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Cadmium Chemical Forms in Two Calcareous Soils Treated with Different Levels of Incubation Time and Moisture Regimes

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Abstract

Sequential extraction is used effectively to determine the chemical forms of heavy metals. Since few studies have been conducted in calcareous soils of Iran, the current research has been carried out to evaluate the effect of moisture regimes and incubation time on the chemical forms of cadmium in two calcareous soils. Treatments included three levels of cadmium (0, 30 and 60 mg/kg of soil as $CdSo_4$), three incubation times (2, 4 and 8 weeks), two soils (clay and sandy clay loam) and two moisture regimes (Waterlogged and Field capacity). The experiment was performed as factorial on the basis of randomized complete blocks design with two replications. At 2, 4, and 8 weeks after treatment, the Tessier *et al.* (1979) sequential extraction method was applied to measure the cadmium concentration in water soluble-exchangeable (WsEx.), iron and manganese oxide (Fe-MnOx.), carbonate (Car.), organic matter (Om.) and residual forms (Res.). The results showed depending on the soil texture, 68 to 72 percent of the cadmium was in water soluble-exchangeable and iron-manganese oxide forms. Flooding condition decreased the concentration of cadmium in water soluble + exchangeable form and increased the concentration of cadmium in the forms of Fe-Mn oxides, carbonate and organic matter. Concentration of cadmium in residual form was higher in clay soil. In sandy clay loam soil, water soluble-exchangeable, carbonate and organic matter forms were higher than clay soil. The iron-manganese oxides form showed no significant difference in two soils at field capacity regime. In flooding conditions, the concentration of the water soluble-exchangeable form decreased and the concentration of other forms increased. In contrast to the oxidizing conditions at the reduction conditions, no significant difference was observed in the residual and organic matter forms in two soils.

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Keywords

Cadmium, Chemical Forms, Flooding, Sequential Extraction, Waterlogged

1. Introduction

Cadmium is a non-essential element which is absorbed by plants [1]. Changing in moisture regimes in soil has a large effect on soil redox potential and as a result on metal solubility [2]. At highly reducing condition in soil, Cd solubility decreases due to formation of Cd-sulphide complexes [3] [4]. Insoluble Fe^{3+} and Mn^{4+} hydrous oxides in aerobic soils provide sorption surface for Cd and other metals' ions [5] [6] [7] [8]. At flooding condition and decreasing redox potential, Mn^{4+} and Fe^{3+} become reduced to more soluble oxidation states Mn^{2+} and Fe^{2+} [6] [7] [8]. Dissolution of Mn and Fe hydrous oxides releases the co-sorbed metal ions into soil solution and increasing metal absorption by plants. Zn dynamic in soil is based on organic matter, pH and soil clay contents. Fe, Mn and Al oxides, clays and organic matter prepare sorption surfaces for adsorbing Zn [9]. By increasing Mn^{2+} and Fe^{2+} in aerobic condition, Zn can be precipitate in forms with less solubility [10]. As the Mn^{2+} and Fe^{2+} forms are more soluble than the oxidized forms, they compete with Zn for sorption sites on the organic matter [17]. Cadmium and Zinc have similar chemical characteristics; they both are absorbed by plants and are retained in soil exchangeable sites as a divalent cation [18]. Adjusting pH by land flooding has positive effects on Zn availability [19]. Submerging alkaline soil causes decreasing in soil pH; organic matter acts as an electron donor while ferric ion acts as an electron receptor [20]. This process increases carbon dioxide and decreases soil pH [21]. Because of the limited diffusion in the standing water on the soil surface, CO_2 is remained in the soil causes mild acidity which neutralizes soil pH and solubilises Zn [22]. Depleting oxygen during the flooding periods decreases Eh [23] [24]. The objectives of this research were to examine the effect of incubation time and moisture regime on cadmium chemical forms in two calcareous soils.

