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INFLUENCE OF MINERAL PHOSPHATE FERTILIZATION ON ACCUMULATION OF CADMIUM IN SOIL

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ABSTRACT

In this current work, the influence of mineral phosphate fertilization on accumulation of cadmium in soil was studied. Rock Phosphate (RP) and Triple super phosphate (TSP) were selected as a common source of P fertilizers and enriched by Cd contamination. An incubation experiment was undertaken for 60 days. Soil was incubated with RP or TSP with 0.0, 20.0, 40.0 and 80.0 kg P_2O_5 ha⁻¹. Soil samples were then taken after 1, 3, 7, 15, 30 and 60 days from incubation course. The most important results gained from the current study were: Cd concentration in RP was enriched 87 times of crustal abundance where Cd concentration in TSP was enriched 73 times crustal abundance. Although the TSP produced higher available P comparing with RP, the differences were not significant. For both TSP and RP applications, Cd extracted by DTPA as a proxy of bioavailable pool of Cd in soil was increased by increasing the P fertilizer rates and by consequence of incubation period. A negative relationship between soil pH and DTPA-Cd has been obtained. The increase of Cd sorption in this study might be attributed to the increase of soil pH caused by the P additions. This might be obvious in the decreasing of DTPA-Cd under higher pH values. The Cd in TSP might be more readably available than that of RP. The concentration of DTPA-Cd in incubated soil increased slightly due to the application of phosphate fertilizers, but the concentration did not reach contamination levels under different treatments.

Key words: Phosphate fertilization, cadmium, Rock Phosphate, Triple super phosphate.

INTRODUCTION

Cadmium (Cd) is a trace element that is naturally present in soils, but can also be introduced into soil through atmospheric deposition, industrial contamination, sewage sludge, irrigation water, and agricultural inputs such as manures, fertilizers, and soil amendments. Agricultural crops accumulate Cd from the soil, with the amount of uptake depending on several factors, including crop genetics, soil Cd concentration, and Cd phytoavailability, which is affected by soil characteristics.

Long-term consumption of foods containing excess levels of Cd may lead to chronic toxicity and adverse health effects. Phosphorus (P) is an essential nutrient for crop production and growth. Next to nitrogen, phosphate is by far the most limiting nutrient for crop production. Phosphate is essential for plant growth and maintaining agricultural productivity. It is a nutrient required in relatively large amounts by plants. Plants need phosphorus for growth, utilization of sugar and starch, photosynthesis, nucleus formation and cell division, fat and albumen formation (Hinsinger et al., 2018). Phosphorus is a component of the complex nucleic acid structure of plants, which regulates protein synthesis (Smith et al., 2018). Phosphorus is, therefore, important in cell division and development of new tissue. Phosphorus is

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associated with complex energy also transformations in the plant. Adding phosphorus to soil low in available phosphorus promotes root growth and winter hardiness, stimulates tillering, and often hastens maturity. For soils deficient in P, application of organic or inorganic fertilizers is needed to achieve optimum crop yields. Although P fertilizers represent the major anthropogenic input of P to agricultural soils, both inorganic Р fertilizers and organic P sources, such as sewage sludge and manure, may contain Cd. In addition to direct inputs of Cd, phosphate fertilization can indirectly affect Cd accumulation in soil through its effects on soil chemistry and microbial interactions. Therefore, the management of P fertilizer application, both in the short and long term, can influence the potential accumulation of Cd in foods.

Rock Phosphate RP is an essential resource for the production of phosphate fertilizers. RP is being imported from various sources around the world. Morocco rock phosphate has three quarters of the world phosphate reserves (Bilali et al., **2005**). The various phosphate minerals present in RP have diverse origins and chemical and physical properties. The phosphorus content or grade of rock phosphate is commonly reported as phosphorus pentoxide (P_2O_5). The principal phosphate minerals in RP are Caphosphates, mainly apatites. Pure fluorapatite contains 42% P2O5, and francolite, the carbonate-substituted form of apatite, may contain 34% P₂O₅.

The RP is, due to its origin, affected by high concentrations of impurities, heavy metals, naturally occurring radionuclides and other so-called trace elements (Selim, 2018). Lowering the cadmium content in fertilizers is the only feasible way of reducing the cadmium input to farmland from this source. This can be achieved either by using raw materials (RP) with a lower cadmium content, or by eliminating the cadmium from the RP or the phosphoric during the production process. acid Obviously, the flow of cadmium to agricultural soils can also be reduced by applying lower amounts of phosphate fertilizer and/or substituting fertilizers by other products containing phosphorus e.g. manure (Mar, 2012). The main object of this work was to study, the influence of mineral phosphate fertilization on accumulation of cadmium in soil.

