



Analysis, spatial distribution and ecological risk assessment of arsenic and some heavy metals of agricultural soils, case study: South of Iran

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Abstract

Purpose In this study, rates of arsenic, cadmium, chromium, copper, lead and zinc contents in agricultural soils from Eghlid County, south of Iran, were determined to assess the soil pollution and potential ecological risk index (PERI) and also spatial distribution of such elements.

Method A total of 100 topsoil specimens were collected from 100 sampling stations. In the laboratory, after acid digestion the element contents in soil samples were determined using ICP-OES. Then, the soil contamination and also ecological risk of the soil were assessed using various indices especially Igeo, PI, IPI, PLI and PERI. Also, the spatial distribution maps of the studied elements in soil specimens were made using the kriging interpolation technique by ArcGIS software (10.4).

Results Based on the results, the mean contents (mg/kg) of the elements in specimens were 1.85, 2.80, 19.04, 19.35, 7.17 and 38.77 for As, Cd, Cr, Cu, Pb and Zn, respectively. Arsenic and Cu contents were comparable to background values, while Cd contents were higher than their corresponding background values. The results of principal component analysis (PCA) and hierarchical cluster analysis (HCA) revealed that Cd had anthropogenic sources; while, other elements originated from natural sources. Pollution index (PI) values of As, Cd, Cr, Cu, Pb and Zn varied in the range of 0.45–1.49, 0.52–32.09, 0.096–0.33, 0.36–1.35, 0.18–0.32 and 0.23–1.59, with mean values of 0.92, 12.17, 0.21, 0.68, 0.21 and 0.96, respectively. The integrated pollution load index (PLI) values of the specimens with an average value of 0.84, indicated that 65% and 35% of soil samples were moderately and low contaminated, respectively. The mean value of PERI with 380.32 implied that the agricultural soils of the study area could be classified of high ecological risk. The spatial distribution of content of the elements showed that Cd had high spatial variability.

Conclusions Although in the short run, the contents of the elements found in the agricultural soil samples may not be alarming for agricultural production and consequently human health, signals it can be observed especially for Cd in the long term due to the impact of anthropogenic activities that lead to the discharge of this element to the environment and can result in its accumulation in agricultural soils. In conclusion, as it is expected that the metal inputs increase in the future, it is recommended that plant analyses be included in the future studies for determining the impact of the amount of bioavailable metals.

Keywords Ecological risk assessment · Heavy metals · Soil contamination · Iran

Introduction

Nowadays, we consider heavy metals as hazardous contaminants due to their bioavailability, their bioaccumulation

potential, their prevalence, and their toxicity, and consequently their adverse effects on the health of the environmental and human health. These elements originate from both natural and anthropogenic sources main among which, the use of chemical and organic fertilizers and pesticides containing toxic heavy metals, mining, power generation, development of industrialization and urbanization, waste spills, smelting, and fuel combustion are the most important sources of metal emissions [4, 22, 25, 37, 50, 52].

Trace elements particularly Cu and Zn are important for their essential functional and structural roles in the biological systems [24, 27, 29]. However, it should be noted that exposure to high levels of Zn and Cu can lead to serious health

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effects such as extensive lesions in the kidneys, nephritis, anuria, hair loss, inflammation in the brain tissue, fatigue, acne, anorexia, panic attacks, allergies, premenstrual syndrome, depressor inverse ion, migraines, anxiety, childhood hyperactivity, kidney and liver dysfunctions, learning disorders, adrenal hyperactivity and insufficiency, autism, and even cancer [1, 2, 24]. Arsenic is a metalloid and as a carcinogen agent does not have any benefits for living organisms even at low levels. Anorexia, fever, hair loss, goiter, fluid loss, herpes, impaired healing, muscle spasms, weakness, decreased production of red and white blood cells, nausea and vomiting and especially kidney and liver damage are the main consequences of the exposure to As [53, 56]. Although Cr(III) plays an important role in the metabolism of the macromolecules, hexavalent chromium (Cr(VI)), is a carcinogen agent and exposure to this element can cause adverse effects on human health, including nose ulcers, wheezing, shortness of breath and asthma [28, 51]. Cadmium and Pb as very toxic elements even at extremely low levels can cause injuries to the kidneys, and may result in poor reproductive capacity, hepatic dysfunctioning, hypertension and tumors [19, 24]. Moreover, learning disabilities, hyperactivity, slow growth, impaired hearing, antisocial behaviors and reduction in children's IQ are the main effects of exposure to Pb [16].