2. Materials and Methods

2.1. Soil

In order to execute this research, two types of soils (top soil, a depth of 0 to 25 cm) were collected from Sarvestan series and Kamfiroz series of Fars province, Iran. Soils in the Classification [11], are Calcic Haploxeralfs and different in terms of texture, Cation exchange capacity (CEC), and calcium carbonate equivalent (CCE). Soil samples were air dried and passed from a 2 mm sieve. Soils texture by the hydrometer method [12], electrical conductivity (EC) in the 1:1 soil - water suspension [13], carbonate calcium equivalent (CCE) by the hydrochloric acid neutralizing method [14], pH by the 1:1 suspension of soil - water [14], organic carbon by the method of Walkaly and Black [15] and available

Fe, Mn, Cu, Zn and Cd extracting with the 0.005 M DTPA [16] were determined (Table 1).

2.2. Test of Incubation Time on Cadmium Chemical Forms at Field Capacity Regime

The experiment was accomplished as factorial on the basis of randomized complete blocks design with tow replications. The factors were three levels of Cd (0, 30 and 60 mg/kg of soil) and three levels of incubation times (2, 4 and 8 weeks). The incubation experiment was carried out in plastic beaker. Each pot (0.5 kg soil) was treated with three levels of Cd from cadmium sulfate source (Merck Co. Germany) and were placed in Field Capacity (33 kPa) situation. The pots were covered by porous plastic sheets. To prevent the fast evaporation of soil samples, the pots were placed in an incubator at 25˚C temperature. The moisture content of the samples was checked every two days and the soils were mixed well every 5 days.

2.3. Test of Incubation Time on Cadmium Chemical Forms at Waterlogged Regime

The experiment was accomplished as factorial on the basis of randomized complete blocks design with tow replications. The factors were three levels of Cd (0, 30 and 60 mg/kg of soil) and three levels of incubation times (2, 4 and 8 weeks). The incubation experiment was carried out in plastic beaker. Each pot (0.5 kg soil) was treated with three levels of Cd from cadmium sulfate source (Merck Co. Germany) and was placed in flooding situation (waterlogged). For flooding

Table 1. Selected chemical properties of soils used.

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

(FD) regime, deionized water was added to the soil samples to create a 5 cm layer of water above the soils. The pots were covered by porous plastic sheets. To prevent the fast evaporation of soil samples, the pots were placed in an incubator at 25˚C temperature. The moisture content of the samples was checked every two days and the soils were mixed well every 5 days.

3. Sequential Extraction Procedure

Soils were sampled at 2, 4 and 8 weeks after the beginning of treatments, The sequential extraction proposed by Tessier [25] was used in this study, The chemical fractions of heavy metals are defined in (**Table 2**). Extractions were put in 100 ml centrifuge tubes. Between each consecutive extraction, the supernatant was centrifuged for 30 min at 4000 r/min and then purified. The total cadmium concentration in soils were determined by digesting 0.5 g soil samples (oven dry weight) with HNO3_HF_HClO4 mixture accompanied by elemental analysis, the concentrations of Cd in all solutions were studied by an atomic absorption spectrophotometer (AA 670).

Statistical Analysis

Statistical analysis was performed with SPSS Version 16.0 statistic software package. Data were demonstrated as means ± standard deviation (SD). Differentiations between groups were performed with analysis of non-parametric test. A value of $P < 0.05$ was regarded statistically significant. The Duncan's multiple range tests used to decide statistical significance of the effects due to treatments and their interaction.

4. Results and Discussion

4.1. Effect of Time on Chemical Forms of Cadmium at Field Capacity Regime

The results showed significant effect of incubation time on the cadmium forms in soil. Through time, some forms followed a steady trend upward or downward (**Figure 1** and **Figure 2**). In both textures and at all levels of cadmium, the water

Table 2. Summary of the sequential extraction method provided by Tessier and *et al.* (1979) to determine the chemical forms of cadmium.

