EFFECT OF RESIDENCE TIME ON PHOSPHATE DISTRIBUTION IN PHOSPHATE/COMPOST TREATED SOIL

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ABSTRACT

Sequential extraction technique of phosphorus using different extractant solutions were carried out to separate various pools of soil phosphorus such as (I) labile (plant available) P_i, (2) inorganic P bound to Fe and Al, (3) inorganic P bound to Ca and Mg, (4) organic P, and (5) residual P. The procedure were developed for some amendments applied in this study containing compost (C), phosphate Rock (PR), Citric acid (CA) in different combination treatments, to recognize plant available P in readily available forms (water soluble and bicarbonate form), refractory forms (NaOH-P, Po, HCL Pi, residual-P). Moreover, the rate process of P released from these systems was also determined to evaluate the rate distribution of P in different forms as affected by compost treatments and residence time and subsequently P availability in such systems.

The obtained results indicated that application of compost treated with 15%PR (T3), the best treatment in overall experiment, increased the extractable phosphorus extracted with H_2O (WS) compared with the other treatments. The acidification of PR by citric acid at different rates of 2 and 4 % applied to sandy soil gradually increased the WS fraction compared with control (PR) through the incubation periods. The higher readily available P was particularly observed after 30 and 120 days of soil incubation period. For these available forms, data showed that the extractable fraction of P by sodium bicarbonate (the exchangeable form) varied significantly for the investigated treatments and time of incubation. The extractable fraction of P by NaOH gave the higher available values particularly for T3 compared with other treatments. In HCl-P pool, results indicated that application of citric acid at rate of 2% was also increased this pool by about 12 % over control. Increasing the rate up to 4% gradually increased this fraction by about 25 % particularly after 15 days of incubation. Data reveared that the extractable fractions of phosphorus by EDTA for the investigated treatments were varied according to treatment applied or incubation time of treatments; nevertheless higher values were noticed again in T3. The application of kinetic study applied in this experiment showed that the concentration of P through the entire reaction time was varied in different forms into two stages which representing different mechanisms controlled P distribution and P availability through the entire reaction time.

Keywords: Residence time, phosphate distribution, phosphate/compost, treated soil

INTRODUCTION

Organic amendments applied in newly reclaimed areas including compost, farmyard manure, plant residues, food processing wastes, and sewage sludge. Many investigators have observed the effects of these amendments on physical, chemical, and biological soil properties. Although a wide variation in results exists in the literature on the effectiveness of

composts to sustain the phosphorus (P) nutrition of crops (Cabrera *et al.*, 1991; Murillo *et al.*, 1997), composting is increasingly recognized as a viable management method for solid organic wastes (He *et al.*, 1996). One of the advantages of composting is the possible recycling of its end-product, composts, in agriculture or horticulture. Because of their high concentration in organic matter and nutrients, composts have been used for years as soil amendments.

A lot of research has focused on compost organic matter quality (Adani *et al.*, 1997; Dinel *et al.*,1996), and on the forms and availability of compost N (Kuo, 1995), while little has been done to unravel the forms and availability of P. Composts may contain P taken up by plant in a soil-compost mixture vary from 10 to 264 % of the amount of P taken up from a water soluble mineral fertilizer used as a reference when it riched with rock phosphate (PR) (Bezzola *et al.*, 1994; Frei *et al.*, 1997; Pommel , 1982; Sikora *et al.*, 1991). This variability is always related to the wide range of compost-soil-plant systems studied and to the different methodologies used. Furthermore the results of a lot of these studies are difficult to interpret because of the lack of information on the forms of P in the added compost.

In addition, the effect of composting on phosphate forms and its availability remains unknown. Since excessive inputs of available P in surface horizons of soils have to be avoided, because they lead to degradation of the quality of surface water (Sharpley & Moyer, 2000), a prerequisite for using compost in a sustainable way is to quantify the amount of P which could be taken up by crops. Until now, chemical extraction methods have been used to assess phosphate availability in composts (Kuo, 1995; McCoy *et al.*, 1986; Pommel, 1982). All these studies considered implicitly that the total compost P could be divided in two pools: one containing available forms and other containing unavailable forms. It has been shown however that in soils, phosphate rocks and sewage sludges, such an arbitrary division cannot be made and that a continum of mobility exists between inorganic P (Pi) present in the soil solution and Pi located in the solid phase (Fardeau, 1996; Frossard *et al.*, 1996; Lookman *et al.*, 1996).

