

A Al-Busaidi and P Cookson

Methods of pH Determination in Calcareous Soils of Oman: The Effect of Electrolyte and Soil/Solution Ratio

Abstract: Determination of pH assists in understanding many reactions that occur in soil. Soil pH values are highly sensitive to the procedure used for determination. In this study, pH was measured in different electrolytes [distilled water (pH_w), $0.01M CaCl_2$ (pH_{Ca}), $1MKCl$ (pH_k), and $0.01M BaCl_2$ (pH_{Ba})] with different soil:electrolyte ratios (i.e. 1:1, 1:2.5, and 1:5). The objective was to determine the effect of each electrolyte and dilution ratio on pH of saline and non-saline soils from Oman. It was found that pH values varied significantly between electrolytes and with different dilution ratios. Linear regression equations were generated between electrolytes, dilution ratios and were mostly significant. Soil pH values determined in different electrolytes were significantly interrelated.

Water appeared as a highly suitable solvent for soil pH measurements because it is simple and values are familiar to soil users. However, alkaline errors and electrode instabilities, due to liquid junction and soluble salt effects, affected soil pH measurements in water.

Soil salinity affected pH measurements, especially in water, and resulted in alkaline errors during pH measurements. Errors were minimized when pH was measured in electrolytes rather than in water.

Keywords: Hydrogenous Determination, Calcareous Soils, Sultanate Oman, Electrolytes, Dilution, Variation.

Introduction

Soil pH is one of the most important parameters used in assessing the suitability of soils for agricultural use. A knowledge of soil pH is fundamental to the understanding of soil systems, because it is an indicator of many soil reactions. Many inferences can be made based on soil pH, including nutrient

طرق تحديد الرقم الهيدروجيني في الترب الكلسية بعمان:
تأثير الرقم الهيدروجيني بمختلف المحاليل والتخفيفات
أحمد البوسعيدي و بيتر كوكسون

المستخلص: يساعد تحديد الرقم الهيدروجيني في فهم كثير من التفاعلات التي تحدث في التربة، وتتأثر القيمة المقاسة للرقم الهيدروجيني للتربة بنوعية الطريقة المتبعة لقياس الرقم الهيدروجيني.

في هذه الدراسة، تم قياس الرقم الهيدروجيني بعدة محاليل مختلفة (ماء مقطر، كالسيوم كلورايد $CaCl_2 0.01$ ، بوتاسيوم كلورايد $1MKCl$ ، باريوم كلورايد $0.01MBaCl_2$) وباستخدام طرق تخفيف مختلفة من نسب التربة والمحلول (1:1، 1:2.5، 1:5). الهدف الرئيسي من هذه الدراسة هو تحديد تأثير هذه المحاليل على الرقم الهيدروجيني للتربة المالحة وغير المالحة بعمان. وقد وجد إن الرقم الهيدروجيني يتغير عند استخدام هذه المحاليل، وبمختلف التخفيفات، وقد تم ربط هذه التغيرات مع بعضها البعض، وأنشئت مختلف المعادلات الخطية بين المحاليل والتخفيفات. معظم هذه المعادلات أوضحت علاقات جيدة مع بعضها البعض مع قيمة عالية لمعامل الارتباط (R^2)

وأوضحت الدراسة أيضاً إن قيم الرقم الهيدروجيني المقاسة بالمحاليل المختلفة قد تغيرت تغيراً ملحوظاً عند استخدام مختلف التخفيفات ولكنها لم تكن عالية كمثل التي قيست بالماء.

والماء هو أكثر تناسلاً لقياس الرقم الهيدروجيني، لأنه بسيط وقيمه سهلة الفهم ومعظم الناس لهم دراية بتفسيراته، ولكنه وعند وجود الأخطاء القلوية يعطي قراءة غير دقيقة نتيجة لوجود الأملاح وانقطاع الإتصال الأيوني. ولا يمكن تفادي هذه التأثيرات عند استخدام الماء كوسط لقياس الرقم الهيدروجيني.

وتؤثر ملوحة التربة في قياس الرقم الهيدروجيني وذلك بتأثيرها على دقة القراءة، وخاصة عند استعمال الماء كوسط لقياسه. هذه التأثيرات يمكن تقليلها أو الحد منها باستخدام المحاليل المختلفة عوضاً عن الماء.

