

تثبيت الفوسفور في الأتربة الكلسية والجبسية والآثار المقارنة للفوسفور والزنك على محصول الذرة الصفراء والتركيب الغذائي

Rate of Phosphate Immobilization in Gypsiferous
and Calcareous soils
and the Comparative Effects of Phosphate and Zinc
on Yields and Nutrient concentration of Corn

by
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أتربة البحر المتوسط الحمراء الخالية من الكلس والجبس ذات الـ PH المعتدل مزجت بكميات متزايدة من الجبس أو الكلس المطحون لتحضير
أتربة محتوَاها من الجبس أو الكلس يحقق النسب التالية :

0 , 5 , 10 , 15 , 20 , 40%

والأتربة المحضرة هذه ذات افطار الحبيبات أقل من (2) ملليمتر أجرى عليها نوعان من التجارب :
التجربة الأولى حول تثبيت الفوسفات . تبين من خلالها أن معدل تثبيت الفوسفور من قبل التربة الجبسية كان أكثر منه من قبل التربة الكلسية .
التجربة الثانية حول تأثير التسميد الفوسفاتي والزنك على نمو الذرة في الأتربة الجبسية والكلسية وتبين من خلالها أن الاستجابة للفوسفور كانت
عالية في الأتربة الجبسية والكلسية معاً . أما إضافة الزنك فقد أظهرت على أنه ضروري جداً لنمو الذرة في الأتربة الجبسية وزيادة مقاومتها للجبس في
التربة .

ABSTRACT

Red Mediterranean Soil (Rhodoxeralf), free of lime and gypsum with PH near 7, was mixed with an increasing amount of
grinded crystalline gypsum or calcium carbonate rocks, to prepare soils with 0, 5, 10, 20 and 40 % of gypsum or calcium
carbonate by weight respectively. Soils prepared were sieved to pass 2 mm sieve openings.

Two kinds of experiments were carried out:

First:

A phosphate immobilization experiment : Where to one kg of various gypsiferous or calcareous soils prepared, was added a constant amount of KH_2PO_4 at a rate of 300 parts per million of P. Distilled water was added regularly, and field capacity was restored weekly. Available P by the NaHCO_3 method (Olsen) was determined, in each soil type regularly, and the experiment lasted for about 210 days. The rate of immobilization of P in Calcareous and gypsiferous was found to be of second order kinetics, and two rate functions. In the first part, the rate of immobilization was fast and the half life of added P was 27 and 12 days for calcareous and gypsiferous soils respectively. In the second part of the curve, the rate of immobilization was found slow for both calcareous and gypsiferous soils. But in general, the rate of P immobilization by the gypsiferous soils was superior to the rate in the calcareous soils.

Second:

A phosphate and zinc experiment on corn.

A Factorial experiment with 4 phosphate and zinc treatments: P_0Zn_0 , P_1Zn_0 , P_2Zn_0 , P_2Zn_1 , where P was added at a rate of $\text{P}_1 = 206$ and $\text{P}_2 = 412$ parts per million as treble superphosphate (48 % P_2O_5) and Zn_1 as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at a rate of 100 parts per million Zn with 3 gypsum or calcium carbonate treatments, where soils with 0, 20 and 40 % of gypsum or CaCO_3 were used. The experiment was run in triplicates, in pots holding 6 kgs or air-dried soils. Three seedlings of hybrid corn were planted in each pot until tasseling stage and early silking. Recently matured leaves were sampled at tasseling stage for mineral analysis and then corn tops were harvested and the total fresh weight recorded. The main results of the experiment were:

1. Phosphate application to calcareous or gypsiferous soils had shown tremendous effect on yield of tops ($P = .01$) or on the P content of plants ($P = .01$).

2. Phosphate application reduced zinc content of corn leaves but to a greater extent in gypsiferous as compared to calcareous soils.

3. The application of zinc to gypsiferous soils increased yields significantly ($P = .01$) helping corn to tolerate better, the high level of gypsum; while zinc had no significant effect on yields of corn grown in calcareous soils.

