

## **Effect of Organic Residues on Superphosphate Fertilizer Reaction and Efficiency in Calcareous Soils. (1) Soil Phosphate Solubility Relationship**

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**Abstract.** This study was conducted to investigate the effect of five types of organic residues on the nature of concentrated superphosphate fertilizer reactions in an alluvial soil (23%  $\text{CaCO}_3$ ) and in a desert soil (8%  $\text{CaCO}_3$ ).

The solubility data showed that, with increasing rates of P, the solubility of P tended towards dicalcium phosphate dihydrate (DCPD) which with time probably changes to hydroxyapatite (HA). Addition of organic residues at rates (1 and 5 mg/g soil) decreased the monocalcium phosphate potentials of native and treated soils with superphosphate, indicating that the organic matter may have successfully retarded the immobilization of applied superphosphate in two highly calcareous soils low in organic matter content.

### **Introduction**

Concentrated Superphosphate (CSP) fertilizer is the most commonly used inorganic phosphate source in calcareous soils. It is highly water soluble and available to plants immediately after soil application. Dicalcium phosphate dihydrate (DCPD) is the main reaction product of applied CSP to calcareous soils [1,2] and it changes with time to octacalcium phosphate, OCP [3] and may finally transform to hydroxyapatite, HAP [1]. Soluble P progressively decreases due to these transformations.

Struthers and Sieling [4] found that organic matter has beneficial action in keeping phosphate available. This beneficial effect has been attributed to: (a) the protective action of organic colloids or gross organic matter in preventing soluble phosphate

phates from coming into contact with active calcium, iron and aluminum; (b) the action of carbon dioxide, produced by organic matter decomposition, in dissolving certain phosphatic materials or in tying up the active cation; (c) formation of organic phosphates, which are less firmly fixed by soils than are inorganic phosphates; and (d) mineralization by bacteria of organic matter containing phosphates with the resultant release of phosphate for plant use.

Martinez *et al.* [5] and Sinha [6] indicated that humic acids, fulvic acids and intermediate products of organic matter decomposition play a significant role in keeping P more soluble for a time through their solubilization action and inhibitory effects on crystallization. Sharif *et al.* [7] and El-Baruni and Olsen [8] reported that premixing concentrated superphosphate with farmyard manure increased the availability of P to plant and extractable P in several field and greenhouse experiments. Moreno *et al.* [3] reported that hydrolysis of DCPD to precipitate OCP was reduced in the presence of organic matter.

The objectives of this investigation were: (i) to study the solubility changes of applied CSP in calcareous soils upon wetting and drying cycles, and (ii) to test the effect of five organic residues which have widely different C/P ratio on retarding CSP immobilization.

## Materials and Methods

### Soils

Two calcareous soils were used in this study: Shatt-Arab clay loam and zubair loamy sand. The soils were collected from surface layer (0-30 cm), air-dried, and crushed to pass a 2 mm sieve before analysis. The initial soil samples were analysed for pH (1:2.5 soil/water ratio); electrical conductivity (in saturated soil-paste extract); organic matter content [9]; calcium carbonate content by acid titration method [10]; cation exchange capacity [9]; partial size analysis [11]; and  $\text{NaHCO}_3$ -extracted P was carried by the blue color method of Murphy and Riley [12]. These characteristics are given in Table 1.

Table 1. Physico-chemical characteristics of soils

Soil	pH 1:2.5	B.C. mmhos/cm	$\text{CaCO}_3$ %	O.M. %	C.B.C. meq/100 gm	$\text{NaHCO}_3$ -P ppm	Texture
Shatt Arab	8.03	5.84	23.0	1.36	15.87	11.78	Clay loam
Zubair	7.82	1.83	8.0	0.13	4.55	9.30	Loamy sand

### Soil – Organic residues mixture

200 gm samples of the air-dry soils (2 mm) were thoroughly mixed, in triplicate, with different rate of air dried sheep; cow; poultry and artificial-organic manures as well as alfalfa hay (oven-dried at 7;°C for 24 hr) equivalent to 0, 1 and 5 mg residue per one gram soil (equivalent to 0, 2.0 and 10 tons per hectare – 15 cm), and placed in round polyethylene containers. Moisture content was raised to field capacity followed by incubation ( $25 \pm 1^\circ\text{C}$ ) for two weeks. Then, the soil residue mixture was air – dried, crushed, and passed through 2 mm sieve. Some chemical properties of organic residues used in this study are given in Table 2.

