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ORIGINAL ARTICLE

Risk assessment of available and total heavy metals contents in various land use in calcareous soils

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Abstract

Heavy metals (HMs) are regarded as a high priority monitoring contaminant and have been identified as a major environmental concern. The forms of land use may have an impact on the movement and accumulation of HMs. The mobility and accumulation of HMs were examined in topsoils of various land use using different soil test methods. Sixty-three soil samples were taken from various land use including garlic, orchard, pasture, potato, vegetable, wheat, and polluted lands. The availability of Cd, Cu, Mn, Ni, Pb, and Zn were determined using $CaCl_2$, HCl, HNO_3, EDTA, and DTPA extractants. Amongst all extractants and land use, the mean available contents of Cd, Cu, Mn, Ni, Pb, and Zn were 0.81, 4.95, 58.60, 2.41, 14.94, and 7.95 mg kg^{-1}, respectively. Among the extractants, the mean contents of all HMs in all land use decreased in following order: HNO_3 (34.39 mg kg^{-1}) > EDTA (19.41 mg kg^{-1}) > HCl (13.52 mg kg^{-1}) > DTPA (5.26 mg kg^{-1}) > $CaCl_2$ (1.36 mg kg^{-1}). Generally, among the various land use, after polluted land (26.2 mg kg^{-1}) the orchard land (17.3 mg kg^{-1}) presented the highest contents of HMs, and the wheat (8.35 mg kg^{-1}) and pasture (9.94 mg kg^{-1}) lands presented the lowest contents. The results from the geo-accumulation index (I_{geo}) and the ecological risk index (*RI*) showed that except for polluted land in other land use the HMs categorized as unpolluted ($I_{geo} < 0$) and low risk (RI ≤ 150). The results from the availability ratio (*AR*) showed that among the extractants, the mean *AR* calculated for all HMs and land use decreased in the following order: HNO_3 (28.08%) > EDTA (26.36%) > HCl (21.55%) > DTPA (7.11%) > $CaCl_2$ (3.19%). It also indicated that the vegetable land (average of all extractants) presented the highest (25.1%) of HMs extractability while the pasture land (average of all extractants) presented the lowest (12.7%). The hazard index (*HI*) showed that for all HMs in various land use the non-carcinogenic risk were not significant. Generally, Pb and Mn are the main contributors to the total health risks, while Zn and Cu were the least risks. When utilizing the EDTA extractant, Mn and Ni were combined into one cluster by using *AR* of HMs, but Cu and Pb were combined into one cluster when using the both EDTA and DTPA extractants. The noteworthy feature of this clustering is the use of *AR* of HMs rather than available ones, which considers both available and total HMs in soil. This study highlights the importance of extractants, land use and *AR* in assessing risk assessment caused by HMs, bioavailability of HMs and exposure health risk. Lastly, we emphasize the significance of employing *AR* to evaluate soil enrichments with HMs and suggest considering available background level of HMs rather than the total background levels that is currently utilized to assess soil contamination.

Keywords Heavy metals availability · Human health risk · Speciation · Various extractants

Introduction

Heavy metals (HMs) such as Cd, Cu, Mn, Ni, Pb, and Zn have been recognized as a main environmental concern because of their high toxicity, persistence, and pervasiveness (Hu et al. 2020). With fast-growing urbanization and industrialization, soil contamination by anthropogenic activities has attracted global attention (Huang et al. 2018; Kazemi Moghaddam et al. 2022; Massas et al. 2013). The accumulation of HMs in soil and aquatic environment ended up in plants and finally in human bodies via food chains (Hooda 2010; Shao et al. 2016). Long-term exposure to HMs resulted in harmful effects on human health such as cancers, kidney disease, and liver disease (Hu et al. 2020; US EPA 2000). In order to investigate the environmental risk assessment of HMs, parameters such as geo-accumulation index (I_{geo}), ecological risk index (*RI*), and availability ratio (*AR*) are widely used (Jia et al. 2018;

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Saroop and Tamchos 2021). The hazard quotient (*HQ*) and the hazard index (*HI*) are usually determined to assess the non-carcinogens risks posed by HMs (Liu et al. 2019). Previous studies determined the risk assessment in different ecosystems (e.g., Ghaderpoori et al. 2020; Marufi et al. 2022; Saleh et al. 2019; Wang et al. 2017; Liu et al. 2019).

Monitoring the environmental risk caused by HMs could be performed by the determination of the available or total content of HMs in soil. The total contents of HMs do not provide information about mobility, bioavailability, and the fate of HMs in soil (Rivera et al. 2016). Determination of the available content of HMs in soil, provided useful information about the mobility of HMs in relation to plant uptake and also their leaching to groundwater (Rivera et al. 2016). The accurate estimation of the HMs availability is a major challenge, since current methods for determination of HMs availability were uncertain. Therefore, it is essential to compare the different methods. One of the widely used extractants for HMs availability is a 0.01 M calcium chloride ($CaCl_2$) solution. Many researchers used this extractant for their studies (e.g., Feng et al. 2005; Jalali and Hourseresht 2017; Kim et al. 2015; Ma et al. 2020; Pueyo et al. 2004; Rivera et al. 2016; Yao et al. 2017; Zhong et al. 2020). This extractant does not change soil pH and reduces analytical interference due to its low concentration (Rivera et al. 2016). Dilute hydrochloric acid (HCl) and nitric acid (HNO_3) are also the other two common extractants for HMs (Kim et al. 2016). Studies such as Annibaldi et al. (2007), Barcellos et al. (2022), Kashem et al. (2007), Kupka et al. (2021), McCready et al. (2003), Sutherland and Tack (2008), and Yang et al. (2009) were used dilute HCl, and Faridullah and Sabir (2012), Jalali and Hurseresht (2020), Li et al. (2015), Shi et al. (2021), and Spijker et al. (2011) were used dilute HNO_3 for HMs extracting from the soil. These extractants increase the extractability of most cationic HMs by decreasing the pH. Widely used chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriamine pentaacetate (DTPA) extractants, with a high level of complexation efficiencies, for most HMs have been used in many studies (e.g., Baldantoni et al. 2010; Beygi and Jalali 2019; Guo et al. 2018; Kim et al. 2016; Lee et al. 2009; Rivera et al. 2016).

The term "land use" refers to a location's human activities, such as agriculture, industry, and habitation. Anthropogenic activities related to land use intensively affected soil quality and nutrient cycling (Yu et al. 2020). One of the important issues related to land use is soil contamination by HMs (Zhao et al. 2022). The mobility and accumulation of HMs could be affected by land use types (Nuralykyzy et al. 2021). Huang et al. (2018) studied the contents of HMs under various land use (farm land, residential land, and forest land). Bai et al. (2010) sampled 148 soils under different land use such as greenhouse, vegetable, maize, and forest. They observed that accumulation of As, Cd, Cr, Cu, Ni, and Zn were more different under various land uses, and higher HMs accumulation observed in greenhouse and vegetable. Nuralykyzy et al. (2021) observed that the highest amount of HMs in different land use was in this order: facility land > farm land > grass land > orchard. Xia et al. (2011) studied the contents of HMs from different types of land use in urban soils. Zheng et al. (2016) investigated the fractionation of HMs and As under various land use. They stated that contents of HMs and As in forest land were significantly lower compared to wetland. They suggested that immense agricultural activities resulted in higher contents of HMs and As in paddy field and dryland. Arfaeinia et al. (2019) determined HMs content of 41 sediment samples under different land use (industrial, urban, agriculture, and natural field). They observed that HMs content in industrial and agricultural land use were significantly higher than urban and natural field.

Earlier studies on HMs availability were mainly focused on predicting HMs contents from physicochemical properties of soils, assessing the relationship between total contents of HMs with their available contents, and identifying the most important factors controlling HMs availability (e.g., Baldantoni et al. 2010; Dutta et al. 2021; Jalali and Hurseresht 2020; Rivera et al. 2016; Zhong et al. 2020). Nearly all of the studies on HMs in various land uses previously mentioned were based on total content of HMs in soil. It was hypnotized that various land use required different managements (e.g., fertilization, pest control, tillage, and so on) hence the availability of HMs varies in various land use. The novelty of this study is that the soils were collected from seven various land use (garlic land, orchard land, pasture land, potato land, vegetable land, wheat land, and polluted land) and the contents of six HMs (Cd, Cu, Mn, Ni, Pb, and Zn) were determined not only by their total contents, but also by using five various available HMs extractants ($CaCl_2$, HCl, HNO_3, EDTA, and DTPA). In addition, the speciation of these HMs in the solution was examined, also the risk assessment parameters regarding these HMs in various land use were examined. Last but not least, in order to assess soil enrichments with HMs in various land uses, we used a variety of soil test methods to determine availability ratio (*AR*) and taking into account background levels of HMs rather than the overall background level currently used to assess soil contamination.

Materials and methods

Study area and soil sampling

Hamedan province (western Iran) lies in a temperate mountainous region. The annual precipitation of about 317.7 mm, with the maximum precipitation, occurs from November to February. The average temperature is 11.6 ℃. Agriculture is one of the main economic activities in this province. In the province of Hamedan, there are 698,614 ha of agricultural land, 822,000 ha of grazing land, and 83,558 ha of orchard land (Ministiry of Agriculture—Jahad 2021). Moreover, this province has 520,053 ha of cereal land, 17,383 ha of leguminous land, 26,157 ha of vegetable land, and 4707 ha of melon land (Ministiry of Agriculture—Jahad 2021). The three largest crops grown in this province are wheat (394,217 ha), potatoes (21,217 ha), and garlic (3318 ha) (Ministiry of Agriculture—Jahad 2021).

A total of 63 soil samples (0–30 cm) were taken from various land use (Fig. 1) including garlic ($n=8$), orchard ($n=10$), pasture ($n=7$), potato ($n=11$), vegetable ($n=9$), and wheat ($n=9$). We also sampled from 9 polluted lands (surrounded by industrial and mining sites) in order to compare them with other soil samples. These soils were taken from 65 soils previously sampled by Jalali and Moradi (2013).