كلمات مدخلية: تحديد الرقم الهيدروجيني، الترب الكلسية، سلطنة عمان، محاليل، تخفيفات، تغيرات.

status, chemical reactions, stage of soil genetic development, presence of micro-organisms, and potential toxicity of environmental contaminants (Moore and Loeppert, 1987).

Measurement of soil pH is highly technique dependent and many soil parameters or experimental factors affect measured values. It is essential that reliable and accurate methods of determination are found.

Ahmed S. Al-Busaidi and Peter Cookson
Department of Soil & Water Sciences,
College of Agriculture, Sultan Qaboos University(SQU),
P.O. Box 34 Al-Khod 123, Sultanate of Oman
Email: ahmed99@squ.edu.om

Deciding how much water to add to different soils when measuring pH is difficult. Soils differ in their capacity to absorb water because of differences in texture and structure. In general, the addition of water to a given amount of soil dilutes the concentration of H⁺ ions, resulting in pH increase. Therefore, the smallest soil/water ratio that can be used without producing technical difficulties is usually preferred. Most pH determinations are performed in a suspension with a soil/water ratio of (1:1 or 1:2), since this condition is closer to the natural conditions than wider ratios.

Measurements of soil pH in distilled water can be affected by the soluble-salt content of soil. The stability of soil pH values is also affected by the interaction of salt and soil/solution ratios. Fluctuations in pH readings can be reduced by measuring soil pH in dilute electrolyte solutions, such as CaCl₂ or KCl instead of distilled water. However, when salt solutions in the range of 0.07 to 1M are used, soil pH values may be 0.5 to 1.5 units lower than when they are measured with distilled water (Foth and Ellis, 1988). The change in pH resulting from the addition of electrolytes [for example 0.01M CaCl₂ (pH_{ca}), 1MKCl (pH_k), and 0.01MBaCl₂ (pH_{ba})] compared to distilled water is known as the salt effect and is measured as:

$$\Delta\text{pH} = \text{soil pH in salt solution} - \text{soil pH in water} \quad (\text{Rowell, 1994}).$$

Many researchers have studied the effect of different electrolytes and soil solution ratios on soil pH in acidic soils. The effects of soil/solution ratios and different electrolytes on soil pH have been less frequently studied in alkaline-calcareous soils. In Oman, soils are mostly alkaline and calcareous, and there are no published studies describing the effect of electrolyte addition and soil suspension dilution ratios on pH determination. Therefore, the objective of this study was to assess the effect of different procedures used to measure soil pH in a range of alkaline and calcareous soils collected in Oman.

Materials and Methods

Soil Sampling and Preparations

Thirty surface (0-10cm) and subsurface (10-20cm) cultivated soil samples were taken from Batinah (Barka) and Interior (Adam) regions. Samples were selected from agricultural areas in order to have a wide range of salinity and textures. All samples were air dried at 25°C and passed through a 2-mm sieve.

Soil pH Determination

Soil pH was determined in distilled water (pH_w), 0.01M CaCl₂ (pH_{ca}), 1MKCl (pH_k) and 0.01M BaCl₂ (pH_{ba}) for all samples. Soil/solution ratios of 1:1, 1:2.5, and 1:5 (w/v) were used for each electrolyte. The suspension was shaken manually every 10 minutes for 30 minutes. Values of pH were recorded after 1 minute of stirring. All pH determinations were performed at room temperature (20 ± 2°C) using a Jenway 3020 pH meter and Phillips combine glass/calomel electrode type CE1, that had previously been calibrated at pH 7.0 and 9.0. The meter was recalibrated if necessary to ensure accuracy.

Electrical conductivity (EC), sodium adsorption ratio (SAR), cation exchange capacity (CEC), calcium carbonate, and soil texture were also determined.

Analysis of Variance (ANOVA) and linear regression analysis were performed using the Statistical Analysis System (SAS) and Statistical Package for Social Sciences (SPSS, Kinnear and Gray, 1997).

Results and Discussion

Factors Affecting Measurements of pH

ANOVA of pH Data

ANOVA for pH results are given in Table 1. There were significant differences in pH when soils were suspended in different electrolytes. This suggests that soils react differently when soil suspensions are modified by electrolyte addition as compared to water alone. This could be explained by differences in electrolyte liquid junction and the release of more H⁺ through different mechanisms, which leads to differences in pH values between electrolyte suspensions.

The table also shows that there was a significant effect of the dilution ratio on electrolyte reactions.

