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PHOSPHATE FERTILIZATION REDUCES ZINC ADSORPTION BY CALCAREOUS SOILS*

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SUMMARY

Zinc adsorption isotherms were constructed for three calcereous soils which varied in carbonate contents, texture, and past history of phosphate fertilization. The equilibrium conditions were 25°C, 0.01 *M* $CaCl_2$ and 6 days.

Higher phosphate fertilization of the soils reduced Zn adsorption. The effect of P was more in the soil with lower carbonate content which suggested that soil carbonates played a dominant role in the Zn adsorption characteristics of the soils.

The adsorption data conformed to the Langmuir equation. Constants (k and b) calculated from the Langmuir isotherm showed that bonding energies (k) were inversely related to extractable P; *i.e.* higher Zn adsorption was associated with lower bonding energy. The Zn adsorption maxima (b) were higher for the soils with higher calcium carbonate equivalent.

Adsorbed Zn was extracted with a single extraction of 0.005 *M* DTPA. The recovery was 91 percent for the Tandojam soil, 82 percent for the Tarnab soil, and 63 percent for the Kala shah Kaku soil, indicating that most of the adsorbed Zn is not irreversibly fixed by the soils and can be utilized by plant during growth.

The results suggest that P-induced Zn deficiency could not be ascribed to precipitation of Zn as insoluble Zn-P compounds in soils. The increased Zn solubility with P fertilization is the evidence that P-Zn interaction does not reside in the growing medium external to plant.

INTRODUCTION

Most Zn deficiency disorders occur in calcareous soils with pH of 7.4 or higher since the solubility of Zn decreases with increasing pH. The Zn content of calcareous soils is often no less and may be higher than that of non-calcareous soils. Adsorption of Zn by carbonates

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may be another reason why Zn availability is low in certain calcareous soils [9 10 11 12].

It has also been observed that Zn deficiency occurs on soils that have received heavy or frequent P applications. Evidence of this has been reported by many workers [2 3 13 16], although some workers have reported evidence to the contrary [4 5].

The mechanism and conditions involved in the development of P induced Zn deficiency are not fully agreed upon. Pauli *et al.*[15] found that $CaCO_3$ influenced the P-Zn relationship within the plant and also affected P-Zn compounds in the growing medium. Reduction in Zn uptake by plants, as applied P and $CaCO_3$ increased has also been reported [13 19]. Most investigators [7 8 22] hold the view that the P-Zn interaction occurs either at the root surface or within the root.

Zinc adsorption isotherms for soils have been studied by some researchers [9 20 21], and some of the investigators have also expressed Zn adsorption data according to the Langmuir model [17 18], but few attempts have been made to study the effect of prolonged P applications on Zn adsorption by soils. The present investigation was undertaken to evaluate Zn adsorption characteristics of three calcareous soils from Pakistan which were being used to evaluate long term effects of phosphorus fertilization.

MATERIALS AND METHODS

Surface soil samples were collected from three calcareous soils having a wide range of carbonate content. The soils were being used for long term phosphate fertilization. The samples were air-dried, screened through a 2-mm screen sieve and sealed in plastic bags to prevent Zn contamination. The samples were brought to Hawaii by air. Some general characteristics of the soils are given in Table 1.

Zinc adsorption isotherms

Three gram triplicate samples of the soils were equilibrated in 50 ml centrifuge tubes containing varied amounts of Zn dissolved in a 0.01 *M* $CaCl_2$ solution. Two drops of toluene were added to retard microbial growth, and the tubes were shaken for 30 minutes twice each day. The equilibration was continued for six days at 25°C. After the equilibration period, the samples were centrifuged, and Zn remaining in solution was determined by an atomic absorption spectrophotometer. The amount of Zn adsorbed was calculated as

TABLE 1

Some general characteristics of the soils used

Soil type	Parent material	pH (1 : 1 H_2O)	$CaCO_3$ equivalent (%)	O.M (%)	DTPA-Extractable Zn (ppm)
Tandojam	Alluvium	8.0	10	0.7	1.3
Kalasha-Kaku	Alluvium	8.1	4	1.7	2.1
Tarnab	Alluvium	8.0	14	1.1	0.8

given below:

$$\text{Zn adsorbed} = A - \frac{R \times S}{g}$$

where A = amount of Zn added μg/g soil, R = Zn remaining in solution μg/ml, S = total equilibrating solution, and g = grams of soil taken

Zinc remaining in solution was plotted against Zn adsorbed on a semi-log scale.

Zinc adsorbed by soils was extracted by the procedure described by Lindsay and Norvell (Agron. Abstr. 1969, P. 84). The extracting solution consisted of 0.005 *M* DTPA (Diethylenetriamine Penta acetic acid), 0.01 *M* $CaCl_2$, and 0.1 *M* TEA (Triethanolamine) adjusted to pH 7.3, with a 2 hour shaking period. Corrections were made for Zn in solutions carried over as entrained solution from centrifugation.

