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Formation of Separate Phases of Calcium Phosphates in Calcareous and some Alluvial Soils of Egypt

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ACTIVITIES of Ca and P species of H_2O extract of 30 surface soil samples, representing alluvial, calcareous and sandy soils of Egypt, showed the dominance of HPO_4^- species overall calculated ones. The predominance area diagram of various Ca – P forms reveals that P activity in the tested soils was regulated by hydroxyapatite (HAP), the most stable compound according to the thermodynamic rules.

Values of the equilibrium constants (log k) calculated for various Ca–P compounds revealed that both dicalcium phosphate dihydrate (DCPD) and dicalcium phosphate unhydrate (DCP) have been precipitated at the beginning of the reaction between soil and solutions of high P concentration. Except few samples, the precipitated compounds transformed rapidly to octacalcium phosphate (OCP), then to tricalcium phosphate (TCP). On the other hand, the common applied low rate of P didn't initiate formation of a separate phase of Ca–P whether the soils were exposed to alternating wetting and drying cycles, or kept at a constant moisture level.

Concentrations (10^{-4}, 1.67×10^{-4} and $10^{-7.8}$ M) of P, Ca and H, respectively, expected to produce supersaturated solutions with respect to hydroxyapatite (HAP) were kept constant throughout the reaction period. Results showed that the solutions attained equilibrium with TCP, and at the same time proved super saturation with HAP. These postulations have been confirmed and examined using X-ray diffraction.

Keywords: Formation, Calcium phosphate, Calcareous soil, Alluvial soil.

Application of phosphorus fertilizers to calcareous soils results in adsorption of P and precipitation of several calcium phosphate compounds (Ca-P), *i.e.,* dicalcium phosphate unhydrate (DCP), dicalcium phosphate dehydrate (DCPD), octacalcium phosphate (OCP), tricalcium phosphate (TCP), and hydroxyapatite (HAP). The exact mechanisms involved are still obscure. Stumm & Leckie (1970) concluded that the adsorption reaction involves three steps: i) chemisorption of phosphate accompanied by heterogeneous formation of nuclei of amorphous calcium phosphate, ii) a slow transformation of these nuclei into crystalline apatite, and iii) crystal growth of apatite . Griffin & Jurinak (1973) and Stumm & Leckie

(1970) who showed that exposure of calcite crystals to phosphate solution resulted in nucleation of hydroxyapatite on some sites. The formation of crystalline apatite usually occurs in a series of steps where the initial precipitate is amorphous to X- radiation and has a Ca / P molar ratio < 1.67 for pure HAP (Fanes *et al.*, 1965).

Webber & Mattingly (1970), and Clark & Turner (1955) found octacalcium phosphate formed at higher P concentration in mixture of the soil and calcium carbonate. They found also that as the initial P concentration was reduced, the solubility followed the calcite line toward equilibrium with hydroxyapatite. Huffman (1962) and Lindsay *et al.* (1962) reported that phosphate fertilizer, when added to soils containing large amounts of calcium and alkaline ones, usually precipitated as metastable DCPD and/or OCP. It has also been shown that when monocalcium phosphate is added to soils, DCPD is the initial reaction product (Lehr & Brown, 1958; Lindsay & Stephenson, 1959 and Lindsay & Moreno, 1960). It is believed that this DCPD is slowly transformed, through hydrolysis, to OCP and finally to HAP (Lehr & Brown, 1958) . Because HAP attains equilibrium with solution so slowly, changes imposed on a soil which would necessitate either dissolution or precipitation of this phosphate compound will require a considerable period of time for any new equilibrium to be established (Weir & Soper, 1963). Bell & Black (1970) showed that, in calcareous soils and when DCPD was placed in contact with them, OCP is formed in 16 weeks as a new phase on the DCPD surfaces. Octacalcium phosphate was the most basic phase formed after 44 weeks.

In this connection, Lehr & Brown (1958) found that octacalcium phosphate (OCP) or hydroxyapatite (HAP) could be identified in fertilizer bands in alkaline soils to which monocalcium phosphate (MCP) had been added. Brown (1981) found that calcium phosphate precipitation from slightly supersaturated solution was induced by addition of HAP seed crystals. Apatite crystal growth was strongly influenced by seed concentration.   .

In addition, Pierzynski *et al.* (1990) in a study on excessively fertilized soils stated that in soils that produce high pH value (> 6.8) P were more soluble than hydroxyapatite and less soluble than OCP. Samples that produce low pH (< 6.8) indicated an equilibrium with amorphous analog of variscit.