Effect of Electrolyte Composition

Figure 1 shows the differences in soil pH when measured in either distilled water (pH_w), 0.01M CaCl₂ (pH_{ca}), 1MKCl (pH_k), or 0.01M BaCl₂ (pH_{ba}). The highest pH as 8.57 was found in water and the lowest value was in CaCl₂ as 8.16. Figure 2 shows significant differences between the mean pH values of different electrolytes measured at three dilution ratios as 1, 2, and 5.

Table 1. Analysis of variance for electrolytes and dilution ratios of different soils.

Dependent variable: pH

Source of variation	DF	Sum of Squares	Mean Squares	F Values ¹
Electrolyte	3	21.537	7.180	224.48
Dilution	2	13.703	6.851	214.23
ELE*Dilution	6	1.856	0.309	9.67

Note: All F values were significant at the 0.1% level of probability

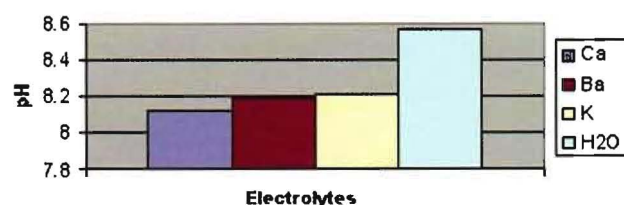


Figure 1: Effect of different electrolytes on soil pH, at average over all dilution ratios.

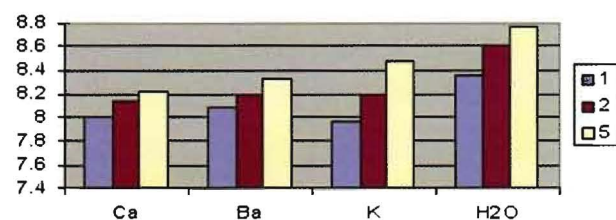


Figure 2: Effect of different electrolytes on soil pH measured in different dilution ratios.

Effect of Electrolytes on pH

Figure 1 shows that on the average, pH_w is significantly higher than the pH values in electrolyte solutions. Electrolytes appeared to release more H⁺ ions from soils than distilled water. This release is probably due to ion exchange between cations held in solution and on soil exchange sites. In particular, soils with varying amounts of exchangeable H and Ca ions, exchange more readily by electrolyte solutions than distilled water. Conyers and Davey (1988) suggested that in neutral soils, at least, direct desorption of H⁺ by Ca²⁺ was the dominant mechanism of pH decrease.

Another probable reason for the lower pH values obtained in electrolyte solutions than distilled water is the liquid junction effect. This arises from the unequal diffusion of electrical charges across the junction between soil suspension and internal electrode solution. Generally, the effect is greater when measuring pH in water than when electrolyte solutions are used (Moore and Loeppert, 1987). Hence, when water is used, soil pH values tend to be

higher than when measured in electrolyte solutions since charges are carried more equally across the junction.

As Schofield and Taylor (1955) pointed out, added CaCl₂ affects the amount of electrolyte in soils but has less effect on solution ionic strength. Addition of KCl and BaCl₂, however, concentrates dissolving solutions whereas water addition simply dilutes the suspension. The use of electrolyte solutions has the advantage of reducing the variability in soluble salt content between soils and so the pH values obtained are less dependent on the soil solution ratio. Furthermore, the addition of electrolytes probably maintained fluctuation conditions during measurement, as compared to addition of water alone, especially in sodium rich soils.

Addition of CaCl₂ electrolyte probably stabilised the dissolution of soil minerals containing CaCO₃, through the common ion effect, more than when KCl and BaCl₂ were added. Thus, variations in Ca²⁺ ion concentration in soil suspensions following KCl and BaCl₂ additions may have influenced the pH values in these electrolyte solutions. However, the position of the equilibrium between soil CaCO₃, CaCl₂, KCl, and BaCl₂ may also be influenced by the length of time which elapses between electrolyte and pH measurement.

Another effect of electrolyte addition compared to water is probably the reduction, at least initially, of the double layer potential surrounding the negatively charged soil surfaces. The result would be to increase the number of H⁺ ions released into the suspension and, hence, decrease the measured pH values.