4. A strong interaction was shown between phosphate and gypsum or calcium carbonate on their effect on the concentration of the three major nutrient cations : potassium, calcium and magnesium.

As a result, the present work suggests that the addition of phosphates is very beneficial to both calcareous and gypsiferous soils; in addition zinc fertilization was found very important for corn grown in gypsiferous soils, thus improving the tolerance to gypsum.

INTRODUCTION

Various lines of evidence have led to the conclusion that the most important metal ions responsible for the binding and immobilization of phosphates in soil are aluminium, iron and calcium. The latter metal ion seems to be the most important under the conditions of calcareous or gypsiferous soils. Aluminium and iron com-

pounds are almost insoluble under the calcareous conditions and will not contribute to any significance on the process reactions leading to immobilization of P (1) .

On first sight, the activity of phosphate in soil solution, in contact with solids of the type CaCO_3 or gypsum should depend on the activity of Ca and on the PH of the soil system. If one assumes that PH is an independent variable, the Ca activi-

ty will depend mostly on the solubility of the solid phase containing C_a ions. Consequently, looking to the table of equilibrium constants of gypsum ($CaSO_4 \cdot 2H_2O$) and Calcite $CaCO_3$ one would notice that the solubility products under the standard conditions are of the order :

for $CaCO_3 = -8.35$

for $CaSO_4 \cdot 2H_2O = -4.61$

Accordingly, $CaSO_4$ is by far more soluble than Calcium carbonate and consequently C_a activity in the soil solution of gypsiferous soils should be greater than its activity in calcareous soil. That would lead to an expectation of higher fixing power of phosphate for gypsiferous soils than calcareous soils, and the response to phosphate fertilization should be greater under the conditions of gypsiferous soils. Some previous work of the author had demonstrated that high levels of gypsum in soils will decrease the P and Z_n content of several crops including corn.

MATERIALS AND METHODS

Two types of experiments were carried out on soils with increasing levels of $CaCO_3$ or gypsum. The first, was to study the rate of immobilization of P, and the second, to study the response of corn plants to application of P and Z_n fertilizers to soils.

Soil Preparation :

To a calcium carbonate and gypsum free clay soil (Rhodoxeralf) - sieved with 2 mm opening sieve diameter, was added grinded and sieved calcium carbonate or gypsum crystals to pass a 2 mm sieve opening diameter, in amounts necessary to prepare soils with 0, 5, 10, 20 and 40 percent of $CaCO_3$ or gypsum by weight.

A. Phosphate immobilization Experiment :

Plastic pots were used to fill 1 kg of each soil types prepared and KH_2PO_4 was added at constant rate of 300 parts per million of p to all types of soils prepared. Field capacity was determined

for each soil type; and distilled water was added at week interval to restore water in all soil pots to field capacity. Soils pots were run in triplicates.

Soil samples were taken regularly for available P determination by the Olsen Method (2). The experiment lasted for about 210 days.

B. P and Z_n fertilizer experiment :

Solids prepared with 0, 20, and 40 percent of gypsum or calcium carbonate were used to fill plastic pots with 6 kgs of airdried soils each. Four fertilizer treatments were used :

P_0Z_{no} no phosphorus zinc was added to the soils.

P_1Z_{no} treble superphosphate (48 % P_2O_5) was added at a rate of 206 parts per million of P to the soils.

P_2Z_{no} Treble superphosphate was added at rate of 412 ppm

P_2Z_{n1} Treble superphosphate was added at rate of 412 ppm P with 100 ppm of Z_n added as $Z_nSO_4 \cdot 7H_2O$ to soils.

All treatments were run in triplicates. A basic dressing of 1g NH_4NO_3 (33 % N) was added per kilo of soil. Two additional top dressings of 1g NH_4NO_3 per kg of soil were added at one month interval, with irrigation. Three seedlings of hybrid-corn were planted in each pot until tasseling and early silking stage, where samples of recently matured leaves were taken for mineral analysis and total tops were harvested and the fresh weight recorded.