Row	Chemical forms	Time (h)	Temperature (˚C)	Soil (g)/Solution Volume (ml)	Used solution
1	Water Soluble and Exchangeable WsEx.	1	25	16	$MgCl_2$ (1 mol/l), pH = 7
2	Carbonate Car.	5	25	16	NaOAc (1 mol/l), pH = 5
3	Iron and Manganese Oxides Fe-MnOx.	6	96	16	$NH_2OH{\cdot}HCl$ (0.04 mol/l) in HOAc (%25 v:v), pH = 2
4	Organic Om.	5.5	85	16	3 ml HNO_3 (0.02 mol/l), 8 ml H_2O_2 (%30), pH = 2, 5 ml NH_4OAc (3.2 mol/l)/HNO_3 (%20 v in v)
5	Residual Res.	2	130	16	(3:1 v/v) $HCl:HNO_3$

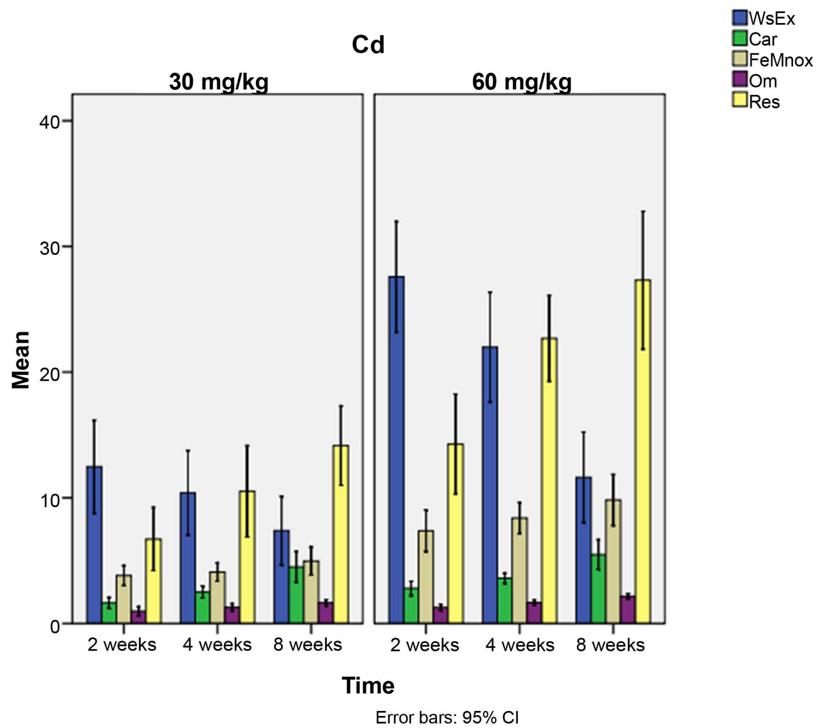

Figure 1. Effect of 30 and 60 mg Cadmium on the chemical forms of Cadmium in Clay soil in three Incubation times at FC condition.

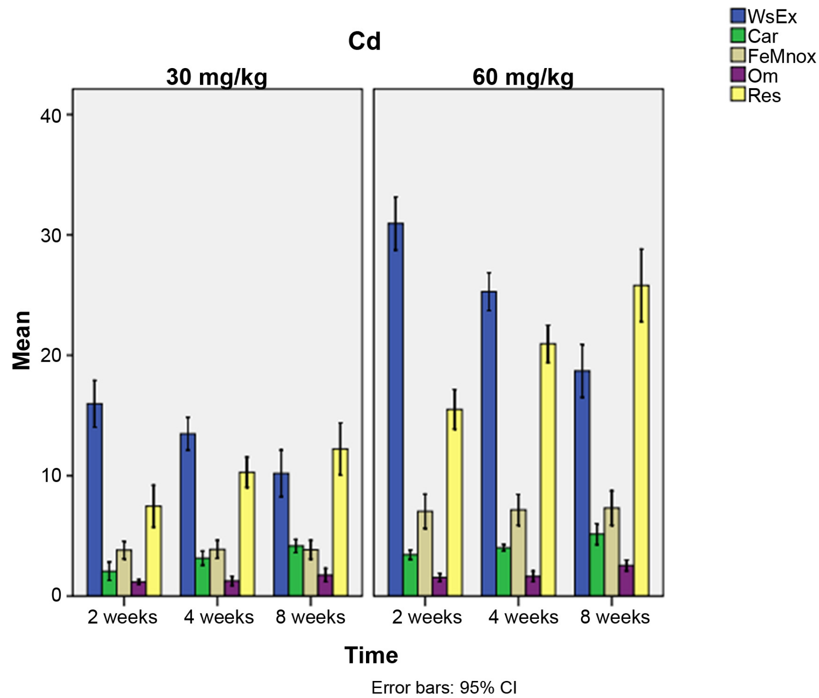

Figure 2. Effect of 30 and 60 mg Cadmium on the chemical forms of Cadmium in sandy clay loam soil in three Incubation times at FC condition.