MATERIALS AND METHODS

A lab experiment was carried out at the Experimental lab of Environ. Agric. Sci. Fac., Arish University, North Sinai, Egypt. Top 20 cm soil sample was collected from the research farm of the Faculty of Environmental Agricultural Sciences, Arish University, North Sinai, Egypt. Soil sample was air dried, ground with a wooden mallet and passed through a 2 mm sieve and stored in clean dry plastic bags for various physical and chemical analyses.

Air dried soil samples, < 2 mm were mixed with 0.149-mm sieve P fertilizer. The experiment was performed in two treatments and triplicate replicates per treatment. Each treatment has been applied for different rates. RP or TSP was homogeneously mixed with 100 g of airdried soil at 0.0, 20.0, 40.0 and 80.0 kg P_2O_5 h⁻¹. The water content of the soil was adjusted to approximately 60% of water holding capacity by adding double distilled water with an automatic pipette and was placed in a 250 ml plastic bottle. The bottles were then kept in lab at 25°C. Throughout the incubation period, water losses exceeding 10% of the initial values were compensated by addition of water by weight to avoid soil- solution system disturbance. Soil samples were taken after 1, 3, 7, 15, 30 and 60 days from incubation course, oven dried and prepared for analysis. Soil pH, EC, Olsen P, DTPA-Cd were measured.

Phosphorous measurements

Phosphate was extracted with 0.5M sodium bicarbonate (NaHCO₃) solution at pH 8.5 (**Olsen** *et al.*, **1954**) as available P and from digested soil as total P. both solutions were assayed using a variation on the phosphomolybdate method (**Drummond and Maher, 1995**) by measuring absorbance in a 1 cm cell at 660 nm (CE 1011 spectrophotometer, Cecil Instruments). All soil measurements were repeated in triplicates and the average results were reported.

Triplicate samples of 4.0 g soil (< 2 mm sieved) were suspended in 8 ml of 0.005 M DTPA (Lindsay and Norvell, 1978) and shaken on an end-over-end shaker, in Oak Ridge polypropylene centrifuge tubes, for 2 hours. Suspensions were then centrifuged at 2500 rpm for 15 min and the supernatant filtered (<0.2 μ m) into polyethylene tubes containing sufficient HNO₃ to produce 2% acid prior to multi-element analysis by ICP-MS.

RESULTS AND DISSUTION

General soil characteristics

The tested soil was sandy in nature with 4.5% clay, 2.3% silt and 93.2% sand fractions. Soil pH was close to neutral with alkaline effect. Soil EC was 0.30 dSm⁻¹ with tiny amount of CaCO₃ (0.05%). Soil organic matter was very low (0.01%) due to arid conditions. Total metal concentrations in acid digest soil were varied depending on specific element. Total Cadmium concentration is 0.101 mgkg⁻¹ which in the range of the earth's crust level considering the tested soil as uncontaminated soil (low background level of Cd).

General characteristic of P fertilizers

The results showed that RP and TSP have a significant amount from Cd. This will defiantly be reflected on the accumulation of Cd in soil. The Cd total concentrations measured in acid digest fertilizer were 23.2 and 19.5 mgkg⁻¹ for RP and TRP, respectively.

Soil Available P

An incubation experiment has been conducted for 60 days. The available P was measured after 1, 3, 7, 15, 30 and 60 days from incubation course (Fig. 1). Depending on the general average values of available P (Fig. 2). The results showed that available P increased up to 7 days of incubation course which rich the maximum value of 6.05 mg kg⁻¹ for RP treatments then the value was declined till the end of incubation course. However, Available P in case of TSP treatment started to decrease from the beginning till the end of incubation course (Fig. 2). The average Olsen P obtained from treating the soil with TSP was 5.74±0.48 which is a little higher than the same value obtained from treating the soil with RP (average Olsen P (P_2O_5) = 5.38 ± 0.44). Although the TSP produced higher available P comparing with RP, the differences were not significant; the T paired test showed probability of 0.26 and T value of -1.26. In contrast, the rate of P added to the soil has a significant effect in available P in both P fertilizer. In general, As the mobile and easily mineralizable fraction of P for plant use, the concentration of Olsen P in the end of incubation course increased significantly as compared to the values at the beginning of incubation period in all P fertilizer addition rates (p < 0.05).