Sequential fractionation techniques are being used increasingly to provide more useful assessments of soil nutrients whether macro and micronutrients such as P distribution (Zaghloul, 1998), lead and zinc heavy metals distribution (Zaghloul, *et al.*, 2006), than is possible with single extractions or total metal concentrations alone. In addition to that, ion fractionation technique is a fairly widely used for understanding the mechanisms of its distribution in different soil system and help to assess bioavailability of trace metals in soils. Sequential P extraction techniques based on the method developed by Chang and Jackson (1957) has been widely used to examine biogeochemical cycling and availability of P. De Groot and De Groot and Golteman (1990) revered that commonly used fractionation schemes which use NaOH to extract Fe-bound P and HCl to extract Ca-bound P, estimate the amount of P bound to Fe and over estimate P bound to Ca minerals, when compared with the methods that utilize selective chelating agents (Golterman and Booman,1988). They also compared an extraction using NaOH to extract Fe-bound P followed by HCl

to extract Ca-bound P (Hieltjes and Lijklema, 1980) with their method using 0.02 M Ca-NTA with dithionate to extract Fe bound P followed by 0.05 M Na-EDTA to extract Ca-bound P. They found that estimates of Fe-bound P were greater using their approach, which resulted in lower estimates of Ca-bound P. They also suggest that this was due to the transformation of Fe-bound P to Ca-bound P driven by the pH change associated with the NaOH extraction step.

In this study, the main objectives are: (1) studying P distribution into different pools in sandy soil treated with RP enriched compost. (2) to declare the effect of acidification of PR with CA at different rates on P distribution in the amended soil. (3) understanding P availability through P distribution into different polls. (4) to represent the effect of residence time on rate of P mobility to different pools. Successive or sequential extraction procedures applied in this experiment using some amendments may improve the predictive capacity of the tests considerably by removing a greater proportion of total P without achieving complete PR dissolution.

MATERIALS AND METHODS

1. Soil sample

In this study, topsoil (0–30 cm) of surface sandy soil was collected from El-Kefaah village, EL-Behera Governorate. This soil is characterized by pH: 8.53; EC: 0.65 dS m^{-1} at 25°C; clay 2.3 %; sand 93 %; silt 4.7% $CaCO_3$ 0.90 %; CEC 3.21 meq 100g^{-1}; organic matter content 0.9 %; total N 241 ppm; total P_2O_5 and K_2o were 60ppm and 329 ppm respectively. Soil sample was air dried and ground to pass through a 2-mm sieve.

2. Treatments and experimental design

Fifty grams of oven-dried soil samples were weighed into 200 ml plastic bottles and mixed with the three phosphocompost types (T$_2$-T$_4$) treated with different rates of phosphate rock as presented in table1. The investigated materials were treated with soil at rate equivalent to five tons per feddan. Also, the application of PR treated with CA at rates of 2 and 4 %(T$_5$-T$_6$) was investigated to evaluate the effect of acidification of PR on P distribution. Worth to mention that PR (T$_1$) was taken as control treatments. The soil and different treatments applied were thoroughly mixed, moistened to approximately 60% of water holding capacity (WHC)and incubated aerobically at 25°C for 1, 2, 4, 8, 12, and 16 weeks. Distilled water was periodically added to maintain the mixtures at approximately 60% of field capacity throughout the study. At the end of each incubation period, treated soil samples were taken and prepared for fractionation study. It is worthy to mention that every treatment was triplicate.

Phosphate distribution study

In the studied samples P distributions were conducted according to Sui and Thompson (1999). After each incubation time, the following fractions were obtained: the water soluble (solution-P), exchangeable (NaHCO$_3$-P), NaOH-P, Fe-Mn oxides, organic, and residual. The method could be summarized as follow:

(1) Solution P, by shaking 1 g soil in 10 ml redistilled water for 16 h, centrifuging, filtering, and measuring P in the filtrate.

(2) $NaHCO_3$–P, by shaking the residue from (1) in 10 ml of 0.5 M $NaHCO_3$ for 16 h, centrifuging, filtering, and measuring P in the filtrate.

Table 1: Some chemical and nutritional properties of the studied Phosphocompost.

Phosphocompost sample (PC)	C/N ratio	Total Macronutrients %			Available Macronutrients		
		N	P	K	N (ppm)	P (ppm)	K (ppm)
C 10%RP(T2)	1:18	1.5	2.2	1.2	590	800	8000
C 15%RP(T3)	1:22	1.7	2.4	1.4	260	1000	7000
C 20%RP(T4)	1:24	1.8	2.8	1.3	1260	1500	7450

PC	pH (1:20)	EC dS m^{-1} (1:20)	Cations				Anions			
			Na^+	K^+	Ca^{++}	Mg^{++}	CO_3^-	HCO_3^-	Cl^-	SO_4^-
C 10%RP(T2)	9.4	1.4	3.1	11.6	1.70	1.3	-	3.0	8.2	6.5
C 15%RP(T3)	8.4	0.9	3.5	9.0	2.40	2.1	-	2.7	5.5	8.8
C 20%RP(T4)	8.6	1.8	3.7	11.4	1.80	2.2	-	2.8	8.2	8.1

(3) NaOH–P, by shaking the residue from (2) in 10 ml of 0.1 M NaOH, centrifuging, filtering, and measuring P in the filtrate after acidifying 5ml (with concentrated HCl) and centrifuging.

(4) Acid P, by shaking the residue from (3) in 10 ml of 1:1mixture of 1 M HCl/1 M H_2SO_4, centrifuging, filtering, and measuring P in the filtrate.

