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Changes in DTPA extractability of added cadmium in two different soil types treated with wheat straw in sterile and unsterile conditions

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Cambios en la extracción de Cd con DTPA en dos suelos tratados con paja de trigo bajo condiciones estériles y no estériles
Alterações na extração de Cd com DTPA em dois solos tratados com palha de trigo em condições de esterilização e não esterilização

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ABSTRACT

Heavy metals in soluble form have the highest bioavailability and toxicity in soil. DTPA-extractable Cd was investigated in two different soil types treated with wheat straw (5%) under sterile and unsterile conditions. Soils were located in Hamadan (Iran, 48º 28' 23" E and 34º 56' 48" N), a fallow cropland with a semi-arid climate, and Lahijan (Iran, 50º 1' 51" E and 37º 11' 59" N), a tea plantation with a temperate climate. DTPA-extractable Cd in contaminated soils (10 mg Cd kg^{-1}) was measured from 1 minute to 3,600 hours. During the soil incubation period, DTPA-extractable Cd was higher in the Lahijan soil, but at the end of the soil incubation period it was higher in the Hamadan soil. The positive effect of wheat residue on DTPA-extractable Cd was higher in the Lahijan unsterile soil at the end of the soil incubation period. The decrease of DTPA extractability of the added Cd was lower in the Lahijan soil incubated under unsterile conditions compared to that under sterile conditions. In contrast, Hamadan sterile soil treated and untreated with wheat residue had the highest DTPA-extractable Cd at the end of the soil incubation period. The decrease in DTPA extractability of the added Cd in soils was exponential with 3 steps. In the 1st step the highest and the lowest rates of DTPA decrease were observed in Hamadan sterile and Lahijan unsterile soils treated with wheat residue. In the 3rd step it was reversed, and the decrease in DTPA extractable Cd was lower in the Hamadan soil compared to the Lahijan soil.

RESUMEN

Las formas solubles de metales pesados son las que tienen mayor biodisponibilidad y toxicidad en suelos. En este trabajo se estudió la extracción de Cd con DTPA en dos suelos diferentes (Lahijan y Hamadan) tratados o no con paja de trigo (5%) bajo condiciones estériles y no estériles, previamente contaminados (10 mg Cd kg^{-1}). Los suelos estudiados se localizaban en Hamadan (Irán, 48º 28' 23" E and 34º 56' 48" N), en barbecho con clima semiárido, y Lahijan (Irán, 50º 1' 51" E and 37º 11' 59" N), en una plantación de té con clima templado. Se midió el Cd extraíble con DTPA en los suelos contaminados durante su incubación en un intervalo de 1 minuto a 3600 horas. La química del Cd soluble que se añadió en los suelos del estudio difirió según el tratamiento. Durante la incubación, el Cd extraíble con DTPA en el suelo Lahijan fue mayor que en el suelo Hamadan pero al final de la incubación fue a la inversa. El efecto positivo del residuo de trigo sobre el Cd extraíble con DTPA fue mayor en el suelo Lahijan bajo condiciones no estériles al final de la incubación. La disminución de la cantidad de Cd extraíble con DTPA fue menor en el suelo Lahijan incubado bajo condiciones no estériles que bajo condiciones estériles. Por

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el contrario, el suelo Hamadan bajo condiciones estériles tuvo la mayor cantidad de Cd extraíble con DTPA al final de la incubación. La disminución de la extracción de Cd con DTPA en los suelos estudiados fue exponencial con 3 etapas. En la primera etapa, la mayor disminución se observó el suelo Hamadan tratado con paja de trigo en condiciones estériles y la menor disminución en el suelo Lahijan en condiciones no estériles. En la tercera etapa esta tendencia se invirtió y se observó una disminución del Cd extraíble con DTPA menor en el suelo Hamadan comparado con el suelo Lahijan.

