

## ORTHOPHOSPHATE CHEMICAL EQUILIBRIA UPON RECLAMATION OF SALT-AFFECTED SOILS IN EL-SALAM CANAL PROJECT, EGYPT

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**ABSTRACT:** Salt-affected soils cover a pronounced area in El-Salam canal project. Phosphorus deficiency is a known problem after reclamation of such soils. Accurate anticipation of soil ortho-P equilibria is a key to a precise correction of P deficiency. The present study aimed to evaluate the effect of reclamation process on soil  $\text{H}_2\text{PO}_4$  potential ( $\text{pK}_{\text{sp}}$ ), quantity-intensity (Q/I) parameters, and dissolution-precipitation aspects for salt-affected soils of El-Salam canal area. Six soils differ in texture,  $\text{CaCO}_3$  content, alkalinity and salinity were reclaimed by intermittent ponding water of El-Salam canal with and without addition of gypsum. The results indicate that gypsum amendment had insignificant effect on ortho-P equilibria as the studied soils contain relatively high amounts of native Ca-bearing compounds. The significant decreases in ionic strength and activities of  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4$  occurred by reclamation were reflected on insignificant increases in  $\text{pK}_{\text{sp}}$ . Soluble ortho-P was decreased to a level lower than adequate for optimum plant growth in all soils. The Q/I plots were displaced in a direction tending to lower equilibrium activity and instant labile ortho-P in all soils. Reclamation process increased the potential buffering capacity of the calcareous coarse and medium textured soils and decreased it in case of the fine textured ones. Soil ortho-P equilibria between solid phase and solution phase after reclamation can be quantitatively predicted by equations calculated from experimental data of Q/I relationships. The initial ortho-P solubility points on the standard solubility-product diagrams of Ca-P compounds revealed that octacalcium phosphate was the most dominant form irrespective of studied soil properties. After reclamation, solubility products of  $\beta$ -tricalcium phosphate and hydroxyapatite control the soluble ortho-P concentrations in all soils. This indicates the susceptibility of  $\text{H}_2\text{PO}_4$  in the soil solution to direct precipitation and probably to chemisorption on the clay particle edges during reclamation. These findings should be considered when fertilizer-P program for the newly reclaimed salt-affected soils is planned.

## INTRODUCTION

El-Salam canal project has economical, demographic and social benefits for Egypt (MPWWR, 1999). Salt-affected soils cover a pronounced portion (290000 faddans) of the area using El-Salam canal water (El-Taweel et al., 1997; Hola, 2000). Land reclamation and intensive agricultural utilization of such area is underway. Reclamation of saline-sodic soils requires replacement of  $\text{Na}^+$  by  $\text{Ca}^{2+}$  on the cation exchange sites of soil colloids along with leaching excess soluble salts out of the root zone by means of adding water to the soil (Wanas and Mansour, 2000). Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is the main amendment used for reclaiming sodic soils in Egypt. Phosphorus deficiency is a major limiting factor to the productivity of the newly reclaimed soils. Accurate prediction of P requirements and correction of P deficiency are still far from being achieved due to the need for more understanding of the chemical behaviour of this nutrient (Holford, 1991; Rietra et al., 2001; Kreller et al., 2002).

Orthophosphate ions ( $\text{H}_2\text{PO}_4$ ) strongly react with various soil components, essentially by processes of adsorption and

formation of solid phosphates. Ortho-P retention includes physical adsorption, chemisorption, precipitation, and penetration into soil particles (Matar et al., 1992). The finite ortho-P quantity in the solution-phase of salt-affected soils has been ascribed to an extreme surface fixation and to direct precipitation reactions. It is demonstrated that the amounts of P sorbed by soil increased with increasing ionic strength and were greater with  $\text{Ca}^{2+}$  than with  $\text{Na}^+$ . These results were attributed to the effects of ionic strength and cations species on the surface charge and the thickness of the double electric layer of the retaining components (El-Mahi and Mustafa, 1980; Kleinman et al., 2002).

Study of soil ortho-P equilibria between solid and solution phases provides excellent opportunity to track dissolution and precipitation reactions which control plant-available ortho-P (Al-Khateeb et al., 1986; Robbins et al., 1999). Three approaches to characterize soil ortho-P equilibria are in general use, chemical potential, quantity-intensity (Q/I) relationships and solubility-product isotherms (Aslyng, 1964; Larsen, 1967; Fixen and Grove, 1990). The term *phosphate potential*

introduced by Schofield (1955) as an index for availability of soil P to plants. It is defined as "the amount of work that must be conducted to move reversibly and isothermally an infinitesimally small amount of a phosphate ion from a pool of phosphates at a specified location at atmospheric pressure to the point under consideration" (Tan, 1998). Schofield suggested the use of chemical potential of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  in the equilibrium liquid phase of soil to evaluate the possible entry of phosphate from the soil solid-phase into soil solution. More information on changes in chemical ortho-P equilibria during reclamation of salt-affected soils is still needed under Egyptian conditions.

The objective of the present study is to explore the changes in soil ortho-P potential, potential buffering capacity, equilibrium activity, instant labile, and dissolution-precipitation behavior during reclamation of salt-affected soils at El-Salam canal project.

#### Mathematical background for assessing soil ortho-P equilibria:

The phosphate potential can be expressed as the solubility-product ( $K_{sp}$ ) of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ :

$$K_{sp} = (a_{\text{Ca}^{2+}})^{0.5} \cdot a_{\text{H}_2\text{PO}_4} \quad [1]$$

where  $a$  denotes to the ion activity and by taking  $-\log$ , this produce changes into

$$-\log K_{sp} = [-0.5 \log a_{\text{Ca}^{2+}}] + [-\log a_{\text{H}_2\text{PO}_4}] \quad [2]$$

or

$$pK_{sp} = 0.5pCa + pH_2PO_4 \quad [3]$$

in which  $p = -\log$ .

Because of  $pK_{sp}$  is, in fact, a solubility-product, it is expected to be useful in estimating solubility of  $\text{H}_2\text{PO}_4$  in soil solution. The application of  $pK_{sp}$  to identify crystalline solid-phase P compounds in soils have been widely used (Lindsay and Moreno, 1960; Lindsay, 1979; Robbins et al., 1999). Diagrams relating phosphate potential,  $pH_2PO_4 + 0.5pCa$ , to lime potential,  $pH - 0.5pCa$ , for the calcium phosphates occurring in neutral and alkaline soils have been constructed, based on the phosphates being stoichiometrically formed from  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$  (Sample et al., 1980). The relationships for saturated solutions are:

for  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (dicalcium phosphate dihydrate, DCPD)

$$(pH - 0.5pCa) - (pH_2PO_4 + 0.5pCa) = 0.65 \quad [4]$$

for  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  (octacalcium phosphate, OCP)

$$5(pH - 0.5pCa) - 3(pH_2PO_4 + 0.5pCa) = 11.7 \quad [5]$$

for  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> ( $\beta$ -tricalcium phosphate,  $\beta$ -TCP)

$$2(\text{pH}-0.5\text{pCa}) - (\text{pH}_2\text{PO}_4+0.5\text{pCa}) = 5.0 \quad [6]$$

for Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> (hydroxyapatite, HA)

$$7(\text{pH}-0.5\text{pCa}) - 3(\text{pH}_2\text{PO}_4+0.5\text{pCa}) = 14.7 \quad [7]$$

In order to determine the mineral form of soil phosphate, a graphical representation of the phosphate potential vs. lime potential for the tested soil can be obtained using the above relationships. If the point lies above the nearest line, then the solution is supersaturated relative to that mineral and precipitation can occur; whereas a point below the line indicates undersaturation of the solution and dissolution is plausible (Fixen and Grove, 1990; Tan, 1998).

