in $CaCl_2$ was 6.39.

4.2 Effects of mixing ratio on soil pH determination

Increased soil and matrix dilution revealed an increasing trend in soil pH, which can be expressed as 1:1.0<1:2.5<1:5.0. This is due to the fact that the H^+ concentration in the soil-matrix suspension decreases with increasing suspension dilution, raising the observed pH. This implies that the pH value will be higher the wider the soil: water ratio. This appears to be due to dilution effects in agreement with the findings of Keaton (1938). The use of $CaCl_2$ as a matrix caused a greater decrease in soil pH in samples with low ionic strength, which is also consistent with earlier research that showed a difference in pH values between water and $CaCl_2$ matrix of up to 1 pH unit (Miller and Kissel, 2010; Rayment and Lyons, 2011). However, for soils with high ionic strength, pH values measured on $CaCl_2$ were quite close to those ofwater. This is in agreement with the findings of Miller and Kissel, 2010 who reported a variation of less than 0.2 pH units for soils with high ionic strength. Al-Busaidi *et al.* (2005) showed similar result where the mean pH values for 1:1.0, 1:2.5 and 1:5.0 dilution ratios recorded as 8.12, 8.29 and 8.44, respectively. Edmeades and Wheeler (1990), reported that a decrease in the solution ratio increases the ionic strength of the solution and a decrease in the pH value of the soil. Libohova *et al.* (2014) found highest pH values in 1:5.0 (water) and lowest in 1:2 ($CaCl_2$). Yu and Ji (1993) found that increasing the soil-water ratio affected the dissociation of adsorbed ions and ultimately increased pH of the suspension.

4.3 Effects of time duration on soil pH determination

The pH values of the surface and sub-surface soil for all matrices were impacted in the case of delayed reading following soil-matrix mixing. In the majority of cases, higher pH values were measured for RA90MM than RA30MM, and after that, the pH values for RA150MM were on the decline. This rise in soil pH between RA90MM and RA30MM may be caused by electrolytes in the soil solution flocculating over time. According to estimates by Beretta *et al.* (2014), soil pH values were higher during first stirring and fell to 3.91% after three minutes of stirring. According to Foth and Ellis (1988), stirred soil suspensions have a lower pH value than non-stirred soil suspensions. Typically, the pH of the soil suspension is lower than that of the supernatant (Tan, 1995). Similar results were also reported by Al-Busaidi *et al.* (2005). It is because soil has a supposedly larger H^+ concentration.

4.4 Relationship between soil pH with other soil properties

The association between available Ca and pH_W, pH_K, and pH_{Ca} was shown to be strongly positive in calcareous surface and subsurface soil, but the link between various micronutrients (Zn, Cu, Fe, and Mn) and pH_W, pH_K, and pH_{Ca} was strongly negative. Such changes in the interaction between soil pH and other soil parameters in soils with diverse responses may be caused by the presence of distinct anions and cations in variable percentages.

4. Conclusions

Due to the use of various matrices in various ratios as well as the use of various reading times after mixing/stirring, considerable differences in the pH of calcareous soils were perceived. Soil pH measured in distilled water, $CaCl_2$ and KCl showed a distinct declining trend following the order $pH_w > pH_{Ca} > pH_K$, respectively. The increase in dilution of the soil and matrix ratio showed increasing tendency of pH which can be stated as $pH_{1:1.0} < pH_{1:2.5} < pH_{1:5.0}$. Soil pH quantified at different time after mixing of the soil and matrix appeared as the highest at 90 minutes after mixing followed by 30 and 150 minutes after mixing.

Acknowledgement

The authors are grateful to Sylhet Agricultural University Research System (SAURES) for the financial support to successfully complete this research.

Conflicts of Interest

The authors declare no conflicts of interest regarding publication of this paper.

References

Aitken, R.L., Moody, P.W. and Mckinley, P.G. 1990. Lime requirement of acidic Queensland soils I. Relationships between soil properties and pH buffer capacity. Aus. J. Soil Res. 28: 695-701.

Al-Busaidi, A., Cookson, P. and Yamamoto, T. 2005. Methods of pH determination in calcareous soils: use of electrolytes and suspension effect. Aus. J. Soil Res. 43: 541-545.