**Table 2. Some chemical properties of organic residues**

Org. residues	pH 1:5	B.C. mmhos/cm	O.M. %	N %	P %	C/N	C/P	moisture %
Sheep	7.54	23.0	61.85	1.78	0.52	20.20	68.10	27.93
Cow	7.73	5.80	45.10	1.81	0.53	14.48	48.42	59.43
Poultry	7.74	15.19	23.19	2.38	0.98	5.66	13.60	11.71
Alfalfa hay	5.84	16.14	59.27	3.34	0.29	10.32	117.78	8.51
Artificial org. Manure	7.87	2.37	34.79	2.00	0.11	10.11	185.21	47.99

### Solubility experiment

Different amounts of concentrated superphosphate, CSP 47%  $\text{P}_2\text{O}_5$  (0, 520 and 2080 ppm P) were thoroughly mixed with each soil-residue container. Then, moisture content was raised to field capacity followed by incubation ( $25 \pm 1^\circ\text{C}$ ) for 1, 5 and 10 wetting and drying cycles. Each sample was irrigated in the ratio 1:1 (soil:water) once more for 24 hr then the irrigated soil was transferred to Buchner funnel fitted with filter paper and filtered under vacuum. The extract was collected in a 250 ml Erlenmeyer flask, and then used for PH, E.C.,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{SO}_4=$ ,  $\text{HCO}_3=$ ,  $\text{CO}_3=$  and P determinations. Calcium and magnesium were determined by EDTA back titration as described by Graham *et al.* [13] to eliminate P interference. Sulphate was determined by Turbidimetric method [9]. Carbonate and bicarbonate were determined by titration with acid and phosphorus concentrations were measured by the ascorbic acid method [12].

The monocalcium phosphate potential ( $\text{PH}_2\text{PO}_4 + 1/2 \text{PCa}$ ) and lime potential ( $\text{PH} - 1/2 \text{PCa}$ ) were calculated from these data using Debye-Huckel equation to obtain activity coefficients. Ion activities were calculated using an alternative prog-

ram employing the Davies equation [14], and E.C. was used as an estimate of ionic strength [15]. Corrections for the following ion pairs were made:  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{MgHPO}_4$ ,  $\text{CaHPO}_4^+$ ,  $\text{MgH}_2\text{PO}_4^0$ , and  $\text{CaH}_2\text{PO}_4^0$ .

Solubility diagrams were constructed for hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , ( $\text{HA}$ ,  $\text{pK}_{\text{sp}} = 116.40$ ), octacalcium phosphate,  $\text{Ca}_8\text{H}_2(\text{PO}_4)_5 \cdot 5 \text{H}_2\text{O}$  ( $\text{OCP}$ ,  $\text{pK}_{\text{sp}} = 46.98$ ), tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$  ( $\text{TCP}$ ,  $\text{pK}_{\text{sp}} = 28.92$ ), and dicalcium phosphate dihydrate,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{DCPD}$ ,  $\text{pK}_{\text{sp}} = 6.60$ ). All equilibrium constants used for ion pairs, hydrolysis species, and mineral isotherms were selected from Lindsay [16].

## Results and Discussion

### Reaction of CSP with soils

The relation between monocalcium phosphate potential ( $\text{PH}_2\text{PO}_4 + 1/2 \text{PCa}$ ) and lime potential ( $\text{PH} - 1/2 \text{PCa}$ ) as shown in Figs. 1 and 2, indicated that phosphate present in unfertilized soils (check treatments) was more than hydroxyapatite ( $\text{HA}$ ) but less soluble than  $\text{OCP}$  and  $\text{TCP}$ . Many workers such as Awad [17], Fixen *et al.* [18] and Olsen *et al.* [8] observed similar results on unfertilized calcareous soils.

