

Buffering capacity of benchmark alluvial and calcareous soils of Egypt

By

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Abstract

The pH-dependent cation exchange capacity (ΔCEC) and pH-buffering capacity (pH-BC) are two crucial properties in soil fertility and pollution issues. However, they are usually measured for variable charge soils but it is rarely measured for the other soil types. The present work aimed at measuring pH-buffering characteristics for benchmark alluvial and calcareous soils of Egypt. Increasing amounts of (0.1 M) NaOH and HCl solutions were added to constant weights of soils, after shaking and equilibration, it was subjected to the measurement of pH and CEC.

The obtained results showed that CEC significantly increased by increasing pH from 3 up to 9. The magnitude of increase (ΔCEC) between pH 6 and 9 for Aswan and Shebien EL-Quom were 8.62 and 16.35 Cmol_c/kg which represent 32.28% and 39.11% of the total soil-CEC (CEC_T), respectively. For calcareous soils of El-Arish and Nubaria, ΔCEC (pH 3-6) were 2.95 and 4.98 Cmol_c/kg which represent 10.5 and 15.47% of their total-CEC, respectively. Significant correlation was found between ΔCEC and clay content. Three buffering capacity indices were calculated in two pH ranges (3-6 and 6-9) and discussed in the present study. The first index is the slope of the pH-CEC curves [$\text{BC}_{\text{CEC}} = \Delta\text{CEC}/\text{dpH}$], second index was calculated as the slope of the soil potentiometric curve [$\text{d}(\text{H}^+)(\text{OH}^-)/\text{dpH}$] BC_{H^+} and the third is the area measured between acid–base titration curves of soil and water BC_{area} . The three buffering capacity indices were significantly correlated to each other but BC_{H^+} was less sensitive to the changes of soil properties as compared to the other indices. Generally, the obtained buffering capacity indices in 3-6 pH range (BC_{3-6}) were much lower than those for BC_{6-9} in alluvial soils, while in calcareous ones the reverse relation ($\text{BC}_{3-6} > \text{BC}_{6-9}$) was recorded. These results could be practically useful in soil management.

Key words: buffering capacity, ΔCEC , alluvial, calcareous soils, pH-dependent CEC

Introduction

Information on the pH-buffer capacity (pH-BC) of a soil is important in the management of soil alkalization or acidification and in soil monitoring. The pH-BC of a soil is its ability to resist pH change on addition of acidic or alkaline reagents to the soils. In spite of its importance, there is an acute lack of pH-BC data for soils of Egypt. Soil pH buffering caused by the protonation and deprotonation of mineral and organic surfaces reduces the change in soil pH when acids or bases are added to the soil. In most mineral soils, significant range of pH-buffering capacity (pH-BC) is generally due to cation exchange reactions (Weaver et al., 2004). Therefore, the higher the soil-CEC the higher the pH-buffering (Chen, 2004). The change in titrable acidity or CEC per unit change in pH (slope b) is used as a measure of the pH-buffering capacity (Bouman, 1995). The soil with low slope (b) from the linear regression of the soils titration curve-had a lower pH-BC or would be sensitive to the additions of acids or bases than those with large b ($\Delta\text{CEC}/\text{dpH}$) which indicated high pH-BC (Weaver et al., 2004). Aitken et al., (1990) concluded that the pH-buffering capacity is governed principally by clay and organic matter (O.M.) content of the soil. Organic matter has bigger effect on pH-BC than that of clay as O.M. can have a buffering capacity 300 times as great as Kaolinite clay mineral (Bache, 1988). Most of the experimental methods reported in the literature to determine the buffer capacity of soils are based on the addition of a fixed volume of acid solutions to the soil for subsequent analysis of pH changes (Kim et al., 2006). Potentiometric titration curves have also been reported to quantify the buffer capacity of different soils (García-Gil et al., 2004).

The present work aims at measuring pH-BC for benchmark alluvial and calcareous soils of Egypt using different methods.

Materials and Methods

Surface soil samples (0-30 cm) depth were collected from alluvial (Aswan, Elminia, Fayoum, Tanta, Sedi Salem and Shebien EL-Quom) and calcareous soils (El-Areish, Nubaryia, Borg El-Arab, North Tahrir and Maryout). The key properties of the studied soils were determined using standard methods (Sparks, 1998) and presented in Table (1). Surface area was determined on fine earth using O-phenanthroline method (Sparks, 1998). Amorphous silica and alumina were extracted and determined according to Page et al., (1982). Free iron oxides were extracted using Dithionite-Citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960) and determined by atomic absorption.

The pH dependent cation exchange capacity (Δ CEC) was measured for alluvial soils according to Page et al., (1982) with some modifications for the pH range. Five grams of ground soil samples were saturated with Na^+ and Cl^- by adding 0.4 M sodium acetate different in pH 3, 6, and 9 and 0.1 M sodium chloride in 60% ethanol. Followed by shaking, centrifuging and decantation of supernatant for three times. The obtained Na and Cl saturated samples were successively extracted by 33 ml portions of 0.25 M magnesium nitrate $\text{Mg}(\text{NO}_3)_2$ through shaking and centrifugation and the extracts were collected. Total sodium [Na^+_T] was determined by flame photometry and total chloride [Cl^-_T] by titration with silver nitrate (Page et al., 1982), in coml. l^{-1} in the extracts, using calibration ranges prepared in the magnesium nitrate background solution. The cation exchange capacity was calculated according to the following equation:

$$\text{CEC (Cmol}_c\text{/kg)} = 10/w [(\text{Na}^+_T) \text{Df}_{\text{Na}^+} - (\text{Cl}^-_T) \text{Df}_{\text{Cl}^-}]$$

Where: w, sample weight; Df, dilution factor, i.e. ratio of the final volume to volume of the aliquot.

