

Salinity–pH Relationships in Calcareous Soils

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علاقة الملوحة بالرقم الهيدروجيني للتربة الكلسية

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خلاصة: يعتبر الرقم الهيدروجيني (pH) للتربة من أهم الخصائص التي يجب توفرها لتقييم خصوبة التربة، فهو يساعد على فهم كثير من التفاعلات التي تحدث في التربة، وله علاقات مختلفة مع مختلف العناصر الموجودة في التربة. في هذه الدراسة، تم جمع ثلاثين عينة من مختلف الترب الزراعية الموجودة بعمان للحصول على مجال أوسع في مدى الرقم الهيدروجيني والملوحة. الهدف الرئيسي من هذه الدراسة هو تحديد العلاقة الموجودة بين الرقم الهيدروجيني والملوحة. في هذه الدراسة اتضح أن هناك علاقة عكسية بين ملوحة التربة و الرقم الهيدروجيني. العامل الرئيسي المساهم في ظهور أو تكوين هذه العلاقة هو وجود أيون الكالسيوم الذي له علاقة عكسية مع الرقم الهيدروجيني و علاقة إيجابية مع ملوحة التربة. وقد تم تحديد الخصائص الأخرى للتربة المؤثرة على الرقم الهيدروجيني مثل سعة التغير الأيوني و الملوحة و كربونات الكالسيوم.

ABSTRACT: Soil pH is the most commonly requested analysis undertaken during farm advisory work. Determination of pH assists in understanding many reactions that occur in soil. Variations in pH between soils have been related to a number of other soil parameters. In this study thirty different soils were collected from agricultural areas to have a wide range of pH, salinity, and texture. The objective was to study the relationship between soil pH and salinity. A negative relationship was found between soil salinity and pH. The main factor contributing to this relationship was probably the presence of soluble Ca^{2+} ion in soil. Variations in soluble Ca^{2+} ion concentrations between soils were negatively related to soil pH and positively related to soil salinity. Other soil properties that may affect pH, including CEC, $CaCO_3$, clay content, gypsum and sodium adsorption ratio (SAR), were also determined.

Keywords: Electrical Conductivity, sodicity, pH, alkaline soil, $CaCO_3$.

Salinization and sodication are important processes in arid regions which often reduce crop yields. Salinity is the concentration of soluble mineral salts present in soils on a unit volume or weight basis (Page *et al.*, 1982), and sodicity is the concentration of Na^+ ions in soil. Soil salinity and sodicity can affect nutrient movement to plants, soil properties, and various soil chemical reactions including pH. In alkaline soils, pH usually increases with an increase in salinity due to the presence of sodium-bicarbonate carbonates (Gupta *et al.*, 1989). However, Tan (1993) reported that increasing sodicity in soil does not necessarily yield a rise in pH. Many sodic soils are neutral in reaction, whereas some are even acid in reaction. The strongly alkaline reaction (pH around 10) of most sodic soils is caused by alkalinization during which sodium carbonate and bicarbonate are formed. Under less alkaline conditions, i.e. where calcium carbonate dominates the soil mineralogy, soil pH has been shown to drop with an increase in salinity (Lai and Stewart,

1990). Several reasons have been proposed for this behavior, including common ion effects (McGeorge, 1938), sulphate complexation (Clark, 1964), variation in ionic strength of soil solutions and junction potential (Mahrous *et al.*, 1983).

In calcareous soils, statistical studies suggest a strong inverse relationship between the concentration of soluble Ca^{2+} ions and pH (Cresser *et al.*, 1993). Since pH is a routinely measured property of cultivated soils, it is essential for soil advisory work that reliable reasons for soils to have a particular pH are understood. The commonly held belief that a reduction in pH of an alkaline soil is beneficial to crop growth may not be entirely suitable for regions where carbonitic soils vary in salinity.

Oman is one of many countries experiencing soil salinity problems (MAF, 1993). Since salinity-pH relationships have not been previously reported from Oman, this paper attempts to determine the nature of this relationship in cultivated calcareous soils.

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TABLE 1

Descriptive statistics for whole data.