## MATERIALS AND METHODS

### Soil samples collection:

The present investigation was a part of comprehensive studies initiated on Oct. 2000. It is the intent to monitor the changes in the chemical behaviour of some nutrients as a function of progressive soil reclamation on El-Salam canal project. Six surface (0-30 cm depth) soils differing mainly

in texture, CaCO<sub>3</sub> content and salinity, with no previous history of P fertilization, were collected from different locations to represent salt-affected soils in the project. Coarse and medium textured soils were collected from Rabaa and El-Tina plain, north Sinai, whereas the fine textured soils were taken from Al-Hussania plain, Shabaab El-Kheregeen project and Al-Matariya region, westsouthern of Manzala lake. The locations of soil samples are illustrated in Fig.1. Soil samples were air-dried, crushed, and passed through a 2-mm sieve, then mixed thoroughly before use in the experiment. Physical and chemical characteristics of these soils are given in Table 1. These characteristics were determined according to the methods recommended by Page (1982) and Richards (1954). Total P was measured after digestion with H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>-HF (Bowman, 1988). Water soluble-P was determined in 1:10 ratio of soil: water extract. In all P determinations, the ascorbic acid blue colour method as given by John (1970) was adopted. Absorbency was determined at a wavelength of 712 nm.

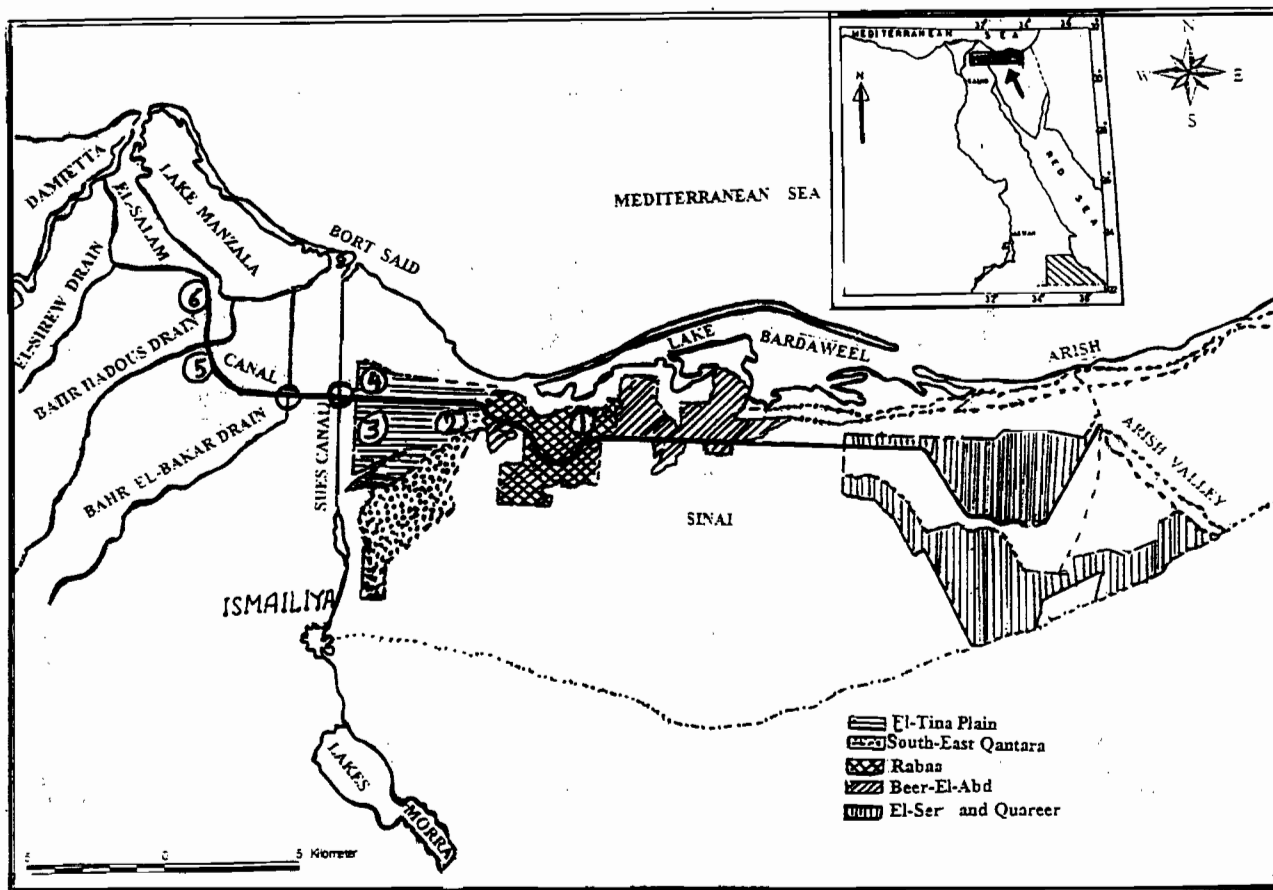


Fig.1 Location of El-Salam canal project and locations of the studied salt-affected soils.