The pH dependent cation exchange capacity (Δ CEC) of calcareous soils was carried out using the method reported by Papanicolaou, (1976). Where 1.0 N CaCl_2 (pH 7.0) was used as the saturating solution; adsorbed Ca^{2+} was replaced by extraction with 1.0 N NaNO_3 (pH 7.0). Total ($\text{Ca}^{2+} + \text{Mg}^{2+}$), Cl^- , and ($\text{CO}_3^{2-} + \text{HCO}_3^-$) were determined in the combined extract (Page et al., 1982). The CEC is calculated as ($\text{Ca}^{2+} + \text{Mg}^{2+}$) minus ($\text{Cl}^- + \text{CO}_3^{2-} + \text{HCO}_3^-$).

Acid-base soil titration curves were obtained by equilibrating constant weights of soil samples with increasing volumes of 0.1 N of HCl and NaOH solutions followed by pH measurements. A reference acid-base titration curve was obtained using distilled water. Potentiometric curves were calculated from the initial data [$d(\text{H}^+)(\text{OH}^-)/\text{dpH}$] according to Van Raij and Peech (1972). Buffering capacity were calculated from the obtained three curves i.e. [pH/CEC], [$\text{pH}/(\text{H}^+)/(\text{OH}^-)$] and [$\text{pH}/\text{ml}_{\text{acid}} - \text{ml}_{\text{base}}$] in both acidic range (pH 3~6) and basic range (pH 6~9).

Three buffering capacity indices were obtained namely; Δ CEC index (BC_{CEC}) as described by Ammann (2003), proton index (BC_{H^+}) according to Oorts et al., (2004) and the area index (BC_{area}) which reported by Raczuk (2001). Fig. (1) represented the methods of obtaining and calculating the three buffering indices from the different soil curves. Regression analysis was performed to determine the relationships between the calculated three buffering indices (SAS, 1985).

Results and Discussion

1- Impact of pH on CEC changes (Δ CEC)

Figure (2) represents pH-CEC curves for the investigated alluvial and calcareous soils, respectively. Consistent increases of CEC with increasing pH were recorded with different rates as a result of deprotonation and negative charge development on the surfaces of soil particles. The magnitude of increments (Δ CEC) in pH range of 6-9 was significantly higher than that obtained from 3-6 pH range from all the investigated alluvial soils which was reversed in the calcareous ones as shown in fig.(3).

On the other hand, The magnitude of Δ CEC in both acidic and basic sides was much higher in alluvial as compared to calcareous soils due to the radical differences in their mineralogical composition. Highly significant correlation was recorded between total Δ CEC (pH 3-9) and clay %, surface area (S.A.), amorphous material (A.M.) %, O.M.% for both alluvial ($r = 0.93, 0.92, 0.94$ and 0.88 , respectively) and calcareous soils ($r = 0.91, 0.97, 0.91$ and 0.79). Furthermore, significant correlations were found between total Δ CEC and both total and active carbonates in calcareous soils ($r = 0.88$ and 0.85). Furthermore, highly significant correlations were found between, Δ CEC in the basic pH range (6-9) and clay %, S.A, A.M and O.M % ($r = 0.96, 0.97, 0.99$ and 0.86), while it were insignificant for the acidic Δ CEC₃₋₆ in alluvial soils. The reverse was true in calcareous soils where the acidic Δ CEC₃₋₆ was more sensitive and correlated to soil properties as well as total and active – CaCO₃ than those for basic Δ CEC₆₋₉ values.

2- Buffering capacity indices

Three Buffering capacity indices were determined and calculated from the original acid-base and potentiometric titration curves. The first BC_{CEC} index is the slope of the pH-CEC curves, the 2nd BC_{H⁺} index is the slope of the potentiometric titration curves (fig. 4) (pH/H⁺-OH⁻) and the third was the area between the acid-base titration curves of both soil and blank (water) BC_{area} index from fig. (5). the three BC index were calculated in both acidic and basic pH ranges i.e. (3-6) and (6-9) for both alluvial and calcareous soils and presented in Table (2). The obtained data indicated that the buffering capacity at the basic pH range 6-9 was much higher [2-3 times] that on the acidic side (pH 3-6) in alluvial soils for all the three BC indices, and the reverse was true for calcareous soils. This finding is in agreement with those reported by Huang et al. (2009). In addition, the buffering capacity values in alluvial soils were much higher than those in calcareous soils due to their higher contents of silicate clay,

SA, AM and OM, while pH-buffering of calcareous soils mainly controlled by CaCO₃ (Doner and Lynn, 1989).