(5) EDTA-P, Inorganic precipitate by shaking the residue with 0,05 M Na $EDTA_2$ for 6 h.

(6) Occluded-P The residue from Fe-Mn oxide fraction is extracted with 10 ml of (0.1M oxalic acid+0.175M ammonium oxalate pH 3.25) and centrifuging.

(7) Residual P, by refluxing the soil residue from (5) in 1 ml of a 5:2 mixture of concentrated HNO_3 and $HClO_4$, and determining P from the digest (Hedley *et al.*, 1982).

All P was determined colorimetrically according to Murphy and Riley (1962) after neutralization when necessary with dilute HCl and NaOH and the neutral pH indicated by the light yellow colour of the solution in the presence of P-nitrophenol indicator. Absorbance for P was determined at a wavelength of 712 nm by spectrophotometer.

All measurements of P were done in triplicate, and data analysis such as standard division SD or regression analysis were performed using the statistical software SAS (SAS, 1985).

RESULTS AND DISCUSSION

Phosphorus fractionation is used to separate the various pools of soil P. These forms can be grouped as follows: (1) labile (plant available) Pi, (2) inorganic P bound to Fe and Al, (3) inorganic P bound to Ca and Mg, (4)

organic P, and (5) residual P. The fractionation procedure, developed for some soil amendments applied to soil system, recognizes plant-available forms (water soluble and bicarbonate P) and refractory forms (NaOH-Po, HCl Pi, residual P) of soil P (Hedley *et al.*, 1982). In this classification, plant-available or labile P includes the sum of Pi and Po and bicarbonate extractions, while refractory or unavailable P includes all of other fractions.

In fractionation procedure, inorganic and organic P in the soil solution is removed with a series of successively stronger reagents: water soluble, sodium bicarbonate (0.5 M $NaHCO_3$), sodium hydroxide (0.1 M NaOH), hydrochloric acid (1.0 M HCl) and an acid digestion (Hedley *et al.*, 1982). The labile P is available to microbial and vegetation communities in the short term because it quickly desorbs from the surface of soil particles. Non-labile P fractions are bound to soil particles and are not as readily available forms for plant uptake.

I. Readily available Pools

In most researches applied, sequential extraction were used to evaluate the distribution of phosphorus, it is assumed that water soluble or solution soil phosphorus and exchangeable pool are the most readily available forms for growing plants. However, barrier to investigate P distribution under this experimental condition. Huguenin-Elie *et al.* (2003) asserted that only 10% of the P taken up by crops was drawn from readily available pools; the bulk was drawn from sparingly soluble pools as a result of solubulization induced by roots.

a. Solution Soil Phosphorus

Data in Figure 1 showed that the mean concentration of solution P at 1 day incubation time varied from 1.4 to 2.9 mg kg^{-1} however, at 15 day of incubation the same values were 6.1 to 8.7 mg kg^{-1} soil. The range of solution P pool at the 30 days incubation was 5.1 to 7.5 mg kg^{-1}, and a similar narrow range of solution P was also found in 60, 90 and 120 days incubation time. According to standard division SD analysis, the variation between PR individually (control) and other treatments at different incubation time was not significant in most cases. However, application of phosphate compost at 15% PR, increased solution P as compared with other treatments. Acidification of PR with 2 and 4% CA increased the water soluble P over control at different incubation times, at 120 days from the incubation, the WS-P increased from 3.96 ppm to 4.92 ppm at rates of 2% and 4% CA respectively.

Worth to mention that the mixture of PR and compost in this pool take the trend: C+PR 15% > C + PR 20% > C+PR 10%.

b. NaHCO₃–P

The $NaHCO_3$–P pool is readily available to plants (Bowman and Cole, 1978). As a general observation in this fraction, the extractable P by $NaHCO_3$ varied significantly due to the applied treatments and time of soil incubation. Data presented in figure 2. Showed that all treatments applied significantly increased HCO_3-P. After 30 days of soil incubation, the application of phosphocompost at different rates of PR was significant led to increase the extractable phosphorus.

Fig. 1. Solution-P as affected by treated PR applied to sandy soil at different incubation time.

It was also noticed that, such increment was pronounced in T3 (C+15 %PR) with an average of increase reached to almost 23 ppm against 19 and 18.3 ppm for C+20%PR and C+ 10 %PR, respectively; Worth to mention that PR only gave the lowest value of 17.8 ppm.

Through the entire time of soil incubation, results indicated that application of PR acidified by citric acid at different rates (2 and 4 %), were gradually increased the extractable P. Numerically, after 1 day of incubation the application of PR treated with 2% CA, increased the extractable P by about 16 mg/ kg. Increasing of CA to 4% gradually increased HCO_3-P to 18.1 mg/ kg, the PR-sandy treatment only gave 12.1 ppm.