Chemical analyses

The pH, electrical conductivity (EC), cation exchange capacity (CEC), calcium carbonate equivalent (CCE), organic matter (OM), clay, silt, and sand contents were all previously measured by Jalali and Moradi (2013) according to methods described by Rowell (1994). The pseudo total contents of Cd, Cu, Mn, Ni, Pb, and Zn were also previously measured by Jalali and Moradi (2013) according to the method described by Sposito et al. (1982).

The available contents of Cd, Cu, Mn, Ni, Pb, and Zn were determined using various available HMs extractants including $CaCl_2$, HCl, HNO_3, EDTA, and DTPA. The procedure for extracting HMs using these extractants presented in Table 1. The suspensions obtained from all above methods were filtered through Whatman no. 42 filter paper, and the concentrations of Cd, Cu, Mn, Ni, Pb, and Zn were determined by the atomic absorption spectrophotometer (Spectra AA-220 Varian).

Speciation

In order to investigate the speciation of HMs in each extractant, in addition to the determination of Cd, Cu, Mn, Ni, Pb, and Zn concentrations, calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chlorine (Cl), bicarbonate (HCO_3), and phosphorus (P) concentrations and pH value were also measured

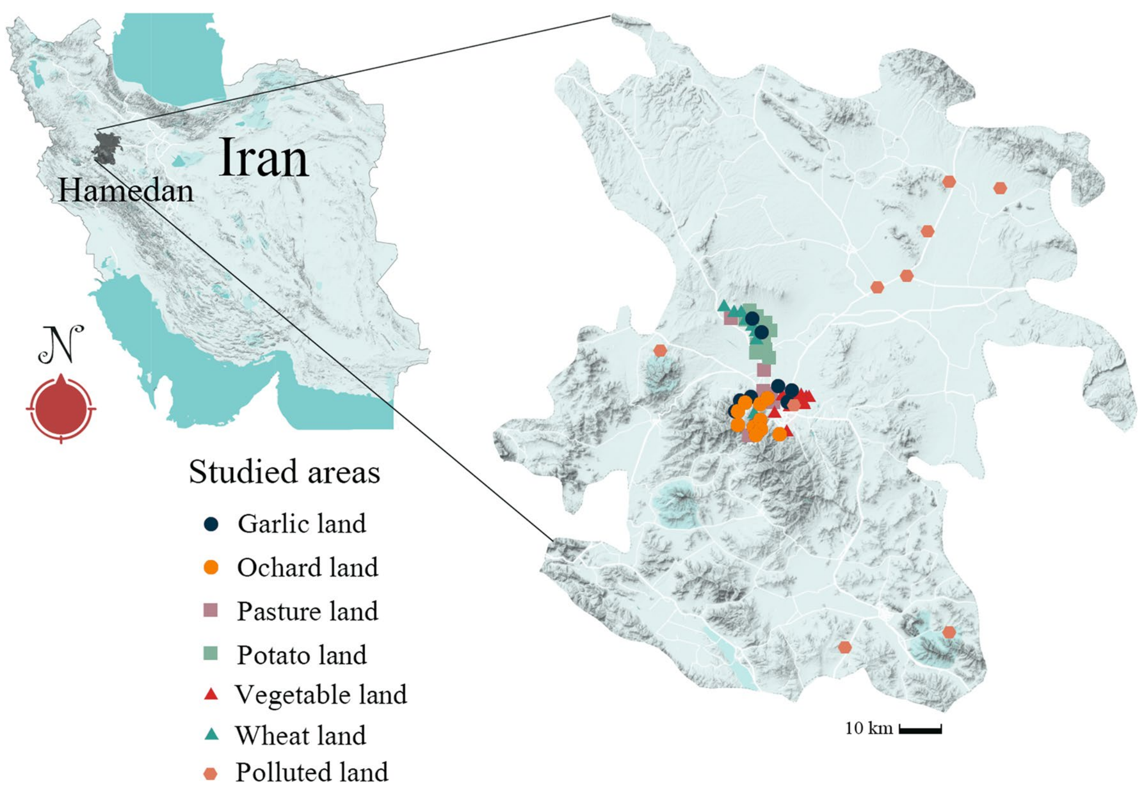


Fig. 1 Location of sampling sites in Hamedan province, Iran

in each extractant. In each land use, two soil samples were selected for the speciation experiment. The concentrations of Ca, Mg, Cl, and HCO_3 were determined using titration methods. Sodium and K concentrations were determined using a flame photometer (Jenway- PFP 7). The P concentration was determined using the molybdenum blue method described by Murphy and Riley (1962) using a UV–visible spectrophotometer (Analytik Jena- spekol 1500). The speciation was performed by the PHREEQC program (Parkhurst and Appelo 1999). The concentration of sulfate (SO_4^{2-}) was not measured, but in the PHREEQC program, based on charge balance, the SO_4^{2-} concentration was calculated.

Risk assessment

Geo-accumulation index

The wieldy used I_{geo} introduced by Muller (1969) to evaluate the current HMs status compared to background levels. The I_{geo} calculated as follow:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{1}$$

where C_n represents the total measured HM content (mg kg^{-1}) in the soil, B_n represents corresponding background level (mg kg^{-1}) in the study area (Beygi and Jalali 2018), and the coefficient 1.5 is used in order to control the fluctuations of B_n values.

Ecological risk index

The *RI* introduced by Hakanson (1980) to evaluate the ecological risks caused by HMs. The *RI* calculated as follow:

$$RI = \sum ER^i; ER^i = TR^i \times C_f^i; C_f^i = \frac{C_n^i}{B_n^i} \tag{2}$$

where C_n^i represents the total measured HM content (mg kg^{-1}) in the soil, B_n^i represents corresponding background level (mg kg^{-1}), C_f^i represents the pollution factor for each HM, TR^i represents the toxic response factor (the toxic response factor for Cd: 30, Cu: 5, Mn: 1, Ni: 5, Pb: 5, and Zn: 1 (Hakanson 1980)), and ER^i represents the ecological risk potential of each HM.

Availability ratio

The *AR* introduced in order to evaluate the availability of HMs in soils. The *AR* calculated as follow:

$$AR = \left(\frac{C_a}{C_n}\right) \times 100 \tag{3}$$

where C_a represents the measured available ($CaCl_2$, HCl, HNO_3, EDTA, or DTPA) contents of HMs in soil (mg kg^{-1}), and C_n represents the total measured HMs contents in the soil (mg kg^{-1}).

Human health risk index

Human health risk assessment introduced in order to determine the non-carcinogens risks of HMs pollutants to human and recommended by the US Environmental Protection Agency (US EPA 1989). The average daily dose (*ADD*) through the ingestion calculated as follow:

$$ADD_{Ingestion} = \frac{C_{soil} \times IR_{soil} \times EF \times ED}{BW \times AT \times 10^6} \tag{4}$$

where C_{soil} represents the total measured HM content in the soil (mg kg^{-1}), IR_{soil} represents ingestion rate of soil (mg day^{-1}), *EF* represents exposure frequency (day $year^{-1}$), *ED* represents exposure duration (year), *BW* represents body weight (kg), *AT* represents average time contact (day), and 10^6 represents the conversion factor from kg to mg.

The ADD through the inhalation calculated as follow:

$$ADD_{Inhalation} = \frac{C_{soil} \times IR_{air} \times PM_{10} \times ET \times EF \times ED}{BW \times AT \times PEF} \tag{5}$$

where IR_{air} represents inhalation rate of air (m^3 day^{-1}), PM_{10} represents ambient particulate matter content in the

Table 1 Extractant methods for determination of heavy metals

Extractants	Soil-to-solution ratio	Equilibration time	References
0.01 M $CaCl_2$	1:10	2 h	Houba et al. (2000)
0.1 M HCl	1:10	1 h	Martens (1968)
0.43 M HNO_3	1:10	2 h	Römkens et al. (2004)
0.05 M EDTA	1:10	1 h	Quevauviller et al. (1996)
(0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M triethanolamine) DTPA	1:2	2 h	Lindsay and Norvell (1978)

air (mg m^{-3}), *ET* represents exposure time (24 h day^{-1}), and *PEF* represents particle emission factor (m^3 kg^{-1}).

The *ADD* through the dermal calculated as follow:

$$ADD_{Dermal} = \frac{C_{soil} \times SA \times ABS \times AF \times EF \times ED}{BW \times AT \times 10^6} \tag{6}$$

where *SA* represents the skin surface area (cm^2), *ABS* represents the skin absorption factor (non-dimensional), and *AF* represents the adherence factor to skin (mg cm^2).

The *HQ* represents non-carcinogenic risk for an individual HM. The *HQ* calculated as follow (non-dimensional):

$$HQ = \frac{ADD}{R_fD} \tag{7}$$

where R_fD represents the reference dose, the maximum permissible dose of HM can be exposure to the human population. There are three R_fD: R_fDo (mg kg^{-1} per day) for ingestion, R_fCi (mg m^{-3}) for inhalation, and R_fDd (mg kg^{-1} per day) for dermal. The R_fDo considered for Cd, Cu, Mn, Ni, Pb, and Zn were 0.001, 0.04, 0.024, 0.02, 0.0014, and 0.3 mg kg^{-1} per day, respectively, the R_fCi considered for Cd, Cu, Mn, Ni, Pb, and Zn were 0.0000571, 0.04, 0.00005, 0.0206, 0.00005, and 0.3 mg m^{-3}, respectively, and the R_fDd considered for Cd, Cu, Mn, Ni, Pb, and Zn were 0.000025, 0.012, 0.00096, 0.0054, 0.00042, and 0.06 mg kg^{-1} per day, respectively (US EPA 1989; Gao et al. 2015; Zeng et al. 2015; Wang et al. 2019; Adimalla 2020; Luo et al. 2021).

Finally, the *HI* calculated by summed the *HQ* calculated for each chemical as follow:

$$HI = \sum HQ_i = HQ_{Ingestion} + HQ_{Inhalaltion} + HQ_{Dermal} \tag{8}$$

All parameters for assessing the human health risk in adults were presented in Table 2.

