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A CHEMICAL AND BIOLOGICAL APPROACH TOWARDS THE DEFINITION OF CALCAREOUS SOILS

I. MOVEMENT AND RETENTION OF P^{32} IN SOILS AS AFFECTED BY PERCENTAGE AND PARTICLE SIZE OF CALCIUM CARBONATE FRACTION

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SUMMARY

Several agricultural problems are associated with the presence of certain levels of $CaCO_3$ in soils. The level of $CaCO_3$ at which the phosphate fixation becomes an apparent agricultural problem, is thought to be an appropriate margine at which the soil can be considered calcareous. Thus, a set of soil mixtures, ranging in $CaCO_3$ content from 1 to 96% was prepared and used in a column study to determine the level at which the $CaCO_3$ fraction becomes a dominant factor controlling P^{32} movement and distribution.

Increasing the percentage of oolitic sand, in the soil mixture, from 1 to 10% caused a sharp drop in P^{32} movement with soil solution and any increase in $CaCO_3$ content above 10% did not show any further drop in P^{32} movement. The amount of P^{32} removed with the soil solution was generally low compared to that retained in soil columns. Studying the distribution of P^{32} in soil columns, after five displacements, has indicated that the migration of P^{32} from the top soil increased by increasing $CaCO_3$ from 1 and 2 to 6%. The amount of P^{32} removed was however retained in lower sections. A very sharp decrease in P^{32} migration from the top soil was observed when $CaCO_3$ content was raised from 8 to 10%.

A similar picture was shown when the $CaCO_3$ material used was in clay size fraction. However the sharp increase in phosphate retention in top soil sections took place at $CaCO_3$ content of 8% rather than at 10%. A limit of 8 to 10% $CaCO_3$ was proposed as an appropriate margine for defining calcareous soils.

INTRODUCTION

Inspite of their importance and spread in the desert and semidesert regions, the calcareous soils have not been well defined.

Soils containing any excess of calcium carbonate, from traces up to more than 50 per cent, have been considered calcareous [4 13]. Such definition is technically inadequate especially when plant growth and production are considered.

Several agricultural problems such as micronutrients deficiencies, lime-induced chlorosis and phosphate fixation are associated with the presence of certain levels of calcium carbonate in soils. The level of calcium carbonate at which these agricultural problems become apparent is thought to be the margin at which the soil can be considered calcareous.

From the amount of phosphorus added as a fertilizer only 10 to 30 per cent is recovered by crops and the rest is fixed in soils. Reversible ionic exchange between phosphate and hydroxyl ions [12] and precipitation as aluminium and iron phosphate [5 11] appear in the literature as the basic types of fixation in acid soils. In calcareous soils precipitation occurs predominantly in the form of calcium phosphate [6]. However the formation of aluminium and iron phosphates along with anion exchange do occur.

Phosphate fixation in soils seems to be a resultant of different factors of which the percentage and particle size of calcium carbonate fraction, the clay type, and content and the soil pH are the most important. It is the goal of this work to find out the level of calcium carbonate at which it becomes the dominant factor controlling phosphate fixation and movement.

EXPERIMENTAL PROCEDURE

Soil materials and preparation of soil columns

Three soil materials were mixed in different proportions to yield soil mixtures of uniform texture and ranging in calcium carbonate content from 1 to 50 per cent; the materials used were namely:

1) Nile loam, which is a dominant component of the alluvial Egyption soils; it contains 22 per cent clay and 1.58 per cent calcium carbonate; it was obtained from the nile bank, near Cairo.

2) Fine oolitic sand, separated by dry sieving of oolitic sand material that was obtained from the north-western coast. The fine oolitic sand contains 96 per cent calcium carbonate.

3) Fine sand, separated by dry seiving of sand that was collected from a desert near Cairo. The fine sand material is mainly quartz and contains 0.39 per cent $CaCO_3$.

The proportions of the soil materials in the mixtures studied are shown in

Table 1. The original soil materials, sand, loam and oolitic sand, were also used for comparison. In another set of mixtures, precipitated calcium carbonate (of about 2 μ in diameter) was used instead of oolitic sand in preparing mixtures having $CaCO_3$ content of 2, 4, 6, 8, and 10 per cent.

The soil materials were very well mixed and packed in plexyglass columns, of 35 cm length and 10 cm in diameter, to a depth of 20 cm (Fig. 1). Soil material required to fill a column to that depth weighed 2 kg. Columns were prepared in duplicates.