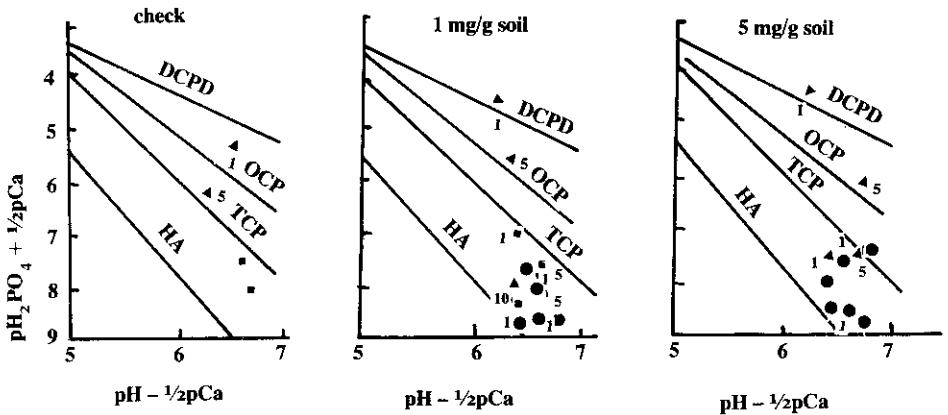


Fig. 1. Phosphate solubility diagram showing the effect of different rates of alfalfa and artificial organic manures on CSP reaction in Shatt Al-Arab clay loamy soil applied at rate of 0 (●), 520 (■) and 2050 ppm (▲) Numbers 1, 5 and 10 indicate wetting and drying cycles

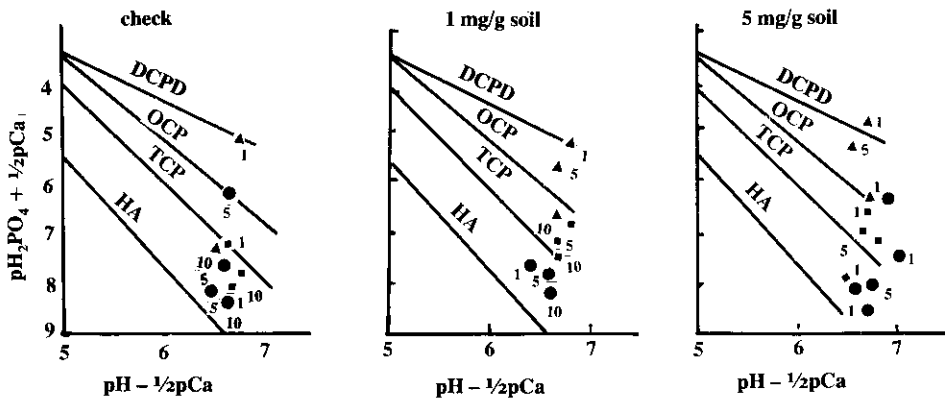


Fig. 2. Phosphate solubility diagram showing the effect of different rates of sheep manure on CSP reaction in Zubair loamy sand soil applied at rate 0 (●), 520 (■) and 2050 (▲). Numbers, 1, 5 and 10 indicate wetting and drying cycles

Results obtained by adding concentrated superphosphate to the alluvial clay loam and to the desert loamy sand soils are also shown in Figs. 1 and 2, respectively. A marked decrease in monocalcium phosphate potential decrease was greater in the desert soil than in the alluvial soil (Figs. 1 and 2). The solubility data, further, showed that after the first wetting and drying cycle, the low P rate (520 ppm P) saturated the desert loamy sand soil with respect to TCP, while the high P rate (2080 ppm P) saturated it with respect to DCPD (Fig. 2). Upon further wetting and drying the low and high P treatments suffered a small increase in the monocalcium phosphate potentials and became supersaturated with respect to OCP at the high P rate during the 5th cycle and then dropped below that line within 10 cycles.

The alluvial clay loam soil, on the other hand (Fig. 1) was undersaturated with respect to TCP at the lower P level, but the higher P rate failed to saturate the soil solution with DCPD; the corresponding points after the first cycle were slightly below the DCPD line then dropped above the HA line within the 10th cycle. These solubility measurements may thus support the suggestion that the solubility of phosphate is related to  $\text{CaCO}_3$  content as well as texture [17,19]. Furthermore, El-Damaty *et al.* [20] found a similar effect due to wetting and drying cycles on the solubility of P applied to two calcareous soils. This could either be due to phosphate compounds losing water on drying and becoming more insoluble [20] or that rewetting processes increased  $\text{CaCO}_3$  solubility and produced a higher Ca ion concentration. It is also known that the adsorption becomes greater on rewetting and there-by drying increases the affinity for P absorption.