Figure (6) showed that the three BC indices were significantly correlated to each other and the highest correlations were recorded between BC_{CEC} and BC_{area}. This indicated that BC_{area} could be used as a simple and fast method to measure the buffering capacity and then could be transformed into ΔCEC using the following best fit regression equations:

$$\begin{aligned}\Delta\text{CEC (pH}_{6.9}) &= 3(0.4 + 0.07 \text{BC}_{\text{area}})_{\text{alluvial}} \cdot \\ \Delta\text{CEC (pH}_{3.6}) &= 3(-0.007 + 0.5 \text{BC}_{\text{area}})_{\text{calcareous}} \cdot\end{aligned}$$

Generally, the basic buffering capacity index for alluvial soils were significantly affected by clay %, OM, AM % and SA. The same was recorded for the acidic buffering capacity indices in calcareous soils with further significant correlations with total and active CaCO₃ % as indicated from Table (3).

Conclusion

In conclusion, it is important to measure pH-buffering capacity for the soils of Egypt and use it in monitoring the other chemical properties such as alkalinity, nutrient availability and capacity load of different pollutants. A simple, fast and economic method was achieved to measure a highly sensitive soil buffering index from the shifting area of soil acid-base titration curves from that of water as a reference (BC_{area}). This index was significantly correlated to the other two indices i.e. BC_{CEC} and BC_{H+} which are more difficult to be measured.

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Table (1). Some characteristics of the investigated soils.

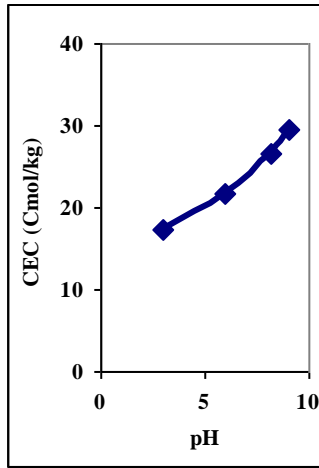
Symbol	Location	pH (1:2.5)	EC (dS/m)	OM g/kg	Clay g/kg	Total CaCO ₃ g/kg	Active CaCO ₃ g/kg	SA (m ² /g)	Total AM g/kg
ASW	Aswan	7.81	1.32	8.5	175	35	33.5	120.31	32
ELM	El-Menia	7.93	2.09	18.2	204	38	35.2	130.45	35.6
FAY	El-Fayium	7.74	2.25	16.5	241	33	31.0	188.83	47.6
TAN	Tanta	7.78	1.13	16.1	314	35.2	32.1	210.32	56.2
SES	Sedi Salem	7.9	2.53	14.3	335	46.6	43.1	215.53	57.1
SEQ	Shebien EL- Quom	7.67	1.22	14.5	425	37.2	32.8	225.11	59.5
ARS	El-Areish	7.73	1.92	13.0	109	123.5	82.2	95.38	12.8
NUB	Nubaryia	7.87	2.34	11.1	165	194.1	95.4	135.45	17.1
BRG	Borg El-Arab	7.81	0.3	11.2	224	280	103.5	137.85	19.8
NHR	North Tahrir	7.75	1.16	4.8	302	410	123.5	141.52	26.9
MAR	Maryout	7.82	0.75	1.4	361	533.1	155.6	144.35	27.4

Table (2). The buffering capacity values for the investigated soils.

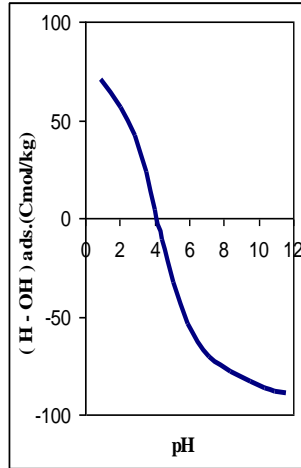
Symbol	Soils samples	CEC index		Proton index		Area index	
		BC= Δ CEC/dpH Cmol/kg/pH		BC=1/(dH/dOH) Cmol/kg/pH		BC=area under acid- base T.C. Cmol/kg/pH	
		pH _(3,6)	pH _(6,9)	pH _(3,6)	pH _(6,9)	pH _(3,6)	pH _(6,9)
ASW	Aswan	1.41	2.54	0.08	0.6	0.16	0.56
ELM	El-Menia	1.7	2.8	0.07	1.0	0.15	0.61
FAY	Fayium	1.5	3.6	0.08	0.92	0.18	0.67
TAN	Tanta	1.33	4.7	0.05	0.86	0.17	0.73
SES	Sedi Salem	2.3	4.9	0.06	0.8	0.21	0.8
SEQ	Shebien EL- Quom	1.9	5.2	0.09	1.09	0.18	0.72
ARS	El-Areish	1.2	0.63	0.31	0.04	0.57	0.09
NUB	Nubaryia	1.34	0.92	0.46	0.07	0.61	0.07
BRG	Borg El-Arab	1.5	0.91	0.32	0.08	0.65	0.08
NHR	North Tahrir	1.6	0.87	0.47	0.05	0.77	0.1
MAR	Maryout	1.7	0.9	0.56	0.09	0.79	0.09

Table (3). Correlation coefficient between buffering index and soil properties.