soluble-exchangeable form decreased significantly from 15.57 and 16.15 to 8.64 and 9.39 ppm for clay and sandy clay loam respectively and the concentration of cadmium in carbonate, organic matter and residual forms increased after 8 weeks of incubation time. The iron and manganese oxides form in both soils did not differ significantly. The correlation coefficients between chemical forms of cadmium and time with Pearson test showed that the carbonate, water soluble-exchangeable and residual forms had the highest correlation coefficient with incubation time in both soils, respectively. Coefficients of correlation between chemical forms of cadmium and incubation time in clay soil were higher than sandy clay loam soil (**Table 3** and **Table 4**). Such data were not unexpected, as the deformations of the soluble metals through time and their conversion into less solubility forms were also reported by other researchers [26] [27] [28]. Lim *et al.* 2002 [29] observed that although increasing the shaking time from 1 to 7, 15, 30, 50 and 65 days did not have a significant effect on the adsorption of lead and cadmium, but it converted high-solubility metal forms into less soluble forms. However, there was no compelling reason to change the concentration of other forms, but it may be possible to attribute changes of other forms to the dynamics of organic compounds of the soil. In other words, the formation and decomposition of organic matter complexes with metal can be effective in combining or releasing metals in the soil and, in turn, affect the relative amount of other forms. This is clear in soils treated with organic wastes. The effect of incubation time on cadmium chemical forms was different. The passing of time reduced the water soluble-exchangeable form in both soils. Lu *et al.* 2005 [30] added 500 mg/kg of copper, zinc and lead and 2.5 mg/kg of cadmium to three areas of tropical regions of China, and examined the chemical forms of these metals during 8-week incubation period. The results showed that, three hours after incubation the main part of metals was in the exchangeable form. Cadmium was slowly converted to other forms while other metals quickly turned into other chemical forms. After adding cadmium to the soils, a significant amount

Table 3. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and incubation time in clay soil at FC condition.

	Time	WsEx	Car	FeMnox	Om	Res
Pearson Correlation	1	−0.628**	0.803**	0.000	0.684**	0.634**
Sig. (2-tailed)		0.000	0.000	1.000	0.000	0.000
N	36	36	36	36	36	36

**Is significant at 0.01 level.

Table 4. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and incubation time in sandy clay loam soil at FC condition.

		Time	WsEx	Car	FeMnox	Om	Res
	Pearson Correlation	1	−0.373*	0.744**	0.000	0.602**	0.417*
Time	Sig. (2-tailed)		0.025	0.000	1.000	0.000	0.011
	N	36	36	36	36	36	36

** and * are significant at 0.01 and 0.05 level respectively.

of Cadmium was entered into the water soluble-exchangeable form and then, gradually separated from this form and entered into other forms. As much as 50% of added cadmium to the soils was extracted in a water soluble-exchangeable form after 2 weeks. With increasing duration time, cadmium concentration in this form was reduced and entered into carbonate and organic and residual forms (Table 3 and Table 4).

4.2. Effect of Incubation Time on Chemical Forms of Cadmium at Waterlogged Regime

Statistical data showed, flooding condition decreased the concentration of cadmium in water soluble + exchangeable form and increased the concentration of cadmium in the forms of Fe-Mn oxides, carbonate and organic matter (Figure 3 and Figure 4). As it can be seen, the iron and manganese oxides form in clay soil is significantly different over the time, but there is no significant difference in sandy clay loam soil. The correlation coefficients between chemical forms of cadmium and incubation time with Pearson test showed that the carbonate, water soluble-exchangeable, residual, organic matter and iron and manganese oxides forms had the highest correlation coefficient with incubation time in clay soils, respectively. In sandy clay loam soil the carbonate, organic matter, water soluble-exchangeable and residual forms had the highest correlation coefficients with incubation time, respectively. The iron and manganese oxides form did not show significant correlation with incubation time in sandy clay loam soil (Table 5 and Table 6). Results from our study show that Cd is associated with carbonates, ferrihydrite, humic acid, and CdS during flooding period. Number of Cd