Houba *et al.* (1990) reasoned that pH values measured in CaCl₂ solutions are less dependent on soil exchange properties than when measured in KCl, since pH_k values are negatively related to the cation exchange capacity (CEC) of calcareous soils. The pH_k - CEC relationship arises from Ca ions being displaced from exchange sites into solution

following the addition of a high concentration of K ions. The resulting increase in Ca ion concentration suppresses the pH of the resulting solution. The extent of exchange of K for Ca is an important factor leading to variable Ca concentration in soil suspensions, and hence reduces the predictability of the common ion effect on the solubility of CaCO_3 .

Effect of Dilution Ratios

Table 1 shows highly significant differences ($p < 0.001$) between pH values measured in electrolytes at different dilution ratios. When averaged over electrolytes, the mean values for 1:1, 1:2.5 and 1:5 dilution ratios became 8.12, 8.29 and 8.44, respectively. The interactions between dilution ratios and electrolytes were highly significant. Hence, dilution ratio should always be specified in any study related to soil pH, because different dilutions are expected to yield different pH values. The general effect of increasing the dilution of the soil suspension was to increase the pH significantly as shown in Figure 3. Addition of more water reduced the H^+ ion concentration and, hence, increased pH. However, since the interaction between dilution and electrolyte was significant, differences in pH values between electrolytes were not due simply to dilution of H^+ ions. This interaction should be interpreted in terms of how soil behaviour changes if different electrolytes are used. Differences between dilution ratios for different soils also influence the pH values because soils vary in their capacity to absorb water. In addition, dilution ratios affect the dissociation of adsorbed ions and, thus, the pH of the suspension. Increasing the dilution ratio probably had two main effects on cations; namely, (1) decrease in the cation concentrations of soil suspensions, and (2) increase in the amount of cations released, except Ca^{2+} , per unit weight of soil. Edmeades and Wheeler (1990), reported that reduction in the dilution ratio causes decrease in the soil pH values as a result of increase in the ionic strength of solutions.

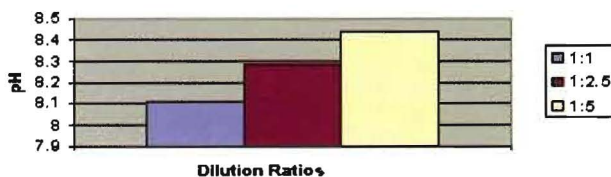


Figure 3: pH of different dilution ratios at average over all electrolytes.

Interactions Between Electrolytes and Dilution Ratios

Figure 4 shows that pH_w values were highest in the whole range of different dilution ratios studied. The differences in pH between electrolytes, at each dilution ratio, were small compared to the differences in water. However, there were interactions between different electrolytes. Values of pH_k were lowest at the 1:1 dilution ratio but higher than pH_{ca} and pH_{ba} at the 1:5 ratio. The possible reasons are:

- 1) as mentioned earlier, since pH_k is affected by the cation exchange capacity of the soil, its response differs when soil suspensions are diluted, mainly through differences in the adsorption power of the soils for exchangeable cations;
- 2) pH_{ca} is less affected by changes in the ion concentration and dilution ratio of the soil suspension than other electrolytes;
- 3) as reported by Aitken and Moody (1991), the relationship between pH_{ca} and pH_w departs from linearity in sandy alkaline soils reflecting the buffering effect of carbonate on pH;
- 4) in calcareous soils, the equilibrium between Ca^{2+} and CaCO_3 in electrolytes differs at different dilution ratios; and finally,
- 5) soil salinity can suppress differences in ion concentrations between soil/water and soil/electrolyte suspensions, and also affects other soil properties.

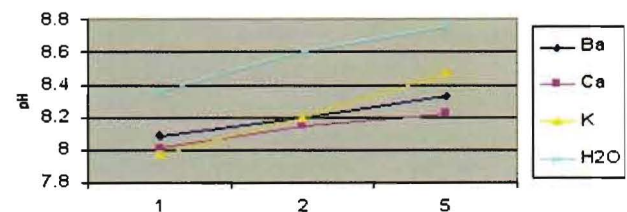


Figure 4: Interactions between different electrolytes at different dilution ratios.