Table 2 Parameters for assessing the human health risk (USEPA 1989)

Parameter	Full name	Unit	Value (adults)
IR_{soil}	Ingestion rate of soil	mg day^{-1}	50
IR_{air}	Inhalation rate of air	m^3 day^{-1}	14.5
PM_{10}	Ambient particulate matter	mg m^{-3}	0.075
EF	Exposure frequency	day $year^{-1}$	250
ED	Exposure duration	year	14
ET	Exposure time	24 h day^{-1}	24
AF	Adherence factor to skin	mg cm^{-2}	0.07
AT	Average time contact	day	5110
BW	Body weight	kg	65.5
SA	Skin surface area	cm^2	4350
PEF	Particle emission factor	m^3 kg^{-1}	1.36E+9
ABS	Skin absorption factor	unitless	0.001

Results and discussion

Soil properties and heavy metals contents

The soil properties in various land use are presented in Table 3. The results indicated that the mean value of pH for all land use was neutral to alkaline. The mean EC for all land use showed low salinity, except for polluted land which was much higher than other land use. The highest mean CEC belonged to polluted land and the lowest belonged to garlic land. The mean percentage of CCE for orchard, pasture, potato, and vegetable lands was similar, with wheat land having the greatest mean and garlic having the lowest mean. The mean OM content across all land uses was low, with garlic land having the greatest mean, and the most prevalent soil textures in garlic land were sandy clay loam and clay. In orchard, pasture, potato, and vegetable lands, sandy loam and sandy clay loam textures were dominant. In wheat land, clay and clay loam textures were dominant, and in polluted land sandy loam and silty loam were dominant textures.

The mean available contents of HMs extracted by various extractants and mean pseudo total content of HMs in various land use presented in Table 4. Among the extractants, the mean available contents of all HMs decreased in the following order: HNO_3 > EDTA > HCl > DTPA > $CaCl_2$. In $CaCl_2$ extractant, the mean contents of HMs in various land use decreased in following order: polluted land > garlic land > potato land > orchard land > wheat land > vegetable land > pasture land. In HCl extractant, the mean contents of HMs in various land use decreased in following order: polluted land > orchard land > garlic land > potato land > vegetable land > pasture land > wheat land. In HNO_3 extractant, the mean contents of HMs in various land use decreased in following order: polluted land > vegetable land > orchard land > potato land > garlic land > pasture land > wheat land. For EDTA, the following order was observed for the mean contents of HMs in various land use polluted land > orchard land > vegetable land > garlic land > potato land > pasture land > wheat land. For DTPA, the following order was observed for the mean contents of HMs in various land use: polluted land = orchard land > vegetable land > potato land > garlic land > wheat land > pasture land. The mean pseudo total contents of HMs had the following order in various land use: polluted land > wheat land > vegetable land > orchard land > pasture land > potato land > garlic land. The results indicated that generally the wheat and pasture lands presented the lowest available content of HMs in various extractants, and polluted and orchard lands presented the highest contents of available HMs. Application of fertilizers to agricultural and orchard lands contributes to

Table 3 The mean soil properties in various land use. The data was taken from Jalali and Moradi (2013)

Land use	pH	EC (dS m^{-1})	CEC ($cmol_c$ kg^{-1})	CCE (%)	OM (%)	Clay (%)	Silt (%)	Sand (%)
Garlic land ($n=8$)	6.84	0.14	16.88	6.74	2.65	21.14	23.58	55.29
Orchard land ($n=10$)	7.16	0.15	21.94	11.97	1.67	29.14	23.69	47.17
Pasture land ($n=7$)	7.00	0.32	18.29	10.18	1.41	20.83	22.55	56.62
Potato land ($n=11$)	7.33	0.21	22.95	10.34	1.18	29.16	19.49	51.35
Vegetable land ($n=9$)	7.09	0.18	19.76	11.61	2.01	23.49	22.04	54.47
Wheat land ($n=9$)	7.41	0.26	24.57	18.46	1.35	40.84	25.58	33.57
Polluted land ($n=9$)	7.09	1.18	29.27	16.42	1.51	24.04	32.44	43.51

HMs accumulation in soils (Acosta et al. 2011a). In orchard land, the application of Cu-based fungicides resulted in the accumulation of Cu in the soils (Fan et al. 2011; Viti et al. 2008). Repeated application of lead arsenate in orchard land, also resulted in the accumulation of Pb and arsenic in soils (Li et al. 2014; Udovic and McBride 2012). Higher accumulation of HMs in vegetable land compared to wheat land could be due to the farmers applying relatively higher rates of chemical and organic fertilizers in vegetable production compared to grain crops (Huang and Jin 2008). Pasture land is an ecological environment which is less exposed the human activities and results in a lower accumulation of HMs (Nuralykyzy et al. 2021). Li et al. (2006) reported that Cd content in their orchard land exceeded the Chinese National Environment Quality Standard for Soil. The total and DTPA content of Cd in their study was higher compared to this study. Yu et al. (2020) reported the total contents of Cd, Cu, Pb, and Zn were 120.4, 72.3, 2848.7, and 11,140.0 mg kg^{-1}, respectively for citrus orchards. They also reported the total contents of Cd, Cu, Pb, and Zn for vegetable fields were 2.0, 26.7, 216.8, and 649.1 mg kg^{-1}, respectively. The values reported by Yu et al. (2020) for HMs in citrus orchards were much higher than the values reported in this study for total contents of HMs in orchard land (Table 2). In addition for vegetable fields, the reported values were also higher compared to values reported in this study, with the exception of Cu content. Nuralykyzy et al. (2021) showed that the total contents of HMs decreased in the following order: facility land > farmland > grassland > orchards.

The available and total background levels of HMs in the studied area were previously calculated by Jalali et al. (2022) and Beygi and Jalali (2018), respectively. Jalali et al. (2022) calculated the available background levels based on DTPA. Figure 2 shows the contents of HMs in various land use along with the background levels for each HM based on the iterative 2-δ technique method (Fig. 2a) and mean + 2 standard deviation method (Fig. 2b). The DTPA background levels calculated for Cd, Cu, Mn, Ni, Pb, and Zn were 0.3, 1.1, 11.6, 0.6, 1.6, and 0.6 mg kg^{-1}, respectively. Considering Cd background level, the mean value of Cd in none of the land use exceeded from background level, except for polluted land which was nearly 3.8 times higher than the background level. The mean contents of Cu in garlic land, orchard land, pasture land, potato land, vegetable land, wheat land, and polluted land were 1.6, 2.2, 1.0, 1.4, 5.1, 1.1, and 2.7 times higher than the Cu background level, respectively. The mean contents of Mn in garlic land, orchard land, pasture land, potato land, vegetable land, wheat land, and polluted land were 1.8, 2.4, 1.1, 2.3, 1.9, 1.7, and 1.5 times higher than Mn background level, respectively. The mean contents of Ni in garlic land, orchard land, potato land, vegetable land, and wheat land were 1.2, 1.3, 1.3, 1.2, and 1.2 times higher than Ni background level, respectively. The pasture and polluted lands mean values were not higher than the background level of Ni. The mean contents of Pb in garlic land, orchard land, pasture land, vegetable land, and polluted land were 1.4, 2.9, 1.3, 4.3, and 7.9 times higher than the Pb background level, respectively. The potato and wheat lands mean values were not higher than the background level of Pb. The highest increases in HMs contents compared to its background level, observed in Zn. The mean contents of Zn in garlic land, orchard land, pasture land, potato land, vegetable land, wheat land, and polluted land were 6.1, 2.6, 3.0, 4.3, 2.6, 5.6, and 5.9 times higher than the Zn background level, respectively. As indicated above, based on available contents (DTPA) of HMs in most land use the HMs contents were higher than their corresponding background levels. The total background levels calculated for Cd, Cu, Mn, Ni, Pb, and Zn were 1.32, 33.67, 407.08, 60.96, 38.46, and 119.99 mg kg^{-1}, respectively (Beygi and Jalali 2018). However, based on total HMs background levels, in most land use and most HMs the total HMs contents were lower than their corresponding background levels, except for polluted land which for all HMs, the contents were higher than their corresponding background levels.

Speciation

As discussed earlier, in each land use two soil samples were selected for the speciation experiment. The percentage of important HMs species in the garlic, orchard, pasture, potato, vegetable, and wheat lands (mean of these land

Table 4 The mean ± standard error of available and total heavy metals in various land use extracted by various extractants