### Effect of organic residues on CSP reactions

Additions of sheep manure at low rate equivalent to 1 mg/gm soil decreased native monocalcium phosphate potential in the sandy loam soil during the first cycle (Fig. 2). A similar decrease in monocalcium phosphate potential towards the TCP isotherm was also found in the clay loam soil (Fig. 1) which has over three times as much free  $\text{CaCO}_3$  (Table 1), indicating the efficiency of organic residues in improving availability of native P in highly calcareous soils. Further decreases in monocalcium phosphate potentials resulted after increasing organic matter rate up to 5 mg/gm soil during the first cycle in both studied soils (Figs. 1 and 2). Increase in native soil P solubility due to organic matter addition to soils has been ascribed to the mineralization of organic P, chemical weathering of soil inorganic phosphate compound by organic acids (solubilizing action) produced during their decomposition [21-22] and displacement of phosphate by organic anions [23-24] formed from the breakdown of organic matter acids. Singh and Sirivastava [25] reported that organic manure has increased the availability of native soil P, and attributed this to pH change due to organic acids produced as a result of decomposition of the organic matter. Present results, however, indicated that both organic matter rates failed to maintain P solubility above the TCP isotherm in both studied soils after 1, 5 and 10 wetting and drying cycles. This might be due to the high calcium carbonate content (Table 1) of the soils, resulting in a much greater capacity to buffer changes in PH. A similar result was obtained by Amer *et al.* [26] and El-Baruni and Olsen [27].

Soils treated with different rates of CSP and organic residues yielded less monocalcium phosphate potentials than soils treated either only with or without organic residues. The degree of this decrease in apparent monocalcium phosphate potentials varied considerably between the two soils and its behavior was strongly influenced by the rate and type of organic residues mixed with the soil. Addition of 1 mg/gm organic residues as sheep, poultry and cow manure with the high P rate was adequate to maintain the clay loam soil superaturated with respect to OCP after the 5th cycle (Figs. 3 and 4); similar to the desert soil receiving no organic matter. Clay loam soil samples, mixed with alfalfa hay or artificial organic manure together with the higher P rate failed to do so. With the same soil higher P rate treatment, however in presence of 5 mg organic residues per one gram soil failed to maintain DCP saturation even after five cycles. The solution was still undersaturated with respect to TCP after the 10th cycle (Figs. 3 and 4).

In the sandy loam calcareous soil, however, the situation was quite different. Addition of the high P rate with 1 mg/gm, organic residues per gram soil saturated it with respect to DCPD during the first cycles (Figs. 5 and 6). Subjecting this soil to