RESUMO

As formas solúveis de metais pesados são aquelas que apresentam maior biodisponibilidade e toxicidade nos solos. Neste trabalho estudou-se a extração do Cd com DTPA em dois solos diferentes (Lahijan e Hamadan), tratados ou não com palha de trigo (5%) sob condições de esterilização e não esterilização, anteriormente contaminados (10 mg kg^{-1} Cd). O Cd extraível com DTPA foi medido em solo contaminado durante uma incubação num intervalo de 1 minuto a 3600 horas. A química do Cd solúvel que foi adicionado aos solos do estudo diferiu de acordo com o tratamento. Durante a incubação, o Cd extraível com DTPA no solo Lahijan foi maior que no solo Hamadan, mas no final da incubação verificou-se o inverso. O efeito positivo do resíduo de trigo no Cd extraível com DTPA foi maior no solo de Lahijan em condições não estéreis no final da incubação. A diminuição da quantidade de Cd extraível com DTPA foi menor no solo de Lahijan incubado sob condições de não esterilização do que sob condições estéreis. Pelo contrário, o solo de Hamadan sob condições de esterilização apresentava a maior quantidade de Cd removível com DTPA no final da incubação. A diminuição da extração de Cd com DTPA nos solos estudados foi exponencial com 3 etapas. Na primeira fase, a maior diminuição foi observada no solo de Hamadan tratado com palha de trigo sob condições estéreis e a menor diminuição no solo Lahijan em condições não estéreis. Na terceira fase, esta tendência é invertida e observa-se uma diminuição do Cd extraível com DTPA inferior no solo de Hamadan em comparação com o solo Lahijan.

KEY WORDS
Bioavailability, calcareous soil, plant residue

PALABRAS CLAVE
Biodisponibilidad, suelo calcáreo, residuo de plantas

PALAVRAS-CHAVE
Biodisponibilidade, solo calcário, resíduos de plantas

1. Introduction

Soil, water and air are the 3 important components of terrestrial ecosystems. The type and level of pollutants added daily to natural habitats has increased continuously with industrialization. Soil pollution is also not far from this trend. Many heavy metals such as Cd and Pb are harmful for soil biota. Cadmium toxicity is high and 2 to 20 times greater than any other heavy metal. According to Kabata-Pendias (2011), the Cd maximum allowable concentration (MAC) and trigger action value (TAV) is in the range of 1-5 mg kg^{-1} and 2-20 mg kg^{-1} respectively, depending on the soil type and country considered. Heavy metals in soil have different behaviors. Harmful effects depend on the organism tolerance, buffering capacity of soil, and chemical speciation, mobility, bioavailability, persistence, and type of heavy metal. Heavy metals that have high mobility, such as Cd, can move through soil profile. Their extractability and mobility are higher in soils with low pH (Jopony and Young 1994), sum of exchangeable bases (SB) (de-Matos et al. 2001), specific surface area (Korte et al. 1976), cation exchange capacity (CEC) and organic matter (OM) content (Sidle and Kardos 1977). Cadmium mobility is also higher in soils with high chelating agents and chloride contents (Wasay et al. 1998; Guevara-Riba et al. 2005). Conversely extractability and mobility of heavy metals are lower in soils with high free iron oxides (Amacher et al. 1986) and clay contents (Korte et al. 1976).

The accumulation of excessive Cd in soil and water decreases organic matter biodegradation (Quenea et al. 2009), reduces microbial biodiversity, changes population structure (Andersson and Nilsson 1972) and reduces enzyme activities (Pradip and Subhasish 2008).

Soil biological activities mainly depend on the more active forms and bioavailable fraction of heavy metals in soil. The contamination factor (Cf) of a heavy metal or the ratio between the more active forms of heavy metals and their total content or residual and inactive forms is used to estimate the relative mobility, availability and retention time of the metal in soil, since the total metal content in soils is not an important or comprehensive environmental risk assessment index (Safari-Sinegani and Jafari Monsef 2016).