In general, a better understanding of the factors influencing the persistence of the metastable phosphates may allow farmers and the fertilizer industry to manipulate management practices such as method of placement so precipitation of P as less soluble forms can be slowed and greater recovery of the fertilizer P could be realized. The study reported herein was carried out to investigate some factors affecting precipitation of calcium phosphate in some calcareous and alluvial soils of Egypt, *i.e.,* P concentration, soil: solution ratio, P : Ca ratio, pH value, and time of reaction.

Material and Methods

Soil sampling

Thirty surface soil samples (0 – 30 cm) represent the most familiar categories of soils of Egypt especially calcareous and alluvial groups were collected. Samples were air – dried, sieved through a 2 – mm screen, and prepared for analysis to characterize their physical and chemical properties.

Experiments

Four laboratory experiments were conducted as follows:

Identification of the native calcium phosphate compounds in the studied soil samples

Five gram portions of air–dried samples have been equilibrated overnight with 50 ml redistilled water after they were shaken for two hours. Then, pH values of the suspensions were measured. The suspensions were centrifuged to collect the supernatant solutions, in which, EC, P and Ca were determined.

Effect of a high P concentration and a wide soil solution ratio

Favourable conditions (a high P concentration of 10^{-3} M and a wide soil: solution ratio of 1: 10) expected to initiate chemical precipitation of Ca-phosphate compounds have been chosen.

Eight soil samples were selected from the studied soils. These samples differ in their characteristics especially $CaCO_3$, clay, and organic matter contents as well as their textural grade. Five gm portions of each soil sample were shaken for half an hour with 50 ml of a mixture of $CaCl_2$ and KH_2PO_4 solutions containing P and Ca of 10^{-3} and 10^{-2} M, respectively, in a water – bath at $30° ± 0.5°$. Before shaking, two drops of chloroform were added to the mixture to retard microbial activity. Reaction times were ½ hr, 6 hr, 24 hr, 7 days, 1, and 2 months. At the end of each reaction time, the mixtures were centrifuged and filtrated after measuring their pH values. The filtrates were analyzed for EC, P and Ca.

Effect of phosphorus stable supersaturated solution

Of the previous eight soil samples, four soil samples were chosen to represent the common soil categories (alluvial, calcareous, and sandy soils). One gm portions of air–dried soil samples were shaken for 30 min with 200 ml of a mixture of KH_2PO_4 and $CaCl_2$ solutions. The initial concentration of P was $10^{-4}M$ with a ratio of P: Ca amounted to 1:1.67. In this case concentration of Ca was 1.67×10^{-4} M, and the pH value was adjusted to 7.8. Sequential centrifugation, using the same mixture has been done daily for 14 days. The collected supernatants were analyzed for EC, P and Ca.

Effect of wetting drying of soil and applied P

Portions of 100 g of soil samples (two alluvial, two calcareous, and one sandy soils) were placed in polyethylene containers. Potassium dihydrogen phosphate equivalent to 31 kg P_2O_5 /feddan was added with sufficient water to maintain moisture at field capacity (FC) and/or saturation percentage (SP) of each soil. The

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soil samples were incubated at $30^o \pm 0.5^o$ for 4 and 8 weeks, followed by extraction of phosphate. Five gram portions of soil samples were shaken for two hours with $0.01^v M$ $CaCl_2$, then pH value was measured and the samples were centrifuged to collect the supernatants. EC, P and Ca were estimated.
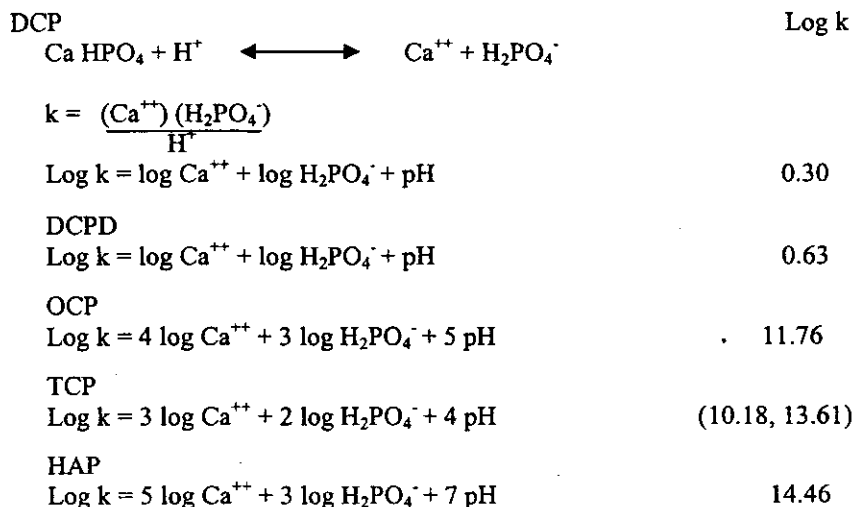
In new soil portions, using previous technique, soil moisture was raised at both of FC or SP and left in the incubator to dry. The cycles of wetting & drying were repeated weekly. After the period of 4 and 8 weeks, pH, EC, P and available P have been measured.