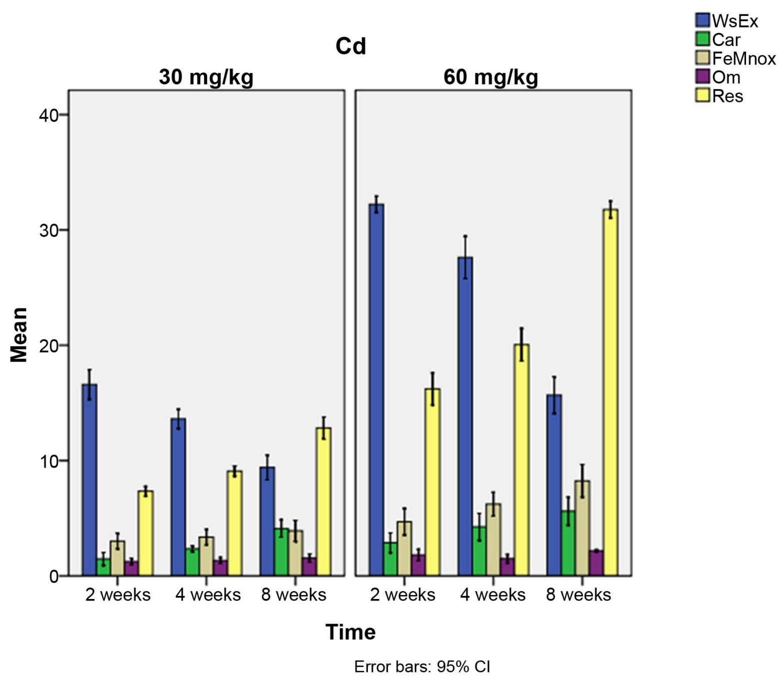

Figure 3. Effect of 30 and 60 mg Cadmium on the chemical forms of Cadmium in Clay soil in three Incubation times at waterlogged condition.

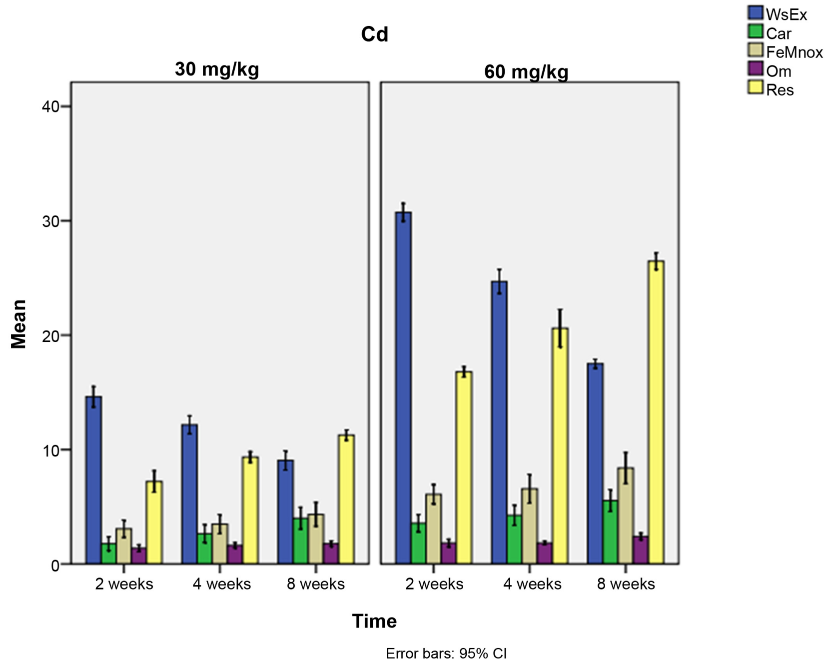

Figure 4. Effect of 30 and 60 mg Cadmium on the chemical forms of Cadmium in sandy clay loam soil in three Incubation times at waterlogged condition.