	Garlic land (n = 8)	Orchard land (n = 10)	Pasture land (n = 7)	Potato land (n = 11)	Vegetable land (n = 9)	Wheat land (n = 9)	Polluted land (n = 9)
$CaCl_2$							
Cd	0.08 ± 0.03^{g}	0.13 ± 0.01^{g}	0.08 ± 0.02^{g}	0.09 ± 0.02^{g}	0.13 ± 0.03^{g}	0.09 ± 0.01^{g}	0.73 ± 0.04^{fg}
Cu	0.27 ± 0.09^{g}	0.53 ± 0.05^{g}	0.34 ± 0.09^{g}	0.21 ± 0.07^{g}	0.46 ± 0.10^{g}	0.12 ± 0.03^{g}	0.16 ± 0.03^{g}
Mn	0.13 ± 0.07^{g}	0.59 ± 0.10^{g}	0.08 ± 0.05^{g}	0.17 ± 0.10^{g}	0.05 ± 0.02^{g}	0.15 ± 0.11^{g}	3.29 ± 0.47^{bc}
Ni	0.63 ± 0.14^{g}	0.35 ± 0.03^{g}	0.31 ± 0.10^{g}	0.49 ± 0.12^{g}	0.32 ± 0.05^{g}	0.55 ± 0.12^{g}	2.32 ± 0.20^{cde}
Pb	3.91 ± 1.29^{b}	1.40 ± 0.18^{d,e,f,g}	1.36 ± 0.37^{d,e,f,g}	2.63 ± 0.30^{c,d}	1.29 ± 0.15^{e,f,g}	1.95 ± 0.15^{def}	28.86 ± 0.72^{a}
Zn	0.06 ± 0.01^{g}	0.10 ± 0.03^{g}	0.14 ± 0.04^{g}	0.09 ± 0.02^{g}	0.11 ± 0.03^{g}	0.10 ± 0.03^{g}	2.27 ± 0.03^{cde}
HCl							
Cd	0.62 ± 0.12^{f}	0.56 ± 0.06^{f}	0.47 ± 0.17^{f}	0.82 ± 0.08^{f}	0.82 ± 0.02^{f}	0.79 ± 0.11^{f}	5.46 ± 0.07^{ef}
Cu	1.92 ± 0.79^{f}	3.33 ± 0.49^{f}	1.45 ± 0.58^{f}	1.54 ± 0.28^{f}	1.37 ± 0.17^{f}	0.89 ± 0.23^{f}	5.38 ± 0.41^{ef}
Mn	51.23 ± 21.5^{b}	88.05 ± 10.0^{a}	37.04 ± 6.9^{b,c,d,e}	49.54 ± 10.3^{b}	40.24 ± 6.7^{b,c,d}	19.64 ± 3.8^{cdef}	81.41 ± 10.7^{a}
Ni	1.98 ± 0.67^{f}	1.99 ± 0.3^{f}	1.55 ± 0.24^{f}	1.41 ± 0.20^{f}	1.44 ± 0.32^{f}	1.76 ± 0.80^{f}	4.65 ± 0.43^{f}
Pb	12.03 ± 2.38^{c,d,e,f}	9.75 ± 1.58^{e,f,d}	9.76 ± 3.48^{e,f,d}	13.52 ± 1.53^{c,d,e,f}	13.19 ± 0.49^{c,d,e,f}	10.07 ± 0.84^{efd}	42.40 ± 2.79^{bc}
Zn	4.17 ± 1.8^{f}	8.02 ± 1.69e^{f}	2.78 ± 0.68^{f}	4.32 ± 1.72^{f}	9.29 ± 5.12^{e,f,d}	2.06 ± 1.49^{f}	19.11 ± 3.76^{cdef}
HNO_3							
Cd	0.42 ± 0.15^{e}	0.15 ± 0.06^{e}	0.45 ± 0.14^{e}	0.50 ± 0.11^{e}	0.46 ± 0.14^{e}	0.55 ± 0.07^{e}	4.44 ± 0.34^{e}
Cu	10.10 ± 2.16^{e}	13.73 ± 1.96^{e}	8.63 ± 1.91^{e}	6.89 ± 0.79^{e}	20.86 ± 5.18^{e}	4.15 ± 0.44^{e}	21.77 ± 10.72^{e}
Mn	135.9 ± 19.8^{b}	198.7 ± 10.2^{a}	119.8 ± 16.3^{b,c}	149.4 ± 12.2^{b}	213.7 ± 7.3^{a}	98.1 ± 9.2^{cd}	151.9 ± 22.9^{b}
Ni	6.10 ± 1.08^{e}	5.77 ± 0.56^{e}	5.07 ± 0.73^{e}	5.24 ± 0.80^{e}	6.43 ± 1.37^{e}	6.01 ± 0.48^{e}	7.00 ± 0.58^{e}
Pb	7.37 ± 1.78^{e}	7.60 ± 2.43^{e}	6.21 ± 2.83^{e}	5.69 ± 0.70^{e}	14.46 ± 1.76^{e}	4.31 ± 1.27^{e}	74.13 ± 5.82^{d}
Zn	13.49 ± 3.47^{e}	16.57 ± 2.86^{e}	7.91 ± 2.20^{e}	18.26 ± 2.86^{e}	31.13 ± 8.72^{e}	5.62 ± 0.84^{e}	29.37 ± 11.72^{e}
EDTA							
Cd	0.68 ± 0.10^{c}	0.57 ± 0.07^{c}	0.62 ± 0.18^{c}	0.91 ± 0.10^{c}	0.72 ± 0.06^{c}	0.82 ± 0.09^{c}	3.93 ± 0.06^{c}
Cu	6.65 ± 1.06^{c}	8.49 ± 1.17^{c}	4.21 ± 0.97^{c}	4.88 ± 0.68^{c}	15.40 ± 3.95^{c}	3.66 ± 0.19^{c}	8.27 ± 2.74^{c}
Mn	68.75 ± 15.77^{b,c}	95.15 ± 10.39^{a,b}	54.68 ± 10.22^{b,c}	50.90 ± 6.27^{b,c}	48.17 ± 4.19^{b,c}	46.57 ± 1.52^{bc}	73.17 ± 7.51^{bc}
Ni	2.21 ± 1.00^{c}	3.70 ± 0.41^{c}	2.04 ± 0.67^{c}	2.54 ± 1.43^{c}	2.87 ± 0.73^{c}	1.25 ± 0.45^{c}	3.48 ± 0.73^{c}
Pb	12.63 ± 1.94^{c}	10.94 ± 1.79^{c}	8.99 ± 1.62^{c}	9.00 ± 0.56^{c}	16.49 ± 1.61^{c}	9.38 ± 0.86^{c}	151.85 ± 2.63^{a}
Zn	8.13 ± 1.27^{c}	6.15 ± 1.13^{c}	5.80 ± 1.26^{c}	11.60 ± 1.85^{c}	20.04 ± 7.37^{c}	4.98 ± 0.42^{c}	24.13 ± 4.56^{bc}
DTPA							
Cd	0.16 ± 0.03^{f}	0.18 ± 0.02^{f}	0.18 ± 0.04^{f}	0.13 ± 0.01^{f}	0.20 ± 0.02^{f}	0.21 ± 0.04^{f}	1.15 ± 0.00^{f}
Cu	1.77 ± 0.38^{f}	2.39 ± 0.53^{f}	1.14 ± 0.21^{f}	1.58 ± 0.08^{f}	5.61 ± 1.72^{f}	1.25 ± 0.09^{f}	2.97 ± 1.37^{f}
Mn	20.90 ± 3.91^{b,c}	28.15 ± 3.35^{a}	12.77 ± 6.21^{d,e}	26.58 ± 1.89^{a,b}	22.45 ± 2.88^{a,b,c}	20.08 ± 3.93^{c}	16.94 ± 6.70^{cd}
Ni	0.72 ± 0.05^{f}	0.77 ± 0.03^{f}	0.53 ± 0.04^{f}	0.80 ± 0.06^{f}	0.72 ± 0.06^{f}	0.75 ± 0.04^{f}	0.46 ± 0.12^{f}
Pb	2.28 ± 0.34^{f}	4.64 ± 1.25^{f}	2.04 ± 0.63^{f}	1.29 ± 0.11^{f}	6.90 ± 1.27^{ef}	1.42 ± 0.08^{f}	12.70 ± 1.22^{de}
Zn	3.68 ± 0.81^{f}	1.58 ± 0.36^{f}	1.81 ± 0.74^{f}	2.55 ± 0.49^{f}	1.53 ± 0.52^{f}	3.35 ± 0.62^{f}	3.54 ± 1.07^{f}
Total							
Cd	0.93 ± 0.14^{c}	1.13 ± 0.08^{c}	1.02 ± 0.25^{c}	1.23 ± 0.13^{c}	1.15 ± 0.06^{c}	1.28 ± 0.15^{c}	8.57 ± 0.16^{c}
Cu	42.35 ± 7.17^{c}	36.23 ± 5.04^{c}	54.36 ± 1.42^{c}	30.95 ± 2.91^{c}	27.66 ± 2.38^{c}	27.94 ± 0.58^{c}	66.64 ± 10.27^{c}
Mn	381.7 ± 24.1^{b}	403.5 ± 16.2^{b}	372.7 ± 6.2^{b}	395.3 ± 20.4^{b}	404.6 ± 28.2^{b}	530.8 ± 25.4^{b}	930.6 ± 50.4^{a}
Ni	38.11 ± 2.37^{b}	46.23 ± 1.95^{c}	48.54 ± 2.66^{c}	42.46 ± 6.35^{c}	48.43 ± 3.70^{c}	60.10 ± 8.81^{c}	62.79 ± 5.45^{c}
Pb	37.01 ± 6.04^{c}	31.05 ± 7.15^{c}	41.31 ± 11.69^{c}	23.15 ± 2.75^{c}	24.42 ± 4.13^{c}	16.59 ± 1.72^{c}	386.50 ± 5.53^{b}
Zn	50.50 ± 7.06^{c}	71.13 ± 7.76^{c}	67.09 ± 5.86^{c}	63.72 ± 13.32^{c}	83.99 ± 24.44^{c}	49.36 ± 5.09^{c}	126.61 ± 14.10^{c}

Values followed by the same letter for each extractant do not differ at the level of 5% (Duncan's test)

use and two soils) compared to polluted land (mean of two soils) in various extractants were presented in Table 5. The results showed that except for EDTA extractant, in all other extractants, the percentage of free HMs species were lower in polluted land compared to other land use. The Mn^{3+} was the only species in all extractants and land use. Generally, among the various extractants, the highest Cd species belonged to $CdCl^{+}$ for all land use. For Cu, Ni, and Zn in