Fresh and humified organic matter (OM) in soils have different effects on various heavy metals. These diverse interactions between heavy metals and soil OM result in differing heavy metal solubility in soils with similar OC contents (Catlett et al. 2002). Fresh organic materials such as manure and plant residue with abundant soluble organic compounds and metals can change the forms and fractions of heavy metal to more active forms (Almas et al. 1999; Clemente et al. 2006; Safari Sinegani et al. 2016). Well transformed organic matter such as compost and peat, having more stable humic materials, could reduce the availability of heavy metals by adsorbing and creating organo-metal complexes (Shuman 1999). Soils with a high level of organic matter leads to higher organically bound Zn, Cu, Cd and Pb fractions extracted with H_2O_2 + HNO_3 (Lu et al. 2005). In our previous study, organically bound Cd (NaOH extractable) was higher in the soils treated with wheat residue compared to that in the untreated soils. Soluble and exchangeable Cd (KNO_3 extractable) was lower in the wheat residue treatment. The carbonate associated form of Cd (EDTA extractable) was lower in the Hamadan (semiarid) soil for wheat residue treatment. However in the Lahijan (temperate) soil it was higher for the wheat residue treatment (Safari-Sinegani and Jafari Monsef 2016). These heavy metal fractions may be extractable by DTPA and available for soil macro- and micro-biota depending on soil type and soil biota tolerance (Lindsay and Norvell 1978; Miles and Parker 1979; Benavides et al. 2005; Honma et al. 2015). In this study the changes of DTPA-extractable Cd in two spiked soils with dissimilar characteristics were examined after the addition of wheat residue (as a common organic matter residue) in sterile and unsterile conditions. The aim was to elucidate the relative importance the soil physicochemical properties on bioavailability of the added Cd in soluble form.

2. Material and methods

In this study, two combined soil samples in three replicates were sampled from the 0-15 cm layer of a fallow cropland in Hamadan (48° 28' 23" E and 34° 56' 48" N) with a semi-arid climate, and a tea plantation in Lahijan (50° 1' 51" E and 37° 11' 59" N) with a temperate climate. Soil samples were air dried, crushed and sieved (2 mm). Before soil treatment, some of the physical, chemical and biological properties of the sampled soils were analyzed with standard methods reported previously (Safari-Sinegani and Jafari Monsef 2016). Briefly, analysis of sand, silt, and clay percentages in the Hamadan (58, 24, and 18%, respectively) and Lahijan (24, 46, 30%, respectively) soils showed that the texture these soils were sandy loam and clay loam respectively. Hamadan soil had higher pH (7.7) and calcium carbonate equivalent (CCE) (19.83%) compared to the Lahijan soil (5.6 and 1.22%, respectively). The cation exchange capacity of the Lahijan soil was (29.7 $cmol_c$ kg^{-1}) higher than the Hamadan soil (12.1 $cmol_c$ kg^{-1}). The Lahijan soil had also higher organic carbon (21.69 g kg^{-1}) and total nitrogen (1.52 g kg^{-1}) than the Hamadan soil (7.91 and 0.74 g kg^{-1} respectively). The numbers of colony forming units (CFU) counted on plates with solid media for bacteria, actinomycetes and fungi were also higher in the Lahijan soil. Log CFU g^{-1} soil for bacteria, actinomycetes and fungi were 6.40, 4.62 and 4.99 respectively in the Lahijan soil, and 6.39, 4.14 and 4.24 respectively in the Hamadan soil. Basal respiration and substrate induced respiration determined by CO_2 trapping in NaOH solution in sealed glass jars were 2.44 and 421.8 mg CO_2 kg^{-1} soil day^{-1} respectively in the Lahijan soil and 1.41 and 232.4 mg CO_2 kg^{-1} soil day^{-1} respectively in the Hamadan soil. Total Cd concentration in two sampled soils (background level) was so low that it was not detectable by HNO_3 (4 M) extraction and atomic absorption on a Varian 220 instrument using an air-acetylene flame, with a detection limit of 0.01 ppm.

Ground and sieved (2 mm) wheat straw electrical conductivity (EC) and pH were measured in a 1:10 extract. Wheat straw properties were as follows: pH 7.27, EC 4.02 (dS m^{-1}), soluble OC 23.3 (g kg^{-1}), total OC 533.33 (g kg^{-1}),

TN 5.78 (g kg^{-1}) and C/N ratio 92.17 (Safari-Sinegani and Jafari Monsef 2016).