Regression Analysis of pH in Water and Electrolytes

The relationships between pH_w and pH values obtained in different electrolytes at the three dilution ratios are shown in Figure 5. Table 2a represents relationships between different electrolytes at different dilution ratios, and corresponding pH_w values in non-saline, saline and mixed soils. The relationships between pH (electrolytes) and pH_w were generally rather poor for the data from all soils. R^2 values ranged from 0.141 for CaCl_2 at 1:5 dilution to 0.539 for BaCl_2 at

1:1 dilution. If soils were separated into non-saline and saline groups, then R^2 values for equations generally increased. CaCl_2 and BaCl_2 tended to yield pH values more closely related to pH_w in saline than non-saline soils at 1:1 dilution, but less closely related at 1:5 dilution because associations generally decreased with increasing dilution. In KCl, dilution ratio appeared to have little effect on R^2 values in non-saline soils, but was slightly reduced in saline soils as dilution increased. In BaCl_2 pH values appeared to be more consistently related to pH_w than either pH_{ca} or pH_k at each dilution ratio. Increasing dilution ratios appeared to give less precise predictions of pH_w in BaCl_2 and CaCl_2 than in KCl for mixed saline and non-saline soils. For saline soils only BaCl_2 at 1:1 dilution gave pH values more closely related to pH_w than other electrolytes ($R^2 = 0.87$). For non-saline soils pH in

BaCl_2 at 1:5 dilution gave pH values more closely related to pH_w than other electrolytes ($R^2 = 0.77$). The apparent differences in significance of regression equations for different electrolytes as compared with water probably reflects, in addition to other factors, differences in CaCO_3 solubility and hydrolysis during measurement. Differences in the degree of alkalinity in soil suspensions could also play a role in producing non-linearity between pH_w and pH electrolytes. Conyers and Davey (1988) found a good relationship between different electrolytes with high R^2 value in acid soils. When their study extended to include alkaline soils, the relationships were more widely scattered and R^2 values dropped. They concluded that the presence of different chemical interferences in alkaline soils made it difficult to reach linearity in relationships between different electrolytes.

Table 2a: The relationships between methods for pH determination.

Variables	Dilution	Regression Equation	R^2	No. of Samples	Soil Salinity
CaCl_2 vs. water	1:1	$\text{pH}_{\text{Ca}} = 0.11\text{pH}_w + 7.03$	0.027NS (1)	11	N (2)
		$\text{pH}_{\text{Ca}} = 0.62\text{pH}_w + 2.97$	0.783***	19	S
		$\text{pH}_{\text{Ca}} = 0.26\text{pH}_w + 5.82$	0.290**	30	M
	1:2.5	$\text{pH}_{\text{Ca}} = 0.33\text{pH}_w + 5.23$	0.389*	11	N
		$\text{pH}_{\text{Ca}} = 0.37\text{pH}_w + 5.03$	0.505***	19	S
		$\text{pH}_{\text{Ca}} = 0.16\text{pH}_w + 6.72$	0.204*	30	M
	1:5	$\text{pH}_{\text{Ca}} = 0.55\text{pH}_w + 3.24$	0.600*	11	N
		$\text{pH}_{\text{Ca}} = 0.26\text{pH}_w + 6.00$	0.280*	19	S
		$\text{pH}_{\text{Ca}} = 0.14\text{pH}_w + 6.96$	0.141*	30	M
KC vs. water	11:1	$\text{pH}_k = 1.07\text{pH}_w - 1.25$	0.654**	11	N
		$\text{pH}_k = 0.53\text{pH}_w + 3.67$	0.460**	19	S
		$\text{pH}_k = 0.25\text{pH}_w + 5.87$	0.151*	30	M
	1:2.5	$\text{pH}_k = 1.11\text{pH}_w - 1.62$	0.635**	11	N
		$\text{pH}_k = 0.47\text{pH}_w + 4.24$	0.411**	19	S
		$\text{pH}_k = 0.29\text{pH}_w + 5.75$	0.205*	30	M
	1:5	$\text{pH}_k = 1.48\text{pH}_w - 4.94$	0.679**	11	N
		$\text{pH}_k = 0.45\text{pH}_w + 4.56$	0.372**	19	S
		$\text{pH}_k = 0.34\text{pH}_w + 5.53$	0.236**	30	M
BaCl_2 vs. Water	1:1	$\text{pH}_{\text{ba}} = 0.4\text{pH}_w + 4.7$	10.343 ^{NS}	11	N
		$\text{pH}_{\text{ba}} = 0.68\text{pH}_w + 2.5$	10.870***	19	S
		$\text{pH}_{\text{ba}} = 0.38\text{pH}_w + 4.94$	0.539***	30	M
	1:2.5	$1:2.5\text{pH}_{\text{ba}} = 0.69\text{pH}_w + 2.12$	0.683**	11	N
		$\text{pH}_{\text{ba}} = 0.41\text{pH}_w + 4.73$	0.568***	19	S
		$\text{pH}_{\text{ba}} = 0.26\text{pH}_w + 5.99$	0.358***	30	M
	1:5	$\text{pH}_{\text{ba}} = 1.1\text{pH}_w - 1.58$	0.772***	11	N
		$\text{pH}_{\text{ba}} = 0.32\text{pH}_w + 5.61$	0.393**	19	S
		$\text{pH}_{\text{ba}} = 0.25\text{pH}_w + 6.13$	0.287**	30	M