Concerning the effect of residence time, results indicated that in all treatments, increasing of incubation period up to 15 days led to gradually decrease the HCO_3-P, the averages of this decrease calculated were ranged between 1-44 % for PR, 8-42%, 34-43% and 9-32% in T2-T4 respectively. The acidification of PR treatments was ranged between 5-47% and 6-48% in T5 and T6 respectively as compared with the same treatments incubated for 15 day which represents the inflection treatment

C. NaOH-P fraction

Sequential extraction procedures using NaOH extractant solution for removal of P in organic form have been used extensively for investigating the chemical partition of phosphorus in soils (Rodolphe *et al.*, 2000). Results indicated that organic P fraction constituted the largest P fraction in different treatments applied in used soil and at different incubation times compared with other fractions. Moreover, in this fraction the differences observed among different treatments had a slightly significance with some exceptions. Data showed that this fraction represents about 5-16% of total P in different treatments, the variations observed were directly due to the investigated treatments applied and incubation time of treated soil. Data also indicated that the application rates of PR added to compost were directly influencing phosphorus extracted by NaOH extractant solution.

Data plotted in Figure 3 represents the effect of incubation time on P extracted by NaOH. After 15 days, the maximum P value was noticed in soil treated with compost+15% PR, where the minimum one was in compost+10% PR compared to control.

By increasing the time of soil incubation to 120 days, a gradual decrease in extractable P was detected in all treatments. Numerically, data indicated that after 15 days, NaOH-P were 27 and 33 ppm in T_2 and T_4 against 38 mg kg^{-1} in T_3. The respective values were decreased by about 37, 33 and 34% after 120 days. The same trend was also noticed in the soil treated with PR acidified with CA. Data indicated that by increasing the incubation time from 15 to 120 days, the extractable P was decreased from 35 and 36 ppm to 23 and 24 ppm in T_5 and T_6 respectively.

The distribution in soil and availability of NaOH-P pool to plant uptake have been reported by different authors. Saleque and Kirk, (1995) in their experiment, reported that rice did not absorb P from the NaOH-P pool in some soils of the Philippines. Paniagua *et al.* (1995) studied the distribution of P pools as affected by the addition of organic active amendments during 10 yr in a maize and bean rotation on a volcanic soil.

Fig. 2 Exchangeable-P as affected by treated PR applied to sandy soil at different incubation time.

They found that no differences in the size of the organic P pools as a result of the addition of organic amendments. Sui *et al.* (1999) observed that a slight increase in NaOH-P due to biosolid application, but not significant. However, Sharpley (1985) reported that mineralization of organic P during the growing season, contributed a similar amount of P (20–74 kg P ha^{-1}) as added in fertilizer (13–100 kg P ha-[1]), and was not inhibited by fertilizer P addition. On the other hand, McGill and Cole (1981) reported that the mineralization of organic-p were occurred only when the supply of inorganic P is limited.

Fig. 3. Extractable NaOH-P as affected by different treatments at 15 and 120 days incubation periods.

D. HCI-P fraction

In sequential extraction procedures, the extractable fraction of phosphorus by HCl extraction solution dissolve P associated with calcium minerals (Concepcio´ n and Delgado, 2005). Figure 4 depicted the HCI-P pool as affected by phosphocompost and PR-CA treatments. Results indicated that the mean concentration of HCI-P ranged from 20 to 40 mg kg^{-1} over the entire incubation time and treatments applied. Despite the increased of the HCI-P pool due to Phosphocompost applied to the studied soil at 10 and 20% PR without significance between these two treatments, the application of compost (C+15% PR) again gave the highest extractable amount of phosphorus. After 15 days of soil incubation, data indicated that

application of (compost+15%PR) increased the HCl-P by about 41 ppm; the same pool values were 35.8 and 35.1 ppm by application of T2 and T3. The control treatment (PR) value, however, was 26.2 mg kg^{-1}.

Data also showed that application of CA to acidified PR in the studied soil sample also increased HCl-P pool over control. The application of rock phosphate treated with citric acid at rate of 2%, increased the extractable phosphorus in this fraction by about 12% as compared with control after 15 days of incubation. Increasing the rate of citric acid to 4% gradually increased the extractable fraction of phosphate by about 25% compared with control treatment. The same trend was also observed in other incubation times for all treatments. On the other hand, increasing the incubation time from 15 to 120 days gradually decreased the HCl-P in all treatments even in PR (control treatment). This result will be discussed in more details in the part of the effect of incubation time on rate of P distribution in different fractions studied. However, in this part it should be mentioned here that after 120 days of incubation, the higher decreasing orders was observed in PR followed by T_2(compost+10%PR) treatments and the lowest one was detected in T_3(compost+15%PR).
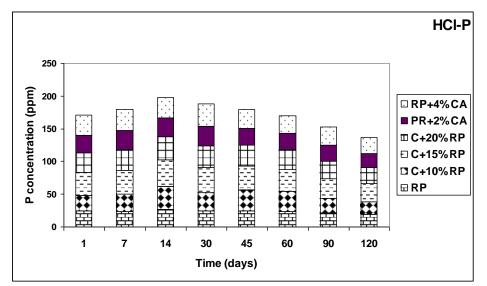

Fig. 4. Extractable HCl-P during the incubation periods as affected by different treatments applied to sandy soil

II. Hardly available Pools
E. EDTA phosphorus

In this technique applied to study P fractionation, using of EDTA extractant solution applied to extract the chelating compounds for determine P related to Fe oxides and Ca-phosphates. It is a modified scheme of Golterman (1996) to study the sediment P fractionation developed. Data of this pool (Figure 5) showed that about 10-18 % of total P was extracted

through the entire reaction time of 120 days. The arrangement of these values was decreased from 10-15% of total P after 1 day of soil incubation. The decreasing order reached to 10-18% after 30 days and followed by increasing order to reach 10-18% of total P in all treatments applied.