Soil Properties	Non-Saline				Saline			
	Minimum	Maximum	Mean	Std. Deviation	Minimum	Maximum	Mean	Std. Deviation
EC _{1:1} (dS/m)	0.29	2.15	0.9259	0.5205	4.50	34.75	10.9804	9.6378
EC _{sp} (dS/m)	0.67	3.70	1.7205	0.8819	4.01	86.80	26.5684	24.5684
SAR	2.66	9.53	6.0437	2.3739	7.31	52.10	20.4657	11.6653
pH _{wa} (1:1)	8.39	8.93	8.6109	0.1587	7.88	8.64	8.1832	0.2340
pH _{wa} (1:2.5)	8.67	9.25	8.8845	0.1799	8.03	8.96	8.4037	0.2710
pH _{ca} (1:1)	7.75	8.13	8.0164	0.1108	7.78	8.25	8.0079	0.1629
pH _{ca} (1:2.5)	7.96	8.29	8.1209	0.1021	7.95	8.36	8.1432	0.1404
pH _k (1:1)	7.72	8.40	7.9282	0.2091	7.68	8.37	7.9805	0.1816
pH _k (1:2.5)	7.94	8.73	8.1964	0.2448	7.88	8.63	8.2011	0.1944
pH _{ba} (1:1)	7.95	8.33	8.1182	0.1073	7.82	8.39	8.0584	0.1701
pH _{ba} (1:2.5)	8.05	8.56	8.2136	0.1466	8.00	8.44	8.1847	0.1444
Na (mmol/l)	5.44	21.74	12.8450	6.0867	27.17	565.22	156.1797	146.7047
Ca (mmol/l)	1.25	6.25	5.7955	1.5076	6.25	100.00	37.8289	28.0650
Mg (mmol/l)	2.08	8.33	3.0301	1.9463	4.17	166.67	70.2852	63.6767
CaCO ₃ (g/g)	0.33	0.60	0.4327	0.0755	0.28	0.58	0.4129	0.0646
CaSO ₄ (cmol/kg)	1.00	1.00	1.0000	0.0000	1.00	10.00	2.0105	2.4644
CEC (cmol/kg)	1.96	16.30	9.3673	5.5536	2.17	21.74	9.2905	5.9732
% Clay	6.00	35.00	16.0909	8.9045	4.00	30.00	11.5789	7.1594

Materials and Methods

SOIL SAMPLING AND PREPARATIONS: Thirty surface (0-10 cm) and subsurface (10-20 cm) agricultural soils were sampled from the Batinah (Barka) and Interior (Adam) regions of Oman. Soils were selected from cultivated areas to have a wide range of pH, 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 for each sample in distilled water (pH_{wa}), 0.01M CaCl₂ (pH_{ca}), 1M KCl (pH_k) and 0.01M BaCl₂ (pH_{ba}) electrolyte solutions. Soil/solution ratios of 1:1 and 1:2.5 (w/v) for each electrolyte were used. The soil/electrolyte suspensions were 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 Jenway 3020 pH meter and Philips combined glass/calomel electrode (type CE1), that had previously been calibrated at pH 7.0 and 9.0. The meter was recalibrated, when necessary, to ensure accuracy.

SOIL ELECTRICAL CONDUCTIVITY DETERMINATION: Soil salinity was assessed by measuring the electrical conductivities in saturated paste extracts (EC_{sp}) and 1:1 (w/v) soil/water suspensions. After adding distilled water and mixing saturated soil pastes were left for 1h to stand and then filtered under vacuum. For each soil/solution ratio, the soil-solution suspensions were shaken automatically for 1h, and EC values of filtered extracts recorded. Measurement of EC in pastes and extracts were performed by using a calibrated Jenway 4020 conductivity meter connected to a conductivity electrode.

DETERMINATION OF SOLUBLE CATIONS AND SODIUM ADSORPTION RATIO (SAR): Concentrations of Na⁺, Ca²⁺, and Mg²⁺ in saturated paste extracts were measured by using an atomic absorption spectrometer (Pye Unicam SP9). The SAR for each soil was calculated by using the equation of Miller (1990):

$$\text{SAR} = \text{millimoles of Na}^+ / [\text{millimoles of (Ca}^{2+} + \text{Mg}^{2+}) / 2]^{-1/2}$$

STATISTICAL ANALYSES: Analysis of variance (ANOVA) was used to determine the significance of differences in pH_{wa}, pH_{ca}, pH_k, pH_{ba} and EC values between soils. The general linear model (GLM) procedure was used to test for Least Significant Differences between means, and for significance of regression equations. Statistical analyses were performed using Statistical Analysis System (SAS) statistical package.