(1) NS not significant ($p > 0.05$), *** significant at ($p < 0.001$), ** significant at ($p < 0.01$), significant at ($p < 0.05$). (2) N = Non-Saline Soils (EC of saturated past), S = Saline Soils, M = Mixed of both Soils.

On the other hand, Table 2b shows the regression equation between different electrolytes at each dilution ratio. In general, pH values of saline soils in CaCl₂ and BaCl₂ were more closely related at each dilution than for non-saline soils. In BaCl₂ and KCl, pH values were closely related, especially in non-saline soils at 1:5 dilution ratio. Increasing dilution ratios tended to increase the significance of these relationships in both saline and non-saline soils. The relation between CaCl₂ and KCl was of lower significance than between other electrolytes. However, at 1:5 dilution in saline soils, pH values in the two electrolytes were relatively highly correlated ($R^2 = 0.72$). In summary, although pH responses in BaCl₂ and CaCl₂ were similar, the largest discrepancy was between KCl and CaCl₂, suggesting that the former two electrolytes behaved dissimilarly.

Generally, salinity had a significant effect in the relationships given in Table 2b. Some saline soils and non-saline soils showed a good relationship with different electrolytes but others did not. The best relationship for non-saline soils was found between KCl versus BaCl₂ at 1:5 ratio. However, for saline soils CaCl₂ versus BaCl₂ at 1:2.5 ratio gave the highest association between pH values. For mixed saline and non-saline soils, CaCl₂ versus BaCl₂ at 1:1 ratio yielded the best association. It can be concluded that soil salinity has a significant effect on pH values but when measured in different electrolytes, the effect can be minimized. Electrolytes perhaps should be used more frequently in pH measurements rather than water because they can give more reliable values for saline soils.

Table 2b: The relationships between methods for pH determination.

Variables	Dilution	Regression Equation	R ²	No. of Samples	Soil Salinity
CaCl ₂ vs. KCl	1:1	$pH_{Ca} = 0.16pH_K + 6.74$	0.093 ^{NS}	11	N
		$pH_{Ca} = 0.67pH_K + 2.70$	0.551*** ¹⁹	S	
		$pH_{Ca} = 0.44pH_K + 4.50$	0.339***	30	M
	1:2.5	$pH_{Ca} = 0.29pH_K + 5.73$	0.605**	11	N
		$pH_{Ca} = 0.5pH_K + 4.03$	0.500***	19	S
		$pH_{Ca} = 0.4pH_K + 4.82$	0.489***	30	M
	1:5	$pH_{Ca} = 0.33pH_K + 5.40$	0.708**	11	N
		$pH_{Ca} = 0.38pH_K + 5.05$	0.325*	19	S
		$pH_{Ca} = 0.35pH_K + 5.23$	0.408***	30	M
CaCl ₂ vs. BaCl ₂	1:1	$pH_{Ca} = 0.87pH_{Ba} + 0.92$	0.716***	11	N
		$pH_{Ca} = 0.94pH_{Ba} + 0.43$	0.964***	19	S
		$pH_{Ca} = 0.9pH_{Ba} + 0.75$	0.888***	30	M
	1:2.5	$pH_{Ca} = 0.57pH_{Ba} + 3.45$	0.819***	11	N
		$pH_{Ca} = 0.95pH_{Ba} + 0.4$	0.985***	19	S
		$pH_{Ca} = 0.8pH_{Ba} + 1.60$	0.887***	30	M
	1:5	$pH_{Ca} = 0.52pH_{Ba} + 3.84$	0.849***	11	N
		$pH_{Ca} = 0.88pH_{Ba} + 0.89$	0.819***	19	S
		$pH_{Ca} = 0.7pH_{Ba} + 2.41$	0.756***	30	M
KCl vs. BaCl ₂	1:1	$pH_K = 1.34pH_{Ba} - 2.95$	0.472*	11	N
		$pH_K = 0.76pH_{Ba} + 1.89$	0.502***	19	S
		$pH_K = 0.8pH_{Ba} + 1.53$	0.399***	30	M
	1:2.5	$pH_K = 1.55pH_{Ba} - 4.53$	0.860***	11	N
		$pH_K = 1.03pH_{Ba} - 0.21$	0.582***	19	S
		$pH_K = 1.2pH_{Ba} - 1.67$	0.674***	30	M
	1:5	$pH_K = 1.39pH_{Ba} - 3.13$	0.931***	11	N
		$pH_K = 1.22pH_{Ba} - 1.70$	0.680***	19	S
		$pH_K = 1.3pH_{Ba} - 2.33$	0.792***	30	M