Table 1. Some physical and chemical properties of surface samples (0-30 cm depth) collected from salt-affected soils of El-Salam canal project

Soil Property	Coarse textured soils		Medium textured soils		Fine textured soils	
Site	1	2	3	4	5	6
Sample number	Rabaa	El-Tina plain	El-Tina plain	El-Tina plain	El-Hussania	Al-Matariya
Clay, gkg <sup>-1</sup>	82	169	287	167	408	520
Silt, gkg <sup>-1</sup>	109	85	223	547	303	290
Sand, gkg <sup>-1</sup>	809	746	490	286	289	190
Texture Class	<i>Loamy sand</i>	<i>Sandy loam</i>	<i>Sandy clay loam</i>	<i>Silty loam</i>	<i>Clay loam</i>	<i>Clayey</i>
CaCO <sub>3</sub> , gkg <sup>-1</sup>	36.2	116.1	101.8	25.4	31.27	39.1
Organic carbon, gkg <sup>-1</sup>	6.61	4.35	12.06	15.95	16.65	22.21
pH (1:2.5 suspension)	7.35	7.85	8.15	7.30	7.55	7.85
EC <sub>e</sub> (soil paste extract), dSm <sup>-1</sup>	117.6	92.6	213.2	262.4	172.7	46.9
Total soluble salts (TSS), g kg <sup>-1</sup>	17.98	11.82	36.75	60.94	44.19	23.52
Soluble ions, cmol <sub>c</sub> kg <sup>-1</sup>						
Ca <sup>2+</sup>	1.26	0.85	8.25	12.91	3.40	1.18
Mg <sup>2+</sup>	2.62	3.57	19.84	26.74	19.47	9.68
Na <sup>+</sup>	84.11	72.13	231.54	272.76	175.39	93.03
K <sup>+</sup>	0.96	0.65	2.38	2.86	3.64	2.84
CO <sub>3</sub> <sup>-</sup>	---	---	---	---	---	---
HCO <sub>3</sub> <sup>-</sup>	0.84	1.70	1.21	1.31	0.69	0.36
Cl <sup>-</sup>	81.24	70.39	240.58	299.38	187.04	97.56
SO <sub>4</sub> <sup>2-</sup>	6.87	5.11	20.02	14.58	14.17	8.81
Exchangeable cations, cmol <sub>c</sub> kg <sup>-1</sup>						
Ca <sup>2+</sup>	5.86	5.89	9.95	10.59	12.48	18.79
Mg <sup>2+</sup>	1.69	2.38	3.98	4.89	9.16	12.97
Na	0.92	1.13	1.99	2.04	4.93	4.99
K <sup>+</sup>	0.58	0.62	0.98	1.09	1.89	2.56
Cation exchange capacity, cmol <sub>c</sub> kg <sup>-1</sup>	9.05	10.02	16.90	18.61	28.46	39.31
Exchangeable Na Percentage (ESP)	10.16	11.28	11.78	10.96	17.32	12.69
Total phosphorus, mg kg <sup>-1</sup>	398	481	606	794	998	1263
Water soluble-P, mg kg <sup>-1</sup>	0.87	0.91	0.78	0.55	0.30	0.32

**Table 2: Theoretical calculations of equilibrium phosphate and lime potential for DCPD, OCP, B-TCP, and HA corresponding to their solubility products (Lindsay,1979)**

Lime potential	Phosphate potential			
	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ <b>DCPD</b>	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ <b>OCP</b>	$\text{Ca}_3(\text{PO}_4)_2$ <b>B-TCP</b>	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ <b>HA</b>
3.75	3.10	2.35	2.41	3.85
4.75	4.10	4.02	4.41	6.18
5.75	5.10	5.98	6.41	8.52
6.75	6.10	7.73	8.41	10.85
7.75	7.10	9.02	10.41	13.18
8.75	8.10	10.68	12.41	15.52
9.75	9.10	12.35	14.41	17.85
10.75	10.10	14.02	16.41	20.18

**Experimental design and statistical analysis:**

The experimental design was a 6 x 3 factorial in a randomized complete block with four replications. Six soil textures were loamy sand, sandy loam, sandy clay loam, silty loam, clay loam and clayey. Three reclamation treatments were non-reclaimed (virgin) soil as control; intermittent leaching with canal water only and leaching coupled with gypsum amendments. Hence, the total number of soil columns is  $72 = 6 \text{ soils} \times 3 \text{ reclamation treatments} \times 4 \text{ replicates}$ . The analysis of variance, regression and correlation for data were done according to the procedures outlined by Gomez and Gomez (1984). Differences among treatments were examined with means separation by the least significant difference (LSD).

**Soil reclamation techniques:**

Eighteen polyvinyl chloride (PVC) columns of 10-cm inner diameter and 40 cm length were used for packing the soil and operating the reclamation processes. The columns were wrapped at the bottom by filter paper followed by cheesecloth to allow drainage of leaching water. The air-dried soil samples were

gradually poured into the columns, and each column received exactly 4kg soil. The soil height in the columns was about 40cm. The soils were wetted to near saturation and were allowed to equilibrate for 2 weeks before leaching. The leaching process was achieved with El-Salam canal water [ $EC = 1.78 \text{ dSm}^{-1}$  and  $SAR = 7.7 (\text{meq/l})^{0.5}$ ]. One set of columns was repeatedly leached with 1.5 fold of soil field capacity portions of water at 3 weeks intervals until their effluents have EC values lower than  $4 \text{ dSm}^{-1}$  (end of reclamation). An additional set of treatments was leached with water until EC of the effluents reach about 30% of the initial value of  $EC_e$  of the soil saturation extract (as recommended by MPWWR, 1999). Then calculated gypsum requirements (based on reducing initial ESP to 5) were thoroughly incorporated into the upper 10-cm of the soil column. Leaching was continued according to the above same manner till full reclamation. To reach approximately the same final effluent EC for all soils, medium and fine textured soils had to be leached as many as 4-6 times over coarse textured soils to reach the target EC. The experiment was extended for almost 9 months. Two weeks after leaching was stopped,



the soils were taken out of column, air-dried, passed through a 2-mm sieve and stored for subsequent studies and chemical analysis.

#### Phosphate potential (pKsp) and Q/I parameters measurements:

Phosphate potential (pKsp) and Q/I parameters were determined according to the method described by Jensen (1970). Five-grams duplicate air-dried soil sample were mixed with 50 ml of 0.01 M CaCl<sub>2</sub> solution having a concentration of KH<sub>2</sub>PO<sub>4</sub> varying from 0 to 200×10<sup>-6</sup> M. Half ml of chloroform was added to each suspension to depress microbial activity. The samples were equilibrated on a reciprocating shaker at room temperature for 23h. The suspensions were centrifuged and filtered through a Whatman No. 42. The pH and electrical conductivity (EC) of the supernatant were measured immediately (Robbins et al., 1999); then P and Ca<sup>2+</sup> in solution were analyzed. The quantity factor (Q) of P sorbed (+ΔQ), or released (-ΔQ) by the soil when reaching equilibrium were obtained from the difference in P concentration between the initial and final solutions after equilibrating with

soil. The intensity factor (I) or ion activity, *a*, in mol/l of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Ca<sup>2+</sup> in equilibrium solutions were calculated from their ion concentrations in the filtrate using the following equation of Bhon et al. (1985):

$$a_i = C_i f_i \quad [8]$$

Where C<sub>i</sub> denotes effective molarity of ionic species *i* and *f<sub>i</sub>* denotes single activity coefficient of ionic species *i* and were estimated using the equation of Davies (1962):

$$\text{Log } f_i = -0.511 Z_i^2 [(m^{0.5}) / (1+m^{0.5}) - (0.3 m)] \quad [9]$$

Where Z denotes charge of ionic species *i*. The values of ionic strength, *m*, were calculated using the EC values in dSm<sup>-1</sup> (Griffin and Jurinak, 1973):

$$m = 0.013 \text{ EC} \quad [10]$$

The concentration of ortho-P ion (H<sub>2</sub>PO<sub>4</sub>) in the equilibrium soil solution was calculated from the total soluble P concentration (P) and Ca concentration (Ca<sup>2+</sup>) and pH using the equation given by Larsen (1965) for alkaline soils as follows: (H<sub>2</sub>PO<sub>4</sub>) = (P) / [(1) + (10<sup>pH-pK<sub>2</sub></sup>) + (Ca<sup>2+</sup>) × (10<sup>pH+pK<sub>c</sub>-pK<sub>2</sub></sup>)] [11]