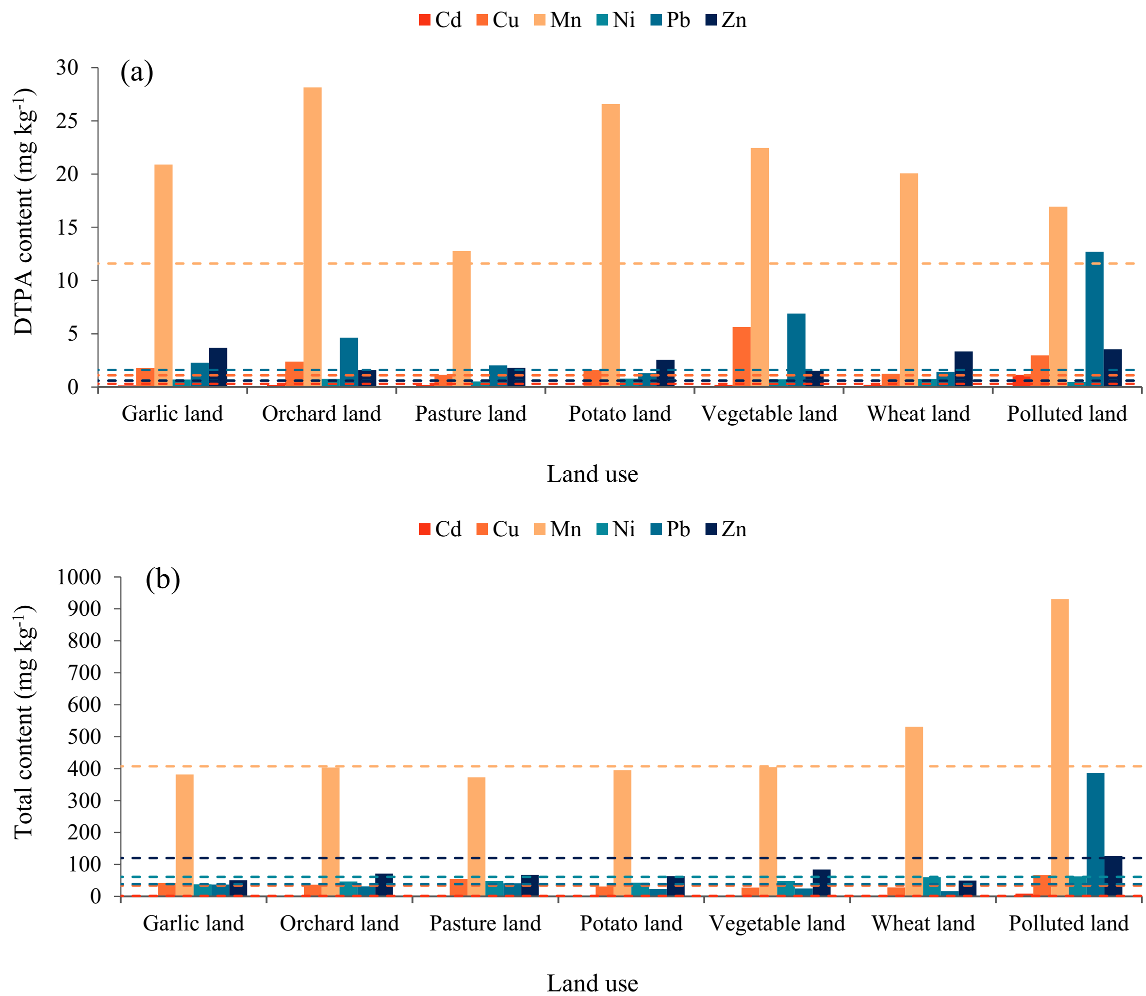


Fig. 2 The DTPA (**a**) and total (**b**) contents of heavy metals in various land use. Dash lines represented the background values for each heavy metal

most extractants the highest species belonged to Cu^{2+}, Ni^{2+}, and Zn^{2+}, respectively. Different Pb species were dominant in different land use and different extractant (Table 5). The equilibrium pH of $CaCl_2$, HCl, HNO_3, EDTA, and DTPA extractants (mean of all land use) were 6.81, 3.90, 1.30, 7.88, and 7.31, respectively. This resulted in a higher percentage of HMs complexes with CO_3 and HCO_3 species in EDTA and DTPA extractants, and zero percentage in HCl and HNO_3 extractants. Jalali and Hurseresht (2020) stated that at pH higher than 7, the negative charges are dominant and may result in reabsorption of HMs in soil, and decreases the availability. However, at lower pH the positive charges are dominant and reabsorption of HMs is not happening. The dissolution of soil minerals and the exchanging of HMs with H^+ are the main mechanisms of HMs availability in low pH.

Risk assessment

Seven classes were introduced based on the I_{geo} value, which including unpolluted ($I_{geo} < 0$), unpolluted to moderately polluted ($0 < I_{geo} \leq 1$), moderately polluted ($1 < I_{geo} \leq 2$), moderately to heavily polluted ($2 < I_{geo} \leq 3$), heavily polluted ($3 < I_{geo} \leq 4$), heavily to extremely polluted ($4 < I_{geo} \leq 5$), and extremely polluted ($5 < I_{geo}$) (Muller 1969). Figure 3a shows the I_{geo} index calculated for HMs in various land use. Among the various land use, the I_{geo} calculated for Cd and Pb in polluted land were categorized as moderately to heavily polluted, and Cu and Mn were categorized as unpolluted to moderately polluted. The I_{geo} calculated for Cu in pasture land was categorized as unpolluted to moderately polluted. All other I_{geo} calculated for HMs in various land use were categorized as unpolluted. Four classes were also

Table 5 The mean percentage of heavy metals species in garlic, orchard, pasture, potato, vegetable, and wheat lands (other land use) compared to polluted land in various extractants

Species	Other land use					Polluted land				
	$CaCl_2$	HCl	HNO_3	EDTA	DTPA	$CaCl_2$	HCl	HNO_3	EDTA	DTPA
Cd^{2+}	22.8	16.1	46.9	49.8	26.0	20.3	15.0	37.3	65.9	19.2
$CdCl^+$	58.3	63.3	3.1	46.2	51.5	50.3	62.9	1.0	33.0	41.6
$CdCl_2$	11.1	18.8	0	2.8	7.6	9.4	20.0	0	0.9	6.8
$CdSO_4$	6.1	0	36.1	0.0	6.1	14.1	0	38.8	0	17.4
Cu^{2+}	61.3	83.5	63.9	15.3	27.9	50.6	2.3	59.8	91.1	21.2
$Cu(OH)_2$	23.9	16.3	0	83.9	65.3	22.2	96.9	0	7.3	63.3
$CuSO_4$	12.7	0	36.1	0	4.5	25.2	0	40.2	0	13.4
Mn^{3+}	100	100	100	100	100	100	100	100	100	100
Ni^{2+}	73.2	87.5	63.1	92.3	34.8	58.8	85.9	55.4	97.5	26.5
$NiSO_4$	13.9	0	36.6	0	5.8	30.0	0	44.1	0	17.9
$NiCl^+$	6.2	12.3	0.1	2.5	2.3	5.3	13.5	0.1	1.3	2.2
$NiHCO_3^+$	6.2	0	0	0	49.0	5.4	0	0	1.1	45.4
Pb^{2+}	18.1	33.6	35.8	32.2	0.8	14.5	27.2	27.7	68.1	0.6
$PbCO_3$	41.8	0	0	0	79.6	38.9	0	0	10.5	74.0
$PbCl^+$	19.3	55.1	1.0	12.9	0.7	15.0	47.6	0.3	14.2	0.5
$PbSO_4$	9.6	0	53.5	0	0.3	19.6	0	56.1	0	1.0
$PbOH^+$	1.1	4.1	0	44.7	0.1	1.0	18.2	0	2.3	0.1
Zn^{2+}	71.2	88.9	57.2	58.2	19.6	55.4	85.3	50.8	97.2	14.2
$ZnSO_4$	14.9	0	33.2	0	3.5	28.3	0	34.2	0.0	9.2
$ZnCl^+$	5.0	9.1	0.1	1.6	1.1	3.5	9.0	0	1.4	0.8
$ZnHCO_3^+$	4.9	0	0	0	22.5	3.5	0	0	1.1	15.2
$Zn(CO3)_2^{-2}$	0.1	0	0	0	30.4	0.1	0	0	0	39.2

introduced based on the *RI* value, which included low risk ($RI \leq 150$), moderate risk ($150 < RI \leq 300$), considerable risk ($300 < RI \leq 600$), and high risk ($RI > 600$). As it was shown in Fig. 3b, only *RI* calculated for Cd in polluted land was categorized as moderate risk, but *RI* calculated for other HMs in various land use were categorized as low risk. According to Liu et al. (2019), the grasslands and forests have moderate levels of Cd, Cr, Cu, and Zn pollution based on I_{geo} index and a high potential for *RI* caused by urbanization.

The *AR* is HMs availability indices normalized by the total contents of HMs. The *AR* reduces the effect of a geogenic factor on HMs availability (Massas et al. 2013). The *AR* is an important indicator providing information about soil enrichment with HMs. Figure 4 shows the *AR* calculated for various available HMs using different extractants. Among the extractants, the mean *AR* calculated for HMs decreased in the following order: HNO_3 (28.08%) > EDTA (26.36%) > HCl (21.55%) > DTPA (7.11%) > $CaCl_2$ (3.19%). The order was the same as the mean contents of HMs discussed in "Soil properties and heavy metals contents". In all extractants, vegetable land had the largest percentage of HMs that could be extracted, followed closely by potato, garlic, orchard, wheat, and polluted lands, with pasture land having the lowest percentage of extractability. According to the *AR* calculated using different extractants, the Cd and Pb generally had the highest percentage of extractability, while the Ni had the lowest. When $CaCl_2$ was used to extract HMs, the results of comparing the *AR* calculated for polluted land with other land use revealed that the percentage of extractability in polluted land (mean of all HMs, 3.68%) was higher than the other land use (mean of all other land use, 3.11%). However, in other extractants, a different result was observed, and the percentage of extractability in polluted land was lower than the other land use. It has been established that HMs accumulation in soil was mostly caused by chemical and organic fertilizers and pesticides containing HMs (Jalali et al. 2021). Due to the excessive and inappropriate use of chemical fertilizer in high-intensive cropping patterns, the likelihood and rate of HMs accumulation in soils were both enhanced (Bai et al. 2010). Cadmium, Cu, Pb, and Zn are examples of HMs that may have accumulated unintentionally in the soil as a result of the usage of agrochemicals such as pesticides and fertilizers. Phosphorus and other HMs are more readily available in Iranian agricultural soils as a result of the heavy application of P fertilizers. According to Jalali and Ahmadi Mohammad Zinli (2011), soils under potato and vegetable farms have higher average Olsen-P values than pasture and wheat fields. Numerous studies (Bai et al. 2010; Jalali et al. 2021; McLaughlin et al. 2021) revealed that one of the primary factors contributing to the accumulation of Cd in soils was the use of phosphate fertilizers with high Cd contents. The information given by