Leaf samples were oven dried to 70°C, grinded and analysed for P, Z_n , K, C_a and Mg. Phosphates in leaves were determined by the phospho-vanadate method; potassium by flame photometry, C_a and Mg by the versenate method and Z_n by atomic absorption method (2).

An analysis of variance was run on yields and results of mineral composition of corn leaves.

RESULTS AND DISCUSSION

Phosphate Immobilization

By plotting on a semi log paper the change in available P as determined by the NaHCO_3 method in both calcareous and gypsiferous soils, it could be noticed as shown in Fig (1) that the average

drop in available P was greater in gypsiferous soils as compared to calcareous. The drop in available P was greatest in the first week after the addition of P.

Using the method used for mixture of radioactive isotopes with two different half life, the curve for either calcareous or gypsiferous soils could be divided into two regions and two rates of

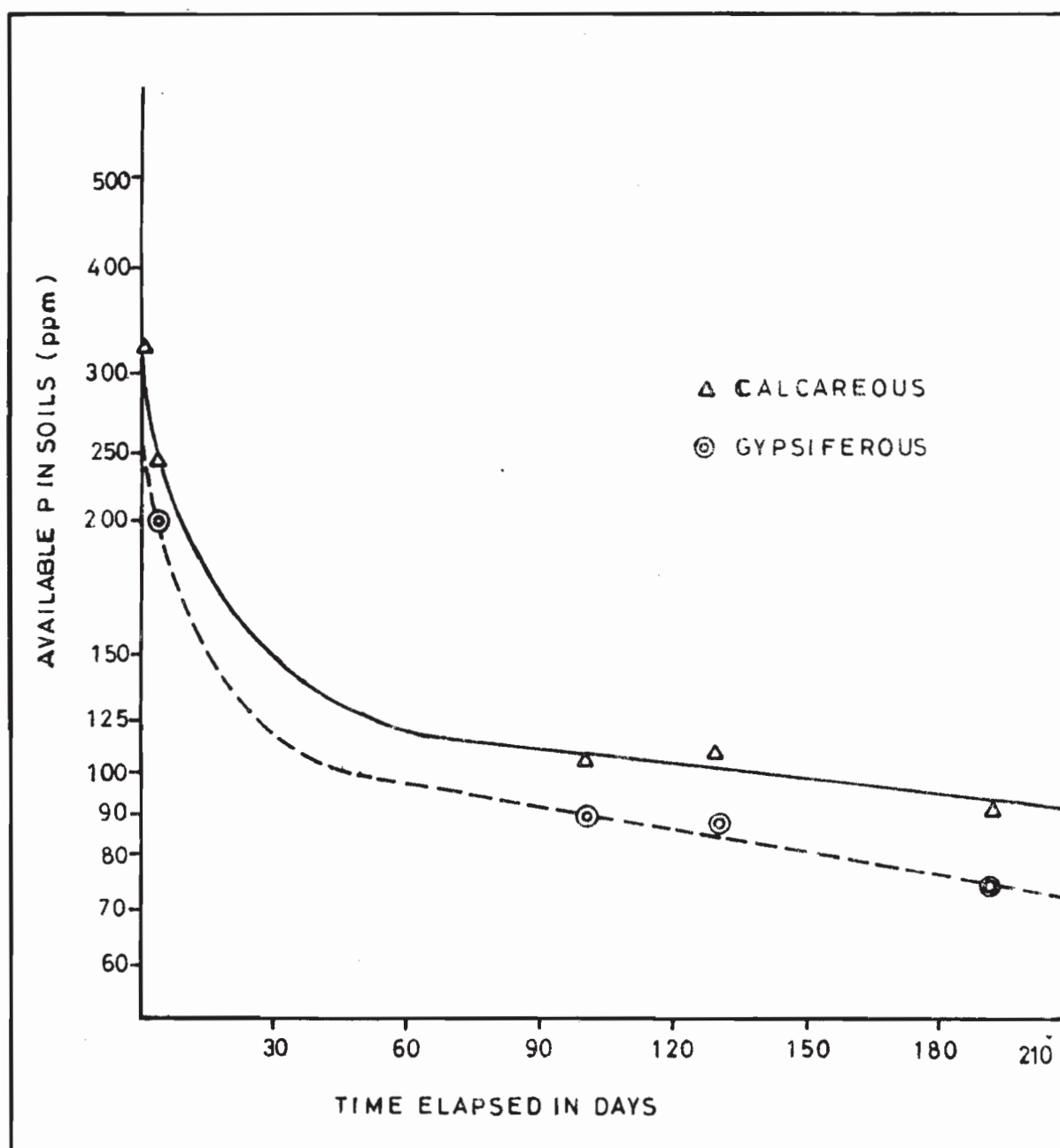


Fig. (1) AVERAGE P IMMOBILIZATION CURVE FOR CALCAREOUS VERSUS GYPSIFEROUS SOILS.

decay : The first region, where rate of immobilization is high and the half life of available P^* Was of the order of 27 days for calcareous soils, and 12 days only for gypsiferous soils. An equation of the type (1) : Could be used to represent P immobilization in calcareous soils of the first region :

$$P = P_0 \cdot e^{-0.81 t}$$

where P is the available P at any time t

P_0 is the available P at $t = 0$ when P fertilizer was added to the soil.

The second region, where the immobilization rate is much slower, and the average half life of P immobilization was about 300 days for both calcareous and gypsiferous soils.