Where pK<sub>2</sub> is -log of the apparent second dissociation constant of phosphoric acid. The pK<sub>2</sub> has been calculated according to the equation of Bjerrum (1958):

$$pK_2 = 7.227 - 1.497 m^{0.5} + 1.09 m \quad [12]$$

Where  $pK_c$  is  $-\log$  of dissociation constant of the calcium phosphate complex ( $\text{CaHPO}_4$ ). Larsen (1965) estimated  $pK_c$  value for 0.01 M  $\text{CaCl}_2$  solution to be 2. The  ${}^a\text{H}_2\text{PO}_4$  for solution P concentrations of each soil were plotted against the corresponding values of  $\pm\Delta Q$  to obtain the Q/I plots. The slope of the Q/I relationship gives the phosphate potential buffering capacity ( $PBC^p$ ) as introduced by Beckett and White (1964). The  $pK_{sp}$  and its components for all equilibrium solutions were calculated in the cases of without adding  $\text{KH}_2\text{PO}_4$  to the 0.01M  $\text{CaCl}_2$  solution.

#### **Solubility-product isotherm:**

For identifying solid-phase P, the calculated phosphate potential ( $0.5p\text{Ca} + p\text{H}_2\text{PO}_4$ ) and lime potential ( $p\text{H} - 0.5p\text{Ca}$ ) were plotted along with the double function solubility diagrams for DCPD, OCP, B-TCP, and HA. The theoretically calculations of equilibrium phosphate and lime potential for DCPD, OCP, B-TCP, and HA corresponding to their solubility products ( $K_{sp}$ ) are shown in Table 2.

## **RESULTS AND DISCUSSIONS**

### **Description of the representative soil samples:**

Table 1 presents some physical and chemical properties of soil samples collected from salt-affected soils of El-Salam canal project. According to the particle size distribution, the studied soils are classified to three groups. First group is composed of loamy sand and sandy loam soils representing coarse textured soils. Second group is medium textured soils comprises of sandy clay loam and silty loam classes. Third group is fine textured soils includes clay loam and clayey classes. <sup>1</sup>

The organic carbon content shows a tendency of increase in the fine textured soils where it reached its maximum of  $22.2\text{gkg}^{-1}$  in the clayey soil. In contrast, calcium carbonate tends to accumulate in the coarse and medium textured soils where it reached its maximum of  $116.1\text{gkg}^{-1}$  in the sandy loam soil. The greatest content of  $\text{CaCO}_3$  could be rendered to the existence of common small to medium shell fragments as an old sea and lake deposits (Hala, 2000).

All of soils are highly to excessively saline and slightly to moderately alkaline as indicated by

values of electric conductivity "EC<sub>e</sub>" (46.9– 262.4 dSm<sup>-1</sup>), and pH (7.30 – 8.15). Soils of El-Tina plain and Al-Matariya were non-sodic since their ESP did not exceed 15, but soil of EI-Hussania was sodic since it ESP exceeded 15 (Richards, 1954). High salinity of the soils may be ascribed to: (1) the high salinity of ground water particularly with the high water table which existed in these soils for a long time, (2) intrusion of saline water from the Mediterranean sea, and other adjacent water bodies such as Suez canal, and Manzala lake, (3) prevalence of arid climate, and (4) inheritance of salts from geological formation of parent materials of soils (El-Taweel et al., 1997; Hola, 2000). The data of soluble ions show that the main cations are Na<sup>+</sup> followed by Mg<sup>2+</sup> and the main anions are Cl<sup>-</sup> followed by SO<sub>4</sub><sup>2-</sup>. This is close resemblance with the ionic composition order of saline water of the sea, Suez canal, Manzala lake and Bardaweel lake (Hola, 2000). However, exchangeable Ca<sup>2+</sup> occupies the first magnitude level followed by Mg<sup>2+</sup> and Na<sup>+</sup> where K<sup>+</sup> is least.

Data of Table 1 also show that total soil P ranges between 398 and 1263 mgPkg<sup>-1</sup>. Generally, total

soil P increases as the clay content of the soil increases. Pierzynski et al. (1990) reported that total P concentration is generally higher in the clay-size fraction of the soils compared with the silt and sand fractions. The values of water soluble-P in 1:10 ratio of soil: water extract are very low (0.32-0.91 mgPkg<sup>-1</sup>) and does not coincide with the trend of total soil P. This may be attributed to the high reactivity of clay mineral surfaces which affects phosphate solubility (Tan, 1998). Behiry (1991) found a negative correlation between soil clay content and saloid-P which refers to water soluble P and easily bound phosphate on solid surfaces.

#### **Ortho-P potential (pK<sub>sp</sub>):**

Tables 3a and 3b show variations in ortho-P potential (pK<sub>sp</sub>) and its components. Two opposite trends can be noticed in all but the clayey soil in some cases. First trend, the concentrations of calcium ion (Ca<sup>2+</sup>) and total soluble phosphorus (P) as well as calcium activity (<sup>a</sup>Ca<sup>2+</sup>) in the equilibrium solutions were significantly lower in the fine textured soils as compared to the coarse and medium textured ones. Second trend, ionic strength (*m*) and ortho-P (H<sub>2</sub>PO<sub>4</sub>) concentration

**Table 3a. Orthophosphate potential (pKsp) and its components in equilibrium solutions of virgin and reclaimed salt-affected soils of El-Salam canal project**