(1) NS - not significant at ($p > 0.05$), *** significant at ($p < 0.001$), ** significant at ($p < 0.01$), significant at ($p < 0.05$). (2) N = Non-Saline Soils (EC of saturated past), S = Saline Soils, M = Mixed of both Soils.

Table 2c shows that the pH values at different dilution ratios within each electrolyte were generally highly interrelated, especially for water and KCl. However, pH in BaCl₂ solutions was more affected by dilution than CaCl₂, KCl and water. The pH relationships tended to be better between 1:2.5 and 1:5 ratios rather than between 1:1 and 1:2.5 or 1:5 for

electrolytes, but not for distilled water. Soil salinity reduced the significance of the relationship between pH in CaCl₂ between 1:1 and 1:2.5 dilution ratios more than for other electrolytes. The overall results from the dilution ratios suggest that soil salinity contributed little to variations in pH when measured in electrolytes.

Table 2c: The relationships between methods for pH determination.

Variables	Dilution	Regression Equation	R ²	No. of Samples	Soil Salinity
Water	1:1,1:2.5	$pH_{1:1} = 0.87pH_{1:2.5} + 0.88$	0.937***	11	N
		$pH_{1:1} = 0.87pH_{1:2.5} + 0.92$	0.955***	19	S
		$pH_{1:1} = 0.87pH_{1:2.5} + 0.87$	0.976***	30	M
	1:1,1:5	$pH_{1:1} = 1.0pH_{1:5} - 0.46$	0.887***	11	N
		$pH_{1:1} = 0.77pH_{1:5} + 1.59$	0.899***	19	S
		$pH_{1:1} = 0.85pH_{1:5} + 0.90$	0.941***	30	M
	1:2.5,1:5	$pH_{1:2.5} = 1.16pH_{1:5} - 1.57$	0.951***	11	N
		$pH_{1:2.5} = 0.91pH_{1:5} + 0.61$	0.983***	19	S
		$pH_{1:2.5} = 0.99pH_{1:5} - 0.03$	0.983***	30	M
CaCl ₂	1:1,1:2.5	$pH_{1:1} = 0.94pH_{1:2.5} + 0.42$	0.604**	11	N
		$pH_{1:1} = 1.15pH_{1:2.5} - 1.35$	0.943***	19	S
		$pH_{1:1} = 1.1pH_{1:2.5} - 0.97$	0.864***	30	M
	1:1,1:5	$pH_{1:1} = 0.68pH_{1:5} + 2.47$	0.415*	11	N
		$pH_{1:1} = 1.08pH_{1:5} - 0.84$	0.871***	19	S
		$pH_{1:1} = 0.98pH_{1:5} - 0.02$	0.750***	30	M
	1:2.5,1:5	$pH_{1:2.5} = 0.85pH_{1:5} + 1.12$	0.959***	11	N
		$pH_{1:2.5} = 0.95pH_{1:5} + 0.35$	0.947***	19	S
		$pH_{1:2.5} = 0.93pH_{1:5} + 0.53$	0.947***	30	M
KCl	1:1,1:2.5	$pH_{1:1} = 0.85pH_{1:2.5} + 0.95$	0.994***	11	N
		$pH_{1:1} = 0.91pH_{1:2.5} + 0.53$	0.945***	19	S
		$pH_{1:1} = 0.88pH_{1:2.5} + 0.72$	0.950***	30	M
	1:1,1:5	$pH_{1:1} = 0.77pH_{1:5} + 1.39$	0.978***	11	N
		$pH_{1:1} = 0.78pH_{1:5} + 1.38$	0.851***	19	S
		$pH_{1:1} = 0.77pH_{1:5} + 1.46$	0.872***	30	M
	1:2.5,1:5	$pH_{1:2.5} = 0.91pH_{1:5} + 0.49$	0.993***	11	N
		$pH_{1:2.5} = 0.89pH_{1:5} + 0.65$	0.972***	19	S
		$pH_{1:2.5} = 0.9pH_{1:5} + 0.60$	0.978***	30	M
BaCl ₂	1:1,1:2.5	$pH_{1:1} = 0.62pH_{1:2.5} + 3.04$	0.713**	11	N
		$pH_{1:1} = 1.12pH_{1:2.5} - 1.14$	0.910***	19	S
		$pH_{1:1} = 0.95pH_{1:2.5} + 0.29$	0.815***	30	M
	1:1,1:5	$pH_{1:1} = 0.43pH_{1:5} + 4.5$	0.565**	11	N
		$pH_{1:1} = 0.99pH_{1:5} - 0.20$	0.716***	19	S
		$pH_{1:1} = 0.74pH_{1:2.5} + 1.94$	0.603***	30	M
	1:2.5,1:5	$pH_{1:2.5} = 0.78pH_{1:5} + 1.75$	0.968***	11	N
		$pH_{1:2.5} = 0.94pH_{1:5} + 0.38$	0.890***	19	S
		$pH_{1:2.5} = 0.86pH_{1:5} + 1.03$	0.911***	30	M