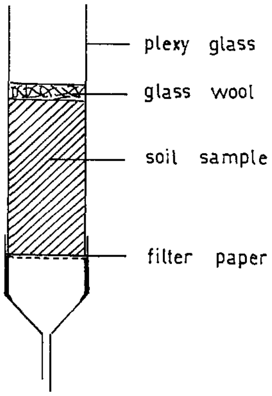

Fig. 1. Soil column.

Dilution, application and detection of P^{32}

An amount of 0.1 mc of a carrier free P^{32} was diluted with 40 ml of KH_2PO_4 (15 g/l) and was added to the top of each column along with 60 ml of water. The total volume of 100 ml solution, added to each column, insured the saturation of the top 5 cm of the soil with water and enriched it with an amount of phosphorus equivalent to 100 kg per acre, calculated on surface bases. Soil columns were then incubated for a week, at room temperature of 25°C. After incubation, the soil columns were leached 5 times on a week interval with 250 ml of water; in the first leachate enough water was added to saturate the column at first then an amount of 250 ml in excess was added.

The displaced soil solutions, of about 200 ml each, were collected and brought to 250-ml volumes. The radioactivity of each displaced solution was counted directly, in 3-ml portions, on a GM tube. A standard solution of known activity was prepared and a 3-ml sample was counted with each set of samples. Small polyethylene cups were used in counting the samples.

After the fifth displacement each soil column was cut into 4 equal segments, of 5 cm thickness each. The soil segments were air dried, mixed, and samples of 0.2 g each were taken for direct counting of radioactivity. Total P^{32} activity per segment was calculated by multiplying the sample count per gram by the total weight of the soil segment.

TABLE 1

Soil mixtures and their percentages of calcium carbonate

Proportions (g) of soil materials in soil mixtures			Percent of $CaCO_3$ in soil
Nile loam	Fine sand	Fine oolitic sand	mixtures
1000	1000	—	1
1000	980	20	2
1000	940	60	4
1000	900	100	6
1000	860	140	8
1000	820	180	10
1000	620	380	20
1000	420	580	30
1000	220	780	40
1000	—	1000	50

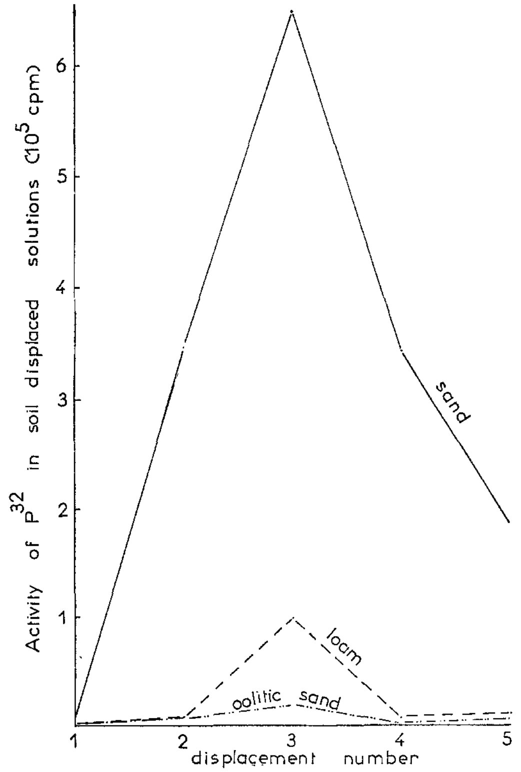

Fig. 2. Movement of P^{32} with the displaced solutions of sand, loam and oolitic sand columns.

RESULTS AND DISCUSSION

Phosphorus movement with soil solution

Detection of P^{32} activity in the displaced soil solution revealed that only traces of P^{32} could be detected in the first displacement of sand columns and no activity at all in those of other columns. The P^{32} activity, as shown in Table 2, increased in the second displacement and reached a maximum in the third displacement of almost all treatments. Movement of P^{32} with each of five displacements of sand, loam and oolitic sand columns is shown in Fig. 2; the P^{32} movement was the highest in sand columns and the lowest in oolitic sand columns.

The effect of increasing amount of $CaCO_3$ on the movement of P^{32} is shown in Fig. 3. Movement as a total of 5 displacements is shown to drop sharply by increasing oolitic sand in the soil mixture from 1 to 10 per cent. No difference could be observed in P^{32} move-

TABLE 2

Movement and distribution of P^{32} in soil columns as affected by percent and size of $CaCO_3$ fraction