Soil texture and Reclamation technique	Calcium concentration (Ca) mol × 10 <sup>-4</sup> /l	$[1] + [10^{pH-pK_2}] + [(Ca) \times 10^{pH-pK_1-pK_2}]$	Phosphorus concentration (P) mol × 10 <sup>-6</sup> /l	Ortho-P concentration (H <sub>2</sub> PO <sub>4</sub> ) mol × 10 <sup>-7</sup> /l	Ionic strength <i>m</i> , mol × 10 <sup>-3</sup> /l	Activity coefficient <i>f<sub>i</sub></i> × 10 <sup>-3</sup>		<sup>a</sup> Ca <sup>2+</sup> mol × 10 <sup>-4</sup> /l	<sup>a</sup> H <sub>2</sub> PO <sub>4</sub> mol × 10 <sup>-7</sup> /l	pH <sub>2</sub> PO <sub>4</sub>	0.5pCa	pKsp
						Ca <sup>2+</sup>	H <sub>2</sub> PO <sub>4</sub>					
<b>Loamy Sand</b>												
Virgin (control)	310	164.22	24.89	1.516	169	322	753	99.8	1.14	6.94	1.00	7.94
Leaching only	240	108.51	1.82	0.167	44	470	828	112.8	0.14	7.86	0.97	8.83
Leaching + gypsum	230	59.68	1.82	0.305	47	462	825	106.3	0.25	7.60	0.99	8.59
<b>Sandy Loam</b>												
Virgin (control)	350	180.14	26.23	1.450	167	323	753	113.1	1.09	6.96	0.97	7.93
Leaching only	240	108.51	1.52	0.140	49	457	822	109.7	0.12	7.94	0.98	8.92
Leaching + gypsum	252	89.40	1.52	0.170	49	457	822	115.2	0.14	7.85	0.97	8.82
<b>Sandy Clay Loam</b>												
Virgin (control)	349	142.98	22.04	1.540	128	346	767	120.8	1.18	6.93	0.96	7.89
Leaching only	250	111.67	1.82	0.162	49	457	822	114.3	0.13	7.88	0.97	8.85
Leaching + gypsum	245	87.65	1.69	0.193	47	462	825	113.2	0.16	7.80	0.97	8.77
<b>Silty loam</b>												
Virgin (control)	336	31.87	14.39	4.510	849	347	767	116.6	3.46	6.46	0.97	7.43
Leaching only	125	45.89	4.74	1.030	41	480	832	60.0	0.86	7.07	1.11	8.18
Leaching + gypsum	140	25.00	4.99	1.990	40	483	834	67.6	1.66	6.78	1.08	7.86
<b>Clay Loam</b>												
Virgin (control)	280	43.63	6.43	1.470	245	297	738	83.2	1.09	6.96	1.04	8.00
Leaching only	110	11.52	0.93	0.807	54	444	816	48.8	0.66	7.18	1.16	8.34
Leaching + gypsum	116	9.59	1.25	1.300	59	433	811	50.2	1.05	6.98	1.15	8.13
<b>Clayey</b>												
Virgin (control)	320	38.43	6.99	1.810	82	393	792	125.8	1.43	6.84	0.95	7.79
Leaching only	224	33.40	2.74	0.820	29	530	853	118.7	0.70	7.16	0.96	8.12
Leaching + gypsum	235	19.83	2.67	1.340	27	535	855	125.7	1.15	6.94	0.95	7.89

**Table 3b. Mean values and LSD of  $pK_{sp}$  and some related components in the equilibrium solutions of virgin and reclaimed salt-affected soils of El-Salam canal project**

Variable	Concentration, mol/l			Ionic strength, mol/lx10 <sup>-3</sup>	Activity, mol/l		$pK_{sp}$
	(Ca) x10 <sup>-4</sup>	(P) x10 <sup>-6</sup>	(H <sub>2</sub> PO <sub>4</sub> ) x10 <sup>-7</sup>		<sup>a</sup> Ca <sup>2+</sup> x10 <sup>-4</sup>	<sup>a</sup> H <sub>2</sub> PO <sub>4</sub> x10 <sup>-7</sup>	
Soil texture:							
Loamy sand	260	9.51	0.663	86.7	103.6	0.51	8.45
Sandy loam	281	9.76	0.587	88.3	112.0	0.45	8.56
Sandy clay loam	281	8.52	0.632	74.7	116.1	0.49	8.50
Silty loam	200	6.03	2.510	310.0	81.4	1.99	7.82
Clay loam	169	2.87	1.192	119.3	60.4	0.93	8.16
Clayey	260	4.13	1.323	46.0	123.4	1.09	7.93
LSD ( $P < 0.05$ )	36	1.31	1.118	24.2	15.7	0.18	NS
Reclamation technique:							
Virgin (control)	324	16.83	2.049	273.3	109.9	1.57	7.83
Leaching only	198	2.26	0.521	44.3	94.1	0.44	8.54
Leaching + gypsum	203	2.32	0.883	44.8	96.4	0.74	8.34
LSD ( $P < 0.05$ )	25	0.93	0.790	17.1	11.1	0.13	NS
Interactions (see Table 3a):							
LSD ( $P < 0.05$ )	62	2.27	NS	41.9	NS	0.31	NS

and ortho-P activity ( ${}^a\text{H}_2\text{PO}_4$ ) were higher in the fine textured soils than the coarse textured soils. The fairly great buffering power of soil clays for controlling hydrogen activity ( ${}^a\text{H}^+$ ) and  ${}^a\text{Ca}^{2+}$  in the equilibrium solution through exchange reactions may be responsible for these trends. Values of the component  $[(1)+(10^{\text{pH}-\text{pK}_2})+(\text{Ca}^{2+})\times(10^{\text{pH}+\text{pK}_c-\text{pK}_2})]$  decreased by an order of magnitude exceeding that of (P) as soil clay content increased substantiates this conclusion. Orlov (1992) reported that the higher the ortho-P potential, the more difficult it becomes for P to enter into soil solution and the less favorable are the conditions for P availability to plants. Based on calculation equations of  $\text{pK}_{sp}$ , the  ${}^a\text{H}_2\text{PO}_4$  in the soil solution would be decreased with an increase in the  ${}^a\text{Ca}^{2+}$ .

Both of the adopted reclamation techniques slightly increased the  $\text{pK}_{sp}$  for all examined soils. There were sharp decreases in the ( $\text{Ca}^{2+}$ ), (P) and ( $\text{H}_2\text{PO}_4$ ) as well as ionic strength ( $m$ ) in the equilibrium solutions of the reclaimed soils as compared with the virgin ones. There is insignificant between leaching with or without gypsum amendments on

ortho-P equilibria. This may be due to these soils having high amounts of native Ca-bearing compounds (Table 1). Hola (2000) reported gypsum contents in these soils as between 22 to as high as  $157\text{gkg}^{-1}$ .

Reclamation of soils by leaching combined with addition of gypsum in comparison with leaching without gypsum showed insignificant increases in ( $\text{Ca}^{2+}$ ), (P), ( $\text{H}_2\text{PO}_4$ ) and  ${}^a\text{Ca}^{2+}$  but significant increase in  ${}^a\text{H}_2\text{PO}_4$  (Table 3b). This may be due to lowering soil pH, which in turn increases the soluble P (Chhabra, et al., 1981; Sanyal and De Datta, 1991).