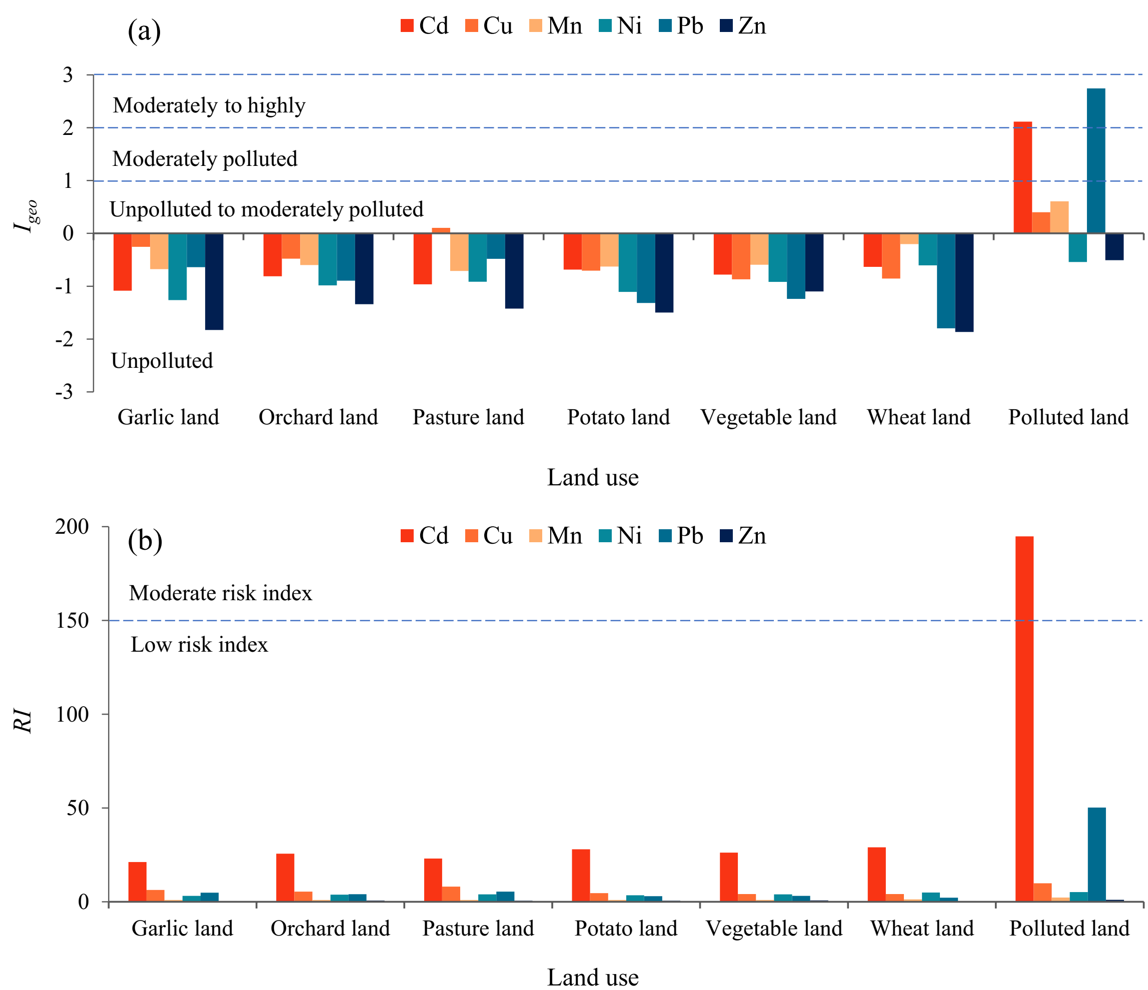


Fig. 3 The geo-accumulation index (**a**) and the ecological risk index (**b**) calculated for heavy metals in various land use

Latifi and Jalali (2018) indicates that K, nitrogen, and sulfur fertilizers do not contain significant amounts of Cd and will consequently have a negligible effect on the accumulation of Cd in soil. Contrarily, a significant source of Cd in agricultural systems comes from P fertilizer (McLaughlin et al. 2021). Latifi and Jalali (2018) investigated the HMs in several nitrogen, K, and P fertilizers that are often applied in Iran. They claimed that HMs were present in higher contents in P fertilizers than in nitrogen and K fertilizers. They found that the average amount of HMs in P fertilizers for Cd, Cu, Mn, Ni, Pb, and Zn were 4.0, 24.4, 272, 14.3, 6.0, and 226 mg kg^{-1}, respectively. Their investigation involved 41 samples of Iranian fertilizers. The amount of P fertilizer used on the garlic, orchard, potato, and wheat lands in the study area is approximately 93, 23, 141, and 35 kg P ha^{-1} $year^{-1}$ (Table 6). As shown in Table 6, the addition of P to the soil in the study area led to increases the content of Cd, Cu, Mn, Ni, and Zn in soils, which ranged from 0.09 to 0.56, 2.3 to 9.2, 6.3 to 38.4, 0.3 to 2.0, 0.1 to 0.8, and 5.2 to 31.9 g ha^{-1} $year^{-1}$, respectively. Potato and garlic lands received higher HMs, as indicated in Table 6. Other sources of HMs addition in soil include manures, biosolids, composts, and other organic fertilizers (McLaughlin et al. 2021). As a result, it implies that extensive and frequent farming operations for crops like potatoes, garlic, and vegetables may have enriched HMs in surface soil.

The values of *HQ* and *HI* for HMs in various land use are presented in Table 7. The highest mean value of *HQ* (mean of all HMs and land use) was found in the following order: ingestion (7.27E–03) > dermal (4.25E–04) > inhalation (3.82E–04). Generally, the highest *HQ* was observed in polluted land (mean of all HMs). The HMs may cause non-carcinogenic effects to the population if *HI* exceeds 1, otherwise, the non-carcinogenic effects of HMs to the population are not significant. As presented in Table 7, the non-carcinogenic risk of all calculated HMs in various land use were less than 1, which shows that the health risks of these HMs are not significant under the conditions and assumptions of the assessment. Generally, Pb and Mn are the main contributors to the total health risks, while Cu and Zn were

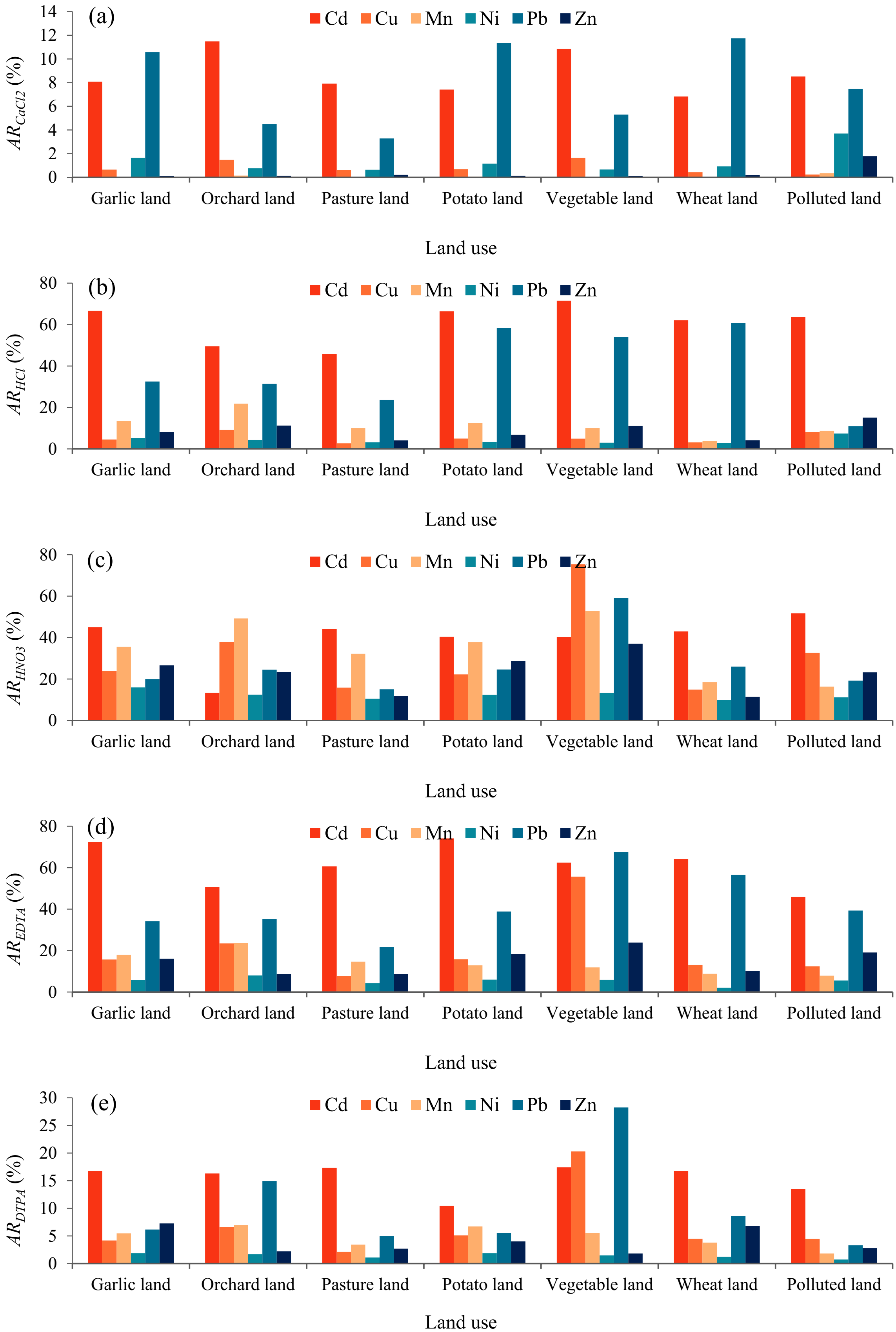


Fig. 4 The availability ratio calculated based on $CaCl_2$ (**a**), HCl (**b**), HNO_3 (**c**), EDTA (**d**), and DTPA (**e**) for heavy metals in various land use

Table 6 The amount of heavy metals added to various land use due to the addition of phosphorus fertilizer (calculated based on the amount of heavy metals in phosphorus fertilizers)

Land use	Added Phosphate (P_2O_5)	Added P	Cd	Cu	Mn	Ni	Pb	Zn
	kg ha^{-1}		mg ha^{-1}					
Garlic land	213.2[a]	93	372	9151.2	25,296	1329.9	558	21,018
Orchard land	52.3[b]	23	92	2263.2	6256	328.9	138	5198
Potato land	322.6[c]	141	564	3468.6	38,352	2016.3	846	31,866
Wheat land	80.54[d]	35	140	3444.0	9520	500.5	210	7910