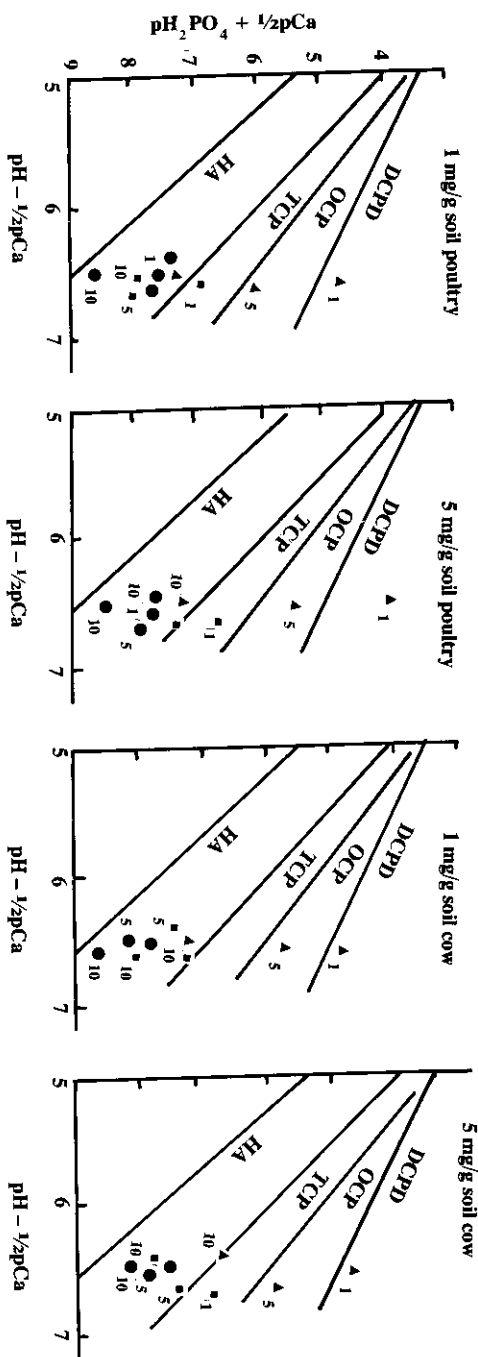


Fig. 3. Phosphate solubility diagram showing the effect of different rates of poultry and cow manures on CSP reaction in Shatt Al-Arab clay loamy soil applied at rate of 0 (●), 520 (■) and 2050 (▲) Numbers 1, 5 and 10 indicate wetting and drying cycles

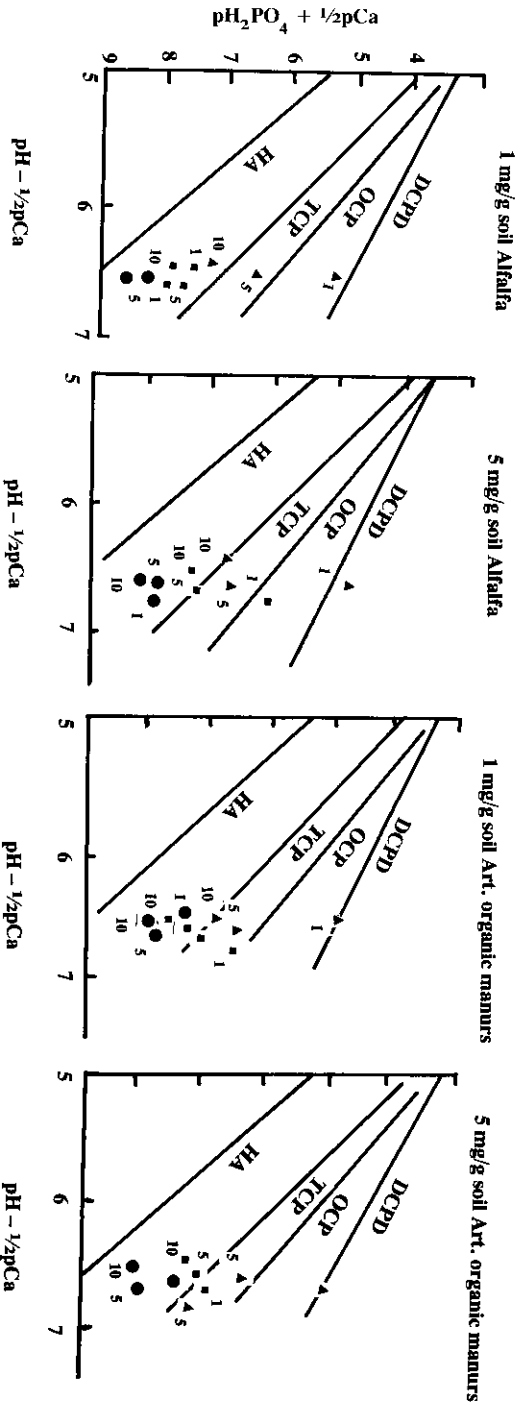


Fig. 4. Phosphate solubility diagram showing the effect of different rates of alfalfa and artificial organic manures on CSP reaction in Shatt Al-Arab clay loamy soil applied at rate of 0 (●), 529 (■) and 2080 ppm P (▲). Numbers 1, 5 and 10 indicate wetting and drying cycles

wetting and drying cycles caused a little increase in monocalcium phosphate potentials and the corresponding points were slightly above the OCP isotherm after the 5th cycle. After the 10th cycle, however, the soil was saturated with respect to TCP. Increasing organic residues rate to 5 mg/gm decreased the monocalcium phosphate potential more compared to treatments received only the high P rate (Figs. 5 and 6). These results are, therefore, concluded that increasing the organic matter of highly calcareous, organic matter-deficient soils can successfully retard the immobilization of applied phosphorus.