It has been shown that, agricultural soils contamination by toxic heavy metals occurs mainly via manures, agrochemicals, compost amendments and biosolids [10, 37, 45], which can halt soil microbial activities [42, 66], reducing soil fertility and inhibiting the seed germination [15, 48] and a nutrient imbalance in plants [13]. On the other hand, toxic heavy metals contamination can result in the accumulation of such elements in crops and consequently their appearance in the food chain which may prove detrimental to the human health [14, 30, 36, 45, 48, 61]. Therefore, it seems that much attention needs to be paid to the issues relating to the agricultural soil contamination by trace elements.

The review of literature shows that in the recent decades, many studies have been carried out on soil contamination analyzing the toxic elements especially in the developed countries [11, 20, 31, 34, 39, 45, 47, 59, 62, 67]. However, few such studies have been performed in the developing countries notably Iran, where traditional agricultural practices and the use of chemical fertilizers are prevalent. Therefore, the present study was conducted in one of the main agricultural and horticultural areas in the southern of Iran known as Eghlid, where soil contamination by heavy metals appears high due to the excessive use of agricultural inputs. The study aimed at (1) analyzing and plotting the spatial distribution of As, Cd, Cr, Cu, Pb and Zn in surface soils collected from Eghlid County; (2) assessing the soil contamination and also the ecological risks of soil using various indices especially Igeo, PI, IPI, PLI and PERI; and (3) identifying the sources of the elements using HCA and PCA.

Materials and methods

Study area

Eghlid County with an area of 7054 km² is located at the northern parts of Fars Province, south of Iran. City of Eghlid is the capital of this county with more than 49000 residents (<https://www.amar.org.ir>). This county is one of the green mountainous areas of Fars Province and located between 52° 41' 53'' eastern longitude and 30° 53' 42'' northern latitude with 2 urban regions (Eghlid and Sedeh), 3 districts, 9 hamlets and 80 villages [46].

Samples collection

After dividing the study area into 2.5 × 2.5 km regular grid squares (systematic sampling), a total of 100 topsoil specimens (5–10 cm depth) were collected between May to June 2017 using a plastic spade and were transferred to a plastic container. Approximately about 1000 g of each specimen was used for elements analysis [58]. The sampling sites are shown in Fig. 1.

Preparation and analysis of soil specimens

After drying the specimens at room temperature (25 °C), and removing their impurities, about 50 g of each soil samples was passed through a nylon sieve (0.15 mm) and then was kept in polyethylene pockets for the analysis of total elements content [37, 61]. In so doing, 1 g of each samples was digested by triacid attack i.e., mixture of 2.5, 5 and 7.5 mL HF, HClO₄ and HNO₃, respectively, at 180 °C for 10 min in a microwave oven. Then, prepared solutions were diluted to 50 mL using double distilled water and finally, the element analysis was performed by ICP-OES (ES-710, Varian, Australia) [6, 37, 38]. Also, pH and EC of the soil specimens were determined in soil-water solution [3, 17], while its organic matter (OM) content was measured through classical redox back-titrimetry procedure [8, 65].