DTPA extractable Cd

The results of DTPA-Cd were presented in Fig. 3. The results showed that, for both TSP and RP application, Cd extracted by DTPA as a proxy of bioavailable pool of Cd in soil was increased by increasing the P fertilizer rates and by consequence of incubation period. However, the final DTPA-Cd values obtained at the end of incubation period were higher than that at control. In terms of P release rose rapidly at the initial time of incubation period



Fig. (1): Changes of available P (Olsen P; mg P₂O₅ kg⁻¹) in tested soil as a function of P sources (RP; rock phosphate and TSP; triple superphosphate) at 0, 20, 40 and 80 kg P₂O₅ h⁻¹ during the incubation course (1, 3, 7, 15, 30 and 60 days). Error bar represents the standard error of triplicates.



Fig. (2): General average changes of available P (Olsen P mg P₂O₅ kg⁻¹ calculated by averaging all values driven from different concentrations of applied P fertilizers) in tested soil treated by rock phosphate (RP) and triple superphosphate (TSP) as a function of incubation course. Error bar represents standard error of triplicates.



Fig. (3): Changes of available (mg DTPA-Cd kg-1) in tested soil as a function of P sources (RP; rock phosphate and TSP; triple superphosphate) at 0, 20, 40 and 80 kg P₂O₅ h⁻¹ during the incubation course (1, 3, 7, 15, 30 and 60 days). Error bar represents the standard error of triplicates.

(typically one day), as expected, and like the Cd, (Figs. 1 and 3). It seems after 60 days of incubation course, the application rate of 80 kg P_2O_5 h⁻¹ of RP had the highest DTPA-Cd value followed by the same rate of TSP at the end of incubation period as well. General results showed average DTPA-Cd obtained from treating the soil with TSP was 0.347 ± 0.063 mg DTPA-Cd kg^{-1} which is a little higher than the same value obtained from treating the soil with RP (DTPA-Cd = 2.53 ± 0.063) (Fig. 4). The difference between RP and TSP in terms of producing DTPA-Cd in soil were significant where T- Paired test showed probability of 0.009 and T value of -4.12.

Moreover, the best fitting relationship between an average DTPA-Cd and incubation intervals was liner for RP (y = 0.0028x + 0.198) with R² of 0.97 where it was polynomial 2nd order equation (y = -0.0001x2 + 0.008x + 0.2803) with R² of 0.71.

The current incubation experiment showed the importance of understanding the release of Cd from fertilizer in unsaturated soils (**Yu** *et al.*, **2019**). Under typical field conditions it is expected that only about 10-20% of Cd will be released quickly in soluble form and that most of the Cd will remain associated with very slowly dissolving solids (**Piveteau**, 2017).

Soil pH and EC

Fig. 5 shows the relationship between DTPA-Cd and soil pH. The results showed a negative relationship between soil pH and DTPA-Cd. Soil pH directly and indirectly influences all chemical processes, and consequently the behavior of trace elements in soils (**Wang et al., 2006**). Soil pH is an important factor in affecting sorption and desorption of heavy metals by soil (**Kunhikrishnan et al., 2012**).

Shaheen (2009) reported that the total amounts of Pb and Cd sorbed within the concentration range used in the sorption experiments were larger in alkaline than in acidic soils from Egypt and Greece which is in consequence in the current results. The increase of Cd sorption in this study might be attributed to the increase of soil pH caused by the P additions. This might be obvious in the decreasing of DTPA-Cd under higher pH values (Fig. 5). Other researchers also reported that the sorption of Pb, Zn, and Cd by variable charge soils was pH dependent (Shaheen and Tsadilas, 2010, Cui et al., 2014, Li et al., 2018). An increase in soil pH causes deprotonatin of



Fig. (4): General average changes of (mg DTPA-Cd kg⁻¹) calculated by averaging all values driven from different concentrations of applied P fertilizers in tested soil treated by rock phosphate (RP) and triple superphosphate (TSP) as a function of incubation course. Error bar represents standard error of triplicates.



Fig. (5): Relationship between (mg DTPA-Cd kg⁻¹) and soil pH for the whole dataset. Broken line represents liner relationship.

hydroxyl groups on the surface of iron and aluminum oxides, and thereby, results in the increase of variable negative charges on soil colloid surfaces. More variable negative charges could attract more Cd toward soil surfaces through electrostatic attraction (**Christensen**, **1984**), thereby, enhancing heavy metal ions sorption by soil clay minerals or iron and aluminum oxides.

On the other hand, increasing soil pH accelerated the transformation of Cd from M^{+2} to MOH^+ and $M(OH)_2$ through hydrolysis, decreased the energy obstacle of the two ions to bind to soil oxides surface, and then increased the specific sorption by soil colloid surface (**NAIDU** *et al.*, **1994**).

Furthermore, increasing soil pH also allowed Cd to form stable complexes with Soil organic matter (SOM) and manganese oxides, and then increased their sorption by soil. **Ma** *et al.* (2010) reported that with increasing pH, more -COOH and -OH in soil colloids dissociated to form -COO- and -O-, which can increase the ability of SOM to complex with M^{+2} , and thus, increase the sorption of M^{+2} .