The comparison between different treatments indicated that regardless the incubation time, T_3 (C+15%RP) always take the higher value as compared with other Phosphocompost treatments or even CA ones by about 15-20% and 30% respectively. Concerning CA treatment, data indicated that after 90 days of incubation using of PR acidified by CA at rate of 2% increase the extractable fraction of P by EDTA by about 41 mg/kg. Increasing the rate of to 4%, the extractable P reached to 44.5 mg kg^{-1}, worth to mention that the control treatment T1 was 36 ppm. However, increasing the incubation time to 120 days, led to decrease the extractable P to 34 and 38 mg kg^{-1}.
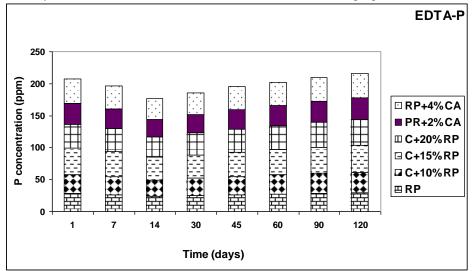

Fig. 5. Extractable EDTA-P during the incubation periods as affected by different treatments.

F. Occluded Phosphorus

Occluded P includes P on sites that are not accessible to outer solution (Torrent *et al.*, 1990). From operational point of view, occluded P is considered the fraction released by the action of reductants after removing most of P adsorbed to Fe oxides and Fe-rich phosphate particles in previous extraction steps.

According to the numerical values of leached phosphate, data depicted in Figure 6 indicated that this pool represent about 12-25 % of total P. After 1 day of incubation time, the occluded-P values decreased by about 12-21 %. After 15 days, gradual increase in this pool values was observed to reach the higher values (13-26% of total P) by the end of incubation period of 120 days in all treatments.

In this pool, the application of Phosphocompost and CA to PR treated soils; results take the same trend in decreasing of P values by increasing the

incubation time from 1 to 15, followed by increasing the extractable fraction of phosphorus P during the incubation periods. Data in Fig. 6 also indicated that in soil treated with compost+15%PR, for example, the extractable-P were decreased from 60 to 51.3 ppm by increasing the incubation time from 1 to 15 days, followed by gradually increasing order reached to 63.6 ppm at 120 days. This treatment, however, showed the higher value as compared with other treatments during the incubation time.

According to the present data of this pool, a reverse trend was observed as compared with readily available forms. In other words occluded-P values were decreased after 1 and 15 days of incubation followed by increasing order in the rest of incubation times. In addition, for different treatments applied in this study it should be mentioned that the increasing order after 1 day of soil incubation takes the order: $T_3 > T_4 = T_6 > T_5 > T_2 > T_1$. After 120 days the same order was $T_3 > T_4 > T_6 > T_5 > T_2 > T_1$. This trend may represent variation in behavior of CA treatments in this pool since T_6 and T_5 gave higher values as compared with T_2 and T_3 especially in the end of the incubation times.
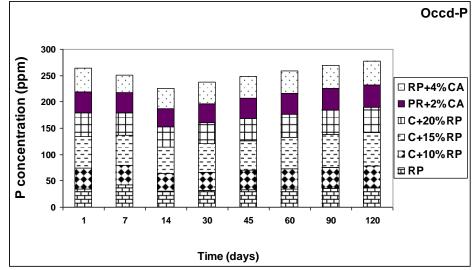

Fig. 6. Occluded phosphate in different treatments at different incubation periods

G. Residual Phosphorus

This fraction contains naturally occurring minerals which may hold macronutrients within their crystalline matrix. Residual P consistently represented the highest fraction of soil P, without any exceptions. Also, this fraction considered to be a non- mobile fraction in the treated samples, which is least harmful fraction among all studied above. The metals concentration found in this fraction were higher than those observed in any of the preceding extractants.

Data in table 2 showed that about 52-60% of the total phosphorus particularly in soil treated with rock phosphate was in the residual form during the incubation periods. These results mean that about 40-48 of the total

phosphorus was automatically distributed in other fractions; the available forms could be uptake by plants. Results also observed that application of Phosphocompost with different rates of rock phosphate gradually decrease the residual fraction of phosphorus. Such phenomenon could be related to the beneficial effects of organic matter in solubilization of most macro and micronutrients in soil system.