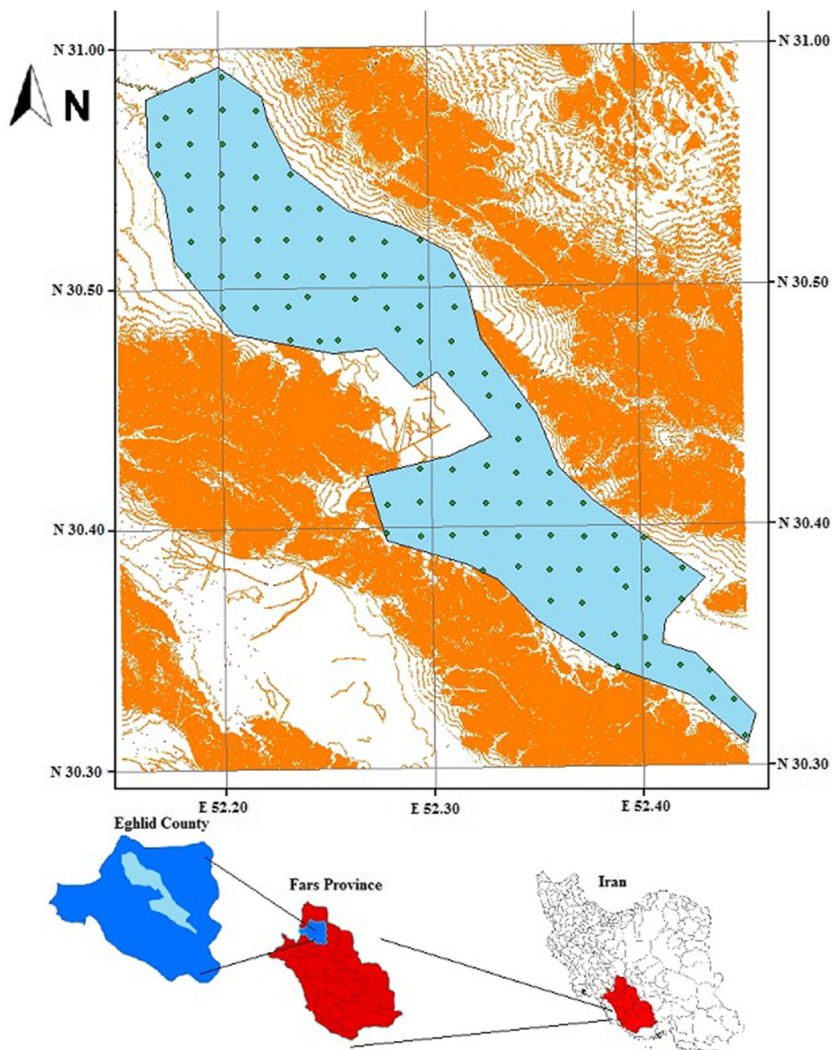
Soil quality assurance (QA) and quality control (QC)

In this study, QA and QC procedures were carried out using standard reference materials (SQC-001, Sigma-Aldrich, Spain) [61]. Recoveries of all the observed elements were good (between 94–101% for As, 92–102% for Cd, 94–101% for Cr, 98–105% for Cu, 93–104% for Pb and 97–106% for Zn, respectively).

Evaluation of the soil contamination and the potential ecological risks

In this study, different indices including Igeo, PERI, PI, IPI and PLI were used to assess the ecological risks and to survey

Fig. 1 Location of sampling sites from the study area



the degree of heavy metal contamination in the soil as described in Eq. 1 to Eq. 6:

Geo-accumulation index (Igeo)

This index is generally used for the assessment of soil contamination and classifies the possible contamination level on a scale of 1–6 [21]. This index is computed in accordance with Eq. 1:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}, \tag{1}$$

where C_n and B_n are the contents of the analyzed elements in the examined environment and the geochemical reference value of each element, respectively. Furthermore, the constant (1.5) was used to minimize the effect of probable variations in the reference values.

The classification of Igeo is presented as follows [7, 32, 40];

Range	Categories
≤ 0	Unpolluted
0–1	Unpolluted to moderately polluted
1–2	Moderately polluted
2–3	Moderately to strongly polluted
3–4	Strongly polluted
4–5	Strongly to very strongly polluted
> 5	Very strongly polluted

Potential ecological risk assessment

PERI is used to assess the degree of toxic and trace elements pollution in soils and sediments [7, 23] and is computed in

accordance with Eqs. 2 to 4:

$$RI = \sum_{i=1}^n Ei \tag{2}$$

$$Ei = Ti \times fi \tag{3}$$

$$fi = \frac{Ci}{Bi}, \tag{4}$$

where the potential ecological risk factor is shown as Ei and the toxic-response factor of the element (10, 30, 2, 5, 5 and 1 for arsenic, cadmium, chromium, copper, lead and zinc, respectively) is indicated as Ti . C_i and B_i stand for the content of the elements in the matrix and the background value of the elements, respectively [18, 2354].