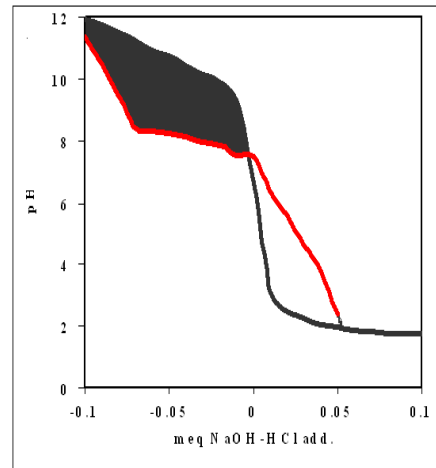
Soil groups	Buffering index	pH	Clay	O.M	SA	AM	Total CaCO ₃	Active CaCO ₃
Alluvial	BC _{CEC}	3-6	0.52	0.61	0.42	0.44	0.90**	0.84*
		6-9	0.96**	0.86**	0.97**	0.99**	0.39	0.29
	BC _{H+}	3-6	0.03	-0.14	-0.18	-0.22	-0.31	-0.38
		6-9	0.55	0.73*	0.44	0.45	0.04	-0.21
	BC _{area}	3-6	0.59	0.63	0.74*	0.72*	0.57	0.68
		6-9	0.80*	0.87**	0.92**	0.93**	0.56	0.54
Calcareous	BC _{CEC}	3-6	0.99**	0.84*	0.85*	0.97**	0.97**	0.94**
		6-9	0.60	0.54	0.96**	0.61	0.55	0.52
	BC _{H+}	3-6	0.76*	0.90**	0.67	0.76*	0.78*	0.83**
		6-9	0.57	0.69	0.71*	0.46	0.56	0.61
	BC _{area}	3-6	0.98**	0.83*	0.74*	0.99**	0.98**	0.94**
		6-9	0.46	0.21	-0.06	0.5	0.48	0.41



$$BC_{CEC} = \Delta CEC / dpH$$



$$BC_{H^+} = 1 / (dH^+ / dOH^-)$$



$$BC_{area} = \text{area under acid-base T.C.}$$

Fig.(1) Calculation methods of the three indices of soil buffering capacity.

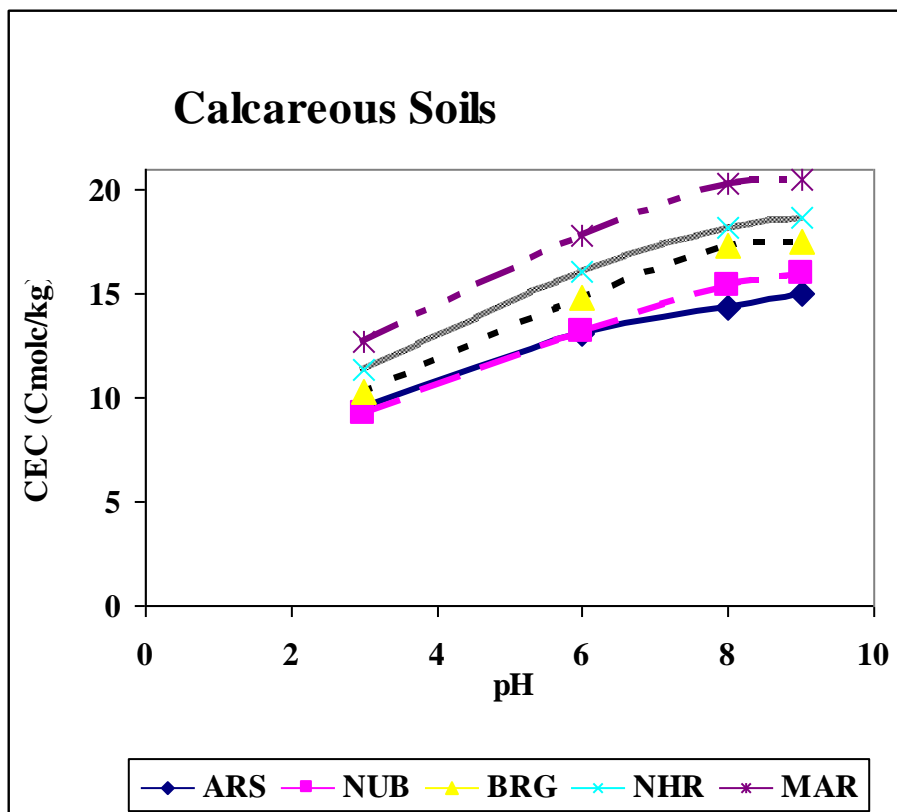
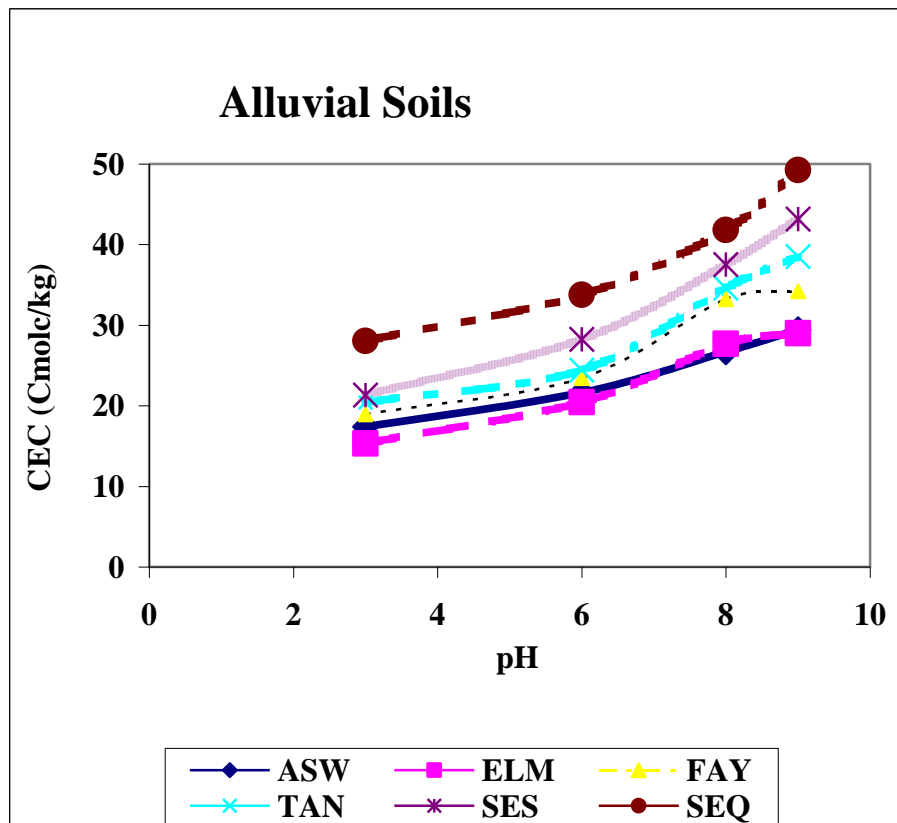