Results and Discussion

SOIL PROPERTIES: Individual soils within the suite analyzed were classified as saline if the EC_{sp} was more than 4.0 dS/m or non-saline if less than 4.0. Minimum and maximum values and variances for each property measured are given in Table 1 for saline and non-saline soils separately. Saline soils were characterized by relatively high SAR values, ranging from 7.31 to 52.10. Values of SAR in non-saline soils ranged from 2.66 to 9.53, suggesting that non-saline soils were also non-sodic. In general, soils were dominated by calcium carbonate, with contents ranging from 28 to 60%. Gypsum contents were low in all soils. The particle size fraction was dominantly sand with clay contributing on average 13.5%.

SALINITY – PH RELATIONSHIPS IN CALCAREOUS SOILS

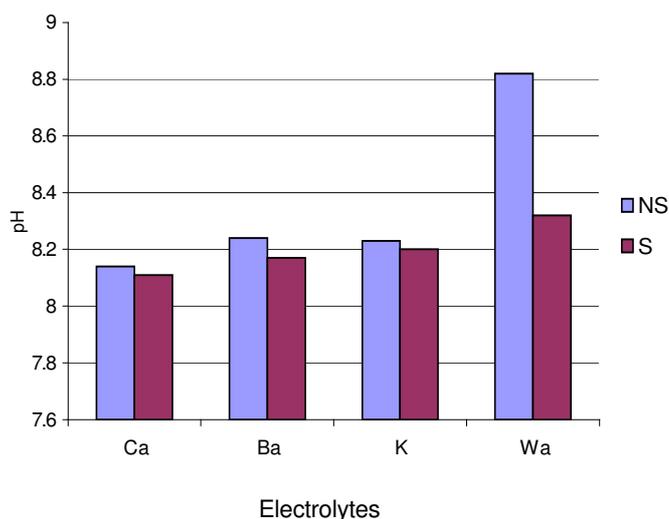


Figure 1. Mean pH values of saline and non-saline soils under different electrolytes.

ELECTROLYTE EFFECT: ANOVA revealed that the mean pH of non-saline soils was 8.36, being significantly higher ($p < 0.05$, $F_{1,695} = 224.48$) than the mean for saline soils, i.e. 8.20. Figure 1 shows that the difference in pH between non-saline and saline soils was greater in the absence of added electrolytes than following their addition. The addition of $BaCl_2$ also resulted in significantly lower pH in saline than non-saline soils ($p < 0.05$, $F_{1,695} = 76.56$). In the presence of $CaCl_2$ or KCl the differences in pH between non-saline and saline soils were not significant.

In general, readings from the pH electrode from non-saline soils tended to fluctuate more than when readings were taken from saline soils. However, pH readings from saline soils in different electrolytes also fluctuated but not to the same extent as in non-saline soils. Electrolytes appeared to suppress fluctuations in pH readings, probably due to, both, reducing the liquid junction effect (especially in water) and minimizing alkaline errors. The reduction in fluctuation between pH values in non-saline and saline soils supports the use of electrolytes especially in non-saline soils.

SOIL SALINITY, SODICITY AND PH RELATIONSHIPS: Sodic soils conditions are believed to occur when the SAR soil extracts exceed 15. In Oman, soil salinization is frequently associated with addition of irrigation water high in sodium to soil. Consequently, non-saline sodic soils are rare in cultivated soil of Oman. Soils, in the collection under study, belong mostly to either non-saline/non-sodic, or saline-sodic categories. Figure 2 shows the relationship between EC_{sp} and SAR for all the soils under investigation. The linear regression line ($SAR = 0.464 EC + 7.077$, $R^2 = 0.83$) fitted to the data collection is highly significant ($p < 0.001$), suggesting that the cause of salinity in these soils was a high concentration of sodium ions.

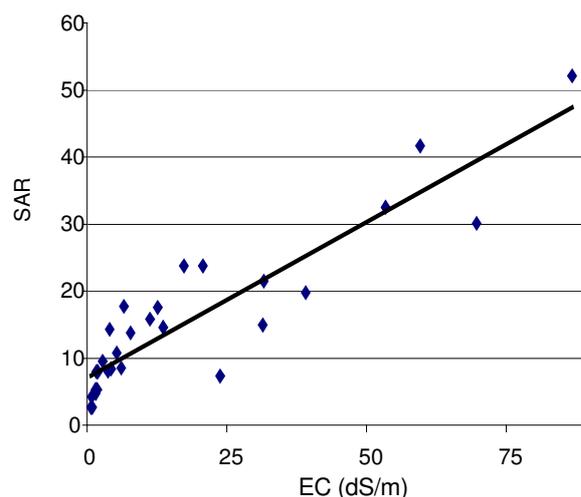


Figure 2. EC – SAR (saturated paste) relationship.

