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Effect of monocalcium phosphate on the concentration of cadmium chemical fractions in two calcareous soils in Iran

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Abstract

This study has been done to see the impact of phosphorus (P) on the concentration of cadmium (Cd) chemical fractions in two sorts of calcareous soils within the Fars province in Iran. Because of these interactions, we looked at the influence of phosphorus on cadmium fractions. Variables were three levels of Cd (0.0, 30.0 and 60.0 mg kg^{-1} of soil from $CdSO_4 \cdot 8H_2O$), three levels of p (0.0, 50.0 and 100.0 mg kg^{-1} of soil from Ca $(H_2PO_4)_2 \cdot H_2O$, three levels Incubation time (2, 4 and 8 weeks) and two sorts of soil (clay and sandy clay loam). The randomized completed block design (RCBD) was used for this research. After 2, 4 and 8 weeks of treatments, the sequential extraction procedure was done to determine cadmium concentration in WsEx (Water Soluble and Exchangeable), Sorb (EDTA extractable), MnOx (Manganese Oxides), Car (Carbonate), OM (Organic matter), AFeOx (Amorphous Iron Oxides), CFeOx (Crystaline Fe oxides) and Res (Residual) fractions. The results showed that 69.0 to 71.0% of the added Cd was removed within the WsEx, Sorb and MnOx fractions. Cadmium concentration in Sorb, OM and Res fraction was higher within clay soil while cadmium concentration within WsEx and Car fractions were higher within sandy clay loam soil. Adding P as monocalcium phosphate reduced cadmium concentration within WsEx and Sorb fractions while increased Car, OM and Res fractions. The presence of phosphorus reduces the concentration of Cd in those forms that are easily released into soil solution (WsEx and Sorb) from where they'll be absorbed by plants and thus decrease cadmium uptake by plants.

1. Introduction

Cd is regarded as one of the most hazardous element among heavy metals (Wu et al., 2016). Although cadmium is thought to be a non-essential metal, plants may easily absorb it (Adriano, 1986). Aerial sources, irrigation, fertilizers, pesticides, and industrial waste all have the potential to pollute soil with cadmium. The use of phosphorus fertilizers in agricultural areas and wastewater-based soil remediation could be the main problems. The buildup of these metals and subsequent presence in the food chain as a result of their long-term biological viability and survival in the soil pose potential health hazards (Basta et al., 2001). Similar to cationic micronutrients (Fe^{2+}, Mn^{2+}, Zn^{2+}, and Cu^{2+}), cadmium is retained at soil exchangeable sites by plants as Cd^{2+} and has characteristics that are essentially identical to those of zinc. In contrast to Zn, which can form layered double hydroxides (LDH) compounds (ZnAl) that become more stable with time (Roberts et al., 2003; Rassaei et al., 2020a), Cd has not yet been discovered to form LDH compounds, and the majority of Cd remains in the labile pool throughout time (Kukier et al., 2010; Rassaei et al., 2020d).

The total amount of heavy metals does not provide information about their impact on the environment or how they travel through contaminated soils (Jeng and Singh, 1993; Kim and McBride, 2006; Rassaei et al., 2019b; Rassaei et al., 2020b). The chemical fractions of heavy metals provide more information about their action within the environment and their mobilization-demobilization (Ma and Rao, 1997). Sequential extraction is employed effectively to work out the chemical types of heavy metals. By using the extractants which boosts from low acidic extraction solution to high acidic extraction solution we will have some data about the bioavailability of metals and their association with soil components (Rassaei et al., 2019a). One of the most important factors in increasing the yield production is phosphorus fertilizer. The low efficacy of phosphorus fertilizers is due to the quick immobilization and low mobility of phosphorus within the soil. Phosphorus fertilizers have an impact on Cd accumulation and availability in soils and crops due to Cd in P fertilizers or due to interactions between Cd-P and soil properties (Grant et al., 1998; Grant and Sheppard, 2008; Rassaei, 2021). According to Jones and Johnston, (1989), applying P fertilizers with a high Cd-P ratio increased the amount of Cd in the soil and the plants. Using P fertilizers and raising the Cd immobile forms decreases the soil's Cd mobility (Dheri et al., 2007; Matusik et al., 2008; Yao et al., 2022). Dheri et al. (2007) reported that using p fertilizer to spinach increased dry matter yield while decreased the Cd concentration within the DTPA-Cd extractable in soil.