2.1. Soil treatments

In this study, a factorial experiment was done on the sampled soils with a completely randomized design. Factors were soil type at two levels (Hamadan and Lahijan soils), sterilization at two levels (sterile and unsterile soils) and wheat straw application at two levels (0, 5%). All of the treated soils were incubated at laboratory temperature and in dark conditions near their field capacity (50-75% of FC). Prior to the application of wheat straw in soil, it was ground and sieved (2 mm size). Half of the soils without treatment and the other half of the soils after treatment with 50 g of milled wheat straw kg^{-1} soil were sterilized. Sterilization was done three times for 30 min on three successive days. Unsterile soils were also studied. All of the treated and untreated soils were wetted with sterilized $CdCl_2$ solution to contamination level 10 mg Cd kg^{-1} soil. Soil moisture content remained near field capacity (50 to 75% of FC) by addition of distilled water for 3600 h incubation in dark conditions and at laboratory temperature. The DTPA extraction method (Lindsay and Norvell 1978) was applied for available Cd after 1, 10 and 30 minutes, and 1, 2, 5, 24, 48, 120, 240, 720, 2160 and 3600 hours and was determined by Atomic Absorption Spectrophotometer (Varian 220). Data were fitted to the simple (one-component) exponential model:

(Eq.1) $$\text{DTPA-extractable } Cd_T = 10^{-kT} * \text{DTPA-extractable } Cd_0$$

where DTPA-extractable Cd_T is DTPA-extractable Cd at time T (mg kg^{-1} soil), k is the decreasing constant, T is time (h) and DTPA-extractable Cd_0 is DTPA-extractable Cd at the start of soil incubation (mg kg^{-1} soil). The linear form of this equation is:

(Eq.2) $$\text{Log } C_T \text{ (mg Cd kg}^{-1}\text{ soil)} = -kT + \text{Log } C_0 \text{ (mg Cd kg}^{-1}\text{ soil)}$$

The means of DTPA-extractable Cd for 3 time intervals (≤ 24 h, 48 to 720 h and 2160 to 3600 h) were calculated for each treatment. These time intervals (≤ 1 day, 2 to 30 days and 90 to 150 days) show fast, moderate and slow reactions of the added Cd in the treated soils. The soluble form of the added Cd in soils is adsorbed and precipitated by initial fast reactions (minutes, hours). It is followed by slow adsorption and immobilization reactions (days, months). Finally its soluble forms in soils depend on desorption/sorption and dissolution/precipitation reactions (months, years) (Brummer et al. 1988; McLaren et al. 1998; Krishnamurti et al. 1999). The prepared data for each time interval was separately processed by Excel and SAS software to perform analysis of variance. The means were compared using Duncan test at 0.05 level of significance.

3. Results and Discussion

Analysis of variance of DTPA-extractable Cd in contaminated soils (10 mg kg^{-1}) showed that soil type, soil sterilization, wheat straw application and their interactions had significant effects on Cd availability in all sampling time intervals (**Table 1**). However the effect of the interaction between soil type and wheat straw application (S*Ws) in the 3rd sampling interval and the effect of the interaction between soil type, wheat straw application and sterilization (S*St*Ws) in the 2nd sampling interval were not significant.