Fig. (2) pH-CEC relationships for alluvial and calcareous soils.

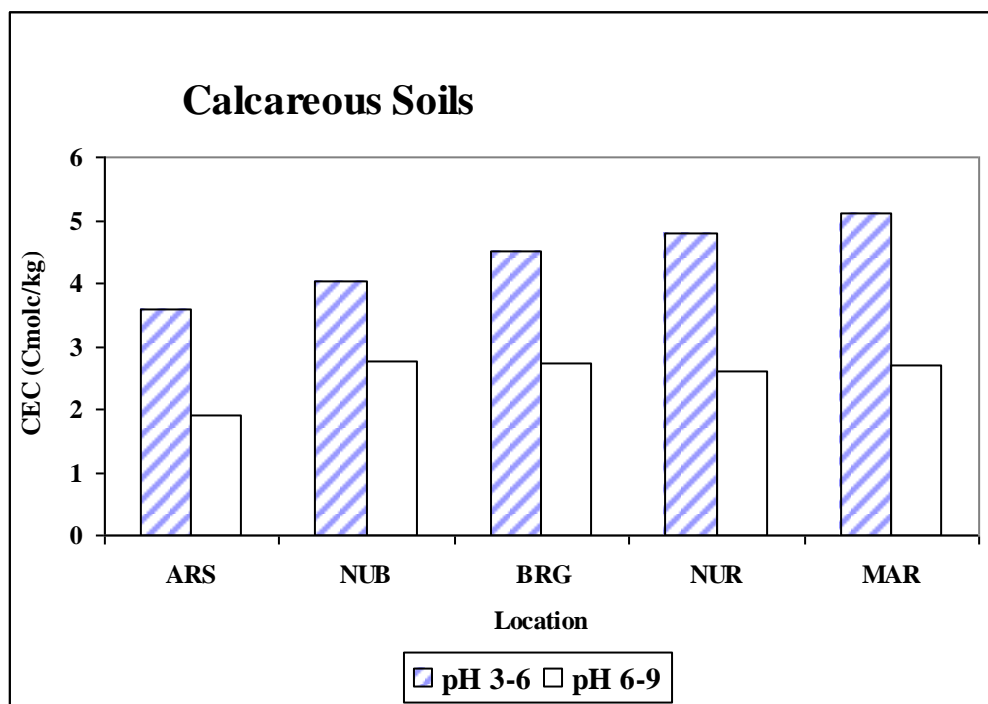
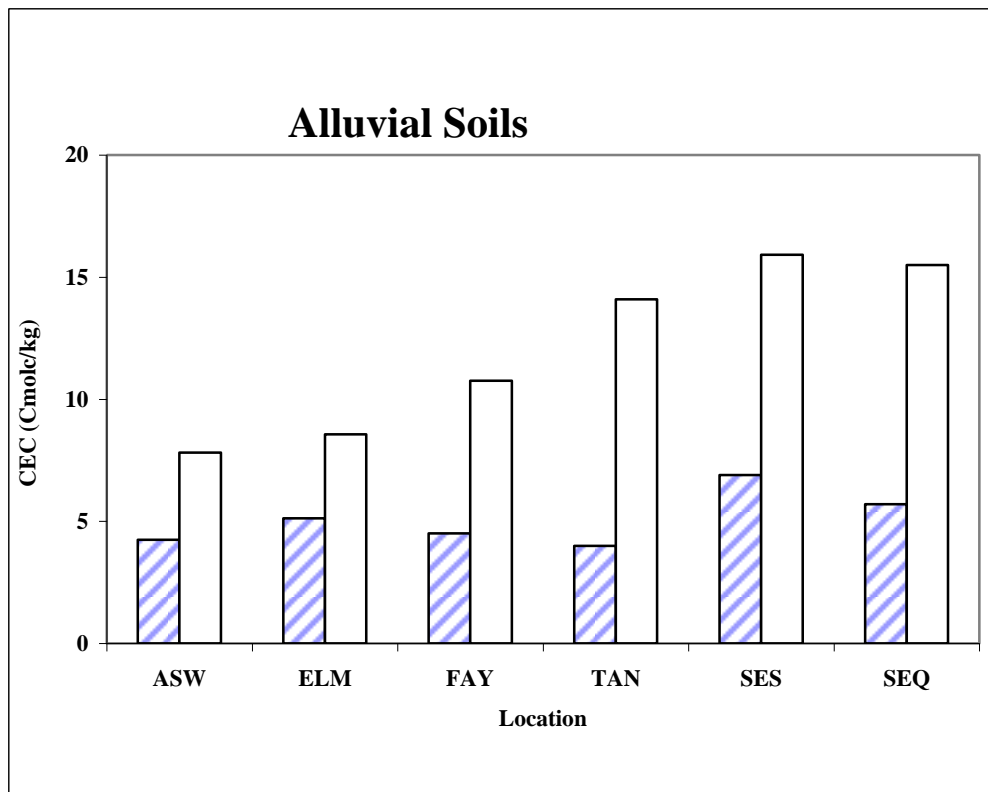