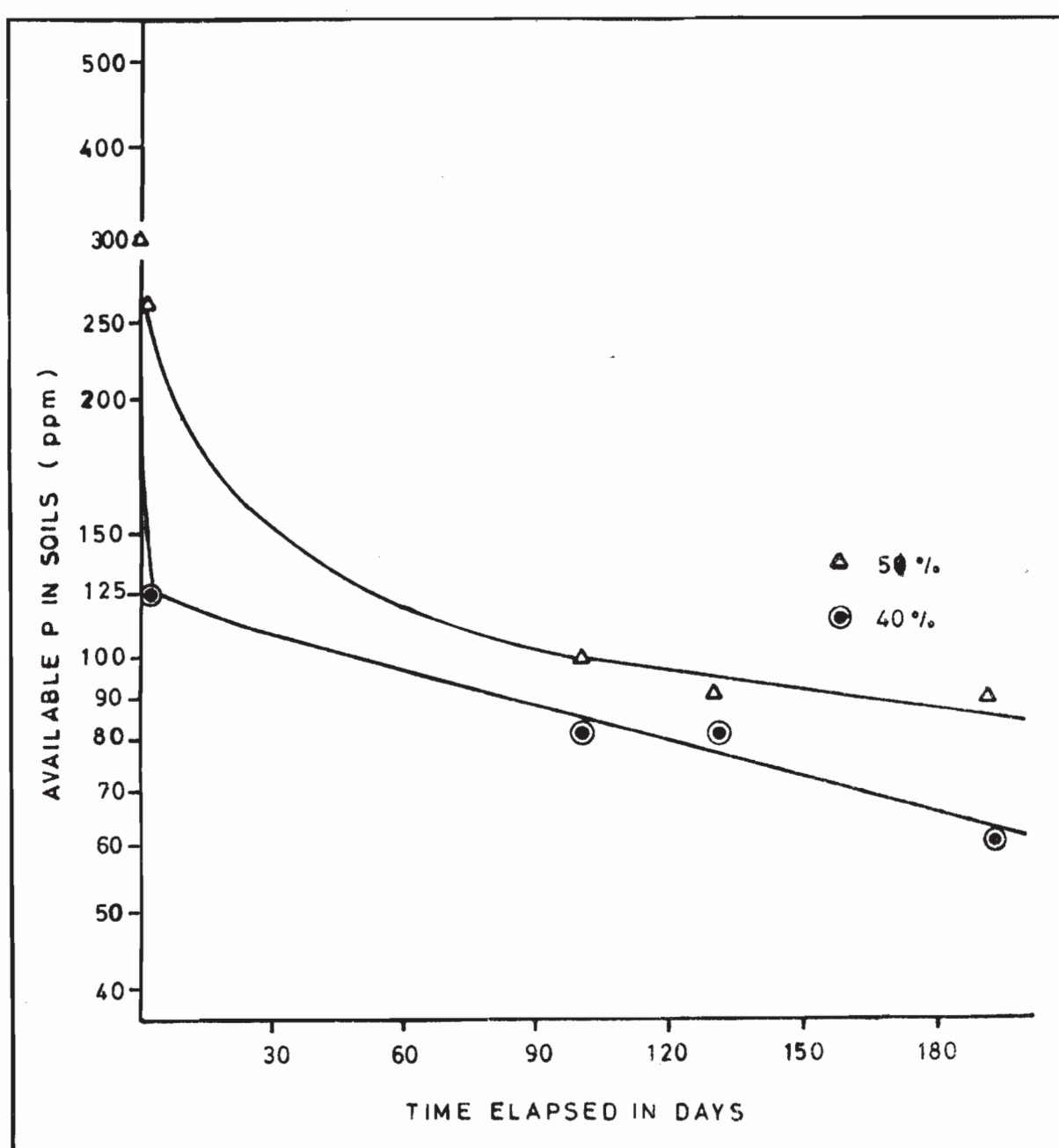


Fig. (2) P IMMOBILIZATION CURVE IN SOILS WITH 5 % (Δ) and 40 % (⊙) OF GYPSUM BY WEIGHT.

By comparing the rate of P immobilization in soils with various levels of gypsum content, it could be notified as shown in Fig (2) that the rate of immobilization was significantly greater in high gypsum soils (40 % by weight) as compared to low gypsum soils (5 %). That state of conditions did not show as clearly for calcareous soils (see Fig.3); where P immobilization was more or

less independent of the levels of CaCO_3 used in the soils.

Under the field conditions. it is expected that immobilizations rate of P could be more rapid, with the more wetting and drying cycles taking place under the irrigation system of arid conditions