Comparison of the means of DTPA-extractable Cd in contaminated soils showed that the Lahijan soil compared to the Hamadan soil had significantly higher available Cd in the 1st and 2nd time intervals but not the 3rd time interval (**Table 2**). DTPA-extractable Cd was higher in the Hamadan soil in all treatments at the end of experiment (after 150 days of soil incubation). The study of the distribution of added Cd among the different fractions in the Hamadan soils previously showed a greater content of HNO_3

Table 1. Analysis variance (mean squares) of DTPA-extractable Cd in contaminated Hamadan and Lahijan soils (with 10 mg Cd kg^{-1} soil) in different treatments in 3 time intervals

Source of variation	Df	≤ 1 day	2 to 30 days	90 to 150 days
Soil type (S)	1	11.756 **	18.774 **	3.330 **
Sterilization (St)	1	3.719 **	5.643 **	2.108 **
Wheat straw (Ws)	1	0.370 **	0.055 **	0.042 *
S*St	1	0.071 **	0.773 **	0.080 **
S*Ws	1	1.220 **	0.429 **	0.011
St*Ws	1	0.765 **	0.181 **	0.454 **
S*St*Ws	1	0.591 **	0.002	0.209 **
Error	**16**	**0.0007**	**0.0043**	**0.0079**

*and ** represents significant effects at 5% and 1% level respectively.

Table 2. Comparison of the means of DTPA-extractable Cd (mg kg^{-1} soil) in contaminated Hamadan and Lahijan soils (with 10 mg Cd kg^{-1} soil) in wheat straw treatments incubated in sterile and unsterile conditions

Soil type	Sterilization	Treatment	Mean	StdDev	Mean	StdDev	Mean	StdDev
			≤ 1 day		2 to 30 days		90 to 150 days	
Hamadan	Sterile	Control	9.50^{f}	0.01	7.38^{f}	0.02	5.17^{a}	0.04
		Wheat straw	8.13^{g}	0.02	6.86^{g}	0.01	5.13^{a}	0.01
	Unsterile	Control	9.72^{e}	0.02	7.84^{d}	0.15	4.38^{b}	0.16
		Wheat straw	9.70^{e}	0.02	7.63^{e}	0.07	4.51^{b}	0.08
Lahijan	Sterile	Control	10.24^{d}	0.06	8.54^{c}	0.03	4.46^{b}	0.08
		Wheat straw	10.40^{c}	0.03	8.52^{c}	0.01	4.12^{c}	0.10
	Unsterile	Control	10.88^{b}	0.02	9.68^{b}	0.07	3.52^{d}	0.01
		Wheat straw	11.12^{a}	0.01	10.04^{a}	0.02	4.11^{c}	0.12

Means with at least one similar letter in each column are not significantly different at 0.05 level.

extractable Cd (52%) than EDTA extractable Cd (31%) after 5 months of soil incubation. In the Hamadan soils the percentages of NaOH extractable (10%) and KNO_3 extractable (7%) fractions were considerably low. But in the Lahijan soil, the KNO_3 extractable fraction was higher (54%) than the HNO_3 extractable (18%), EDTA extractable (14%) and NaOH extractable (14%) fractions. Thus soil pH and carbonates may play an important role in precipitation of soluble Cd in semiarid soils (Safari-Sinegani and Jafari Monsef 2016), although in the Lahijan soil, adsorption is more important than precipitation of soluble Cd. This finding does not support our new finding for DTPA-extractable Cd content in the Lahijan soil in the 3rd time interval. Here after 150 days of soil incubation the DTPA-extractable Cd in the Lahijan soil was significantly lower than that in the Hamadan soil. These studies show that all KNO_3 extractable Cd in Lahijan soil is not extractable with DTPA. On the other hand, the other fractions (especially EDTA extractable Cd) in calcareous (Hamadan) soil may be extractable with DTPA. Once again in this study it is revealed that the chemistry of Cd in the temperate (Lahijan) and the semiarid (Hamadan) soils is different, with DTPA reacting and extracting Cd differently. However this finding needs to be more studied.

DTPA extractability of the added Cd was moderately higher in both unsterile soils compared to sterile soils in the 1st and 2nd time intervals (**Table 2**). The positive effect of sterilization on the decreasing rate of DTPA-extractable Cd was found in the studied soils in the 1st and 2nd time intervals. This positive effect was higher in the Lahijan soil than in the Hamadan soil. However DTPA-extractable Cd in the 3rd time interval was significantly higher in the sterile Lahijan and Hamadan soils. On the other hand, the effect of application of wheat straw on the DTPA-extractable Cd in sterile soil was not so obvious and it was different in various treatments and time intervals. However it had positive effect on DTPA-extractable Cd in unsterile Lahijan soil. It may be due to the increase in soil biological activity (Safari-Sinegani and Afzalpour 2014) and or formation soluble organo-Cd complexes (Martínez et al. 2003).