These hypotheses result in the successful examination of soil extractable Cd concentration differences over time. This experiment was performed to quantify the effect of P and short-term incubation time on soil Cd fractions in two sort of calcareous soils in Iran. Advancing our knowledge of the impact of p on soil Cd fractions may provide greater insight into appropriate strategies to boost the management in using of p fertilizer and Cd accumulation in soils. The objectives of this paper are to (1) investigate the effect of incubation time; (2) evaluate the effect of soil texture; (3) examine the effect of P on Cd fractions within the two sorts of calcareous soils.

2. Materials and Methods

2.1. Area description

The Sarvestan plain, located 80 kilometers south of Shiraz in Fars, Iran, is located between latitudes 29°11' and 29°25' north and 52°45' and 53°25' east. The approximate area of this area is 95000 ha. Temperatures in the climate vary (the mean monthly maximum ranges from 6.30°C to 29.50°C), and November to May is when most rain falls (346 mm on average). The terms xeric and thermic refer to the soil's warmth and moisture (Rassaei et al., 2019a). This region's geology is evidenced by lucostrin deposits, calcareous marls, and gypsiferous marls.

The Kamfirouz Plain, also known as Kamfirouz, is located 110 km north-west of Shiraz in Fars, Iran, between latitudes 30°25' and 30°10' N and longitudes 52°20' and 52°10' E, along the eastern and western banks of the Chour River and north of the Doroodzan Dam. The community in question is 11300 acres large. The mean precipitation is 580 mm, with the minimum and maximum amounts being 370 and 800 mm, respectively. The winters are pleasant and humid, and the summers are warm. Typically, the soil in this area is calcareous (carbonate). In Fars, Iran, Kamfirouz is renowned for its rice farming. The land in this area is used for rice farming.

2.2. Soil

2.2.1. Sample collection

For this investigation, two different types of topsoil samples (a depth of 0–25 cm) were taken from the Sarvistan and Kamfiroz series in the Iranian province of Fars. Accoriding to the FAO-WRB soil system the studied soils were classified as Calcic Luvisol (IUSS Working Group WRB, 2015). Soil samples were sieved by a 2 mm sieve. They were then relentlessly dried in an oven at 105°C, chilled, and kept until analysis (Allen et al., 1974).

2.2.2. Sample Analysis

Soil texture was analyzed by the hydrometer method (Gee and Bauder, 1986), pH within the 1:1 suspension of soil and water (Richards, 1969), electrical conductivity (EC) in the 1:1 suspension extract of soil and water (Gupta, 2000), organic carbon by the tactic of Walkley and Black (Nelson and Sommers, 1982), carbonate equivalent (CCE) by the method of neutralizing with acid (Richards, 1969) and available Mn, Fe, Zn, Cu, and Cd extracted with the 0.005M DTPA solution (Lindsay and Norvell, 1978) were calculated (Table 1; Rassaei et al., 2020c).

2.3. Preparation of Cd-P test

The study was performed in a randomized completed block design (RCBD) with two replications. The treatments were three levels of P (0.0, 50.0 and 100.0 mg kg^{-1} of soil), three levels of Cd (0.0, 30.0 and 60.0 mg kg^{-1} of soil), two types of soils (clay and sandy clay loam) and three incubation time levels (2, 4 and 8 weeks). The incubation experiment was performed in the plastic beakers. Each beaker (equal to 0.50 kg soil) was treated with three Cd levels from source of cadmium sulphate ($CdSO_4 \cdot 8H_2O$, Merck Co. Germany) and three P levels from source of monocalcium phosphate ($Ca(H_2PO_4)_2 \cdot H_2O$, Merck Co. Germany). The beakers were placed alternatively in FC (33 kpa) conditions (by weighing the beakers on the first day and comparing their weight in the following days with the initial weight). During the incubation process, the beakers were covered with the porous plastic membrane and placed in an