Methods of analysis

The following determinations were performed on saturation soil extracts and filtrates of all experiments.
- EC: conductimetrically using HACH conductivity/TDS-meter
- Ca: chelometrically with EDTA (Jackson, 1973).
- P: spectrophototometry using Troug and Meyer method (Jackson, 1973).

Data were computed to calculate activity of P and Ca species. Equilibrium constants (log K) of calcium phosphate compounds were calculated using the following dissociation equations:

DCP   Log k

$$Ca\,HPO_4 + H^+ \longleftrightarrow Ca^{++} + H_2PO_4^-$$

$$k = \frac{(Ca^{++})\,(H_2PO_4^-)}{H^+}$$

$Log\ k = log\ Ca^{++} + log\ H_2PO_4^- + pH$ 0.30

DCPD
$Log\ k = log\ Ca^{++} + log\ H_2PO_4^- + pH$ 0.63

OCP
$Log\ k = 4\ log\ Ca^{++} + 3\ log\ H_2PO_4^- + 5\ pH$.   11.76

TCP
$Log\ k = 3\ log\ Ca^{++} + 2\ log\ H_2PO_4^- + 4\ pH$ (10.18, 13.61)

HAP
$Log\ k = 5\ log\ Ca^{++} + 3\ log\ H_2PO_4^- + 7\ pH$ 14.46

The obtained equilibrium constants were compared with those of the theoretical values (Lindsay, 1979) to identify the calcium phosphate compounds.

Results and Discussion

The studied soil samples were selected from different locations; along Nile Valley, Delta, and desertic area, which represent different types of agricultural soils of Egypt. These samples proved wide differences in their properties pertaining studied subject. Total contents of carbonate, clay and organic matter, ranged from 0.5-38.0 %, 0.3- 44.7 % and 0.1-3.9 %, respectively. All the studied soil samples have slightly alkaline reaction with pH values ranging between 7.2 to 8.2.

Identification of the native Ca - P compounds in the tested soils

Since P concentrations of 0.01 M CaCl$_2$ solution were below the detection limits of the available analytical methods, distilled water was used as an extractant. Using distilled water, instead of 0.01 M CaCl$_2$, to extract soil P resulted in variations in activity of Ca^{++} ion which ranged between 0.095 x 10^{-3} – 2.11 x 10^{-3} M, hence, it could be involved in determining slightly soluble compound governing phosphate activity. Activities of P species and Ca^{++} ion were calculated using the results of chemical analysis of H$_2$O extract. The data showed that HPO$_4^-$ was the dominant phosphate species among the calculated ones, H$_2$PO$_4^-$, PO$_4^{---}$, H$_3$PO$_4$, CaPO$_4^-$, CaHPO$_4$, and CaH$_2$PO$_4^+$. On average, HPO$_4^-$ representing 64.6 % of the total soluble P, followed by H$_2$PO$_4^-$, 16.7 % and CaHPO$_4$, 16.3%.

Figure 1 shows the solubility diagram constructed by Lindsay in which the predominance areas of various Ca-P compounds were outlined. By plotting phosphate activity (log H$_2$PO$_4$ - pH) versus calcium activity (log Ca + 2 pH) of the studied soil extracts on the solubility diagram, an inverse highly significant relation was obtained (r = - 0.64 M), as expressed in the following regression equation:

Log H$_2$PO$_4^-$ - pH = - 0.2 – 1.16 (log Ca^{++} + 2 pH)   (r = 0.64***)
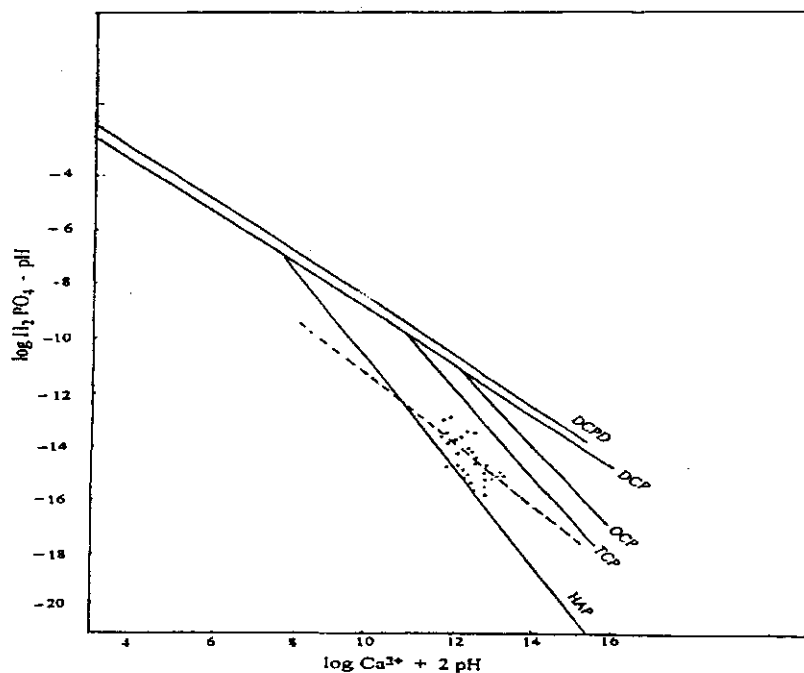

Fig.1. Phosphorus activity of the studied soils compared with the solubility of various calcium phosphates. The diagram was constructed by Lindsay (1979).

The slope (-1.16) of the regression line representing the studied soil samples was not-identical to any of the theoretical ones of the pure Ca-P compounds. However, phosphate activity in the solution of the tested soils, as shown in Fig. 1 was regulated by hydroxyapatite (HAP). According to the thermodynamic rules, this compound is the most stable Ca-P one, which is in agreement with El-Sayed (1982).

Calcium phosphate involved in the interaction between the added soluble P and soils
   Effect of a high P concentration and a wide soil solution ratio
The obtained Ca-concentrations ranged from 7.20 x 10^{-3} - 12.38 x 10^{-3} *M* which is considered nearly constant. An initial rapid drop was observed in P concentration of the equilibrated solution of all tested soils, followed by a short period of a relatively little change in concentration preceded the flat part of the curves in which a gradual decrease in concentration was persisted until the end of the reaction period (Fig.2). The highest drop was observed for soil samples contain either high $CaCO_3$ and/or clay content which have higher ability to adsorb P, as reported by Helal (1993). A highly significant and positive correlation (r = 0.883**) was obtained between the initially sorbed P, after ½ hr, and clay content. Also, a positive and significant (r = 0.714**) second order relation was obtained between sorbed P and total calcium carbonate content.

Sorbed P (ug /g) = 53.9 + 4.56 (clay %)   (r = 0.883**)
Sorbed P (ug /g) = 90.61 + 13.65 ($CaCO_3$ %) – 0.3 ($CaCO_3$ %)   (r = .714**)

A slight increase was observed in pH values of the reactant solutions at the beginning of the reaction (up to 2 hr). The pH values ranged between 6.11, and 6.92. The slight increase in pH values verify that adsorbed phosphate ions replace (OH_2), not OH^-, groups which act as a lewis acid site (Sposito, 1984) and enhance ligand exchange.