The Cd release is mirrored in the soil during incubation periods by a very similar time course for electrical conductivity (EC) (Fig. 6), which is an index of total salts released from the fertilizer.

EC is a measure of the total concentration of dissolved ions. As expected, the largest increase in EC is seen in the experiment with the high fertilizer rate. This finding could be embedded in Fig. 6 where DTPA-Cd mirror the total amount of P added to the soil. The EC values tracked the DTPA-Cd values where slightly positive nonsignificant relationship has been found between DTPA-Cd and EC. The high EC values noted with solution could be due to the dissolved ions in the eluting solution itself.

Unexpected results have been found in the relationship between available P and EC

as it was expected that increasing EC was a result of increasing the rate of fertilizers (Fig. 7). These unexpected results could be attributed from influence of different soil properties such as CaCO₃, soil organic matter, Fe, Mn oxides (Marzouk et al., 2013). Overall, applying both TRP and RP to the soil increased Cd concentration extracted by DTPA. Fig. 8 shows the relationship between DTPA-Cd and Applied P as TR and TRP at different rates. The results showed highly significant liner relationship (p<0.01) for both fertilizers. Moreover, the average values of DTPA-Cd under TRP application $(0.35\pm0.06 \text{ mg kg}^{-1})$ were much higher than that of RP $(0.25\pm0.06 \text{ mgkg}^{-1})$ although the total amount of Cd in RP (23.2 mg kg⁻¹) is more than Cd exist in TRP (19.5 mgkg⁻¹).

This finding may suggest that the Cd in TRP might be more readably available than that of RP. Rock Phosphate reactivity is a measure of the rate of dissolution of phosphate rocks under standard laboratory conditions or in a given soil and under given field conditions (**Rajan and Chien**, **2001**). The dissolution rate of phosphate rocks is mostly affected by soil properties and plant characters. The chemical composition and particle size of phosphate rocks control their reactivity.

Sedimentary origin phosphate rocks are generally most reactive and suitable for direct application. Calcium carbonate is the most abundant accessory mineral in phosphate rocks.

As calcium carbonate is more soluble than the most chemically reactive phosphate mineral, its dissolution increases the calcium content and pH at the phosphate mineral surface. So, calcium carbonate can reduce the rate of phosphate rock dissolution in some soils. Sedimentary phosphate rocks show a very complex structure as a result of their different origin in nature and even within a particular geological deposit. Thus, they have extremely variable chemical





Fig. (6): Relationship between (mg DTPA-Cd kg⁻¹) and soil EC (dSm⁻¹) for the whole dataset. Broken line represents liner relationship.



Fig. (7): Relationship between available P (mg P₂O₅ kg⁻¹) and soil EC (dSm⁻¹) for the whole dataset. Broken line represents liner relationship.



Fig. (8): Relationship between average (mg DTPA-Cd kg⁻¹) values and total soil P (kg P₂O₅ h⁻¹) for the TR and TSP applications.

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constituents and may contain elements such as heavy metals and even radionuclides that upon dissolution of the phosphate rock in the soil may be harmful at some concentrations (**Hellal** *et al.*, **2019**). This could explain the highest level of extractable Cd by diluted DTPA gained from soil treated by TRP comparing to extractable Cd by diluted DTPA from the soil treated by RP.

Correlation coefficient matrix has been used for multi correlation analysis using

principle component analysis (Table 1). The results show that a significant negative correlation between pH and Cd measured in DTPA solution, DTPA-Cd and TP added to the soil (p < 0.01). Moreover, available P had a positive significant correlation with Cd measured in DTPA solution, DTPA-Cd and TP added to the soil (p < 0.01). in addition, it has been observed that a significant positive correlation between DTPA-Cd and TP which confirm the source of Cd was obtained from the added P fertilizers.

Table (1):	Correlation	matrix betwo	een all meas	surements in	incubation	experiment.
						1

Item	PH	EC dsm ⁻¹	Avi. P mgkg ⁻¹	Cd mgL ⁻¹	DTPA-Cd mgkg ⁻¹
EC dsm ⁻¹	-0.319				
	0.027				
Avi. P	0.023	-0.27			
	0.875	0.064			
Cd mgL ⁻¹	-0.689	0.201	0.442		
0	0.000	0.171	0.002		
DTPA-Cd mgkg ⁻¹	-0.688	0.192	0.448	1	
	0.001	0.192	0.001	0.000	
TP møkg ⁻¹	-0 443	-0.03	0 523	0 757	0 762
•••••B••B	0.002	0.842	0.000	0.000	0.000

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