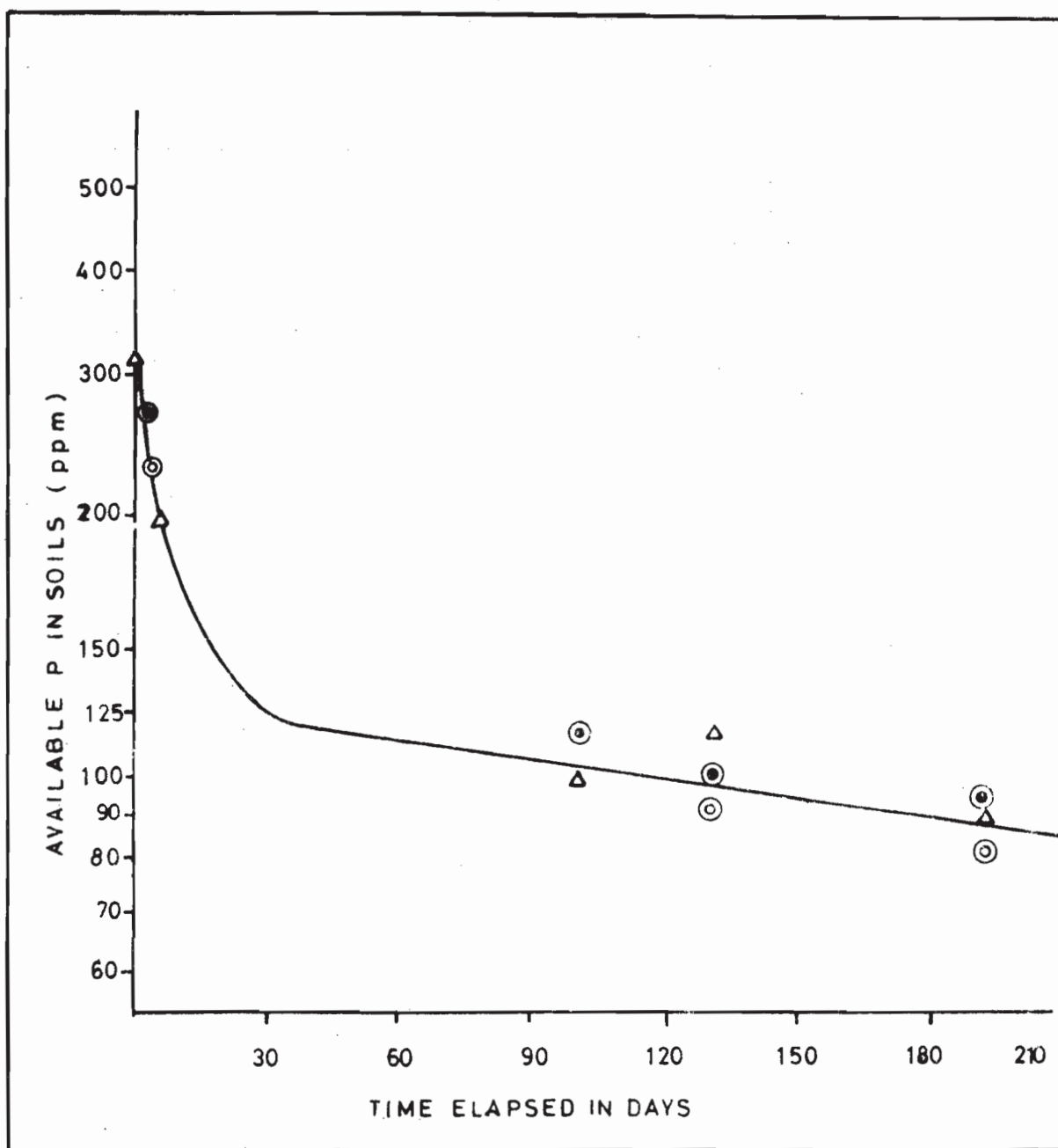


Fig. (3) P IMMOBILIZATION CURVE OF CALCAREOUS SOILS WITH 5 to 40 PERCENT of CaCO_3 .

Response of Corn to Phosphate and Zinc

In a previous work published by the author (7,8) it was found that the P content of corn leaves dropped markedly as the soil content in gypsum increased and especially for soils with 40 % gypsum. And as expected, the response of corn grows in both calcareous and gypsiferous soils to application of P was very significant at the 0.01 level (see table 1 and 2); but the interaction between P and gypsum content of soils was more significant (0.01 level) than the interaction of P with CaCO_3 in soil (0.05 level).

Gypsiferous soils are expected to have a very high concentration of calcium in the soil solution, even to a greater degree than the calcareous soils.

Gypsum as mentioned is much more soluble in water than calcium carbonate. Several researches have found that a high concentration of Ca in the soil solution, with the possibility of its accumulation on the root surfaces, could give to a reduction in P absorption by plants roots and thereby depress the root elongation.

In the absence of Zn application to soils, the maximum yield of corn was obtained similarly with the P1 treatments for both calcareous and gypsiferous soil

Table (1) Fresh weight of corn plant tops grown in soils with various levels of gypsum, with phosphate and zinc treatments, (g/pot).

Gypsum %
in Soil

Fertilizer Treatments					
P ₀	P ₁	P ₂	P ₂	P ₂ Zn	Mean
0	17.	512.	606.	618.	584.3
20	31.	454.	453.	618.	518.7
40	14.	397	403.	501.	433.7
Mean	20.7	454.3	487.3	579.	

LSD .05 = 69 g/Pot LSD .01 = 94 g/Prt

Table (2) Fresh weight of corn plant tops grown in soils with various levels of Calcium carbonate with phosphate and zinc treatments, (g/pot).