The classification of E_r^i and RI are presented as follows [23]

E_r^i		RI	
Range	Categories	Range	Categories
< 40	Low	< 150	Low ecological risk
40 ≤ < 80	Moderate	150 ≤ < 300	Moderate ecological risk
80 ≤ < 160	Appreciable	300 ≤ < 600	High ecological risk
160 ≤ < 320	High	≥ 600	Significantly highest ecological risk
≤ 320	Serious		

In the current study, to evaluate contamination level of the elements and also to determine the general contamination class for a sample, PI for each element and IPI and PLI for all the analyzed elements were computed in accordance with Eqs. 5 and 6, respectively [11, 33]:

$$PI = \frac{C}{S} \tag{5}$$

$$PLI = (PI_1 \times PI_2 \times PI_3 \times \dots \times PIN)^n \tag{6}$$

where C is the determined content of each analyzed element (mg/kg), S is the reference value of the corresponding element (mg/kg) and n is the number of the studied elements.

The PI, and PLI of each element are categorized between low to high contamination and unpolluted to extremely polluted, respectively as follows [49, 60];

PI		PLI	
Range	Categories	Range	Categories
≤ 1	Low contamination	< 1	unpolluted
1 < ≤ 3	Moderate contamination	1 ≤ < 2	Moderately polluted
> 3	High contamination	2 ≤ < 3	Strongly polluted
		≥ 3	Extremely polluted

The IPI values i.e., the average value of the pollution index of the analyzed elements (Eq. 7) is categorized as follows [26, 37, 55];

$$IPI = mean(PIi) \tag{7}$$

Range	Categories
< 1	Low
1 < < 2	Middle
> 2	High

Statistical analyses

All analyses were done by SPSS software version 20.0 (SPSS Inc., USA). The mean and the standard deviations (SD) of the metals contents were computed for every sampling site. The Kolmogorov-Smirnov (K-S) test was used to assess the normality of the data. Also, correlations between the contents of the elements among soil samples were calculated using Pearson’s correlation coefficient (PCC).

Element source identification

In the current work, PCA was conducted to find out the contamination sources, and PCA and HCA were used to distinguish the different groups of elements.

Preparation of the spatial distribution maps of the elements

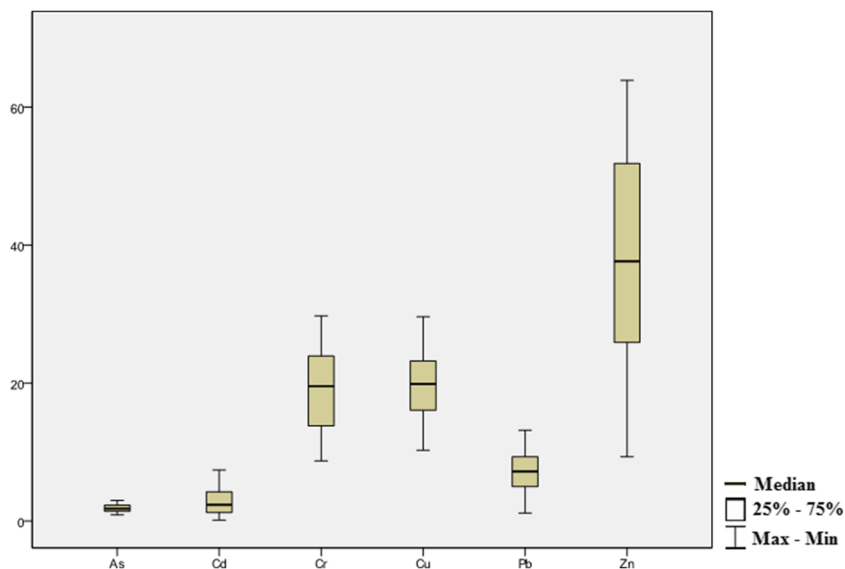
In so doing, the spatial distribution maps of the elements were made using the kriging interpolation technique by ArcGIS software (Version 10.4, ESRI Inc., USA).