RESULTS AND DISCUSSION

Zinc adsorption isotherms

Zinc adsorption isotherms for three calcareous soils each with two levels of P are given in Fig. 1, where the amount of Zn adsorbed is plotted against the amount remaining in solution on a semi-log scale. Zinc adsorption progressively increased with increasing solution concentration of Zn. The ability of soils to adsorb Zn was reduced with higher extractable P. At a given Zn concentration in solution (1 ppm), the reduction was 5 per cent for the Tandojam, 12 per cent for the Kala Shah Kaku, and 7 per cent for the Tarnab soil, respectively. The highest reduction in adsorption was for the soil with the lowest carbonate content, indicating that carbonates played a dominant role in Zn adsorption characteristics of the soils. The relative Zn adsorption was in the order of: Tarnab > Tandojam > Kala Shah Kaku. Total carbonate content of the soils also increased in the same order.

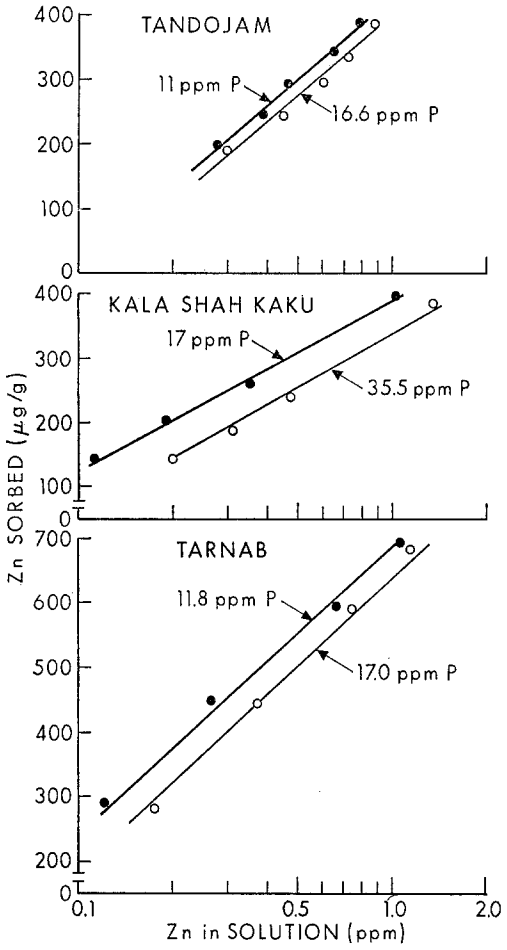

Fig. 1. Zinc adsorbed by three calcareous soils in relation to Zn remaining in solution and $NaHCO_3$-extractable P.

The reduction in Zn adsorption with P was apparently due to the formation of readily soluble Zn-P compounds in the soils. Recently, Lindsay[11] has shown that $Zn_3(PO_4)_2.H_2O$ is relatively more soluble than soil Zn, and this compound could be an excellent source of Zn as well as P. Increased solubility of Zn with P applications has also been reported by several other investigators[1 5 6].

The results do not agree with the findings by Spencer[19], who concluded that Zn is immobilized in the soil external to the roots by the phosphate and lime, but substantiate the conclusions by most

of the workers that the P-Zn interaction problem is not in the soil external to plant[15].

Application of Langmuir Equation

The Langmuir adsorption equation can be written in the form:

$$\frac{C}{x/m} = \frac{1}{kb} + C\,\frac{1}{b},$$

where C = the equilibrium concentration of Zn in soil solution

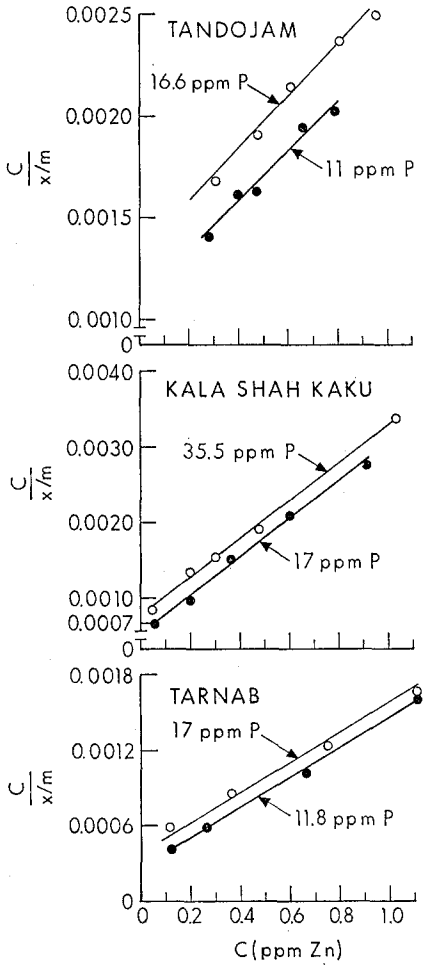

Fig. 2. Langmuir isotherm for Zn adsorbed by calcareous soils at different extractable P levels.