Figure 3 shows the relationship between pH_{wa} and $\log EC$ (1:1) for all soils studied. The linear regression equation is given in equation 1 below. The negative relationship between pH_{wa} and salinity was significant ($p < 0.001$), for saline and non-saline soils analyzed separately. In both groups, soils with lower pH_{wa} tended to be more saline, than those of higher pH_{wa} values. It can be concluded that pH_{wa} values in the calcareous soils in investigation were inversely related to salinity.

The inverse relationship between pH and salinity was less apparent when pH was measured in different electrolyte solutions. However, pH measured in electrolyte solutions were considerably less closely related to EC (1:1) values than when measured in water. It appears that measurements of pH in water are highly sensitive to differences in soil salinity whereas the measurements of pH in electrolyte solutions are indicative of electrolyte-soil interactions which are not similar to soil-water interactions.

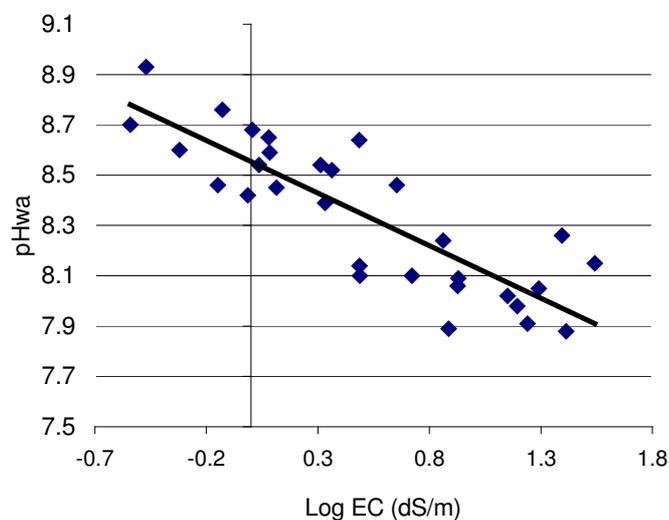


Figure 3. Soil EC – pH relationship.

The calculated regression relationship between pH and EC (1:1) is given in equation 1:

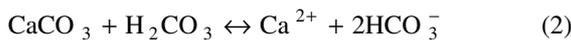
$$\text{pH}_{\text{wa}} = 8.81 - 0.4881 \log \text{EC}_{(1:1)}, R^2 = 0.77 \quad (1)$$

This equation is not entirely supported by other published research. According to Gupta *et al.*, (1989) sodium ions react in calcareous soils to form sodium carbonate and bicarbonate, which by hydrolyzing at pH values more than of 8.8, leads to a direct relationship between soil salinity and pH. In the absence of concentrations of sodium ions, soil pH has also been found to decrease as salinity increases. Since the inverse pH-salinity relationship depends on the absence of high concentrations of sodium ions in soil then in the present study, where soils were both saline and saline-sodic, no direct relationship between the two variables was expected. However, finding an inverse relationship suggests that sodium, as either carbonate or bicarbonate, were either not present in the soils or did not hydrolyze rapidly enough, during pH measurement, to have an appreciable effect on pH.

Many factors have been found to contribute to pH-salinity relationships in calcareous soils. Among these, the following are relevant to the present study of arid soils:

In the presence of sodium ions, pH of calcareous soils often exceeds 8.5 and may reach as high as 12. This situation was not encountered in the present study since the pH value of the most saline-sodic soil was only 8.2, suggesting that formation of sodium carbonate and bicarbonates from the reaction between calcium carbonate and sodium did not occur in the soils.