During composting processes, small chain of organic acids released in soil systems and could attack PR to be more soluble to considerable amount of phosphorus during the incubation periods. This excess amount of P will redistribute and recharged into different pools. Results revealed that the decreasing values of residual fraction were varied through the first 15 days of incubation, the minimum reduction was observed in this fraction in the soil treated with compost+15% PR by about 20-25%, followed by 27-34% for compost+20%PR and 35-44% for the soil treated with compost+10%PR. It Also, the acidification of rock phosphate by citric acid at different rates (2% and 4%), gradually decrease the residual fraction of phosphorus. In this treatment the majority of phosphorus was mostly accounted 35-53% in the residual forms. As a general conclusion, it has been suggested that the greater proportion of P in the residual phase become unavailable in the soils (Ma and Rao, 1997). These observations are consistent with those obtained by Gupta and Chen, 1975; Tessier *et al.*, 1979; and Ma and Rao 1997, who suggested that the majority of ions in soils and sediments were often of detrital nature. Also the obtained results were in agreement with that observed by Hickey and Kittrick (1984), Harrison (1987), Ma and Rao (1997).

Table 2: Effect of incubation time on the change of Residual-P(ppm) in the treated soil.

Treatments	Time (days)							
	1	7	14	30	45	60	90	120
RP	58.37	54.59	52.08	53.46	55.49	56.01	57.65	59.09
C+10%RP	41.26	40.22	34.75	36.83	38.41	39.67	42.06	43.77
C+15%RP	22.85	21.96	19.68	20.46	21.42	22.19	23.52	24.96
C+20%RP	32.56	30.46	27.48	29.13	30.33	31.07	32.71	33.56
PR+2%CA	51.75	49.22	44.11	45.10	47.03	49.84	51.33	52.89
RP+4%CA	43.31	42.14	36.78	37.58	38.84	41.63	42.74	44.07

The fractionation of phosphorus by various extractant reagents always reflected lower concentration of the extractable fraction as compared with the residual one. This finding may be due to the lower solubility product of phosphate in soil, since the chemical composition of the rock phosphate mainly hydroxyl apatite and fluroapatite.

Effect of residence time on P redistribution into different fractions in treated sandy soil through the kinetic approach:

Bioavailability of macro or micronutrients is often rate limited by contact time (i.e., residence time) in soils and sediments. Specifically, under Egyptian conditions residence time directly influenced the distribution of P in soils and

subsequently its bioavailability (Zaghloul, 1998). This study tries to evaluate the effect of residence time on P redistribution into different fractions determined by sequential extraction procedure.

Data in Figure 7 represents P concentration in the forms of water soluble, exchangeable, NaOH and HCl as affected by time of soil incubation. In these fig, plotting of reaction time in days against P concentration for these four fractions, the curves were generally straight or concave in the beginning of reaction up to 15 days, the inflection point or the 1st period, and then the curves almost become straight in the rest of reaction time (15-120 days). In some cases, however, the curves become convex in the 1st period particularly in case of $NaHCO_3$-P fraction. This result implies that two reaction types take place throughout the entire reaction time of 120 days. In contrast, in hardily available pools depicted in fig 8, in most cases data plotted take the convex shape in the 1st period till the inflection point after 15 days this trend was clearly observed in residual pool, followed by straight line at higher reaction period.

Consequently, modified Freundlich model (MFE) in the form of $q = b\ t^{kd}$ where q and t represent amount of P in soil system at time t, k_d and b constants were applied, the linear form of this model is: $\log q = b + k_d \log t$.

The MFE model and various modified forms of this equation have been applied to experimental data by several researchers (Cooke, 1966; Kuo and Lotse, 1974; Barrow and Shaw, 1975; Evan and Jurinak, 1976; Elkhatib and Hern, 1993; Zaghloul, 1998). This model was applied in this experiment for each period i.e. 1-15 days (the 1st period) and 30-120 days as a (the 2nd period) to each fraction and for different treatments applied.

Data in Table 3, represents the rate constants of MFE for the 1st and 2nd stages, coefficient of determination R^2, standard error SE for different treatments applied at different fractions. The coefficient of determination ranged between 0.91** and 0.99** and the SE ranged between 0.01-0.07 in all cases. According to R^2 and SE, the tested MFE showed high conformity to describe kinetic data for different treatments.

Concerning the rate constant of MFE in the 1st stage of different fractions, data showed that in water soluble fraction, this constant gave high rate of P availability in both T_3 and T_6 while other treatments showed almost equality ranged between 0.33-0.37 mg kg^{-1} min^{-1}.

In $NaHCO_3$-P fraction, again acidification of rock phosphate by 2% and 4% citric acid gradually increased P availability in this fraction, followed by T_1 and then T_2 and T_2. This result perhaps represents the important role of citric acid (CA) in the first period. Although other fraction almost show the same of the importance of CA in readily available forms, the HCL-P fraction showed the least rate of P availability compared with other fractions tested.

In hardily available forms, data showed that EDTA-P pool showed no difference between different treatments; (0.05 mg kg^{-1} $min^{-1)}$. In occluded pool, however, slightly increase was observed ranged between 0.05 and 0.09 mg kg^{-1} min^{-1} in T1 till T_3 and then decrease order in T_4, T_5 and T_6. Worth to mention that residual pool takes the same trend of EDTA-P pool.