(1) NS - not significant at ($p > 0.05$), *** significant at ($p < 0.001$), ** significant at ($p < 0.01$), significant at ($p < 0.05$). (2) N = Non-Saline Soils (EC of saturated past), S = Saline Soils, M = Mixed of both Soils.

Conclusions

Soils in Oman are mostly calcareous, and might, at first, be expected to vary little in terms of their pH value. However, this study found statistically significant differences between soils depending on how pH is measured.

Addition of different electrolytes (i.e. CaCl₂, KCl and BaCl₂) reduced measured soil pH compared to water alone. The reduction in pH was probably due to the release of more H⁺ and Ca²⁺ ions to the soil suspension following electrolyte addition, reduced liquid junction potentials and reduced variability of soluble salt content between soils. In the presence of electrolytes, pH values were also less dependent on the soil solution ratio than in water. Furthermore, the addition of electrolytes probably helped to maintain soils in a fluctuated state during actual measurement by reducing the suspension effect.

Differences in pH between electrolytes at specific dilution ratios were, in general, greater in non-saline than in saline soils. The most probable reason was that pH was sensitive to decreases in ionic strength as solutions became more dilute.

Conversion between pH measured in different electrolytes and water was achieved using the following equations:

between pH_{ba} and pH_w (non-saline soils)

$$pH_{ba} = 1.1pH_w - 1.58 \quad (1:5 \text{ dilution ratio}) \quad R^2 = 0.772$$

between pH_k and pH_w (non-saline soils)

$$pH_k = 1.48pH_w - 4.94 \quad (1:5 \text{ dilution ratio}) \quad R^2 = 0.679$$

between pH_{ca} and pH_{ba} (saline soils)

$$pH_{ca} = 0.95pH_{ba} + 0.40 \quad (1:2.5 \text{ dilution ratio}) \quad R^2 = 0.985$$

Use of electrolytes gave less variable values of suspension pH than when measured in water. Electrolytes have many advantages over water, in minimizing liquid junction, reducing fluctuations in pH measurements and decreasing the salt affect so pH values are less affected by dilution ratios.

Soil dilution ratios had more effect when pH was measured in water than in electrolytes. Dilution relationships found between pH measured in 1:1 and 1:5 dilution ratios were statistically less significant than between either 1:1 or 1:5 and 1:2.5. The effect of dilution ratios on pH in water was more

pronounced than for added electrolytes. The exact dilution to use appears to depend on soil properties and whether an electrolyte is to be used.

Finally, soil pH is an extensive field for research and much work can be done to clarify the interactions between pH and other soil properties. The present study should be considered only as a commencement of the work needed in order to fully understand pH behaviour in the soils of Oman. For analytical and advisory purposes, the influence of different measurement procedures on the soil pH needs to be fully explored.

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