In general the DTPA extractability of the added Cd decreased exponentially in all treatments. The exponential model was suitably fitted to DTPA-extractable Cd (**Table 3**). The best linearized model was obtained for data in the Lahijan sterile soil treated and untreated with wheat residue ($R^2 \geq 0.95$). However, the Lahijan unsterile soil showed the largest decrease, consistent with high initial and low final DTPA-extractable Cd. In contrast, the suitability of the fitted model for data in the Hamadan sterile soil was the lowest one. The determination coefficients (R^2) were 0.62 and 0.73 for the Hamadan sterile soil treated and untreated with wheat residue, respectively. The statistical analysis showed that these linear correlation coefficients (Rs) were statistically significant. According to the studied exponential models and **Figures 1 and 2** the decrease of DTPA-extractable Cd had 3 steps. During the 1st step DTPA-extractable Cd decreased quickly, during the 2nd step it decreased moderately, and during the 3nd step there was a slow linear decrease with incubation time. This could be attributed to the differing Cd reaction mechanisms in each step. During the 1st step the cation exchange reaction may be the most important process. This reaction is strongly dependent on the metal concentration and its affinity to soil solids. The cation exchange reaction may reach equilibrium in less than 24 h (Polcaro et al. 2004).

Table 3. Linearized equations of the decreasing exponential models for DTPA-extractable Cd in the studied sterile and unsterile soils in wheat residue treatments

Soil type	Sterilization	Untreated with wheat straw
Hamadan	Sterile	Log C (mg Cd kg^{-1} soil) = -8*10^{-05}T (h) + 0.9434 R^2 = 0.73**
	Unsterile	Log C (mg Cd kg^{-1} soil) = -0.0001T (h) + 0.9613 R^2 = 0.91**
Lahijan	Sterile	Log C (mg Cd kg^{-1} soil) = -0.0001T (h) + 0.9544 R^2 = 0.95**
	Unsterile	Log C (mg Cd kg^{-1} soil) = -0.0002T (h) + 1.0094 R^2 = 0.94**
Soil type	**Sterilization**	**Treated with wheat straw**
Hamadan	Sterile	Log C (mg Cd kg^{-1} soil) = -8*10-05T (h) + 0.9226 R^2 = 0.62**
	Unsterile	Log C (mg Cd kg^{-1} soil) = -0.0001T (h) + 0.9551 R^2 = 0.90**
Lahijan	Sterile	Log C (mg Cd kg^{-1} soil) = -0.0001T (h) + 0.9545 R^2 = 0.96**
	Unsterile	Log C (mg Cd kg^{-1} soil) = -0.0002T (h) + 1.0163 R^2 = 0.92**