Results and discussion

Soil properties

The statistical summary of soil properties data for the analyzed elements in the soil specimens of Eghlid County, together with pH, EC, OM values, are shown in Table 1. The K–S test confirmed that all the parameters are normally distributed. The median, minimum and maximum levels and the lower and upper quartile of all the analyzed elements are illustrated on the box–whisker plot diagram as shown in Fig. 2. The results revealed that the level of elements (mg/kg) varied between

Fig. 2 Contents of studied elements (mg/kg) plotted in box and Whisker method



0.90 and 2.98 for As, 0.12 and 7.38 for Cd, 8.67 and 29.76 for Cr, 10.25 and 38.33 for Cu, 6.33 and 11.07 for Pb and 9.31 and 63.87 for Zn, with an average content of 1.85, 2.80, 19.04, 19.35, 7.17 and 38.77 mg/kg, respectively. The pH values ranged between 7.21 and 8.99 with a mean value 8.28 (100% of the soils having pH above 7.0), while, the levels of EC ($\mu\text{S}/\text{cm}$) and OM (%) were detected in amounts ranging from 201 to 954 and 1 to 2.77, respectively. Based on the results, 64% of the topsoil samples had low salinity (200–400 $\mu\text{S}/\text{cm}$), 31% had mild salinity (400–800 $\mu\text{S}/\text{cm}$) and 5% had high salinity (800–1600 $\mu\text{S}/\text{cm}$) and all presented low OM contents.

Pollution assessment

The Igeo and PERI values for each element are given in Tables 2 and 3.

As shown in Table 2, based on the mean values of Igeo, the soil samples in the Eghlid County could be classified from unpolluted to strongly polluted. The results pointed to a high accumulation of cadmium, in the samples, as illustrated by its respective average value of geo-accumulation index (3.02 ± 2.62). In contrast, the Igeo value of As (-0.69), Cr (-2.84), Cu (-1.12), Pb (-2.84) and Zn (-0.64), suggested that the agricultural soils of Eghlid County are not contaminated by such elements.

Based on the results, the observed mean ecological risk index value (380.32) indicated that the agricultural soils of Eghlid County could be classified as “at high ecological risk”. In this regard, Cd with the highest mean ecological risk index (365), confirmed the results achieved through the Igeo index. Besides, as the mean PI value of arsenic was found to be 0.92, and since 64% of the agricultural topsoil specimens were categorized as low contaminated; therefore, no obvious arsenic pollution was considered in the studied samples. The mean PI

Table 1 Soil properties and coefficients of variations in agricultural soils in the Eghlid County and the reference value

	Units	Min	Max	Median	Mean	SD	CV (%)	K-S _p	Reference value (mg/kg) ^a
As	mg/kg	0.9	2.98	1.81	1.85	0.59	32	0.558	2
Cd	mg/kg	0.12	7.38	2.36	2.80	2.12	76	0.086	0.23
Cr	mg/kg	8.67	29.76	19.55	19.04	6.31	33	0.657	90
Cu	mg/kg	10.25	38.33	19.86	19.35	5.05	26	0.159	28.3
Pb	mg/kg	6.33	11.07	7.14	7.17	0.40	5	0.055	34.2
Zn	mg/kg	9.31	63.87	37.63	38.77	14.58	38	0.101	40.2
pH	-	7.21	8.99	8.23	8.28	0.37	4	0.514	
EC	$\mu\text{S}/\text{cm}$	201	954	365	427.15	168.52	39	0.061	
OM	%	1	2.77	2.20	2.13	0.48	22	0.326	

a[5, 14, 54, 57]

Table 2 Igeo values for elements in agricultural soil samples of Eghlid County

Elements	Igeo value		Class	Soil quality
	Min	Max		
As	-1.74	-0.01	0	unpolluted
Cd	-1.51	4.42	4	Strongly polluted
Cr	-4.06	-2.18	0	Unpolluted
Cu	-2.06	-0.15	0	Unpolluted
Pb	-3.06	-2.18	0	Unpolluted
Zn	-2.74	0.08	0	Unpolluted

value of Cd (12) indicates that 80% of the topsoil specimens are highly contaminated with this element. Considering the mean PI value of Cr of 0.21, it should be noted that 100% of the topsoil specimens are low contaminated with this element. The mean PI value of Cu (0.68) implies that 98% of the topsoil specimens can be classified as low contaminated soil while the mean PI value of Pb (0.21) indicates that 100% of topsoil specimens can be classified as low contaminated soil. However, the mean PI value of Zn (0.96) can mean that 54% and 46% of topsoil specimens may be classified as low contaminated and moderately contaminated soils, respectively. Finally, it can be admitted that the mean IPI value of all the studied soil specimens (2.52) may be taken to indicate that 62% of the samples can be categorized as highly contaminated soil. In other words, 21, 17 and 62 sampling sites can be regarded a low, moderate and high IPI, respectively. Furthermore, the mean PLI value of all the studied soil samples (0.84) showed that 65% of the specimens can be considered as moderately polluted soil (Table 4).