In agreement with above findings Mattingly [28] reported that when farmyard manure was applied to a calcareous soil, P concentration in the soil solution was approximately three times greater, for the same amount of labile P, than when the soil received only superphosphate.

Organic matter may also increase P solubility through calcium chelation that causes either a permanent or a temporary delay in the formation of basic calcium phosphates. Moreno *et al.* [3] indicated that hydrolysis of DCPD to precipitate OCP was reduced in the presence of organic matter.

The effect of sheep, cow and poultry manures (with C/P ration less than 100) on added P solubility was less variable than that of alfalfa hay and artificial organic manure (with C/P ratio more than 100).

The latter organic residues produced a similar decline in potentials at low and high rates as in the former, but their corresponding points moved less towards the more soluble calcium phosphate. these results could be due to the use of organic residues of widely different C/P ratio which affected the kinetics of microbial immobilization and remobilization of inorganic P during their decomposition [29]. In accordance with previous results, Parsad and Thomas [30] showed that addition of alfalfa hay, cow or poultry manures increased phosphate availability but the poultry manure was the most effective, presumably because it decomposes more rapidly. White and Ayoub [31] found that decomposing organic residues of C/P ratio of 123 could not change soil extractable-P, while organic residues of C/P ratio of 506 decreased it.

In general, however, effect of organic residues was less marked in the alluvial soil (1.36% organic matter) than in the desert soil (0.13% organic matter). This could be due to the higher calcium carbonate content of the former soil.

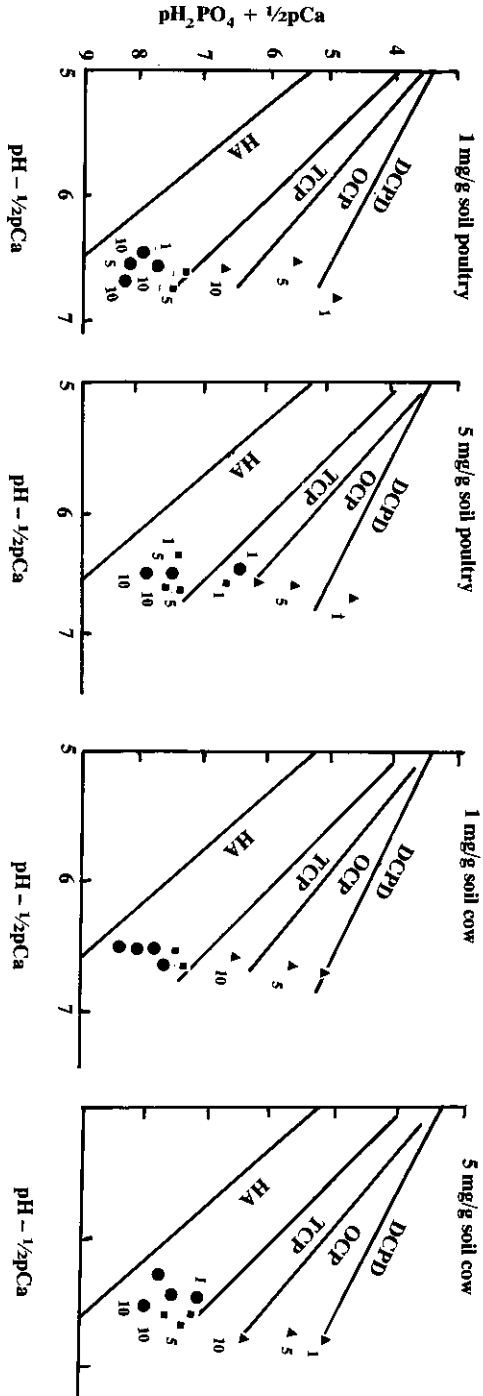


Fig. 5. Phosphate solubility diagram showing the effect of different rates of poultry and cow manures on CSP reaction in Zubair clay loamy soil applied at rate of 0 (●), 520 (■) and 2050 ppm P (▲) Numbers 1, 5 and 10 indicate wetting and drying cycles