[a]Samavatean et al. (2011)

[b]Banaeian and Zangeneh (2011)

[c]Hamedani et al. (2011)

[d]Ghasemi-Mobtaker et al. (2020)

Table 7 The hazard quotient (*HQ*) and the hazard index (*HI*) for non-carcinogenic risk (adults) calculated in various land use

	Garlic land ($n=8$)	Orchard land ($n=10$)	Pasture land ($n=7$)	Potato land ($n=11$)	Vegetable land ($n=9$)	Wheat land ($n=9$)	Polluted land ($n=9$)
$HQ_{Ingestion}$							
Cd	4.88E-04	5.89E-04	5.31E-04	6.44E-04	6.03E-04	6.68E-04	4.48E-03
Cu	5.54E-04	4.74E-04	7.11E-04	4.05E-04	3.62E-04	3.65E-04	8.71E-04
Mn	8.32E-03	8.79E-03	8.12E-03	8.61E-03	8.82E-03	1.16E-02	2.03E-02
Ni	9.96E-04	1.21E-03	1.27E-03	1.11E-03	1.27E-03	1.57E-03	1.64E-03
Pb	1.38E-02	1.16E-02	1.54E-02	8.64E-03	9.12E-03	6.20E-03	1.44E-01
Zn	8.83E-05	1.24E-04	1.17E-04	1.11E-04	1.46E-04	8.60E-05	2.21E-04
$HQ_{Inhalation}$							
Cd	3.28E-06	3.96E-06	3.57E-06	4.33E-06	4.05E-06	4.49E-06	3.01E-05
Cu	2.12E-07	1.82E-07	2.73E-07	1.55E-07	1.39E-07	1.40E-07	3.34E-07
Mn	1.53E-03	1.62E-03	1.50E-03	1.59E-03	1.62E-03	2.13E-03	3.74E-03
Ni	3.71E-07	4.50E-07	4.73E-07	4.14E-07	4.72E-07	5.85E-07	6.12E-07
Pb	1.49E-04	1.25E-04	1.66E-04	9.29E-05	9.80E-05	6.66E-05	1.55E-03
Zn	3.39E-08	4.76E-08	4.49E-08	4.26E-08	5.62E-08	3.30E-08	8.47E-08
HQ_{Dermal}							
Cd	1.19E-04	1.44E-04	1.29E-04	1.57E-04	1.47E-04	1.63E-04	1.09E-03
Cu	1.12E-05	9.61E-06	1.44E-05	8.21E-06	7.34E-06	7.41E-06	1.77E-05
Mn	1.27E-03	1.34E-03	1.24E-03	1.31E-03	1.34E-03	1.76E-03	3.09E-03
Ni	2.25E-05	2.73E-05	2.86E-05	2.50E-05	2.86E-05	3.54E-05	3.70E-05
Pb	2.81E-04	2.35E-04	3.13E-04	1.75E-04	1.85E-04	1.26E-04	2.93E-03
Zn	2.69E-06	3.77E-06	3.56E-06	3.38E-06	4.46E-06	2.62E-06	6.72E-06
HI							
Cd	6.10E-04	7.37E-04	6.64E-04	8.05E-04	7.54E-04	8.35E-04	5.60E-03
Cu	5.65E-04	4.83E-04	7.25E-04	4.13E-04	3.69E-04	3.73E-04	8.89E-04
Mn	1.11E-02	1.17E-02	1.09E-02	1.15E-02	1.18E-02	1.55E-02	2.71E-02
Ni	1.02E-03	1.24E-03	1.30E-03	1.14E-03	1.30E-03	1.61E-03	1.68E-03
Pb	1.42E-02	1.20E-02	1.59E-02	8.91E-03	9.40E-03	6.39E-03	1.49E-01
Zn	9.10E-05	1.28E-04	1.21E-04	1.14E-04	1.51E-04	8.87E-05	2.27E-04

the least risks. Among different land use, the following order was observed for *HI*: polluted land > pasture land > garlic land > orchard land > wheat land > vegetable land > potato land. Liu et al. (2019) observed that the highest mean calculated *HQ* belonged to ingestion followed by inhalation and dermal contact. Huang et al. (2018) studied the health risk assessment of HMs in various land use. They reported that the *HI* value calculated for adults was all lower than 1, however, this value for children in residential and farm land were higher than 1. Jiang et al. (2021) also noted that Cu and

Zn are the least significant supporters to *HI*, while Cd and Pb are the main contributors. They stated that for Pb and Zn the ingestion is the main channel of absorption and for Cd and Cu the dermal absorption is the main channel. They added that Cd and Pb's higher toxicity was the reason why they had higher *HI* than Cu and Zn.

Correlation analysis

Pearson's correlation analysis of *AR* of HMs with soil properties was performed for EDTA and DTPA extractants. In EDTA extractant, the *AR* of Cu and Zn showed no significant correlation with any soil properties, while other HMs were mostly correlated with EC, CCE, clay, and sand. In DTPA extractant, which is a common soil extractant in soil testing, the *AR* of Ni showed no significant correlation with any soil properties, while the *AR* of other HMs were mostly correlated with pH, CEC, OM, silt, and sand (results not shown). Massas et al. (2013) observed that the DTPA extractable Mn and Zn were negatively correlated with pH. They also reported that the DTPA extractable Fe and Zn were negatively correlated with clay and positively correlated with OM, whereas DTPA extractable Pb was also positively correlated with CCE. Rivera et al. (2016) observed that the Cd and Cu extracted by EDTA positively correlated with EC and Zn negatively correlated with clay. Zhong et al. (2020) stated that pH and EC were the most important factors affecting HMs availability. They observed significant negative correlations for the *AR* of Cd, Cr, Cu, Ni, Pb, and Zn with pH, and significant positive correlations for the *AR* of Cd, Cr, Cu, Ni, and Zn with EC. Such results were also reported in other studies (e.g., Jalali et al. 2022; Zhen et al. 2019). Decreasing the soil pH resulted in decreasing the negative charges on minerals, oxides, and organic surfaces, which resulted in decreasing in HM ions sorption and increasing the competition for free HM ions with other cations, therefore the availability of the HMs increased (Zhen et al. 2019; Zhong et al. 2020). Lowering soil pH, increases competition between free HM ions with other cations, thereby increasing the availability of the HMs (Zhen et al. 2019; Zhong et al. 2020). Increasing EC increases HMs availability. Complex formation of anions with HMs and competition of cations with HMs derived from high ECs increases the availability of HM (Acosta et al. 2011b). Soil OM can significantly affect HMs availability. Organics matter contain many functional groups that can adsorb HMs through complexation reactions, sometimes reducing the availability of HMs and sometimes increasing their availability (Antoniadis et al. 2017; Zeng et al. 2011). Higher clay and silt contents lead to lower HMs availability, while higher sand contents lead to higher HMs availability and higher contents of minerals provided more sites for HMs adsorption. The presence of calcium carbonate decreases the HMs availability by increasing the pH and formation of insoluble metal carbonates (Hooda 2010).

The relationship between *AR*, calculated based on EDTA and DTPA for HMs in various land use is presented in Fig. 5. Cadmium, Cu, Mn, and Pb all showed a significant correlation (combined of all land use), and Cu and Pb showed a strong relationship, indicating that these two extractants had similar abilities in extracting Cd, Mn, and especially Cu and Pb from soils (Fig. 5).

The multivariate analyses were performed for the *AR* of HMs calculated based on EDTA and DTPA for the combination of various land use and the dendrograms were presented in Fig. 6. According to the results, Mn and Ni were included in the same cluster when using the EDTA extractant, whereas Cu and Pb were included in the same cluster when using both EDTA and DTPA extractants were used (Fig. 6). The noteworthy feature of this cluster is the use of *AR* of HMs rather than available ones, which considers both available and total HMs in soil.

Environmental implications

Our results show the significance of soil properties, different land use, and extractants when assessing soil enrichment with HMs. It was indicated that in DTPA extractant, which is a common soil extractant and used to extract micro nutrients and well correlated with plant response, the *AR* of HMs were mostly correlated with some soil parameters. Thus, soil parameters can be used to predict available form of HMs. It was advised to take into account both the total HMs contents and their available forms in order to assess the status of HMs because their availability varies depending on the type of land use and the extractant being employed. This led to the calculation of *AR*, which can describe the status of HMs more accurately than a single extractor. The relationships between various soil tests found in this study can be utilized to report the amounts of HMs for another soil test method. Certain laboratories may use a particular soil-test method to assess available HMs in soil samples. Advantages of correlation between different methods to extract HMs from soil arise from the need for cross-method interpretation. Traditionally, the level of total HMs in soil is compared to the total background level to assess soil contamination due to the presence of HMs in soil, but background levels of available HMs were used for the first time in this study. Based on available background of HMs (DTPA), it was noted that in most land uses, HMs content were higher than the corresponding background values. It was indicated that the greatest increase in HM levels compared to background levels was observed with Zn and that the mean contents of Zn in all land use were higher than the Zn background level. As a result of human activities, HMs