Activities of Ca and P in equilibrium solution were calculated and used to predict the equilibrium constants (log k) of calcium phosphate. The obtained (log k) values showed an apparent equilibrium, at the beginning of the reaction, with DCPD and DCP (Fig.3). After 24 hr a deviation from equilibrium was observed. At the subsequent period, the tested solutions attained equilibrium with OCP, the more stable compound, which persisted to a period of approximately one month, then the solutions showed a tendency to be in equilibrium with the TCP. So, it is possible to derive that the solutions of these samples didn't attain a real equilibrium throughout the reaction period of 2 months. On the other hand, solutions of samples showed a persistence in equilibrium with DCP until the end of the experiment. In conclusion, all tested samples didn't attain equilibrium state with HAP, the most stable and predominant compound.
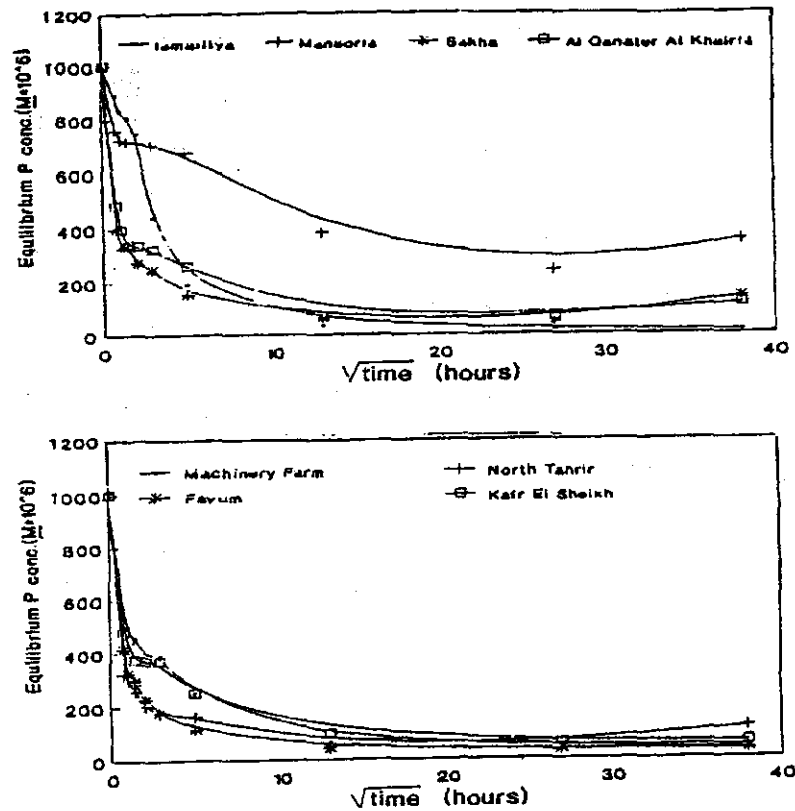
Fig.2. Equilibrium phosphorus concentration of the soil solution of the tested soils as a function of square root of time.

Effect of wetting/drying of soil and applied P

Effect of common rate of P fertilizer application (31 kg P_2O_5 /f) under moisture levels of field capacity (FC) and saturation percentage (SP), with and without alternating wetting or drying, on the formation of a separate phase of calcium phosphate was studied in this experiment. A glance on the chemical analyses of 0.01 M $CaCl_2$ extract shows the following:

1. In general, the extractable- P decreases as the time of reaction increases for both moisture levels (FC and SP) that could be attributed to the formation of less soluble compound.

2. As the moisture level increases (SP), extractable-P, in most cases, slightly increases.

3. The effect of alternating cycles of wetting and drying could be revealed by statistical analysis of the constant moisture level.

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The calculated equilibrium constants (log k) of various Ca-P compounds were more or less the same whether the soils were treated with P or not. Therefore, applied P had no effect on the equilibrium constants. This means that the normal low rate of the applied P didn't initiate the formation of a separate phase of Ca-P compounds. In general, the calculated values were not in coincidence with those of the theoretical ones of the studied compounds. The tested solutions were unsaturated with respect to DCP, DCPD, and OCP. The obtained values of TCP were little lower than those of the theoretical ones. On the other hand, the solutions were supersaturated with respect to HAP, the most expected compound to control P activity in soil according to the thermodynamic rules. It could be postulated that the surface of HAP is associated with strongly adsorbed materials which modify its solubility. Such materials normally present in the soil. Greenland & Hayes (1978) reported that interpretation, which is based on the comparison with colloids of carefully "cleaned" surfaces, could be misleading. That is because soil colloids are invariably formed in a "dirty" environmental, and a part from materials newly formed in the soil, will have the opportunity to adsorb any several materials to which they are exposed.
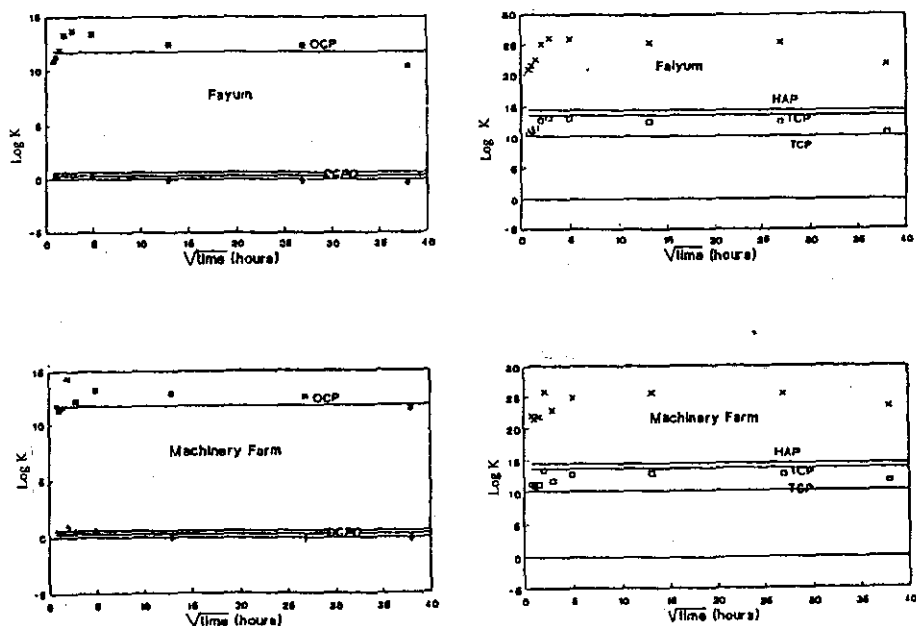