Table 5. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and incubation time in clay soil at waterlogged condition.

		Time	WsEx	Car	FeMnox	Om	Res
	Pearson Correlation	1	−0.598**	0.810**	0.357*	0.362*	0.525**
Time	Sig. (2-tailed)		0.000	0.000	0.033	0.030	0.001
	N	36	36	36	36	36	36

** and * are significant at 0.01 and 0.05 level respectively.

Table 6. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and incubation time in sandy clay loam soil at waterlogged condition.

		Time	WsEx	Car	FeMnox	Om	Res
	Pearson Correlation	1	−0.536**	0.774**	0.157	0.582**	0.360*
Time	Sig. (2-tailed)		0.001	0.000	0.361	0.000	0.031
	N	36	36	36	36	36	36

** and * are significant at 0.01 and 0.05 level respectively.

complexes with humic acids released into soil solution during flooding condition due to slight decrease in pH and remarkable increase in Eh. Carbonate minerals and organic matters adsorb the amount of Cd released from humic substances. These findings are supported by results from studies by *Jung and Thornton* 1997 [31] that showed under anaerobic conditions (flooding), Cd largely bound to Fe-Mn (hydr) oxides. Flooding leads to decreasing exchangeable Cd while increasing the concentration of Cd in Fe-Mn (hydr) oxides and organic matter forms. Evolution of reducing condition in soil causes a decrease Cd solubility over the formation of CdS complexes [3] [4]. *Guo et al.* 1997 [32] showed that with decreasing Eh in 60 days suspension experiments, Cd bound to carbonate, humic substances and sulfide increased while Cd bound to Fe-Mn (hydr) oxides form decreased.

4.3. Effect of Different Levels of Cadmium on the Chemical Forms of Cadmium

In both soils, and at all times, with increasing cadmium levels, all the chemical forms of cadmium increased significantly. Increasing in all chemical forms of cadmium, at the beginning of the experiment indicates a rapid achievement of the balance and precipitation of cadmium in the form of mineral phases. This shows the high capacity of the soils to absorb and maintain cadmium. However, in soils with light texture, the presence of metals such as cadmium in the more usable forms has been reported by other researchers [33] [34] [35] but the effect of cadmium levels on the chemical forms of this element has been considered less. In the present experimental conditions, the effect of cadmium levels on the distribution of the chemical forms of Cadmium can be attributed to the different capacities of soil components for the storage of cadmium. In other words, due to the limited capacity of some soil components to maintain cadmium, by increasing the level of this element, cadmium enters the components that have more capacity to maintain the element. As can be seen, the correlation between cadmium levels and water soluble-exchangeable, iron and manganese oxides and organic matter forms in clay soil are higher than sandy clay loam and in sandy clay loam the residual form is higher than clay soil at field capacity regime (**Table 7** and **Table 8**). Correlation between cadmium levels and all cadmium chemical forms in sandy clay loam are higher than clay soil at waterlogged regime (**Table 9** and **Table 10**).

Table 7. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and cadmium levels in clay soil at FC condition.

		Cd	WsEx	Car	FeMnox	Om	Res
Cd	Pearson Correlation	1	0.788**	0.508**	0.888**	0.487**	0.637**
	Sig. (2-tailed)		0.000	0.002	0.000	0.003	0.000
	N	36	36	36	36	36	36

**Is significant at 0.01 level.

Table 8. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and cadmium levels in sandy clay loam soil at FC condition.

		Cd	WsEx	Car	FeMnox	Om	Res
Cd	Pearson Correlation	1	0.753**	0.508**	0.858**	0.411**	0.641**
	Sig. (2-tailed)		0.000	0.002	0.000	0.004	0.000
	N	36	36	36	36	36	36

**Is significant at 0.01 level.

Table 9. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and cadmium levels in clay soil at waterlogged condition.