Correlation coefficient analysis

Pearson's correlation matrix for the six elements of the soil samples is shown in Table 5. As shown in the Table, in the agricultural area, positive correlations were found between As

Table 3 PERI values for elements in agricultural soil samples of Eghlid County

Elements	RI value		Risk grade
	Min	Max	
As	4.50	14.90	Low ecological risk
Cd	15.65	962.61	high ecological risk
Cr	0.19	0.661	Low ecological risk
Cu	1.81	6.77	Low ecological risk
Pb	0.92	1.62	Low ecological risk
Zn	0.23	1.59	

and Cu ($r_{As-Cu} = 0.379, p < 0.01$), between Cr and Cu ($r_{Cr-Cu} = 0.357, p < 0.01$), and between Cu and Zn ($r_{Cu-Zn} = 0.356, p < 0.01$). Also, the strongest positive correlation was found between Cr and Zn ($r_{Cr-Zn} = 0.701, p < 0.01$), which may suggest a common origin for these elements.

Element source identification

In the current work, PCA was conducted to find out the contamination sources. The PCA results for the element contents in the agricultural soil samples are listed in Table 6. Also, loading plots of the components are illustrated in Fig. 3. As shown, the analyzed element contents are grouped into a three-component model, which accounts for 71% of the total variance. The PC1 explains 30.76% of all the data variation and shows the highest positive loadings for Zn (0.840), Cr (0.821) and Cu (0.705), while it reflects moderate and low positive loadings for As (0.400) and for Pb (0.231), respectively. Therefore, it can be admitted that since the average contents of Cr, Cu and Zn are lower than the background values, PC1 indicates lithogenic component of the elements. The PC2 explains 22.28% of all the data variation showing strong loadings with As while, the PC3 with 18.24% of all the data variation, for the two important factors (unequivocally isolated of cadmium from other elements and a higher mean content of this element than the average shale) suggests that Cd could have an anthropogenic origin.

Based on the results of HCA analysis (Fig. 4), three different clusters (CI to CIII) could be identified. Although, CI contained As, Pb and Zn, CII contained only cadmium, which mainly originates from a different source and CIII contained Cr and Cu. The results of principal component analyses agreed with that of the hierarchical cluster analysis. Therefore, these analyzes suggest that the studied elements could be classified from group 1 (G1) to group 3 (G3) with respect to source identification. G1, clustered by As, Pb and Zn was associated with lithogenic components. Therefore, it can be concluded that these elements originate from natural sources. G2, clustered by Cd, might be resulted from some human impacts in the study region. Besides, G3, clustered by Cr and Cu.

Spatial distribution of the analyzed elements

In this work, the contents of all the analyzed elements in the whole agricultural areas of Eghlid County were interpolated by kriging technique (Fig. 5).

Based on the spatial distribution patterns the elements in the study area, it can be argued that the contents of As, Cu and Cr are decreasing from the center to the borders, while, this pattern could not be seen for the other elements.

Table 4 PI, IPI and PLI of elements in agricultural soil of Eghlid County

	PI			Number of samples			IPI			Number of samples			PLI			Number of samples			
	Min	Max	Mean	Low	Middle	High	Min	Max	Mean	Low	Middle	High	Min	Max	Mean	Low	Moderate	High	Extremely high
As	0.45	1.49	0.92	64	36	0	0.32	6.20	2.52	21	17	62	0.20	1.61	0.84	35	65	0	0
Cd	0.52	32.09	12.17	13	7	80													
Cr	0.096	0.33	0.21	100	0	0													
Cu	0.36	1.35	0.68	98	2	0													
Pb	0.18	0.32	0.21	100	0	0													
Zn	0.23	1.59	0.96	54	46	0													