Fig. 7. Rate of P redistribution through the entire reaction time in WS, Exchangeable, NaOH and HCl-P in treated sandy soil.

Fig. 8. Rate of P redistribution in EDTA, occluded and Residual pools extracted in from treated soils through the entire reaction time.

In the 2nd stage, data of WS pool indicated that a gradual increase in rate of P availability was observed. Data in table 3 showed that K_d of MFE increased from 39, 41, and 47 mg kg^{-1} min^{-1} to 0.50 mg kg^{-1} min^{-1} in T_1, T_2, T_3 and T_4 , where T_5 and T_6 showed decreasing order reached to 0.36 and 0.39 mg kg^{-1} min^{-1}.   In contrast, in NaHCO$_3$-P, T_5 and T_6 showed the highest values reached to 0.62 and 0.85 mg kg^{-1} min^{-1} against 0.33, 0.32, 0.31 and 0.34 mg kg^{-1} min^{-1} in T_1 till T_4 respectively. Among the above mentioned fractions, data indicated that a decreasing order was observed in both NaOH-P and HCl-P in relation to WS-P and NaHCo$_3$-P. In the 1st pool most treatments gave k_d values ranged between 0.22 and 0.27 mg kg^{-1} min^{-1}, while the other pool gave k_d values ranged between 0.15 - 0.25 mg kg^{-1} min^{-1}, the higher values in both pools were detected for T_3.

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In hardly available pool of EDTA, the k_d of the 2nd stage had a slight gradually increased in T_1, T_2 and T_3 ranged between 0.10 and 0.13 mg kg^{-1} min^{-1}, followed by a steady state condition in T_4 and then decreased to 0.12 and 0.07 mg kg^{-1} min^{-1} in T_5 and T_6. However, the occluded and residual pools gave almost the same values ranged between 0.12 and 0.13 mg kg^{-1} min^{-1} in all treatments with some exception observed in T_1.

Table 3. Rate constants of modified Freundlich equation, coefficient of determination (R^2) and standard error (SE) in readily available forms (A) and hardly available forms (B) of P redistribution in different fractions.

(A) readily available forms

WS-P

Parameters	T1	T2	T3	T4	T5	T6
Stage 1	0.41	0.48	0.34	0.37	0.37	0.48
Stage 2	0.39++	0.41	0.47	0.50	0.36	0.39
R^2	0.99**	0.98**	0.97**	0.97**	0.99**	0.95**
SE	0.04	0.05	0.04	0.05	0.01	0.07

NaHCO3-P

	T1	T2	T3	T4	T5	T6
Stage 1	0.14	0.05	0.05	0.06	0.2	0.2
Stage 2	0.33	0.32	0.31	0.34	0.62	0.85
R^2	0.93**	0.91**	0.94**	0.98**	0.97**	0.94**
SE	0.03	0.01	0.01	0.06	0.03	0.04

NaOH-P

	T1	T2	T3	T4	T5	T6
Stage 1	0.19	0.11	0.08	0.11	0.19	0.14
Stage 2	0.22	0.27	0.25	0.22	0.23	0.23
R^2	0.99**	0.93**	0.97**	0.99**	0.97**	0.92**
SE	0.07	0.02	0.01	0.06	0.02	0.03

HCl-P

	T1	T2	T3	T4	T5	T6
Stage 1	0.12	0.07	0.05	0.04	0.03	0.03
Stage 2	0.2	0.22	0.25	0.23	0.17	0.15
R^2	0.99**	0.92**	0.90**	0.91**	0.99**	0.95**
SE	0.06	0.02	0.02	0.01	0.01	0.06

***: stage 2^-1

(B) Hardly available forms

EDTA-P

	T1	T2	T3	T4	T5	T6
Stage 1	0.05++	0.05	0.05	0.05	0.05	0.05
Stage 2	0.10	0.12	0.13	0.13	0.12	0.07
R^2	0.97**	0.97**	0.92**	0.98**	0.93**	0.97**
SE	0.02	0.03	0.02	0.02	0.02	0.03

Occluded-P

	T1	T2	T3	T4	T5	T6
Stage 1	0.05	0.08	0.09	0.05	0.02	0.10
Stage 2	0.12	0.13	0.13	0.13	0.13	0.13
R^2	0.97**	0.96**	0.98**	0.91**	0.94**	0.91
SE	0.02	0.01	0.02	0.03	0.01	0.02

Residual-P

	T1	T2	T3	T4	T5	T6
Stage 1	0.05	0.05	0.05	0.05	0.02	0.05
Stage 2	0.09	0.12	0.12	0.12	0.12	0.10
R^2	0.97**	0.94**	0.98**	0.97**	0.98**	0.96**
SE	0.02	0.02	0.02	0.02	0.03	0.02

++: stage 1^-1

T1: treated soil with PR **T4: treated soil with compost+20%PR**
T2: treated soil with compost+10%PR **T5: treated soil with PR+2%citric acid**
T3: treated soil with compost+15%PR **T6: treated soil with PR+4%citric acid**

CONCLUSIONS

The results of the present investigation showed that the sequential extraction technique, allows us to clear up phosphorus/ compost relations in soil system of newly reclaimed areas. Data observed indicated that, the association of phosphorus into different pools controlled by residence time and type of treatments applied. Results also indicated that application of T_3 (compost+15% PR) in sand soil increased the readily available pool compared with ether control (PR) or other treatments applied. Moreover, the acidification of PR may increase P-bioavailability compared with PR individually (control treatments).