TABLE 2

Adsorption maxima (b) and bonding energy constants (k) as affected by P levels and total carbonates

Soil type	$CaCO_3$ (%)	Olsen's P (ppm)	Adsorption maxima (b) ($\mu g/g$)	Bonding energy (k) (ml/μg)
Tandojam	10	11.0	927	1.1
		16.6	877	0.8
Kalashah Kaku	4	17.0	392	3.5
		35.5	382	1.8
Tarnab	14	11.8	862	4.5
		17.0	847	2.4

(ppm), x/m = the quantity of Zn adsorbed ($\mu g/g$ soil), b = the zinc adsorption maximum, and k = constant related to the bonding energy

When the adsorption data were plotted according to the Langmuir equation, a frequently reported linear relationship was obtained irrespective of the P levels (Fig. 2). All data fit very well since the Langmuir isotherm holds good for low concentrations of absorbent (for Zn concentration < 0.3 ppm, the Tandojam soil did not conform to this equation). The good fit of the data according to the Langmuir equation would suggest that Zn adsorption was taking place on one type of adsorption site.

The results also indicate that at any given solution concentration of Zn the slopes of the lines are unrelated to extractable P, showing that the adsorption maximum (Zn adsorption capacity) of the soil is not affected by P fertilization. However, the higher P level has displaced the line, indicating a change in the value of bonding energy (k). This was further confirmed when the Langmuir coefficients (b and k) were calculated for the data in Fig. 2. These calculations are given in Table 2. Within experimental error, the adsorption maxima are nearly the same for the two P levels within each soil. The relative bonding energy indicated by the k values was higher for the samples with low extractable P, showing that high Zn adsorption was associated with low bonding energy. This finding is similar to that of Shuman[17 18].

The data in Table 2 further indicate that, irrespective of P, Zn

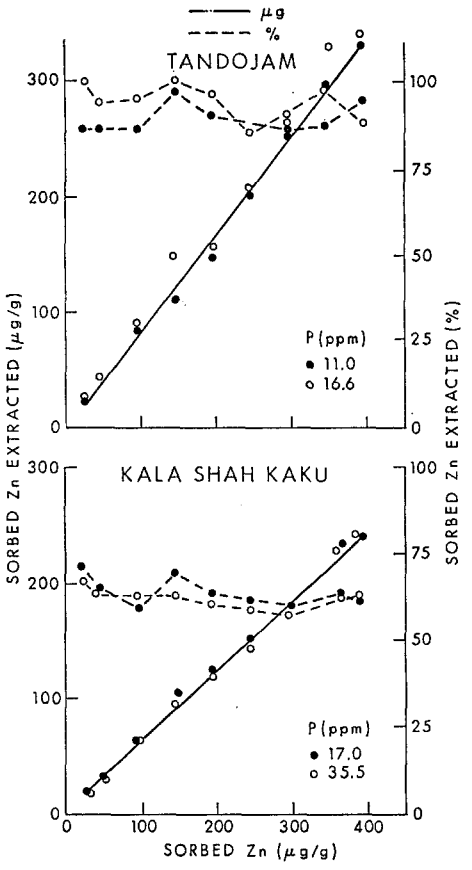

Fig. 3. Recovery of adsorbed Zn from Tandojam and Kala Shah Kaku soils by a single extraction with 0.005 *M* DTPA.

adsorption maxima were much higher for the soils with a high content of total carbonate. Udo *et al.*[20] also reported a significant correlation between Zn adsorption maxima and the carbonate content of 10 Arizona soils.

Recovery of adsorbed Zn

A single extraction of DTPA in 0.01 *M* $CaCl_2$ was used to extract adsorbed Zn. The results are presented in Figs. 3 and 4. A linear relationship was observed between amounts of Zn adsorbed and amounts extracted. In all soils the effect of P on per cent Zn extraction did not show a definite trend.

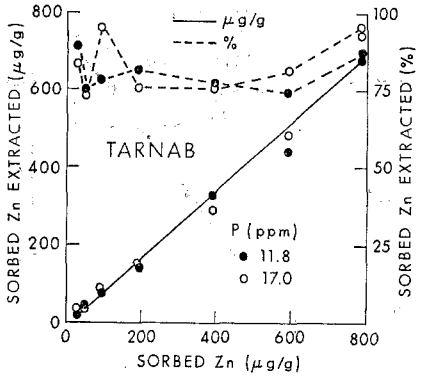

Fig. 4. Recovery of adsorbed Zn from Tarnab soil by a single extraction with 0.005 *M* DTPA.

The average recovery was 91 per cent for the Tandojam soil, 82 per cent for the Tarnab soil, and 63 per cent for the Kala Shah Kaku soil. The high recovery of added Zn from the Tandojam soil was due to the low Zn fixation capacity of the soil because of its sandy texture. The low recovery from the Kala Shah Kaku soil could be attributed to a high content of illite clay. Thus most of the adsorbed Zn must have been irreversibly fixed by illite in forms or on sites which were not DTPA extractable. Newton and Melsted[14] in their comparative study on Zn adsorption by different clays concluded that illite had a higher Zn adsorption capacity than bentonite and kaolinite clays.

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