As shown in Fig. 5, the hot-spot areas of As are mainly observed in the central and southeast parts of Eghlid County, while, the distribution pattern of Cd with high spatial variability is different from other elements. The hot-spot areas of this element are mainly observed in the central part, as well as the northeast and southwest parts of Eghlid County and can be associated with anthropogenic activities especially agronomic practices that could cause heavy metals contamination. However, agronomic practices, especially the use of soil manures or inorganic fertilizers, may also be considered as an important source of Cr and Cu [35, 37, 41, 43, 44]. For the distribution of Cd, more areas on the map are shaded brown, suggesting that the mean contents of this element (2.80 mg/kg) are higher than the reference values (0.10 mg/kg) over the whole region.

The spatial distribution pattern of Pb is characterized by decreasing contents from the central part to the northern and southern parts, while, increasing in the content of Zn from southern to northern parts of the study region, are probably related to the geological structure.

As shown in Table 1, there is a distinct change in the contents of analyzed elements among the soil specimens, and the median concentrations of As, Cd, Cr, Cu, Pb and Zn are 1.81, 2.36, 19.55, 19.86, 7.14 and 37.63 mg/kg, respectively, which follows a descending order as Zn > Cu > Cr > Pb > Cd > As. Also, in terms of median values, the content of arsenic is

Table 5 The correlation matrix between the elements in soil specimens

Element	As	Cd	Cr	Cu	Pb	Zn
As	1					
Cd	0.018	1				
Cr	0.101	-0.048	1			
Cu	0.379**	-0.038	0.357**	1		
Pb	-0.054	-0.084	0.052	0.101	1	
Zn	0.119	0.040	0.701**	0.356**	0.187	1

**p < 0.01 (2-tailed)

comparable to the reference values (global average shale) [57], indicating this element in the soil specimens of the Eghlid County may be influenced by external factors less, while, the levels of the other elements (Cd, Cr, Cu, Pb and Zn, respectively) are 12.17-, 0.21, 0.68, 0.21 and 0.96 folds higher than their related reference values. Furthermore, the Cd value is considerably enriched when compared with that obtained by Azimzadeh and Khademi (2013). Therefore, such high concentrations coupled with high standard deviation values suggest anthropogenic origin sources for this element. The Pb with 5% has the lowest coefficient of variability (CV) followed by Cu, As, Cr, Zn and Cd (26, 32, 33, 38 and 76%, respectively). The results indicate that, Cd has the greatest variation among the topsoil samples and thus would have the highest possibility of being influenced by the extrinsic factors especially human activities (anthropogenic sources) such as industrial and agronomic practices [9, 12, 64]. Also, the CV value of Pb suggests that this element has a weak variation and its concentration is almost constant across the

Component Plot in Rotated Space

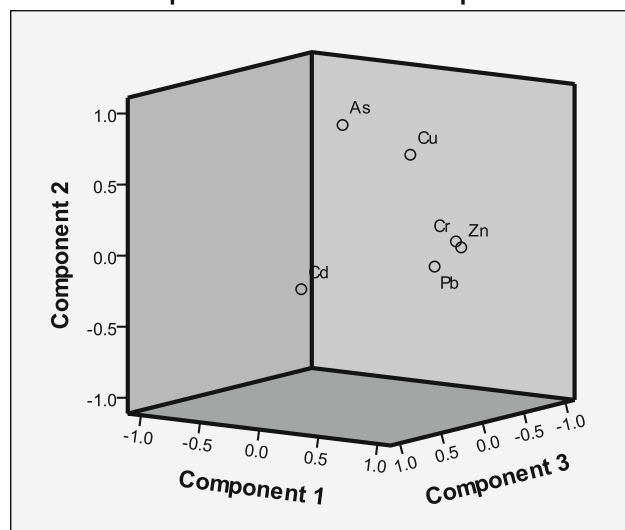


Fig. 3 Loading plot of analyzed elements in the space described by three principal component (PC1, PC2 and PC3)