Fig.(3) Cation exchange capacity (Δ CEC) at pH ranges of 3-6 and 6-9 for the benchmark alluvial and calcareous soils.

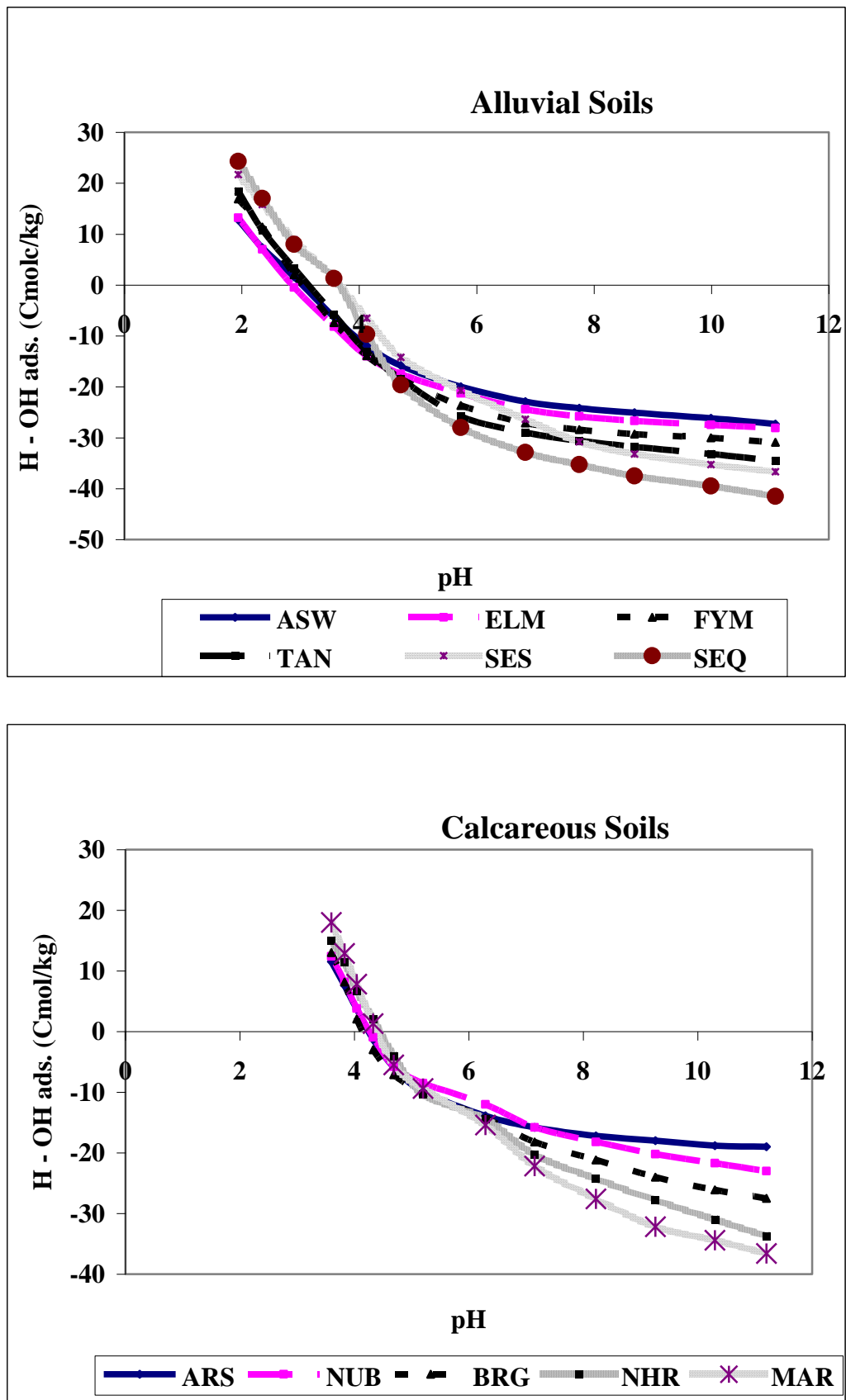


Fig. (4) Potentiometric titration curves for alluvial and calcareous soils.