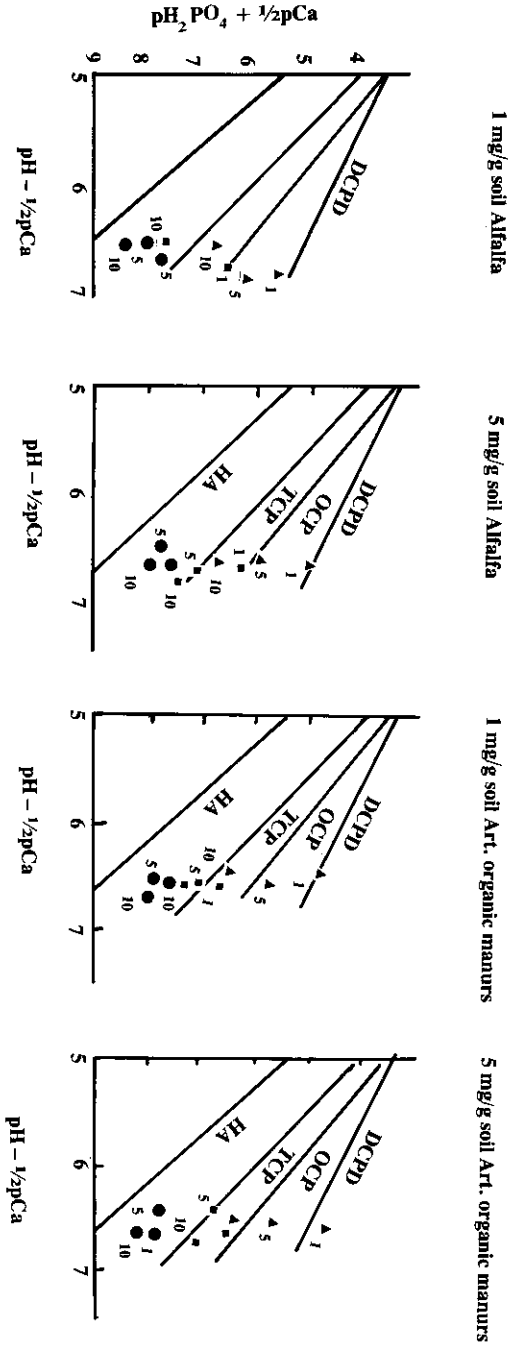


Fig. 6. Phosphate solubility diagram showing the effect of different rates of alfalfa and artificial organic manures on CSP reaction in Zubair loamy sand soil applied at rate of 0 (●), 520 (=) and 2080 ppm P (▲) Numbers 1, 5 and 10 indicate wetting and drying cycles

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## تأثير المخلفات العضوية على تفاعل وكفاءة سهاد السوبر فوسفات المركز في الترب الكلسية

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ملخص البحث . وجهت هذه الدراسة لاختبار تأثير خمس مخلفات عضوية على طبيعة تفاعل سهاد السوبر فوسفات المركز في ترب رسوبية (٢٣٪ كربونات الكالسيوم) وتربة صحراوية (٨٪ كربونات الكالسيوم). فوضحت نتائج الذائبة أنه بزيادة معدل الفوسفور المضاف نتيجة إذابة الفوسفور نحو تكوين فوسفات ثنائي الكالسيوم المائية ولكن مع الوقت يتحول هذا المركب ليكون هيدروكسي أبتايت .

إن إضافة المخلفات العضوية بمستوى (١٥ ملجم / جم تربة) أدى إلى إنخفاض جهد فوسفات أحادي الكالسيوم لكلا المعاملتين المسمدة وغير المسمدة بسهاد السوبر فوسفات مما يؤكد أن إضافة المادة العضوية للترب العالية المحتوى بالكالسيوم والمنخفضة المحتوى بالمادة العضوية تعمل على عرقلة تدهور سهاد السوبر فوسفات المركز.