Treatment	Activity of P^{32}									
	soil leachates (100 cpm)					soil segments (10000 cpm)				
	2	3	4	5	total	1	2	3	4	total
Sand	3481	6415	3465	1858	15320	136	97	88	243	564
Loam	56	977	50	90	1173	41	102	339	207	689
O. Sand	54	182	5	18	260	652	15	4	3	674
S. Loam	127	956	1309	1079	3470	144	139	338	211	832
2% O.S.	26	915	790	561	2292	100	81	266	198	645
4% O.S.	38	510	369	386	1303	59	59	255	312	685
6% O.S.	38	530	225	210	1004	79	52	186	292	609
8% O.S.	23	536	68	56	683	52	63	232	217	564
10% O.S.	26	167	18	84	295	705	140	85	25	955
20% O.S.	26	187	53	28	293	550	143	23	5	721
30% O.S.	13	182	180	35	310	680	64	16	4	764
40% O.S.	18	209	90	35	352	571	31	8	15	625
50% O.S.	13	139	9	28	189	576	35	26	9	646
2% f. $CaCO_3$	13	70	18	140	231	327	356	118	82	883
4% f. $CaCO_3$	8	84	18	70	180	259	230	291	41	821
6% f. $CaCO_3$	–	106	9	42	157	192	450	162	25	829
8% f. $CaCO_3$	–	196	14	280	490	510	82	48	45	685
10% f. $CaCO_3$	–	56	31	42	129	500	25	35	20	580

O.S. = oolitic sand f. $CaCO_3$ = fine calcium carbonate material

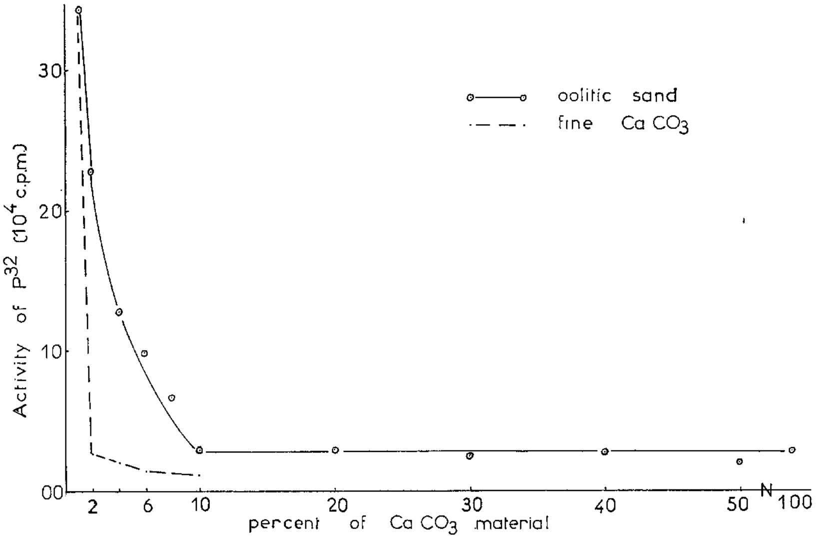

Fig. 3. Effect of $CaCO_3$ material on P^{32} movement (total of 5 displacements).

ment with any increase in $CaCO_3$ material above this percentage. It thus seems that the effect of $CaCO_3$, on phosphate movent, becomes dominant at 10 per cent and any increase in $CaCO_3$ beyond this percentage is apparently less effective.

When the oolitic sand was replaced by fine $CaCO_3$ particles, the movement of P^{32} with the soil solution droped to a minimum by the slightest addition of $CaCO_3$. Increasing $CaCO_3$ in this case from 2 to 4, 6, 8 and 10 per cent was less effective (Fig. 3). Such an effect is expected since phosphate fixation in soils is a function of particle size of $CaCO_3$ fraction (Boischot *et al.*[2]). Murphy[9] has found a similar effect for particle size of kaolinite on phosphorus fixation.

Distribution of P^{32} in the soil columns

P^{32} removed with the soil solution was generally low compared to that retained in the soil columns. Thus the study of P^{32} distribution in the soil columns was necessary. The study of P^{32} distribution in soil columns (Table 2) has shown that the totals of P^{32} retained in loam and oolitic sand columns were almost the same. However, most of the added P^{32} was retained in the top section of the oolitic sand columns while more than 90 per cent of it has migrated to lower sections of loam ones. About 50 and 25 per cent of retained P^{32} in the loam columns were detected in the third and fourth sections respectively. It seems that the Gibbs free energy of P retained in the loam columns is higher than that of oolitic sand columns and hence, more mobile. The activity of P^{32} retained in sand columns was far less than that retained in loam or oolitic sand columns with more than 40 per cent of it being detected in the lowest section. Sand loam mixtures behaved as the average of their components.