Reclamation, sharply decreased the  $0.01M$   $\text{CaCl}_2$  extractable ortho-P concentrations in all tested soils which were appreciably lower than the  $0.2\text{--}0.3\text{mgPkg}^{-1}$  required for optimum plant growth (Nishimoto et al., 1977; Robbins et al., 1999). This may be attributable to the reclamation having a diminishing ionic strength, thereby expanding the double electric layer of soil colloids and accentuating the electrostatic repulsive forces. Hence, easily-held ortho-P anions onto solid-phase swarms closer to solution-phase and become more exposed to direct precipitation or to

movement along with other leached soluble ions (Sparks, 1999; Celi et al., 2000). Under salt-affected soil conditions in Egypt, Mohammed (1980) found a negative significant correlation between soil salinity and water soluble-P. The significant increases of activity coefficients ( $f_i$ ) of  $\text{Ca}^{2+}$  and ortho-P due to reclamation are negatively reflected on  $pK_{sp}$ . Minkina (1997) demonstrated that although there was a sharp decrease in the (P) in the 0.01M NaCl+CaCl<sub>2</sub> equilibrium solution occurred by different means of sodic soil reclamation, the  $pK_{sp}$  has changed insignificantly. Moreover, changes in ( $\text{Ca}^{2+}$ ), (P), ( $\text{H}_2\text{PO}_4$ ) and pH were variable and were reflected on the values of  $pK_{sp}$ .

#### **Quantity-intensity parameters of ortho-P:**

An alternative model to describe soil P equilibria is the quantity/intensity (Q/I) relationship (Sui and Thompson, 2000). The quantity-intensity graphs given in figure 2 allow to assess three important characteristics of soil ortho-P equilibria (Orlov, 1992). First, the capacity factor or the instant labile phosphates (ILP) capable to be dissolved in 0.01M CaCl<sub>2</sub> solution, and it is the value

of the intercept of the straight line on the y-axis. Second, the intensity factor or  ${}^a\text{H}_2\text{PO}_4$  at equilibrium, i.e. equilibrium phosphate activity (EPA) which is represented by the point of intersection of the graph on the x-axis. At EPA the phosphate ions in liquid-phase are not sorbed or fixed on soil components from such a solution and solid-phase phosphates do not enter such a solution. Third, phosphate potential buffering capacity ( $PBC^p$ ) which is the slope of the graph ( $dQ/dI$ ). The  $PBC^p$  of a soil indicates its ability to resist a change in the P concentration of the solution phase. A summary of the data obtained from the Q/I plots of the studied soils are presented in Tables 4 & 5.

Reclamation displaced Q/I plots in a direction tending to lower EPA and ILP in all soils. However, reclamation increased  $PBC^p$  of coarse and medium textured soils and decreased it in the fine textured ones. These trends reflect differences between soils in their chemical properties caused by differences in their clay contents (Table 1), and thereby their power to retain soluble-P. It has been demonstrated that the high clay contents of soils are associated with their high capacity to react

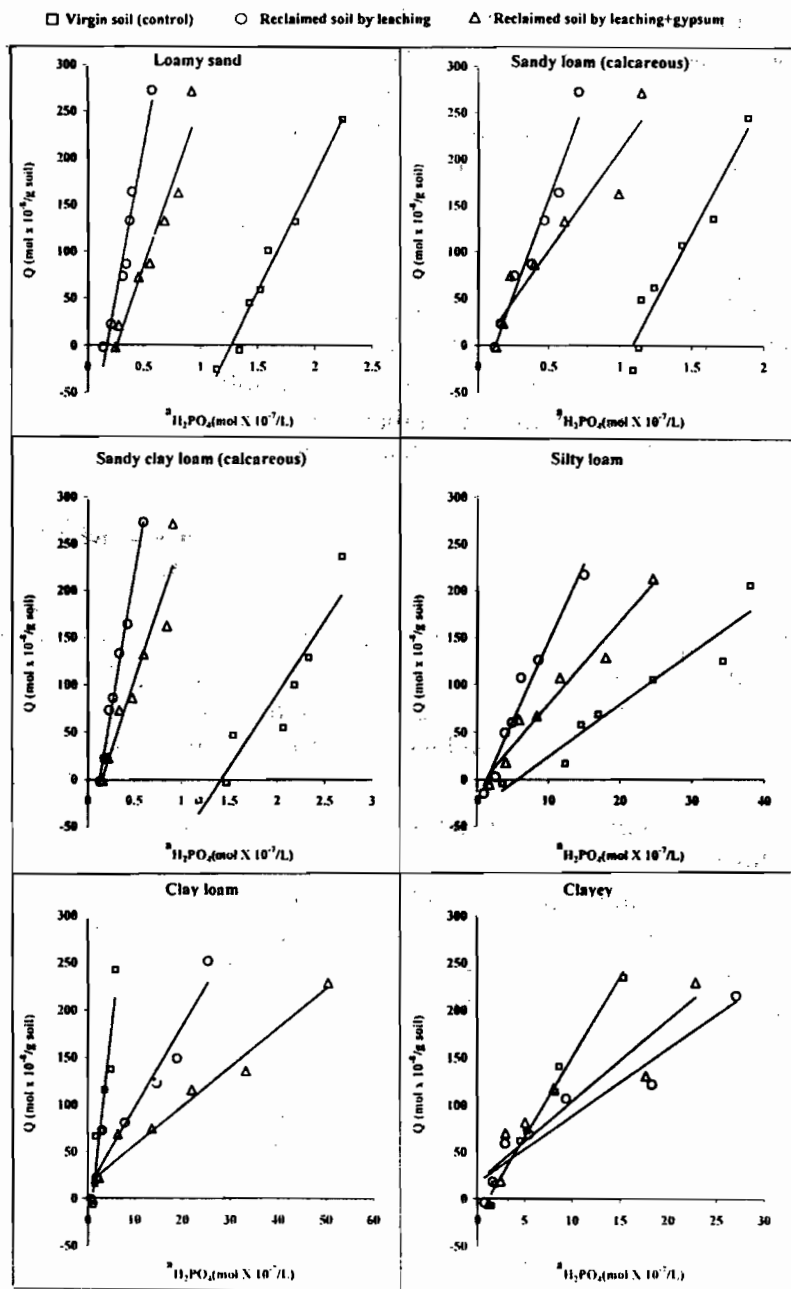


Fig. 2. Quantity-intensity plots of ortho-P in virgin and reclaimed salt-affected soils of El-Salam canal project.