Table 1
Selected chemical properties of soils

Amount		Properties
Sarvestan series	Kamfiroz series	
12	51.8	Sand (%)
34.8	25.5	Silt (%)
53.2	22.7	Clay (%)
Clay	Sandy Clay Loam	Texture
2.61	3.4	OM (%)[1]
34.1	52.3	CCE (%)[2]
30.31	8.34	CEC (Cmol kg^{-1})[3]
0.76	0.74	EC (dS. m^{-1})[4]
7.38	7.92	pH(1:1)
12.3	8.8	P(mg/kg)
4.4	3.3	Fe(mg/kg)
8.7	5.4	Mn(mg/kg)
0.51	0.33	Zn(mg/kg)
1.42	0.93	Cu(mg/kg)
nd	nd	Cd(mg/kg)

1 – Organic matter
2 – Calcium carbonate equivalent
3 – Cation exchange capacity
4 – Electrical conductivity

incubator under the constant temperature (25°C) to prevent the rapid evaporation of samples while allowing air to pass through.

2.4. Sequential extraction method

After 2, 4, and 8 weeks of incubation, the modified Ma and Uren, (1998) sequential extraction method was used to measure the concentration of Cd in the following fractions: water soluble-exchangeable (WsEx), EDTA extractable (Sorb.), manganese oxide (MnOx), carbonate (Car), organic matter (OM), amorphous Fe oxide-bound (AFeOX), crystalline Fe oxide-bound (CFeOX), and Residual (Res). Table 2 provides an operational definition of the chemical percentages of heavy metals. The 100 ml centrifuge tubes were used for the extractions. The supernatants were centrifuged at 4000 rpm for 30 minutes and then filtered between each subsequent extraction. After digesting 0.5 g of oven-dried soil samples with an HF-HNO_3-$HClO_4$ mixture, elemental analysis was used to quantify the total metal and consequently the Cd contents in the soils. By using an atomic absorption spectrophotometer (Shimadzu-AA 670, Japan), the total Cd concentrations in the solutions were examined.

2.5. Data analysis

Data analyses were meted out with SPSS Version 16.0 statistic software package (IBM, USA). Cadmium concentration in chemical fractions was analyzed by one-way analysis of variance. The experiment was randomized completed block design (RCBD) with 2 varieties of soil treatments (clay and sandy clay loam) × three incubation time (2, 4 and 8 weeks) × three Cd levels (0.0, 30.0 and 60.0 mg kg^{-1}) × three P levels (0.0, 50.0 and 100.0 mg kg^{-1}) and two replicates for every sample. Repeated measures ANOVA was performed to check the effect of treatment and soil over time using time as repeated measure. The means were compared by the Duncan's tests to see the statistical significance of the results as a result of treatments with Cd, p and their interaction. The p value < 0.05 was contemplated statistically significant.

3. Result and discussion

3.1. Effect of incubation time on Cd fractions

Data shows significant effect of incubation time on the Cd fractions in soil samples. The Cd concentration at 0.0 level Cd treatments (control) was non-detectable in all studies. Within the clay soil, the mean soil extractable Cd concentration in WsEx, Sorb, Car, Om and Res fractions across the duration of the examination was significantly ($p \leq 0.01$) different with incubation time. The Cd concentration within the MnOx fraction wasn't significantly different with incubation time ($p = 0.343$, $p > 0.05$). Within the sandy clay loam soil samples, the mean of the soil extractable Cd concentration in WsEx, Car, OM and Res. fractions across the duration of the examination was significantly different with incubation time ($p < 0.01$). Cd concentration within the Sorb fraction was significantly different with incubation time at $p \leq 0.05$. Cadmium concentration within the MnOx fraction wasn't significantly different with incubation time ($p = 0.303$, $p > 0.05$). This data indicated that in both soil samples the MnOx fraction failed to differ significantly with time period. The Cd concentration within the AFeOx and CFeOx fractions were below the detection limit of the atomic absorption spectrophotometer in both soil samples which is because of the low tendency of Cd to enter into these fractions at this short term incubation time. In both clay and sandy clay loam soil the WsEx and Sor fractions decreased with passing incubation time while the Car, Om and Res fractions increased (Figs 1 and 2). Within all treatments, there was a general increase within the concentration of Cd-WsEx and Cd-Sorb fractions during the primary period of time of the examination. Cd-WsEx was then followed a sharp decline movement in soil extractable Cd concentration over eight weeks incubation period.