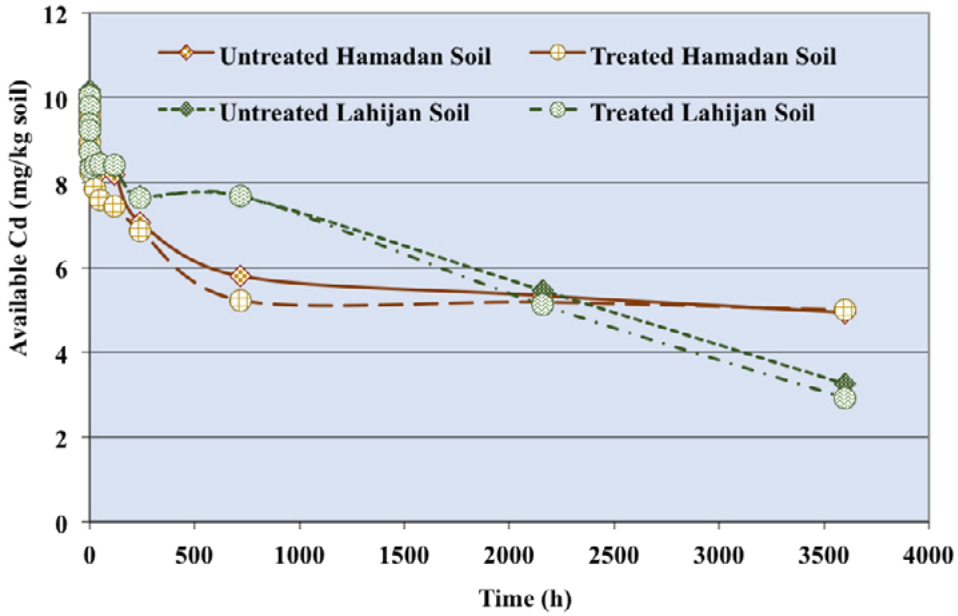

Figure 1. Decrease in availability (DTPA-extractable Cd) of added soluble Cd (10 mg kg^{-1}) in treated and untreated Hamadan and Lahijan soils with wheat straw (5%) and incubated for 3600 h under sterile conditions.

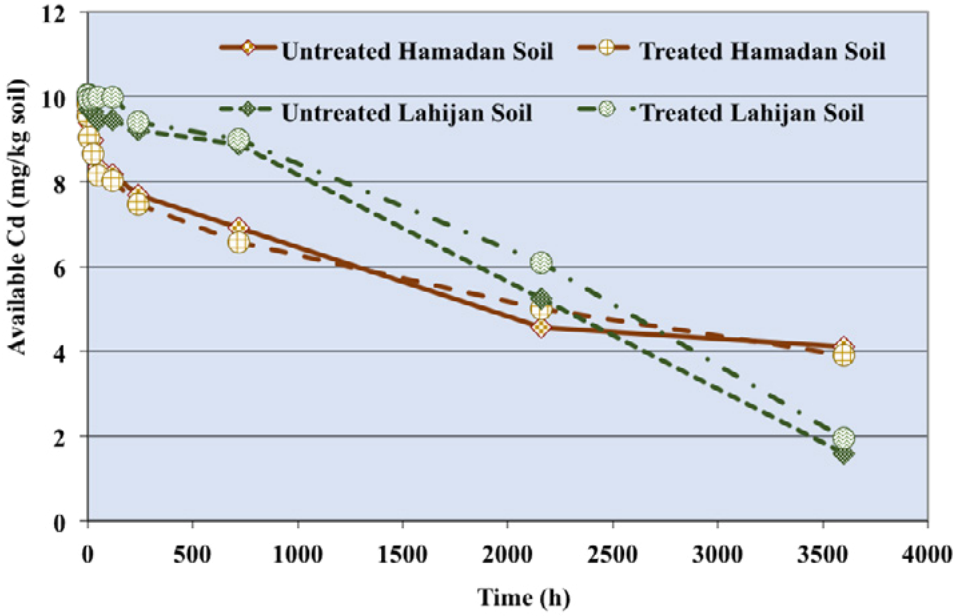

Figure 2. Decrease in availability (DTPA-extractable Cd) of added soluble Cd (10 mg kg^{-1}) in treated and untreated Hamadan and Lahijan soils with wheat straw (5%) and incubated for 3600 h under unsterile conditions.

Since the affinity of Cd is relatively low among heavy metals (Yong and Phadungchewit 1993; Lu and Xu 2009), Cd bioavailability remains high in the cation exchange reactions. In the 1st and 2nd steps cadmium availability was higher in the Lahijan soil compared to the Hamadan soil incubated under sterile and unsterile conditions. The difference between DTPA-extractable Cd in the Lahijan and Hamadan soils was more obvious for the unsterile soil (**Table 2 and Figure 2**). This finding may be related to the greater importance of the Cd cation exchange reaction

in the Lahijan soil. This soil had a higher clay content and CEC. Our previous study showed that the added Cd to this soil remained higher in KNO_3-extractable form (soluble-exchangeable fraction) over 3600 h incubation (Safari-Sinegani and Jafari Monsef 2016). This reaction may play an important role in Cd availability remaining high in the Lahijan soil compared to the Hamadan soil. Soils with higher clay contents, especially in higher pH environments, have a greater capacity for heavy metal adsorption, but in low pH conditions, the adsorption of metals decreased significantly due to competition with the hydrogen cation (Lu and Xu 2009; Safari Sinegani and Araki 2009; Wuana and Okieimen 2011).