Beretta, A., Bassahum, D., Musselli, R. 2014. Measure Soil pH at Rest or Stirring the Soil: water Mixture. Agrocienc. Urug. 18(2): 90-94.

Conyers, M.K. and Davey, B.G. 1988. Observations on some routine methods for soil pH determination. Soil Sci. 145: 29-36.

Davis, L.E. 1943. Measurement of pH with the glass electrode as affected by soil moisture. Soil Sci. 56(6): 405-422.

Edmeades, D.C. and Wheeler, D.M. 1990. Measurement of pH in New Zealand soils: an examination of the effect of electrolyte, electrolyte strength, and soil: solution ratio. N. Z. J. Agric. Res. 33(1): 105-109.

Forstner, U. and Allen, H.E., Huang, C.P., Bailey, G.W., Bowers, A.R. 1995. Land contamination by metals global scope and magnitude of problem in Metal Speciation and Contamination of soil. CRC press, Inc. Boca Raton, FL, USA.1-33.

Foth, H.D., Ellis, B.G.1988. Soil fertility, soil pH and its management. Wiley: New York. 36-59

Gomez, K. A. and Gomez, A.A. 1984. Statistical procedures for agricultural research. John Wiley & Son.

Jones, J.R. and Benton, J. 2012. Plant Nutrition and Soil Fertility Manual 2nd Edition. CSIRO Publishing.

Keaton, C.M. 1938. A theory explaining the relation of soil- water ratios to pH values. Soil Sci. 46(3): 259-266.

Kome, G.K., Enang, R.K. and Palmer, B. 2018. Models relating soil pH measurements in H_20, KCl and $CaCl_2$ for volcanic ash soils of Cameroon. Kfuban Yerima Meli Gilles. Geoderma Reg. 14: 185.

Kulikowska, D. and Klimiuk, E. 2008. The effect of landfill age on municipal leachate composition. Bioresour. Technol. 99(13): 5981-5985.

Libohova, Z., Wills, S., Odgers, N.P., Ferguson, R., Nesser, R., Thompson, J. A. and Hempel, J.W. 2014. Converting pH 1:1 H_2O and 1:2$CaCl_2$ to 1:5 H_2O to contribute to a harmonized global soil database. Geoderma. 213: 544-550.

McLean, E.O. 1982. Soil pH and Lime requirement. In page A.L. (Ed), Methods of Soil Analysis, Part2. Chemical and Microbiological Properties, American Society of Agronomy, Soil Science Society of America, Madison, Wisconsin. 199-224.

Miller, R.O. and Kissel, D.E. 2010. Comparison of soil pH methods on soils of North America. Soil Sci. Soc. Am. J. 74: 310-316.

Moore, T.J. and Leoppert, R.H. 1987. Significance of potassium chloride pH of calcareous soils. Soil Sci. Soc. Am. J. 51: 908-912.

Puri, A.N. and Asghar, A.G. 1938. Influence of salts and soil–water ratio on pH value of soils. Soil Sci. 46: 249-257.

Rayments, G.E., Lyons, D.J. 2011. Soil Chemical methods. CSIRO publishing Victoria Australia.

Reuter, D.J., Peverill, K.I. and Sparrow, W., 1999. In soil analysis, An interpretation manual, CSIRO Publication Sydney, Australia. Soil pH. 104-106.

Stumm, W. and Morgan, J.J. 2012. Aquatic chemistry: chemical equilibria and rates in natural waters (Vol. 126). John Wiley & Sons.

Suarez, D.L.,1977. Ion activity products of Calcium Carbonate in waters below the root zone. Soil Sci. Soc. Am. J. 41: 310-315.

Sumner, M.E. 1994. Measurement of soil pH: Problems and solutions. Commun. Soil Sci. Plant Anal. 25: 859-879.

Tan, H.K. 1995.Soil sampling, preparation, and analysis. Soil pH measurement. Marcel Dekker, New York. 96-113.

Yu, T.R. and Ji, G.L. 1993. Electrochemical methods in soil and water research. 'Glass electrodes and their applications'. pp. 147-182.

Yusuf, A.J., Galadima, A., Garba, Z.N. and Nasir, L. 2018. Determination of some heavy metals in soil sample from Illela Garage in Sokoto state Nigeria. Res. J. Chem. Sci. 5(2): 8-10.