Table 2
Summary of sequential extraction method provided by Ma and Uren (1998) to determine the chemical forms of cadmium

Used solution	Shaking Time	Soil to Solution ratio	Chemical Forms	Row
1M $MgCl_2$, pH = 7.0	1	2:20	Water soluble-Exchangeable (WsEx)	1
1% NaCaHEDTA in 1 M NH_4OAc, pH = 8.3	2	2:20	EDTA extractable (Sorb.)	2
0.2% Quinol in 1 M NH_4OAc, pH = 7.0	2	2:20	Manganese Oxide (MnOx.)	3
0.5 M NaOAc + 0.5 M HOAc, pH = 4.74	3	2:20	Carbonate (Car.)	4
5 ml H_2O_2 30%, pH = 4.74, digested twice at 85°C and extracted by 0.5 M NaOAc – 0.5 M HOAc	1	2:20	Organic matter (OM)	5
0.175 M $(NH_4)_2C_2O_4$ + 0.100 M $H_2C_2O_4$, pH = 3.25	4	2:20	Amorphous Iron Oxides (AFeOx.)	6
0.175 M $(NH_4)_2C_2O_4$ + 0.100 M $H_2C_2O_4$ + 0.1 M Ascorbic acid, boiling Water bath	0.5	2:20	Crystaline Iron oxides (CFeOx.)	7
(3:1 v/v) $HCl:HNO_3$	2	2:20	Residual (Res.)	8

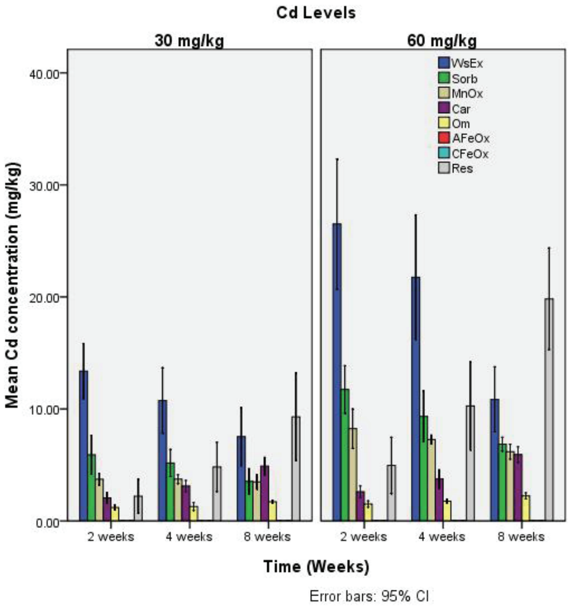

Fig. 1. Effect of incubation time on cadmium chemical fractions in clay soil

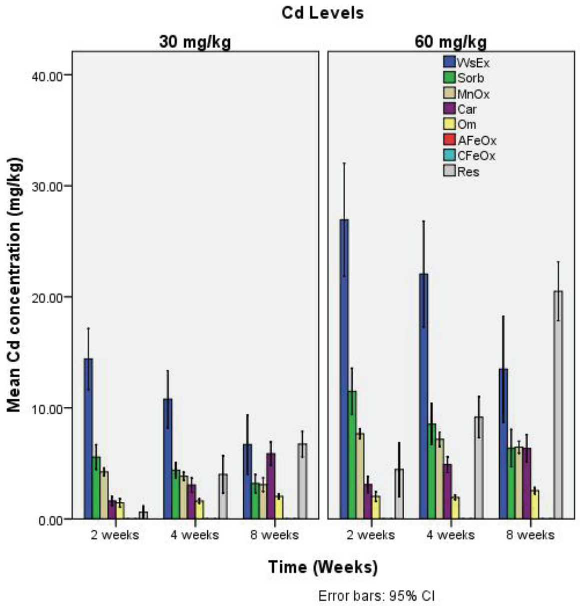

Fig. 2. Effect of incubation time on cadmium chemical fractions in sandy clay loam soil