**Table 4. Ortho-P quantity-intensity (Q/I) plot parameters of virgin and reclaimed salt-affected soils in El-Salam canal project**

Soil texture	Potential buffering capacity (PBC), l/g			Phosphate activity at equilibrium (EPA), mol $\times 10^{-7}$ /l			Instant labile phosphate (ILP), mg P/kg		
	control	leaching	leaching + gypsum	control	leaching	leaching + gypsum	control	leaching	leaching + gypsum
Loamy sand	24.9	64.6	34.9	1.27	0.17	0.26	98.3	34.9	28.5
Sandy loam	29.3	41.9	21.8	1.09	0.13	0.04	91.0	16.2	2.4
Sandy clay loam	15.4	57.4	29.8	1.42	0.13	0.15	67.8	22.3	14.0
Silty loam	0.6	1.7	0.9	5.62	1.28	0.94	9.6	6.6	2.6
Clay loam	4.3	0.9	0.4	0.92			12.4		
Clayey	1.7	0.7	0.9	1.10			5.8		

— Means that the values of EPA are negative whereas the values of ILP are positive.

**Table 5. Prediction equations of instant labile phosphate (ILP) vs. equilibrium phosphate activity (EPA) for the newly reclaimed salt-affected soil of El-Salam canal project**

Soil texture	Reclamation technique	Prediction equation*	r <sup>2</sup> value
Loamy sand	Leaching only	$y = 645.76 x - 112.56$	0.9603
	Leaching + gypsum	$y = 349.31 x - 92.039$	0.8583
Sandy loam	Leaching only	$y = 419.12 x - 52.293$	0.9327
	Leaching + gypsum	$y = 217.57 x - 7.6886$	0.8491
Sandy clay loam	Leaching only	$y = 574.33 x - 71.864$	0.8165
	Leaching + gypsum	$y = 298.25 x - 45.11$	0.9438
Silty loam	Leaching only	$y = 16.674 x - 21.353$	0.9189
	Leaching + gypsum	$y = 8.7778 x - 8.2352$	0.9483
Clay loam	Leaching only	$y = 8.6333 x + 10.367$	0.8390
	Leaching + gypsum	$y = 4.1418 x + 15.716$	0.9051
Clayey	Leaching only	$y = 7.1171 x + 17.332$	0.8582
	Leaching + gypsum	$y = 8.5754 x + 18.296$	0.8125

\*y is ILP whereas x is EPA

with soluble-P (Behiry, 199; Mc Dewell et al., 2001). Orth-P retention by clays can include chemisorption on the clay particle edges. As the soils taken from areas around El-Salam canal were shown to have montmorillonite dominating clay mineralogy assemblage (El-Taweel et al., 1997), leaching of such soils may enhance P retention.

Retention of soluble phosphate by clay minerals involves a reaction with the particle lattice either through exchange of the orthophosphate ions ( $\text{H}_2\text{PO}_4^-$ ) by the hydroxyl ions ( $\text{OH}^-$ ) attached to aluminum and iron hydroxides; or by substitution of the triphosphate ions ( $\text{PO}_4^{3-}$ ) in place of the silicate ions ( $\text{SiO}_4^{4-}$ ) (Tahoun, et al., 1975; Tahoun, 1976a; Tan, 1998). Nair (1996) reported that buffering action of soils had no direct relationship to clay or humus content or soil pH. The ortho-P equilibria between solid phase and solution phase following reclamation can be quantitatively predicted by equations computed from the experimental data of Q/I relationships (Table 5).

### Dissolution-precipitation behaviour of ortho-P:

The study of soil ortho-P dissolution-precipitation behaviour is particularly useful for understanding the fate of soluble-P over time. Effective fertilizer-P use has to be based on a sound knowledge of the fate of soluble-P added to soil (Matar, et al., 1992, Sparks, 1999).

Figure 3 shows that the ortho-P solubility points before reclamation were below the  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  dicalcium phosphate dihydrate (DCPD) isotherm in the loamy sand soil and calcareous coarse textured soils of the sandy loam and sandy clay loam soil and well along the  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  octacalcium phosphate (OCP) isotherm in medium and fine textured soils. Reclamation shifted ortho-P solubility to be below the OCP isotherm in all soils and the  $\beta\text{-Ca}_3(\text{PO}_4)_2$   $\beta$ -tricalcium phosphate ( $\beta$ -TCP) isotherm in only one the clay loam soil. This may indicate that direct precipitation of soluble ortho-P is the main mechanism of P fixation under the conditions of these soils.

The vertical shifts in the solubility points may have been primarily due to a combination of

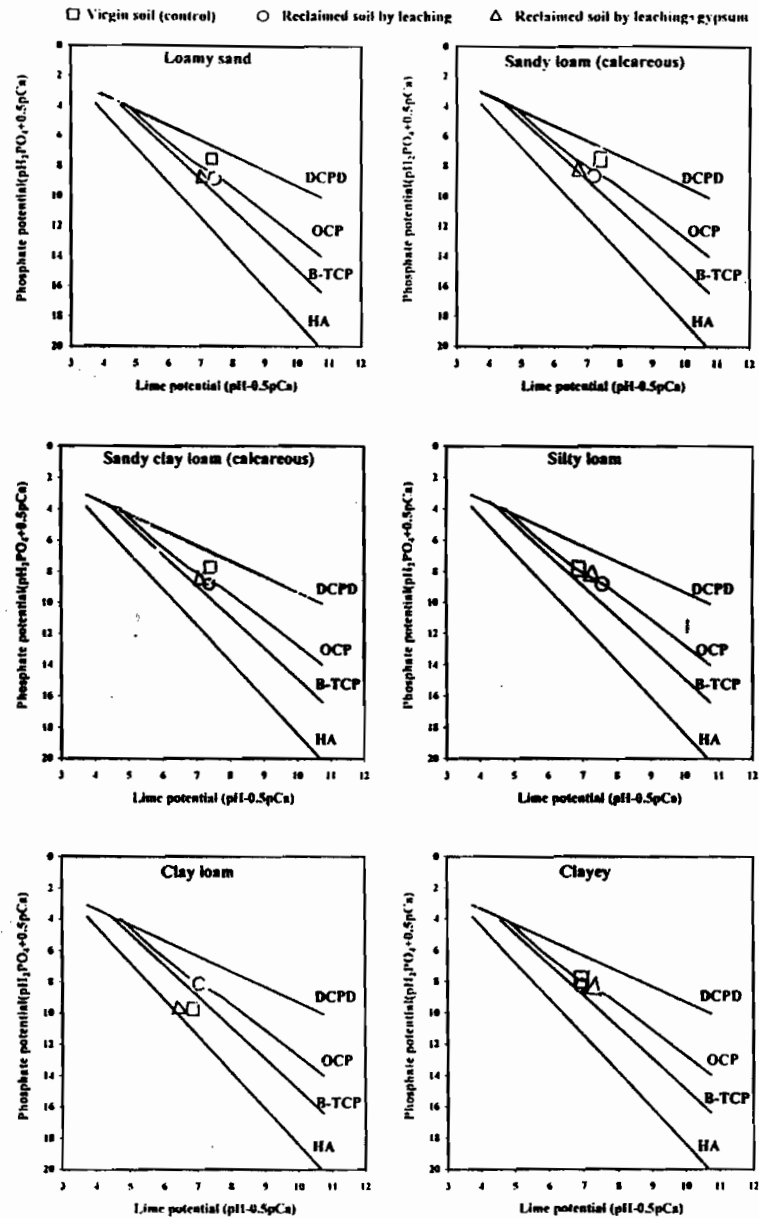


Fig. 3. Solubility isotherms for Ca-P compounds in solid-solution systems of virgin and reclaimed salt-affected soils of El-Salam canal project.