CaCO_3 %
In Soil

Fertilizer Treatments					
P ₀	P ₁	P ₂	P ₂ Zn	Mean	
0	14.	569.	509.	457.	516.3
20	12.	496.	438.	398.	448.
40	9.	436.	357.	376.	392.7
Mean	11.7	500.3	434.7.	410.3	

LSD .05 = 56 g/Pot

LSD .01 = 76 g/pot

The main difference between gypsiferous and calcareous soils was in their response to soil application of Zinc. The original rhodoxeralf soil,

free of lime and gypsum did not show any response to Zn and are usually well supplied with available Zinc. Similarly, the addition of ZnSO₄ did not have any significant effect on yield of corn grown in all types of calcareous soils used. However, Zn application had a very significant effect on yield of corn grown in gypsiferous soils at 0.01 level. Yields obtained from Zn-treated gypsiferous soils (20 percent of gypsum) were of the same level reached in non-gypsiferous soils. But for soils with 40 % percent of gypsum the application of Zn, although it increased the corn yield significantly, the levels reached were still below the maximum yield obtained with nongypsiferous soils. That would suggest that zinc could not be the only limiting factor affecting growth and development of corn plants grown in highly gypsiferous soils; and presumably other variables affecting growth could be at stake and need further exploration.

Effect of P and Zn on Nutrient Content of Corn

The application of Phosphate to calcareous and gypsiferous soils raised fresh yield of corn as well as its phosphorus content significantly at the 0.01 level to a concentration level far above the deficiency level of 0.11 % for fresh matured leaves of corn as tasseling stage as determined by Lawton et al (5)

The application of the P₂ level, raised even further the P content of plants to a level ranging between 0.26 and 0.4 percent (table 3 and 4), without any effect on yields. Gypsum in soil had a significant effect (at 0.05 level) on the P concentration in corn leaves, however the CaCO₃ did not have any significant effect. (3) The interaction between soil gypsum or soil CaCO₃ and phosphorus applied to soils was significant (at 0.01 level) for P concentration in corn leaves.

Table (3) Effect of gypsum and phosphate levels and zinc on mineral contents of corn leaves at tasseling stages.

Treatments		Plant nutrient concentrations					
		P %	Mg %	Ca %	K%	zn	Mn
P ₀	0% Gypsum	0.1 124	1.38	2.18	1.35	61	92
	20% G	0.1 54	1.35	1.73	1.62	72	80
	40% G	0.2 12	1.44	1.92	1.73	75	42
P ₁	0% G	0.3 55	0.87	0.60	0.27	47	97
	20% G	0.3 59	0.87	0.60	0.30	35	101
	40% G	0.263	0.85	0.56	0.28	14	58
P ₂	0% G	0.396	0.70	0.55	0.29	22	73
	20% G	0.4 07	0.75	0.60	0.21	34	96
	40% G	0.3 31	0.72	0.47	0.27	23	61
P ₂ Zn	0% G	0.3 92	0.56	0.76	0.46	68	55
	20% G	0.3 75	0.77	0.73	0.47	72	82
	40% g	0,3 32	0.81	0.67	0.31	84	68
LSD.05 =		0.055	0.26	0.33	0.10	24.7	54.7
LSD. 01 =		0.076	0.39	0.45	0.14	34.0	40.2

Talbe (4) Effect of Calcium carbonate and phosphate levels and zinc on mineral contents of corn leaves at tasseling stages.

Treatments		Plant nutrient concentrations					
		P%	Mg%	Ca%	K%	Zn ppm	Mn
P ₀	0% CaCO ₃	0.0 23	0.76	2.35	1.43	95	64
	20% CaCO ₃	0.1 36	1.28	2.36	2.03	73	48
	40% CaCO ₃	0.2 68	3.04	2.87	2.34	50	50
P ₁	0% CaCO ₃	0.3 04	0.78	0.75	0.56	40	79
	20% CaCO ₃	0.2 55	0.59	0.76	0.51	48	75
	40% CaCO ₃	0.2 84	0.67	0.75	0.36	52	74
P ₂	0% CaCO ₃	0.3 65	0.74	0.59	0.63	47	71
	20% CaCO ₃	0.3 41	0.69	0.71	0.44	48	61
	40% CaCO ₃	0.3 23	0.76	0.57	0.34	48	57
P ₂ Zn	0% CaCO ₃	0.3 87	0.68	0.47	0.62	72	39
	20% CaCO ₃	0.3 44	0.72	0.60	0.40	85	71
	40% CaCO ₃	0.3 50	0.73	0.55	0.37	94	62
LSD.05 =		0.06		0.41	0.16	32.8	
LSD.01 =		0.08		0.56	0.22	45.2	

Table (5) Analysis of Variance for main effects of soil gypsum, phosphate and zinc added to soil and their first order interaction on mineral concentrations of corn leaves. (mean squares).