Table 3
Correlation coefficients between cadmium fractions (mg kg^{-}soil) and incubation time in clay and sandy clay loam soil

Soil			WsEx	Sor	MnOx	Car	Om	AFeOx	CFeOx	Res
Sandy Clay Loam	Time	Pearson Correlation	–.560**	–.499**	–.262	.780**	.464**	.[a]	.[a]	.598**
		Sig. (2-tailed)	.000	.002	.123	.000	.004	.	.	.000
		N	36	36	36	36	36	36	36	36
Clay	Time	Pearson Correlation	–.580**	–.483**	–.230	.871**	.624**	.[a]	.[a]	.699**
		Sig. (2-tailed)	.000	.003	.178	.000	.000	.	.	.000
		N	36	36	36	36	36	36	36	36

**. Correlation is significant at the 0.01 level (2-tailed).
a. Cannot be computed because at least one of the variables is constant.
*. Correlation is significant at the 0.05 level (2-tailed).

The correlation between Cd fractions and incubation time indicated that the Car>Res>WsEx>OM>Sor fractions have the good coefficient of correlation with the incubation times within the clay soil, within the order given in both sample soil. The MnOx fraction has not shown a big correlation with the incubation time within the both sample soil (Table 3). Lu et al. (2005) added 500 mg·kg^{-1} of Cu, Zn and Pb and 2.5 mg·kg^{-1} of Cd to soils in three areas of tropical regions of China, and examined the chemical fractions of those metals during an 8-week time period. Their results showed three hours after incubation most of the metals were within the exchangeable fraction. Cadmium was slowly converted into other fractions while the opposite metals were quickly transformed.

3.2. Effect of P on Cd fractions

Adding P to the tested soil samples reduced the Cd concentration within the WsEx and Sorb fractions while increased Car, OM and Res fractions but had no significant effect on MnOx fractions (Figs 3 and 4). Changes within the Cd concentration in chemical fractions as influenced by monocalcium phosphate followed an analogous trend in both tested soils which suggests that soil properties don't have a big effect on the influence of P. The correlation between P and Cd concentration in Cd chemical fractions in both sample soils has shown in Table 4. The coefficient of correlation between P and WsEx, Car, OM and Res fractions in sandy clay loam soil was beyond clay soil. Within the sandy clay loam, the effect of P level on Cd concentration in Cd chemical fractions is OM>WsEx>Res>Car>Sorb supported the coefficient of correlation while within the clay soil the arrangement is WsEx>Sorb >Res>OM>Car. It seems that the formation of cadmium phosphate ($Cd_3(PO_4)_2$) and Octavite ($CdCO_3$) minerals in soils with high levels of phosphorus and also in Cd contaminated soils with added phosphorus controls the solubility of Cd in these soils. Studies show that cadmium phosphate with a solubility coefficient of 38.1 is more practical than ottavite with a solubility coefficient of 11.3 in reducing Cd solubility in contaminant soils. Phosphorus appears to be able to transmit a portion of the Cd in soil via ottavite formation into the carbonate fraction and a portion of that via cadmium phosphate formation into the residual fraction. Zhao et al. (2020) showed that application of calcium magnesium phosphate fertilizer can effectively inhibit Cd accumulation in root protoplasts by promoting iron plaque formation on the root surface, reduce Cd concentration and increase free amino acids in rice grains. Yao et al. (2022) showed that exchangeable and carbonate bound fractions of Cd and Pb in the soil sample after slow-release phosphate amendments application significantly reduced, while the residual fraction increased, indicating the stability of heavy metals increased. Lambert et al. (1997) added phosphorus from Apatite and potassium phosphate into sewage sludge and examined the cadmium and copper chemical forms. The authors reported that adding potassium phosphate with 1:4 ratio (P: Cd) reduced the Cd concentration within the exchangeable, manganese and iron chemical forms and increased the carbonate and residual forms.