Fig.3. Calculated equilibrium constants (log k) for the different Ca-P compounds (DCP, DCPD, OCP, TCP and HAP) compared with the theoretical values (solid lines) as a function of $\sqrt{\text{tim}}$.

Effect of stable supersaturated P solution

The current experiment was designed to study the effect of the constant concentrations (10^{-4}, 1.67×10^{-4}, and $10^{-7.8}$ M) of P, Ca, and H, respectively, on the precipitation of the slightly Ca-P compounds on surfaces of either, $CaCO_3$ or soil. The results of the equilibrium solutions show that, except for observations of the first three days, Ca concentrations fluctuate in a narrow range varied between 0.64 – 0.88, 0.38 – 0.425, 0.155- 0.28 mM, for pure $CaCO_3$, calcareous and non calcareous soil, respectively. Phosphorus concentrations for all equilibrated solutions, either with $CaCO_3$ or soil, were almost constant (varied between 0.097 – 0.121 m M), except those of the first three days.

Equilibrium constants (log k) of the various Ca-P compounds (Fig. 4) show that the solutions equilibrated with pure $CaCO_3$ were; undersaturated with respect to DCPD and DCP, and supersaturated with respect to the HAP. Comparing with the theoretical values, the obtained (log k) were little higher than that of TCP, while close to that of OCP. Based on these results, OCP is the only precipitated solid phase of Ca-P.
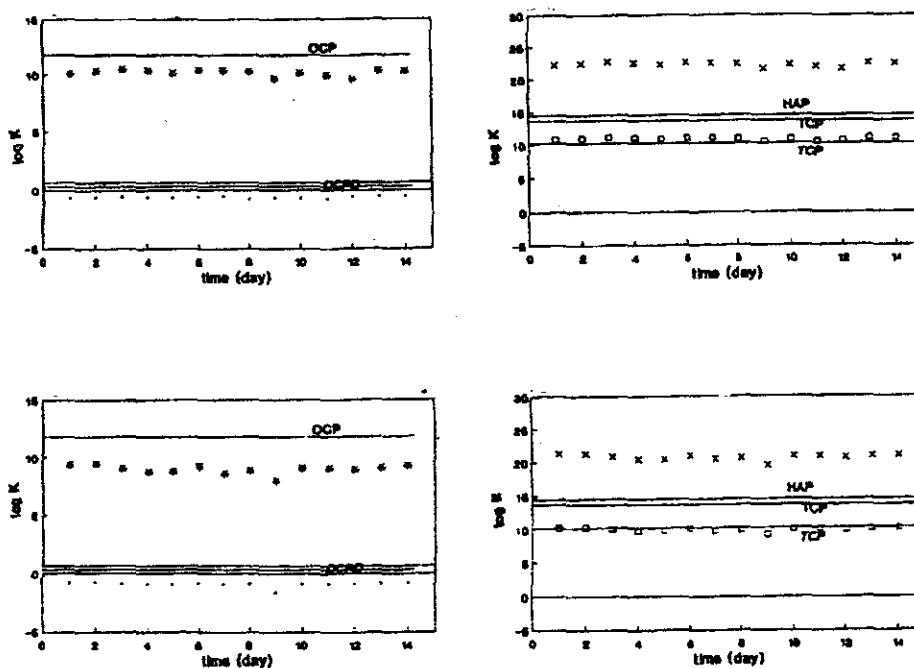

Fig. 4. Equilibrium constants (log k) of the studies Ca-P compounds calculated for the supersaturated solutions equilibrated with the soil samples as a function of time. Solid lines represent the theoretical values (log k) of the various Ca-P.