Source of Variation	Degree of Freedom	Plant Nutrients in Corn				
		P%	Ca%	Mg%	K%	Zn Ppm
P	3	8.92**	4.02**	0.93**	3.54**	4869.5**
G	2	0.53*	0.05	0.02	0.01	214.5
R	2	0.09	0.01	0.03	0.005	42.5
PXG	6	0.58**	0.04	0.01	0.004**	447.8

*,** Significant at the 5 and 1% level respectively.

Table (6) Analysis of Variance for main effects of Soil Calcium carbonate, Phosphate and Zinc added to soil and their first order interaction on mineral concentrations of corn leaves. (mean squares).

Source of Variation	Degrees of Freedom	Plant Nutrients in corn				
		P%	Ca%	Mg%	K%	Zn ppm
P	3	6.98**	8.08**	2.19**	4.82**	1936.**
Ca	2	0.42	0.06	1.11	0.005	258.
R	2	0.03	0.13	0.30	0.01	12305
RxCa	6	0.85**	0.08	1.07*	0.27**	686.8

*,** significant at the 5 and 1% level respectively.

On the other hand if it is well understood that excess application of P could reduce significantly Zn uptake by corn (1) either through inhibition of Zn uptake or by curtailing its translocation into root xylem or by lowering its rate of absorption by roots. In the present work the application of P led to a reduction in Zn concentration significantly in corn leaves (at 0.01 level) 2 to 3 times, but at the same time P increased yields of corn by about 40 folds. That made the total uptake of Zn by corn to be greater in the P treated soils. The effect of P on the plant Zn concentration was difficult to interpret because large increase in yields were associated with P which could cause a dilution effect on Zn concentration. The Zn concentration in corn leaves dropped to 47 or 48 parts per million for soils fertilized with P1 and P2 treatments respectively; while the level reached in gypsiferous soils was very low and of the order 29 and 26 parts per million for P1 and P2 treatments. Although the level of Zn in corn leaves or plants grown in gypsiferous soils remained above the critical level for corn (15 parts per million), as determined by (Melsted et al (2) the application of $ZnSO_4$ to gypsiferous soils raised yields significantly (at the 0.01 level) and raised at the same time the Zn concentration in corn leaves very significantly (at 0.01 level) to an average of 90 and 78 parts per million for plants in calcareous and gypsiferous soils respectively. From the analysis of variance summarized in table 5 and 6 it showed clearly that except for the P treatments, neither gypsum, nor the $CaCO_3$ had a significant effect on Zn concentration of corn leaves.

Concerning the relative distribution of the three major cations in plants : potassium, calcium and magnesium, it was obvious from table (5) and (6) that application of Phosphate to soils lowered very significantly (at 0.01 level) the concentration of all three cations in corn leaves; with the presence of a strong interaction between P and gypsum or $CaCO_3$. Except for K concentration in

corn leaves, the Mg and Ca concentrations remained above the adequacy levels for optimum yields of corn.

CONCLUSIONS:

1. Calcareous and especially gypsiferous soils tend to immobilize phosphate fertilizers added, and the maintenance of an adequate level of available P in soil is a must for reaching high yields under the irrigated agriculture.
2. The application of $ZnSO_4$ to gypsiferous soils was found very beneficial in tolerating higher levels of gypsum in soils and improving yields. The application of phosphates and zinc compounds could be added to the soil before sowing.

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Importance and Purposes : Gypsiferous Soils are quite widespread in the Euphrates Valley. in Syria. The Fertilization of such soils is basic for a good crop production.

The purpose of the present work is to compare under controlled conditions, the rate of im- mobilization of P in calcareous and gypsiferous conditions, and the response of corn, a semi tolerant plant to gypsum, and application of phosphates and zinc to soils.

* According to Larsen : The half life of available P is the time elapsed for the immobilization of half of the available P in soils as determined in pot test or by other methods.