4. Conclusions

A significant portion of the additional Cd was removed from the WsEx and Sorb fractions, but over time, it gradually changed into other non-labile Cd fractions. After two weeks, the WsEx fraction had removed over 50% of the additional Cd. With longer incubation times, the Cd concentration in the WsEx and Sorb fractions changed into the Car, OM, and Res fractions. Increasing Cd levels led to higher Cd concentrations in both soil samples across all Cd chemical components. The maximum ability of the soil samples to adsorb and retain Cd can be seen when all of the Cd chemical fractions are increased at the beginning of the experiment. Phosphorous raised the Car, OM, and Res fractions while increasing the WsEx and Sorb fractions' Cd concentrations, but had no discernible effect on the MnOx fraction.

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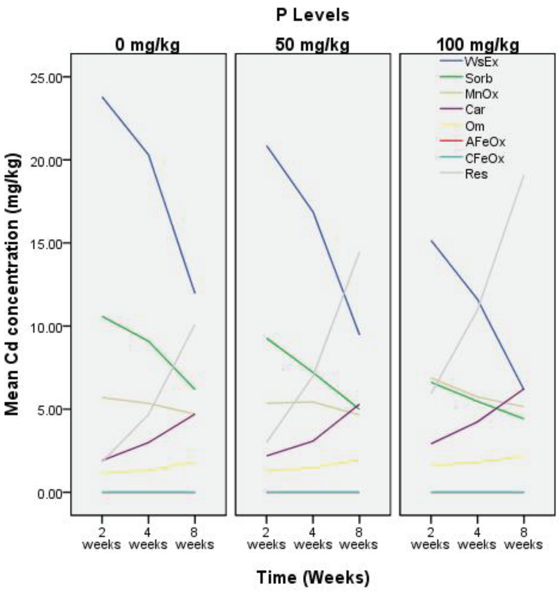

Fig. 3. Effect of phosphorus on cadmium chemical forms in clay soil

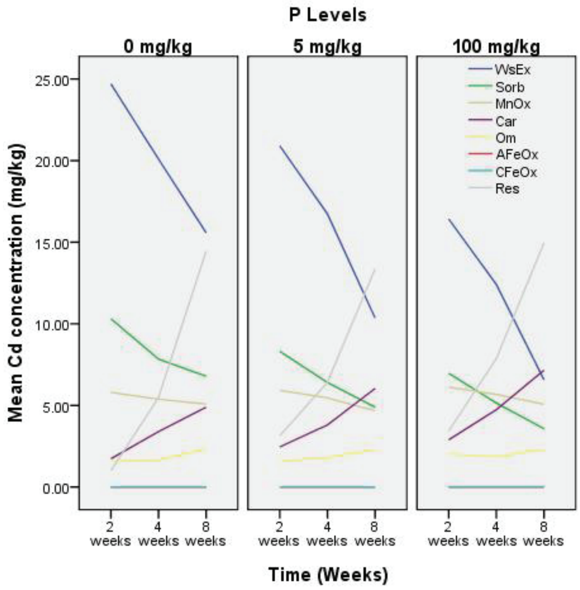

Fig. 4. Effect of phosphorus on cadmium chemical forms in sandy clay loam soil

Table 4
Correlation coefficients between cadmium fractions (mg kg^{-1} soil) and phosphorus.

Soil			WsEx	Sor	MnOx	Car	Om	AFeOx	CFeOx	Res
		Pearson Correlation	-.427**	-.388*	.078	.408*	.430**	.[a]	.[a]	.426**
Sandy Clay Loam	P	Sig. (2-tailed)	.009	.019	.650	.013	.009	.	.	.010
		N	36	36	36	36	36	36	36	36
		Pearson Correlation	-.417*	-.415*	.135	.356*	.409*	.[a]	.[a]	.412*
Clay	P	Sig. (2-tailed)	.011	.012	.434	.033	.013	.	.	.013
		N	36	36	36	36	36	36	36	36

**. Correlation is significant at the 0.01 level (2-tailed).
a. Cannot be computed because at least one of the variables is constant.
*. Correlation is significant at the 0.05 level (2-tailed).

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