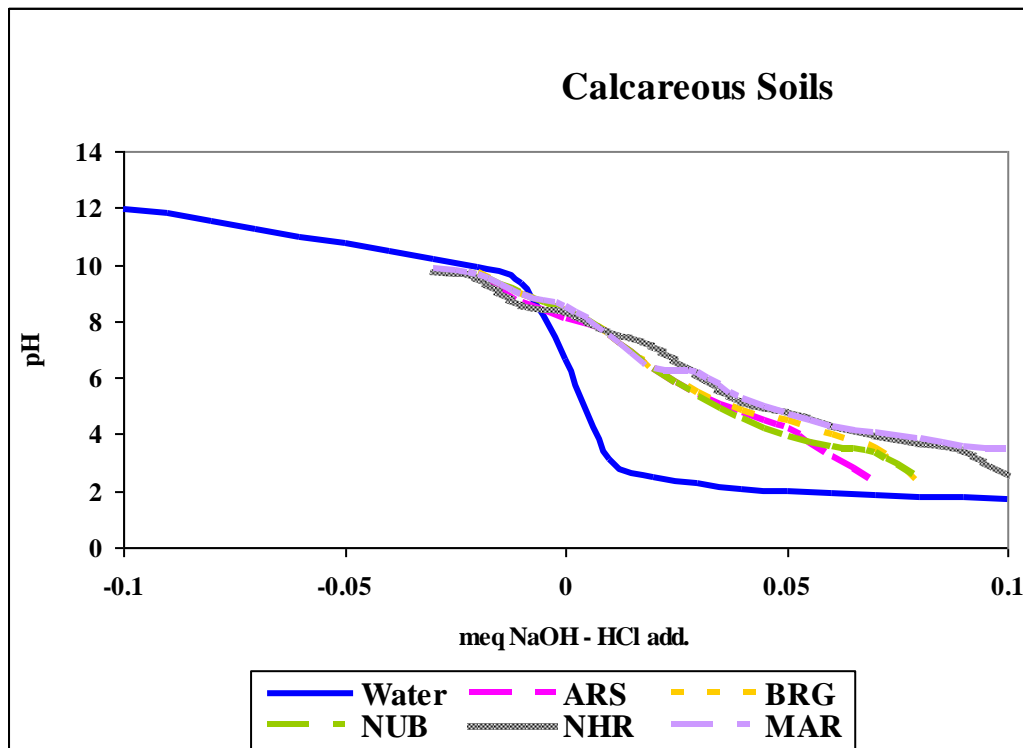
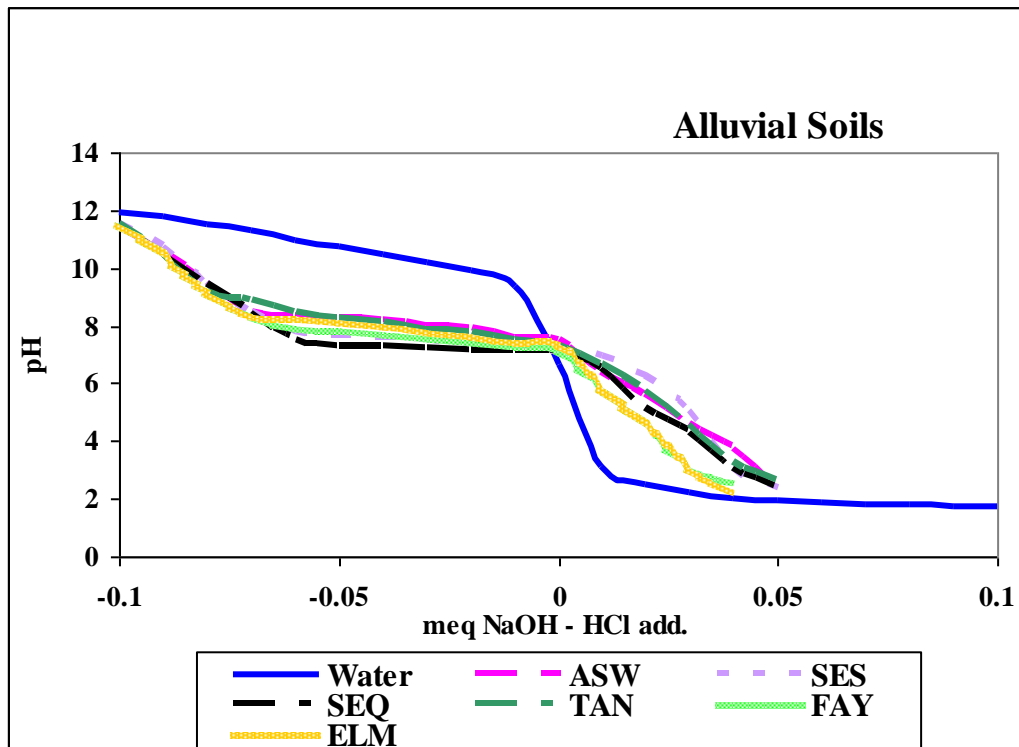


Fig. (5) Acid – base titration curves for alluvial and calcareous soils.