The other most important reaction of heavy metal in soil is precipitation (Yong and Phadungchewit 1993; Ottosen et al. 2001). It is a relatively fast reaction that decreases heavy metal bioavailability in soils. The decrease of Cd availability was higher in the Hamadan soil compared to the Lahijan soil during the 1st and 2nd steps (**Figures 1 and 2**). The Hamadan soil, with its higher pH and carbonate minerals, had a greater capacity for the precipitation of heavy metals. The soluble and exchangeable fraction of Cd (KNO_3 extractable) in the Hamadan soil was significantly lower than this fraction in the Lahijan soil (Safari-Sinegani and Jafari Monsef 2016). Calcareous soils thus have a high capacity for heavy metal precipitation. The soluble form of the heavy metal transformed to precipitated forms in calcareous soils after a few days, and these soils are useful for heavy metal sequestration. However at the end of soil incubation, the Hamadan soil had higher DTPA-extractable Cd.

The other transformation reactions of the added soluble heavy metal in soil are biosorption and immobilization by soil microorganisms (Volesky and Holan 1995; Ledin et al. 1999; Wang et al. 2014). These reactions are slow and strongly depend on all of the soil properties affecting its biological activities. The differences between Cd availability in sterile and unsterile soils may show the importance of biosorption and immobilization of Cd in soils especially at the 1st and 2nd steps of sampling time. Generally DTPA-extractable Cd was higher in soils incubated under unsterile conditions. This effect of soil microorganisms was more obvious in the Lahijan soils (**Table 2 and Figure 2**). The unsterile Lahijan soil had the highest DTPA-extractable Cd in each sampling time except in the final sampling time (**Table 2** and **Figures 1 and 2**). The addition of wheat straw may elevate Cd availability compared to that in untreated soils by increasing soil biological activity. This effect was observed in the Lahijan soil but not in the Hamadan soil (**Figure 2**). The addition of organic matter in soil cannot increase the DTPA-extractable Cd and other heavy metals (Wuana and Okieimen 2011). This is due to the formation of low molecular anions such as phosphates during organic matter decomposition, which can precipitate heavy metals in more stable species. On the other hand, the addition of degradable plant residue (wheat straw) may increase dissolved organic matter (DOM) by soil microorganisms (Safari-Sinegani and Afzalpour 2014). Mahara et al. (2007) showed that organic materials with a low molecular weight were more effective in the formation of cadmium complexes. The addition of soluble organic matter from sewage sludge prevented the adsorption of heavy metals in acid soils to a lesser degree than in calcareous soils (Karaca 2004). This effect was smaller in coarse-textured soils than fine textured soils.

4. Conclusions

Contaminated (10 mg Cd kg^{-1}) Lahijan soil compared to Hamadan soil had higher DTPA-extractable Cd in the 1st and 2nd time intervals. However, at the end of the soil incubation period (3rd time interval) the Hamadan soil had higher DTPA-extractable Cd.

DTPA-extractable Cd was considerable higher in the unsterile Lahijan soil. The addition of wheat straw to the Lahijan soil, especially under unsterile conditions, increased DTPA-extractable Cd. This could be related to an increase in soil biological activity and/or the formation of soluble organo-Cd complexes.

Higher KNO_3 extractable Cd in contaminated Lahijan soil coupled with lower DTPA-extractable

Cd in this soil compared to the Hamadan soil at the end of the soil incubation period show the difference in Cd chemistry in Lahijan (the temperate) and Hamadan (the semiarid) soils. These findings need to be investigated further.

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