Soil aeration can influence CO₂ exchange in soils. High pH values are rarely attributed to CaCO₃ in aerated soils. When the aeration is poor, as in many alkali soils, and carbon dioxide is absent, then CaCO₃ may produce pH values of 8.5 or higher (Foth and Ellis, 1988). In Oman, soils are mostly light textured, rarely poorly aerated and appear to experience generally free exchange of carbon dioxide with the atmosphere. Hence CO₂ consumes OH⁻ ions, and thus restrains the rise of pH [OH⁻ + CO₂ ↔ HCO₃⁻]. In addition to that, the presence of CaCO₃ in the soil is also a major source of gaseous CO₂, through the reaction with carbonic acid:



Calcareous soils were highly buffered with respect to calcium. When calcium ions are present on exchange sites and in sufficient quantity in the soil solution, calcium carbonate will precipitate. As long as calcium dominates the cation exchange complex rather than sodium, the soil pH is buffered and unlikely to rise above 8.5. The buffering effect of calcium leads to precipitation of calcium carbonate through the following reaction:

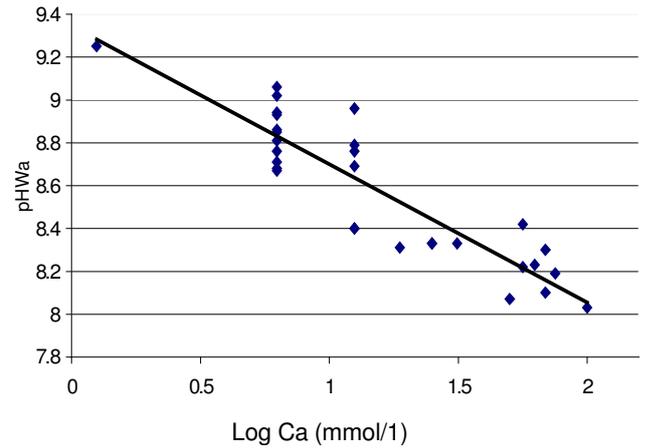
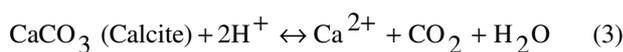


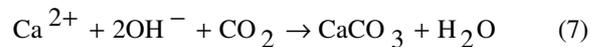
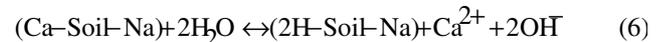
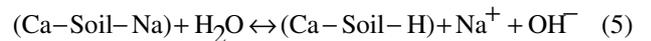
Figure 4: pH of water at 1:2.5 dilution ratio with log Ca.

Under more acid conditions, the equilibrium will start to move from left to right, effectively increasing soil pH. Conversely, if hydroxide ions are generated they will react with hydrogen ions thus forcing the equilibrium to the left (Figure 4). The equilibrium relation between pH and the partial pressure of CO₂ (i.e. Pco₂) in the air for the system CaCO₃-H₂O-CO₂ can be expressed as follows:

$$\text{pH} = -1/21 \log(\text{Ca}) - 1/21 \log \text{Pco}_2 + \log K \quad (4)$$

where K is an equilibrium constant.

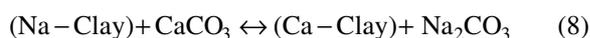
The relationships between soil pH, salinity, CaCO₃ and Ca²⁺ in a heterogeneous system, such as a calcareous soil, can be represented by Equations 5, 6 and 7. The calcium hydroxide activity is fixed by Pco₂ but the individual ionic activities of calcium and hydrogen may increase or decrease as influenced by soluble salts and exchange reactions



If sufficient calcium comes into solution at high pH, calcium carbonate will precipitate. Through the reaction presented in Equation (3), H⁺ are liberated passing from right to left, which neutralizes the hydroxide ion produced by the hydrolysis reaction in Equation 5. Displacement of Na⁺ by hydrolysis liberates hydroxide, which remains in solution, thus raising the solution pH.

Increases in soil pH above 8.5 are associated with high concentrations of exchangeable sodium ions (SAR > 15%), and low EC (< 4 dS/m). A high concentration of sodium chloride in the soil solution suppresses the displacement of exchangeable sodium by hydrogen (Equation 6) as a consequence of the ratio law (Cresser *et al.*, 1993).

In the case of accumulation of sodium ions in soil, calcium and magnesium can be displaced by sodium. However, the calcium and magnesium thus replaced are not converted into soluble calcium and magnesium salts, but probably precipitated principally as carbonates, and a lesser extent as silicates. Consequently, the leaching process may not remove any significant amount of calcium and magnesium from the soil. Reducing soluble sodium salts by leaching gives an opportunity for calcium minerals to react with sodium exchange complex. Consequently, sodium is gradually replaced by calcium with the formation of Na_2CO_3 and NaHCO_3 as follows:



Sodium carbonate and bicarbonate formed by these reactions have to be leached into the subsoil and lost to drainage.