Values of the equilibrium constants (log k) of the solutions equilibrated with soil samples were; undersaturated with respect to DCP, DCPD and OCP, and supersaturated with respect to the HAP. On the other hand, all soil solutions were in equilibrium with TCP throughout the reaction period. Based on these results, formation of a crystalline phase of HAP may be possible in longer periods since all solutions were supersaturated with respect to the mineral.

To confirm the previous postulation concerning the possible formed P compounds. Both reacted and non-reacted solid $CaCO_3$ with soluble P were examined using X-ray diffraction analysis. Diffraction pattern of unreacted $CaCO_3$ shows only one peak of $CaCO_3$, while, that of reacted $CaCO_3$ shows; a) a peak of a crystalline OCP that is coincident with the results of the equilibrium solution, and b) a beak of a weakly crystalline HAP. These results indicate that such weakly crystalline or amorphous HAP compound might be formed out and can't be detected by chemical analyses. Also, these results imply that formation of a well crystalline form, or transformation of an amorphous form to the well crystalline one, needs more time. Since the solubility of the amorphous form is higher than that of the well crystalline one, supersaturation of the solution with respect to HAP may be due to the formation of an amorphous compound. The inconstant values obtained with the previous experiments could be attributed to the fact that a well crystalline form of HAP has not been formed yet. The obtained two peaks of the OCP and HAP compounds refereed to the transformation of the precipitated Ca-P to the basic more form.

Referances

Bell, L.C. and Black, C.A. (1970) Transformation of dibasic calcium phosphate dihydrate and octacalcium phosphate in slightly acid and alkaline soil. *Soil Sci. Soc. Am. Proc.* **34**, 583.

Brown, J.L. (1981) Calcium phosphate precipitation: b- Effect of Common and foreign ions on hydroxyapatite crystal growth. *Soil Sci. Soc. Am. J.* **45**, 482.

Clark, J.S. and Turner, R.C. (1955) Reaction between solid calcium carbonate and orthophosphate solution. *C. and J. Chem.* **33**, 665.

El-Sayed, M.H. (1982) The phosphate equilibrium in the soil of Egypt. *Research Bull.* **1869**, 1.

Fanes, E.D.; Gillessen, I.H. and Posner, A.S. (1965) Intermediate states in the precipitation of hydroxyapatite. *Nature* **208**, 365.

Greenland, D.J. and Hayes, M.H.B. (1978) *"The Chemistry of Soil Constituents"*, John wily & sons

Griffin, R.A. and Jurinak, J.J. (1973) The interaction of phosphate with calcite. *Soil Sci. Soc. Am. Proc.* **37**, 847.

Helal, M.I.D. (1993) Phosphate adsorption in alluvial soils of Egypt. *Fayoum J.Agric. Res. & Dev.* **7** (1), 205.

Huffman, E.O. (1962) Reactions of phosphate in soils: *Recent research by T.V.A Proceedings of the Fertilizer Socity* **71**, 5.

Jackson, M.I. (1973) *"Soil Chemical Analysis"*, Prentice- Hall, Inc. Limited, New York.

Lehr, J.R. and Brown, W.E. (1958) Calcium phosphate fertilizers. II. A petrographic study of their alterations in soil. *Soil Sci. Soc. Am. Proc.* **22**, 29.

Lindsay, W.L. (1979) *"Chemical Equilibria in Soils"*, John Wily & Sons, Inc., New York.

Lindsay, W.L. and Moreno, E.C. (1960) Phosphate phase equilibria in soil. *Soil Sci. Soc. Am. Proc.* **24**, 177.

Lindsay, W.L. and Stephenson, H.F. (1959) Nature of the reactions of monocalcium phosphate in soils. *IV. Ibid* **23**, 440.

Lindsay, W.L.; Frazier, A.W. and Stephenson, H.F. (1962) Identification of reaction products from phosphate fertilizers in soils. *Soil Sci. Soc. Am. Proc.* **26**, 446.

Pierzynski, G.M.; Logan, T.J. and Traina, S.J. (1990) Phosphorous chemistry and mineralogy in excessively fertilzed soils: solubility equilibria. *Soil Sci. Soc. Am. J.* **54**, 1589.