changes in pH and changes in activities of  $\text{H}_2\text{PO}_4$  and  $\text{Ca}^{2+}$  (Table 2) in soils solutions. These were reflected on the ratio of Ca : H :  $\text{PO}_4$  and consequently the precipitation of  $\beta$ -TCP and HA forms. Al-Khateeb et al. (1986) equilibrated some soils with  $\text{KH}_2\text{PO}_4$  to assess solid-phase phosphates after 3000 h; and concluded that the dominant precipitation forms were DCPD, OCP and  $\beta$ -TCP. Tahoun et al. (1975, 1976a, 1976b) utilized X-ray diffraction and microscopy to identify the reaction products of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  in some Egyptian soils, and found that OCP and HA were the main reaction products in calcareous soils and metavariscite in kaolinitic soils. Minkina (1997) reported that soil tillage as well as gypsum application to a sodic soil is substantially reflected in the secondary precipitation processes of soluble soil phosphate.

### CONCLUSION AND PRACTICAL IMPLICATIONS

The results of this work demonstrates that reclamation of salt-affected soils in El-Salam canal project by leaching with or without addition of gypsum affects the ortho-P equilibria to decreasing

available P lowers than adequate for optimum plant growth. There is insignificant effect of gypsum amendments on ortho-P equilibria since these soils have already high amounts of Ca-bearing compounds. The equilibrium of ortho-P between solid phase and solution phase after reclamation can be quantitatively predicted by equations calculated from the experimental data of Q/I relationships. It seems that direct precipitation and surface reaction mechanisms are involved in converting soil solution- $\text{H}_2\text{PO}_4$  into merely soluble solid-phase phosphate is considered as an inherent character of the studied soils. These findings should be considered when planning fertilizer-P programs for newly reclaimed salt-affected soils of this area.

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الاتزان الكيميائي للأرثوفوسفات عقب استصلاح الأراضي المتأثرة بالأملاح في  
مشروع ترعة السلام بمصر  
شوقي محمد متولي

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تشغل الأراضي المتأثرة بالأملاح ما يزيد عن نصف المساحة الإجمالية لمشروع ترعة السلام ، إلا أن مشكلة نقص نيسر الفوسفور تعوق إنتاجيتها بعد الاستصلاح. إن التنبؤ الدقيق باتزان الارثوفوسفات بين طوري التربة الصلب والسائل يعتبر المنخل الصحيح لتحديد الأسلوب الأمثل لعلاج نقص نيسر الفوسفور. تهدف هذه الدراسة إلى تقييم تأثير عمليات استصلاح الأراضي المتأثرة بالأملاح في زمام ترعة السلام على جهد الارثوفوسفات ومعايير  $Q/I$  وسلوك ذوبانها أو ترسيبها. ولهذا الغرض جمعت عينات تربة سطحية من عدة مناطق على امتداد الترعة تمثل جميع أنواع الأراضي المتأثرة بالأملاح في المشروع، واختير منها ستة مناطق حيث روعي اختلاف القوام، نسبة كربونات الكالسيوم ونسبة الصوديوم المتبادل والتركيز الكلي للاملاح الذائبة . بعد الإعداد الأولي للعينات وضعت في أعمدة بلاستيكية وتم استصلاحها بالفضيل المنقطع مع أو بدون إضافة الاحتياجات الجبسية. ولقد استعملت مياه ترعة السلام كما هي للفضيل لجعل ظروف الاستصلاح المعملية أقرب ما يمكن للواقع الحقلية. وقد امتدت فترة الاستصلاح إلى نحو تسعة أشهر.

أظهرت النتائج أن الاستصلاح أدى إلى انخفاض القوة الأيونية لمحاليل الاتزان وزيادة معاملات نشاط أيونات الكالسيوم و الارثوفوسفات للذائبة مما انعكس ذلك على زيادة جهدها الكيميائي في جميع الأراضي المختبرة. لم يكن لإضافة الجبس تأثير معنوي على اتزان الارثوفوسفات ربما بسبب احتواء هذه الأراضي على كميات كبيرة نسبيا من المعادن الحاملة للكالسيوم. كما حدث تعديل في مواضع وميول منحنيات  $Q/I$  تجاه انخفاض نشاط الارثوفوسفات عند الاتزان ورصيد الفوسفور فوري النيسر نتيجة الاستصلاح في جميع الأراضي ؛ بينما زاد جهد السعة لتنظيمية للأراضي الجيرية ذات القوام الخفيف والمتوسط وعلى العكس انخفضت هذه القيمة في حالة الأراضي ذات القوام الطيني الثقيل. وتشير النتائج إلى أن مواضع نقاط ذوبان الارثوفوسفات على الدياگرامات القياسية الخاصة بإذابة معادن فوسفات الكالسيوم في الأراضي إلى سيادة معادن فوسفات ثنائي الكالسيوم في جميع أنواع الأراضي المختبرة قبل استصلاحها. وقد تغير الاتزان في الأراضي المستصلحة بحيث أصبح تركيز الارثوفوسفات يحكمه اتزان إذابة معادن فوسفات ثلاثي الكالسيوم بصفة عامة، إلا أن تكوين الهيدروكسي أباتيت كان نادر الحدوث. وهذا يثبت تعرض الارثوفوسفات الذائبة في محلول التربة لتفاعلات الترسيب المباشر وربما أيضا لتفاعلات التثبيت الكيميائي على حواف حبيبات الطين أثناء فترة استصلاح.

مما تقدم يمكن استخلاص أن عمليات الاستصلاح تؤدي إلى نقص كميته الارثوفوسفات الميسرة إلى دون المستوى الضروري للنمو المثالي للنبات؛ ولم تؤثر طريقة الاستصلاح أو صفات التربة على تعديل هذا الاتجاه. ويمكن التنبؤ كميًا باتزان الارثوفوسفات بين الطور الصلب والمحلول الأرضي بعد الاستصلاح باستخدام معادلات محسوبة من البيانات التجريبية لعلاقات  $Q/I$ . ومن الناحية التطبيقية يجب أخذ تلك النتائج في الاعتبار عند تخطيط برامج التسميد الفوسفاتي للأراضي المتأثرة بالأملاح حديثة الاستصلاح في مناطق مشروع ترعة السلام.