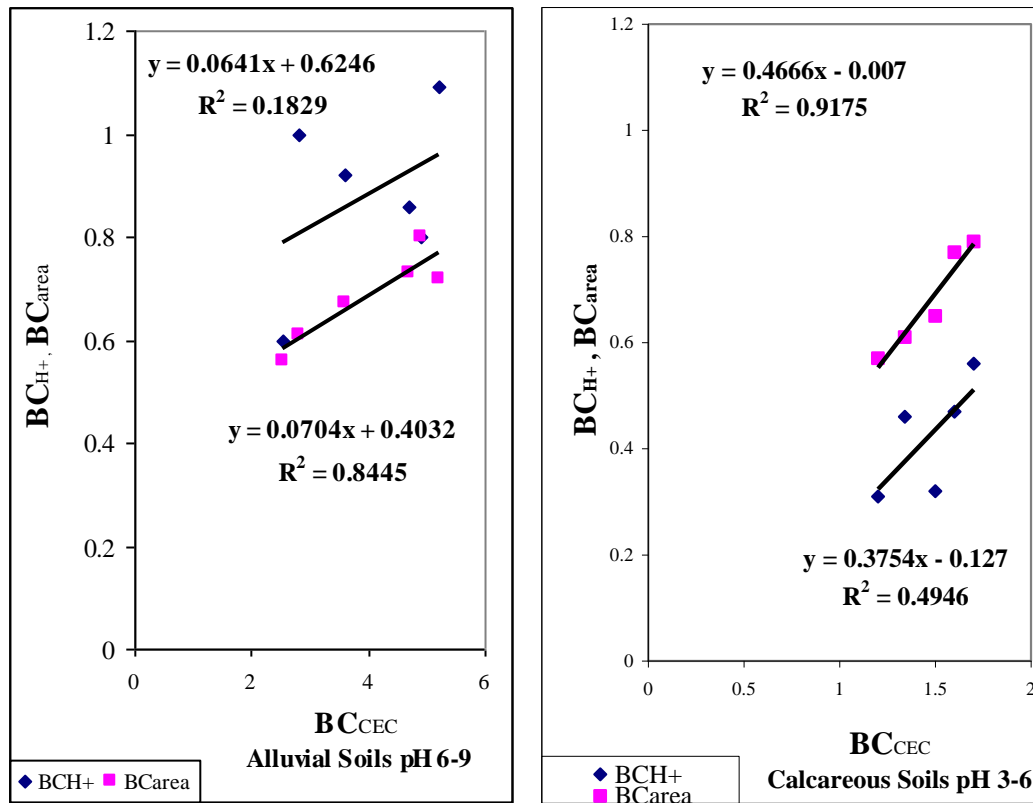


Fig.(6) Linear regressions among the different buffering index in alluvial and calcareous soil groups.

تقدير السعة التنظيمية لنماذج الأراضي الرسوبية والجيرية في مصر

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من الخواص الهامة لدراسة خصوبة التربة وتلوثها دراسة السعة التبادلية الكاتيونية وكذلك السعة التنظيمية المعتمدة على رقم حموضة التربة. وعادة ما تقاس هذه الخصائص للأراضي متغيرة الشحنة ونادراً ما تقاس لأنواع الأراضي الأخرى. والهدف من هذه الدراسة هو قياس خصائص السعة التنظيمية المعتمدة على رقم حموضة التربة لنماذج الأراضي الرسوبية النهرية والجيرية في مصر ، وذلك من خلال إضافة كميات متزايدة من محلول NaOH (ع0.1) ومحلول HCl (ع0.1) لأوزان ثابتة من التربة ثم الرج وبعد الإتزان تم قياس رقم pH , CEC.

أوضحت النتائج المتحصل عليها أن CEC تزداد زيادة معنوية بزيادة رقم pH من (9-3) وكانت هذه الزيادة كبيرة جداً عند رقم pH يتراوح من (9-6) حيث كانت الزيادة في ΔCEC عند pH (9-6) لأراضي أسوان وشبين الكوم من 8.62 إلى 16.35 $Cmol_c/kg$ وهذه الزيادة تمثل (32.28 , 35.8 %) من CEC_T على التوالي ، بينما تراوحت هذه القيمة في الأراضي الجيرية للعريش والنوبارية بين 2.95 إلى 4.98 $Cmol_c/kg$ وكانت تمثل (10.5 ، 15.47 %) من CEC_T على التوالي وكانت العلاقة معنوية بين ΔCEC والمحتوى الطيني.

كذلك تم حساب السعة التنظيمية المعتمدة على رقم pH باستخدام مدى من pH (6-3) وكذلك من (9-6) وتم بحثها في هذه الدراسة وذلك من خلال ثلاث معاملات للسعة التنظيمية. المعامل الأول هو ميل منحنى pH-CEC [$BC_{CEC} = \Delta CEC / dpH$] ، المعامل الثاني هو ميل منحنى المعاير [$BC_{H+} = d(H)(OH) / dpH$] ، والثالث هو قياس المساحة المحصوره بين منحي المعاير في الجانب الحامضي والقلوي للتربة وبين منحنى المعاير للماء BC_{area} . وكانت المعاملات الثلاث للسعة التنظيمية ذات علاقة معنوية ببعضها البعض، إلا أن BC_{H+} كانت أقل حساسية للتغير في خصائص التربة مقارنة بالمعاملات الأخرى. وعموماً فإن قيم السعة التنظيمية المتحصل عليها في المدى من (6-3) أقل كثيراً من النتائج المتحصل عليها في المدى من (9-6) للأراضي الرسوبية بينما أظهرت الأراضي الجيرية اتجاهاً عكسياً. وتفيد هذه النتائج من الناحية التطبيقية في التخطيط للإدارة الجيدة للأراضي.