		Cd	WsEx	Car	FeMnox	Om	Res
	Pearson Correlation	1	0.738**	0.500**	0.811**	0.486**	0.790**
Cd	Sig. (2-tailed)		0.000	0.002	0.000	0.003	0.000
	N	36	36	36	36	36	36

**Is significant at 0.01 level.

Table 10. Correlation coefficients between chemical forms of cadmium (mg/kg soil) and cadmium levels in sandy clay loam soil at waterlogged condition.

		Cd	WsEx	Car	FeMnox	Om	Res
	Pearson Correlation	1	0.793**	0.538**	0.821**	0.542**	0.880**
Cd	Sig. (2-tailed)		0.000	0.001	0.000	0.001	0.000
	N	36	36	36	36	36	36

**Is significant at 0.01 level.

4.4. Effect of Soil Texture on Cadmium Chemical Forms

The average of the data showed that the concentration of cadmium in residual form was higher in clay soil. In sandy clay loam soil, water soluble-exchangeable, carbonate and organic matter forms were higher than clay soil. The Iron-manganese oxides form showed no significant difference in two soils at field capacity regime (Table 11). In flooding conditions, the concentration of the water soluble-exchangeable form decreased and the concentration of other forms increased. In contrast to the oxidizing conditions, at the reduction conditions no significant difference was observed in the residual and organic matter forms in two soils (Table 12). Also, the results showed that in all treatment for clay soil

Table 11. Impact of soil texture on chemical forms of cadmium at FC condition.

Cadmium Chemical Forms mg/Kg					
Soil	WsEx	Car	Fe-MnOx	Om	Res
Sandy clay loam	20/32a	3/48a	5/29a	1/75a	13/18b
Clay	18/14b	3/14b	5/15a	1/46b	15/96a

The numbers in each column have a common alphabet do not differ significantly from the Duncan test at 5% level.

Table 12. Impact of soil texture on chemical forms of cadmium at waterlogged condition.

Cadmium Chemical Forms mg/Kg					
Soil	WsEx	Car	Fe-MnOx	Om	Res
Sandy clay loam	18/89a	3/99a	5/72a	1/98a	15/10a
Clay	17/34b	3/56b	5/65a	1/82a	16/26a

The numbers in each column have a common alphabet do not differ significantly from the Duncan test at 5% level.

and sandy clay loam, 68.98% and 70.89% of added cadmium to soils were extracted by three first extractants. With a little attention to these data, it becomes clear that in both soils, a major portion of cadmium was associated with water soluble-exchangeable, Iron-manganese oxides and carbonates forms, which indicate of high bioavailability of cadmium in the soils. Because these forms compared to others are extracted with a weaker extractor s which are not very acidic. Through the mentioned forms, the water soluble-exchangeable was the dominant form. Almost all cadmium was removed by three first relatively weak extractors. The higher concentration of Cadmium in water soluble-exchangeable and carbonate forms in the sandy clay loam also reflects the greater bioavailability of cadmium in light texture soils, which has been reported by other researchers [35] [36] [37].

5. Conclusion

After adding cadmium to the soils, a significant amount of this metal was entered into water soluble-exchangeable form and gradually separated from this form and entered into other forms. As much as 50% of the added cadmium was extracted in the water soluble-exchangeable form after two weeks. With increasing time, the cadmium concentration in this form was reduced and cadmium was entered into carbonate, organic and residual forms. In both textures and at all times, with increasing cadmium levels, all the chemical forms of cadmium increased significantly. The increase of all chemical forms of cadmium at the beginning of the experiment indicates a rapid achievement of the equilibrium and precipitation of cadmium in the form of mineral phases, which shows the high capacity of the soils to absorb and maintain cadmium. Flooding condition decreased the concentration of cadmium in water soluble + exchangeable form and increased the concentration of cadmium in the forms of Fe-Mn oxides, carbonate and organic matter. Concentration of cadmium in residual form was higher in clay soil. In sandy clay loam soil, water soluble-exchangeable, carbonate and organic matter forms were higher than clay soil. The iron-manganese oxides form showed no significant difference in two soils at field capacity regime. In flooding conditions, the concentration of the water soluble-exchangeable form decreased and the concentration of other forms increased. In contrast to the oxidizing conditions at the reduction conditions, no significant difference was observed in the residual and organic matter forms in two soils.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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