Piper, C.S. (1950) *" Soil and Plant Analysis"*, International Science Publication Inc., New York.

Stumm, W. and Leckie, J.O. (1970) Phosphate exchange with sediments ; its role in the productivity of surface waters. *Proc. Fifth International Water Pollution Research Conference,* San Francisco, August 1971, Pergamon Press.

Stumm, W. and Morgan, J.J. (1970) *"Aquatic Chemistry"*, J. Wily & sons Inc., New York.

Walkley, A. and Black, I.A. (1934) Organic matter determination for soils. *J. Soil Sci.* **37**, 29.

Webber, M.D. and Mattingly, G.E. (1970) Inorganic soil phosphorus : II. Changes in monocalcium phosphate and lime potentials on mixing and liming soils. *J. Soil Sci.* **21**, 121.

Weir, C.C. and Soper, R.J. (1963) Solubility studies of phosphorus in some calcareous Mantilla soils. *J. Soil. Sci.* **14**, 256.

تكوين طور منفصل من فوسفات الكالسيوم فى بعض أراضى مصر الجيرية و الرسوبية و الرملية

محمد عبدالعزيز طــه ضيف ، محمد ابـراهيم هـــلال ، محمد ابراهيم النـجار وحسن احمد خاطر

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يهدف هذا البحث الى اختبار بعض العوامل المؤثرة فى ترسيب مركبات فوسفات الكالسيوم على أسطح كربونات الكالسيوم فى التربة ، و العوامل المختبرة هى تركيز الفوسفور ، نسبة التربة : الماء ، نسبة الفوسفور : الكالسيوم ، رقم الحموضة ، زمن التفاعل ، وقد استخدمت التحاليل الكيماوية للمحاليل المتزنة عند أزمنة التفاعل المختلفة لتوصيف المركبات الفوسفاتية المترسبة.

استخــدم فى هــذا البحث ثلاثون عينة سطحية (صفر – ٣٠ سم) تمثل الترب الرسوبية ، الجيرية و الرملية فى مصر . فى البداية أجرى تحليل كيماوى للمستخلص المائى لهذه العينات (بنسبة ١ : ١٠) للتعرف على مركب فوسفات الكالسيوم المتحكم فى نشاط الفوسفور فى المحلول الأرضى . اتضح من حساب نشاط الكالسيوم وصور الفوسفور المختلفة فى المحلول الأرضى ، و باستخدام الشكل الذى يمثل منحنيات الذوبان لمركبات فوسفات الكالسيوم المختلفة أن مركب الهيدروكسى أباتيت هو المتحكم فى نشاط الفوسفور فى محاليل هذه الترب.

أظهرت قيم ثوابت الاتزان (log k) المحسوبة لمركبات فوسفات الكالسيوم المختلفة فى الترب المتزنة مع محاليل تحتوى على تركيز عالى من الفوسفور ($١٠^{-٣}$ مولار) ، ترسب كل من الداى كالسيوم فوسفات، داى هيدرات ، الداى كالسيوم فوسفات أنهيدريت فى بداية التفاعل باستثناء عدد قليل من العينات تحولت هذه المركبات بسرعة الى مركب الأوكتا كالسيوم فوسفات ثم التراى كالسيوم فوسفات ، وهذا يدل على أن محاليل هذه العينات لم تصل بعد الى حالة الأتزان الحقيقية.

لم تسفر اضافة الفوسفور بمعدل قليل يماثل الكمية المعتاد اضافتها كسماد للتربة عن تكوين أيا من مركبات فوسفات الكالسيوم الشحيحة الذوبان ، كذلك لم يكن لتوالى عمليات الترطيب و التجفيف و لا لمستوى الرطوبة (سعة حقلية ، تشبع) تأثير واضح فى تغيير حالة الأتزان و التى استدل عليها من قيم log K المتحصل عليها .

عند الحفاظ على محلول الأتزان فوق مشبع ($١٠^{-٤}$ ، ١,٦٧ X $١٠^{-٤}$ ، $١٠^{-٧,٨}$ مولا ر) لكل من الفوسفور ، الكالسيوم ، والهيدروجين ، على التوالى) بالنسبة للهيدروكسى أباتيت طوال فترة التجربة، اتضح أن المحاليل كانت متزنة مع التراى كالسيوم فوسفات ، وفى نفس الوقت فوق مشبعة بالنسبة للهيدروكسى أباتيت و قد تأكدت هذه الاستناجات من اختبارات أشـــعة اكـــس .