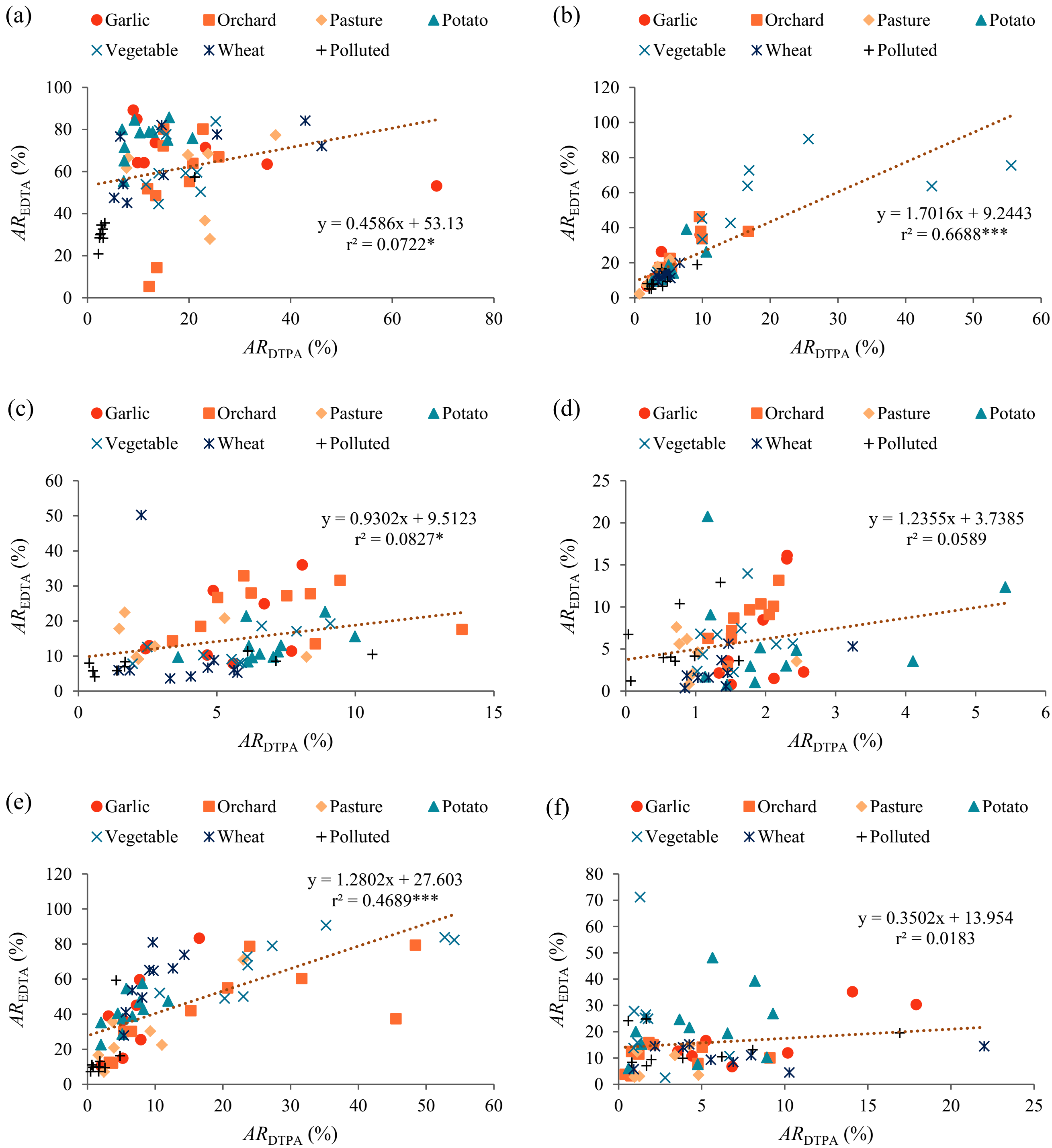
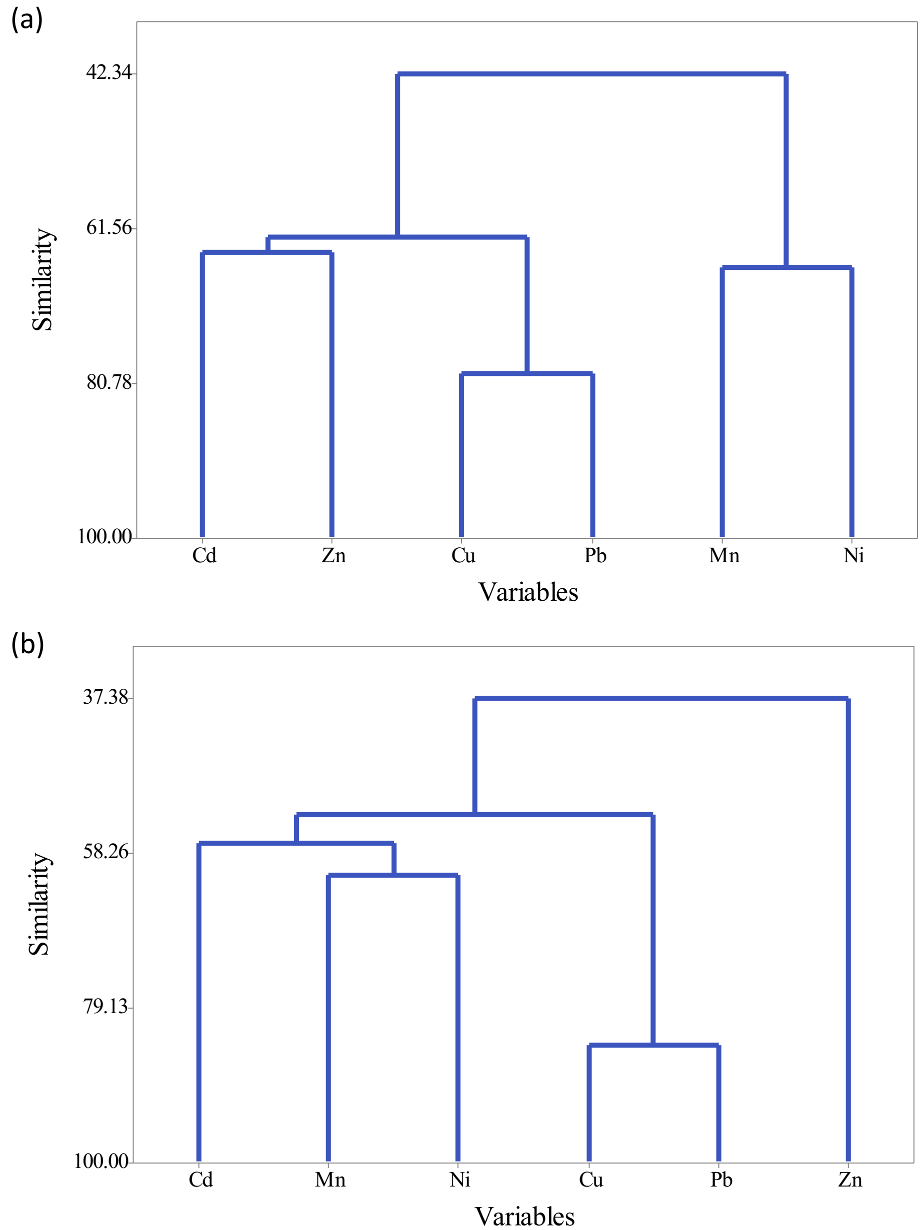


Fig. 5 The relationship between availability ratio, calculated based on EDTA and DTPA for Cd (**a**), Cu (**b**), Mn (**c**), Ni (**d**), Pb (**e**), and Zn (**f**). Dot lines represented the linear relation fitted to all land use. * and *** denote levels of significance at $P<0.05$ and $P<0.001$

can be found at levels well above background levels in a variety of environmental conditions (Vareda et al. 2019). This indicates that the greatest impact of anthropogenic activity has resulted in an increase in available Zn content, and further research should be conducted to trace sources of Zn contamination in these land use. Available forms of HMs are not only considered toxic but are mobile and can penetrate soil profiles and contaminate groundwater. They accumulate in ecosystems and are mostly toxic, so they can be dangerous when accumulated in living organisms

Fig. 6 Dendrogram of heavy metals availability ratio calculated based on EDTA (**a**) and DTPA (**b**) extractants



(Vareda et al. 2019). The highest abundance of Cd species belonged to $CdCl^+$, which with its high mobility, could be a risk for plant uptake and leaching from soil profile resulting in contamination of groundwater. Although, the content of Cd was not much higher than the background levels; however, based on risk assessment parameters, Cd along with Pb resented higher risk compared to other HMs. Regarding various land use, still, the HI was low for all HMs in all land use; however, other risk assessment parameters highlighted the risk of polluted land. Nevertheless, in this study, we only looked at the influence of some total and available HMs content on human health risk in a few land uses. Further research should concentrate on HMs availability and toxicity in various land uses from concurrent exposure to numerous HMs in order to have a comprehensive understanding of the possible risk.

Conclusions

In this study, we evaluated the speciation and risk assessment of Cd, Cu, Mn, Ni, Pb, and Zn extracted with $CaCl_2$, HCl, HNO_3, EDTA, and DTPA extractants in various land use. Based on available contents (DTPA) of HMs in most land use, the HMs content were higher than their corresponding background levels, while, based on total HMs background levels, in most land use (except polluted land use) the total contents of most HMs were lower than their corresponding background levels. The speciation of HMs indicated that the highest abundance of Cd species belonged to $CdCl^+$, which with its high mobility, could be a risk for plant uptake and leaching from soil profile resulting in contamination of groundwater. Further studies should focus on HMs availability and toxicity in different land uses by simultaneous exposure to multiple HMs to better understand the potential risks of HMs. The *AR* parameter considering both available and total HMs content was calculated and provided important information about soil enrichment with HMs in different land use. Among the extractants, the mean *AR* calculated for HMs decreased in following order: $HNO_3 > EDTA > HCl > DTPA > CaCl_2$. In assessing anthropogenic activity, it is very important to consider not only the total HMs content, but also the available HMs content. There were strong correlations between *AR*, calculated based on EDTA and DTPA for Cu and Pb in all land use, indicating that these two extractants had similar abilities in extracting Cu and Pb from soils having different Cu and Pb contents. In DTPA extractant, the *AR* of Ni showed no significant correlation with any soil properties, while the *AR* of other HMs were mostly correlated with soil properties. These correlations can be used to estimate the content of HMs in soils in various land use zones with diverse physical and chemical properties. Although most soils can exhibit this relationship, it is clear that different soils have different *ARs* due to the presence of different soil components, so further studies are needed to determine its exact strength. The extensive agricultural activities in garlic, orchard, potato, vegetable, and wheat lands may result in higher contents of Cd, Cu, Mn, Ni, Pb, and Zn and higher potential risk to humans and the environment compared to pasture land. However, the heavy industrial and mining activities in polluted land may result in higher contents of HMs and potential risk compared to other land use. It can also conclude that for evaluating the anthropogenic activities not only considering the total contents of HMs but also the available contents of HMs could be very important.

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Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

Research involves human and animal participant This manuscript does not contain any animal research.

Consent to participate Informed consent was obtained from all individual participants included in the study.

Consent to publish This manuscript does not contain any individual person's data in any form.

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