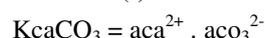
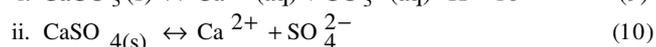
Soil solution salinity and ionic strength effects on soil pH. McGeorge (1935) showed that pH_{wa} decreases with increasing concentrations of NaCl. He speculated that the pH of the soil increased as the salt concentration of the soil solution was reduced because of an increase in the hydrolysis of the sodium clay complex. No definite relationship could be found between soluble salts concentration in soil and pH_{wa} , probably due to the wide variation in the composition of the salts present in different soils (McGeorge, 1938).

Salinity increases the ionic strength of the soil solution and consequently suppresses the activity coefficient of ions in solution. This would result in increasing the pH values, but increasing ionic strength mainly decreases the pH values because salinity decreases the junction potential.

Garrels and Christ (1990) found a direct relationship between calcite solubility and ionic strength under the influence of sodium chloride. The following factors - sulfate complexing, the absence of equilibrium conditions, and the presence of more soluble forms of calcium carbonate - may account for the differences between pH values of different calcareous soils (Clark, 1964).

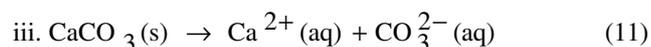
Presence of gypsum in soil can reduce pH and affect sodium solubility. Generally, gypsum is found only in arid soils where leaching is restricted. Application of gypsum to sodium-affected soils in the pH range of 8.5 to 10 raises soluble Ca^{2+} above that of the calcite and leads to the precipitation of calcite with the release of hydrogen ions as presented in Equation (3). The pH then drops to the range of 7.5 to 8.0 where gypsum and calcite can coexist. In this way soluble Ca^{2+} is restored to approximately $10^{-2.5}$ M, keeping the soil colloids flocculated and predominantly calcium saturated. Displaced Na^+ can then be leached from the soil as drainage is supplied (Suhayda *et al.*, 1997).

The common-ion effect on Ca solubility (i.e. the addition of Ca to soil solutions from sources other than CaCO_3 or exchange sites) can lead to an increase in the concentration of Ca that supersaturates the solution and causes precipitation. This is the case when CaCO_3 precipitates in the presence of Ca^{2+} ions from a combination of CaCO_3 and CaSO_4 sources. Precipitation continues until the product of Ca^{2+} and CO_3^{2-} ion activities is reduced to the equilibrium constant (of 10^{-10}). In this case, reactions 9, 10 and 11 occur, with the formation of Ca^{2+} ions.



where $a_{\text{Ca}^{2+}}$ and $a_{\text{CO}_3^{2-}}$ are activities of Ca^{2+} and CO_3^{2-} ions, respectively.

If $K < 10^{-10}$ then



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 showed that statistically significant differences in pH are found between soils. The soils investigated varied from being virtually non-saline to being excessively saline. Soil extract was negatively related to pH in all electrolytes, especially to pH_{wa} ($R^2 = 0.77$). A possible reason for the negative relationship was that soils were influenced by increased solubility of Ca^{2+} ions in saline conditions under ambient atmospheric CO_2 concentrations that lead to a release of hydrogen ions.

Other soil parameters such as CaCO_3 , gypsum and clay contents were also studied but their influence on soil pH did not appear to be as prominent as the concentration of soluble Ca^{2+} ions.

The pH of calcareous soils has not generally been studied extensively because soil scientists once believed that the presence of a powerful buffer, such as calcium carbonate, would prevent significant changes in pH. However, it is becoming to be recognized that the behavior of carbonate and bicarbonate anions of different elements, including major soil cations such as Ca^{2+} , Mg^{2+} , and Na^+ , can cause significant changes in pH. The present study should be considered only as a commencement of the work needed in order to fully understand pH behavior in the soils of Oman.

Finally, more research is needed on the chemical reactions in calcareous soils in general, especially on pH dependent reactions. A comparison between pH dependent reactions in calcareous and acidic soils would help in highlighting areas of differences in soil behavior.

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