Increasing the amount of calcium carbonate material in the soil mixture from 2 to 4 and 6 per cent increased the downward movement of P^{32} to lowest sections. Although the movement of P^{32} to the fourth segment increased by increasing the $CaCO_3$ content from 1 and 2 to 4 and 6 per cent, little variation could be observed in the activities of the top sections of these columns. On the other hand, increasing $CaCO_3$ content from 6 to 8 per cent reduced the movement of P^{32} from the third to the fourth soil section; the amount of P^{32} retained in both of these sections was almost the same.

At 10 per cent $CaCO_3$ less than 30 per cent of the added P^{32} could migrate from the top section, with less than 3 per cent of P^{32} being detected in the lowest section; while more than 90 per cent of the added P^{32} was detected in the lower sections at 2, 4, 6 and 8 per cent $CaCO_3$. Compared to few hundred thousands counts per minute detected in the top sections of columns containing 8 per cent $CaCO_3$ or less, the 10 per cent $CaCO_3$ column retained more than 7 milion cpm in the top section.

The relative amounts of P^{32} moving from the top-soil section decreased by increasing $CaCO_3$ from 10 to 20, 30, 40, and 50 per cent. However little or no variation could be observed in the amount of P^{32} reaching the lowest section. (Fig.4).

Increasing $CaCO_3$ in the soil mixture from 2 to 6 per cent is thought to increase the amount of Ca ions released into the soil solution which in turn replaces Na and other exchangable cations on clay surfaces. Thus the increase of $CaCO_3$ within that range may lead to the increase of Na to Ca ratio in soil solution, bringing out a situation in which phosphates are more soluble and hence more mobile.

The observed increase in the pH of soil paste from 8.4 to 8.7 and 8.8 by increasing $CaCO_3$ content from 1 to 2 and 6 per cent, as

TABLE 3

pH values of some selected soil columns as determined in the top soil sections, at the end of the experiment

Selected soil column	pH of the top section
Loam	8.20
Sand loam	8.40
Oolitic sand	8.50
2% oolitic sand	8.70
4% oolitic sand	8.75
6% oolitic sand	8.80
8% oolitic sand	9.00
10% oolitic sand	8.75
30% oolitic sand	8.55
50% oolitic sand	8.35

shown in Table 3, supports the idea of Ca and Na exchange; Na released into solution increases the pH. Calcium phosphate solutions has been shown by Bjerrum [1] to be more acidic than the corresponding sodium phosphate solutions; which supports the idea of the increase in soil pH due to the exchange of Ca for Na.

Increasing the content of $CaCO_3$ forward from 8 to 10 per cent is thought to increase the local concentration of Ca ions in the top soil to the limit at which the phosphates change from the dicalcium form to the insoluble form of tricalcium phosphate. McGeorgy [7] indicated that soluble phosphates are fixed rapidly, in alkaline calcareous soils, as tribasic calcium phosphates which change slowly to calcium carbonate-phosphate. Olsen [10] believed that a precipitate of unknown composition, of probably a large surface area is formed when P concentration as K_2HPO_4 exceeds $2 \times 10^{-4} M$. Boischot [2] has found the initial reaction of dilute phosphate solutions with $CaCO_3$ to be a sort of adsorption onto the surface of $CaCO_3$ particles. He has however added that precipitation occures when $Ca(H_2PO_4)_2$ concentration exceeds $5 \times 10^{-5} M$, at pH 8.3 to 8.5.

Effect of fine $CaCO_3$ material on P^{32} distribution

It was shown in Fig. 3 that only traces of P^{32} were detected in the displaced soil solution of columns receiving any amount of fine $CaCO_3$ material. However a considerable amount was removed from the top soil of columns containing 2, 4 and 6 per cent $CaCO_3$ (Fig4.). The