As a general conclusion increasing of time of soil incubation, led to decrease readily available and increase the hardly ones with different percentages according to treatment applied and the type of fraction studied. The residual pool in all cases take the higher values.

The kinetic study applied in this experiment indicated that the reaction rate of P redistribution through the entire reaction take tow directions regardless the type of pool. This phenomenon representing different mechanisms controlled P redistribution under such conditions. However, the more available pools i.e. water soluble, exchangeable, NaOH, and HCl-P take a reverse trend compared to hardily available pools investigated.

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تـأثير زمـن التفاعـل علـى توزيـع الفوسـفور مـن بعـض الأراضـي المعاملـة بالفوسفور/الكمبوست

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أجريت تجربة معملية لدراسة توزيع الفوسفور في ارض رملية معاملة بأنواع مختلفة من الكمبوست المحضر حديثا و صخر الفوسفات المعامل بحامض الستريك بإضافات وتركيزات مختلفة وحضنت تلك المعاملات لفترات مختلفة(واحد الى 120 يوم) وذلك باستخدام طريقة الاستخلاص المتتابع للحصول على الصور :- 1- المتحركة -2- الغير عضوية المرتبطة بالحديد والالومونيوم -3- الغير عضوية المرتبطة بالكالسيوم والماغنسيوم-4- الصورة العضوية -5- الصورة المتبقية وذلك بغرض التعرف على مدى تيسر الفوسفور تحت ظروف التجربة المطبقة.أيضا فقد تم أجراء دراسة كينيتيكية لمعرفة معدل انطلاق الفوسفور من المعاملات المختلفة بغرض الربط بين معدل توزيع العنصر و أزمنة التحصين المدروسة فى الصور السابق ذكرها.

أوضحت النتائج المتحصل عليها الآتي:-

استخدام الكمبوست المضاف بنسبة تحتوى على 15% صخر فوسفاتي (أحسن معاملة على مدار التجربة) أعطت أعلى محتوى فوسفور في الصورة الميسرة مقارنة بالأراضي المضاف إليها الكمبوست بمعدل أعلى(20% صخر الفوسفات) أو حتى الأقل(10% صخر الفوسفات).

أن الأراضي المعاملة بصخر الفوسفات المضاف الية حامض الستريك 4% أعطى نسبة فوسفور أعلى في كافة الصور السابق ذكرها مقارنه بتلك المعاملة 2% حامض الستريك خلال فترات التحضين المختلفة.كذلك فان استخدام حامض الستريك (في بعض الحالات) أعطى معدلات عالية من الفوسفور المنطلق في الصور الميسرة مقارنه بالكنترول (صخر الفوسفات) خاصة بعد 30 يوم أو 120 يوم من التحضين .

الفوسفور المستخلص بكربونات الصوديوم (المتبادل) اختلف اختلافاً معنوياً باختلاف المعاملات و باختلاف زمن التحضين.

بملاحظة أزمنة التحضين المختلفة ومدى تأثيرها على تيسر الفوسفور أوضحت النتائج انه عند زمن 14 يوم زادت كل الصور الصالحة في محتواها من العنصر مقارنة بالأزمنة الأخرى خاصة في تلك المعاملة السابقة الذكر (كمبوست 15%) .

وأوضحت ان كمية الفوسفور المنطلقة باستخدام هيدروكسيد الصوديوم اختلف بصورة متباينة بين المعاملات المختلفة وأزمنة التحضين المختلفة إلا انه بشكل عام فان الأرض الرملية المعاملة بالكمبوست 15% صخر الفوسفات أعطت مرة أخرى افضل النتائج.

صورة الفوسفات المرتبطة بحامض الهيدروكلوريك في المعاملات المختلفة اختلفت بشكل واضح وتأثرت بتحميض صخر الفوسفات وزمن التفاعل ووصلت إلى زيادة مقدارها 25% بزيادة كمية حامض الستريك المضاف للصخر.

الدراسة الكينيتكية التي طبقت في هذا البحث اوضحت أن تركيز الفوسفات خلال زمن التفاعل المدروس (120 يوم) اختلف في المعاملات المدروسة والصور المختلفة واخذ شكل منحنى مقسم الى قسمين مما يدل على وجود اكثر من ميكانيكية تتحكم في توزيع الفوسفور خلال زمن التفاعل وبالتالي تؤثر تأثير مباشر على تيسر الفوسفور.   9815