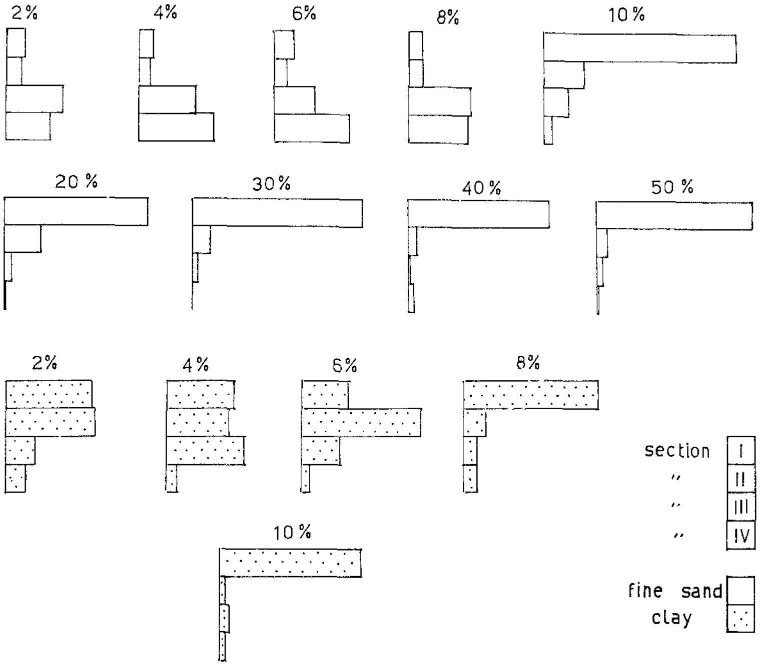

Fig. 4. P^{32} distribution in soil sections as affected by percent and size of $CaCO_3$. (Four mm ↔ means 10^6 cpm)

amount of P^{32} removed from the top section increased while that recovered in the lowest section decreased, with the increase of $CaCO_3$ from 2 to 6 per cent. In other words most of the transported P^{32} was retained in the mid soil sections. On the other hand, raising the fine $CaCO_3$ content to 8 and 10 per cent caused the retention of more than 80 per cent of P^{32} in the top section, compared to only 30 per cent or less being retained in top soil at $CaCO_3$ content of 6 per cent or less. It is thought that the solubility of $CaCO_3$ along with cation exchange control the local concentration and distribution of Ca ions and consequently control the P^{32} movement and distribution within the soil columns.

Burd[3] had defined calcareous soils as those containing large amounts of exchangable calcium and limited amounts of kaolinite and hydrated oxides and in which calcium plays a dominant role in determining phosphate solubility. Morsy[8] found no correlation between the amount of P^{32} retained in Egyptian soils and $CaCO_3$ content within the range of 2 to 6 per cent. On the other hand, there was a significant correlation between soluble phosphate and $CaCO_3$ content within the same range. These results agree to a large extent with the work in hand, since there was no observed variation in the P^{32} retained on top of soil columns containing 2 to 8 per cent oolitic sand.

According to these results and in consideration of Burd's views in defining calcareous soil, it is thought that $CaCO_3$ becomes a dominant factor in controlling phosphate movement and distribution at a percentage of 8 to 10 per cent depending on the size distribution of $CaCO_3$ particles. It is suggested to consider soils containing 8 to 10 per cent or more of $CaCO_3$ as calcareous. However that proposed limitation is worthy for more consideration.

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LITERATURE CITED

1 Bjerrum, N., Investigation on the solubility of calcium phosphate. 19*th* Scandinavian Scientist Meeting in Helsingfors, Aug. 1936. Selected papers edited by friends and co-workers, Copenhagen (1949).

2 Boischot, P., Coppenet, M., and Herbert, J., The fixation of phosphoric acid on calcium carbonate in soils. Plant and Soil **2**, 311–322 (1950).

3 Burd, J. S., Chemistry of the phosphate ion in soil system. Soil Sci. **65**, 227–248 (1948).

4 Fuller, W. H., Reaction of nitrogenous fertilizers in calcareous soils. Agr. Food Chem. **11**, 188–193 (1963).

5 Low, P. F. and Black, C. A., Phosphate induced decomposition of kaolinite. SSSA Proc. **12**, 180 (1947).

6 McGeorge, W. T. and Brazeale, J. F., The relation of phosphate availablity, soil permeability and carbon dioxide to the fertility of calcareous soils. Ariz. Agr. Exp. Stat. Tech. Bull. **36** (1932).

7 McGeorge, W. T., Studies on plant food availability in alkaline calcareous soils: Seedling tests and soil analysis. Arizona Agr. Exp. Sta. Tech. Bull. **94** (1942).

8 Morsy, M. Y., Phosphorus status in Egyptian soils. M. Sc. Thesis, Soils Dept., Cairo Univ. (1967).

9 Murphy, H. F., The role of kaolinite in phosphate fixation. Hilgardia. **12**, 343 (1939).

10 Olsen, S. R., Inorganic phosphorus in alkaline and calcareous soils. Agronomy: A Series of Monographs, no. IV. Soil and Fertilizer Phosphorus, 89–122 (1953).

11 Perkins, A. T. and King, H. H., Phosphate fixation by soil minerals. III: Particle size. Soil Sci. Soc. Am. Proc. **9**, 61 (1944).

12 Stout, R., Alteration in the crystal structure of clay as a result of phosphate fixation. Soil Sci. Soc. Am. Proc. **4**, 177 (1939).

13 Soil Sci. Soc. Am., Report of definitions approved by the commete on terminology. Soil Sci. Soc. Am. Proc. **20**, 431 (1956).