Table 6 Total variance described and component models of the elements

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	2.091	34.844	34.844	2.091	34.844	34.844	1.846	30.759	30.759
2	1.151	19.180	54.023	1.151	19.180	54.023	1.337	22.283	53.042
3	1.035	17.258	71.281	1.035	17.258	71.281	1.094	18.239	71.281
4	0.904	15.061	86.343						
5	0.542	9.039	95.382						
6	0.277	4.618	100.000						

Elements	Component Matrix			Rotated Component Matrix		
	PC1	PC2	PC3	PC1	PC2	PC3
As	0.400	0.712	-0.349	-0.008	0.883	0.092
Cd	-0.041	0.332	0.791	0.160	-0.148	0.831
Cr	0.821	-0.190	0.240	0.865	0.135	-0.030
Cu	0.705	0.308	-0.261	0.417	0.687	-0.118
Pb	0.231	-0.590	-0.298	0.274	-0.186	-0.616
Zn	0.840	-0.234	0.272	0.907	0.097	-0.033

Extraction method: principal component analysis (significant loading factors are marked in bold)

study area. On the other hand, the lower CV% of Pb and Cu compared with the other elements implies that the distribution of these metals in agricultural soil specimens is relatively homogenous in the study area. Similarly, Cai et al. (2015) reported that Cd has the greatest variation among the

agricultural soil samples of Shunde, China and thus would be influenced by the extrinsic factors. Also, the comparison of metal content in the agricultural soil samples of Eghlid County with the farming soil specimens collected from Poland indicated that the average levels of arsenic, chromium,

Fig. 4 Dendrogram of the CA of Eghlid County soils based on heavy metal

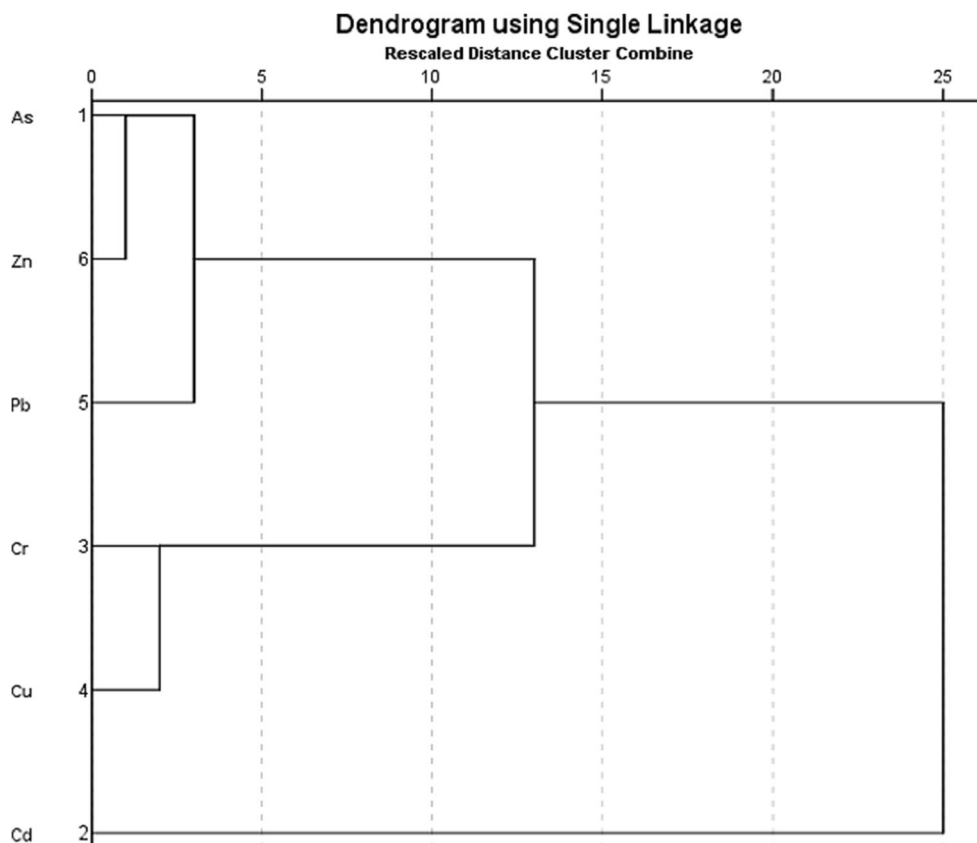
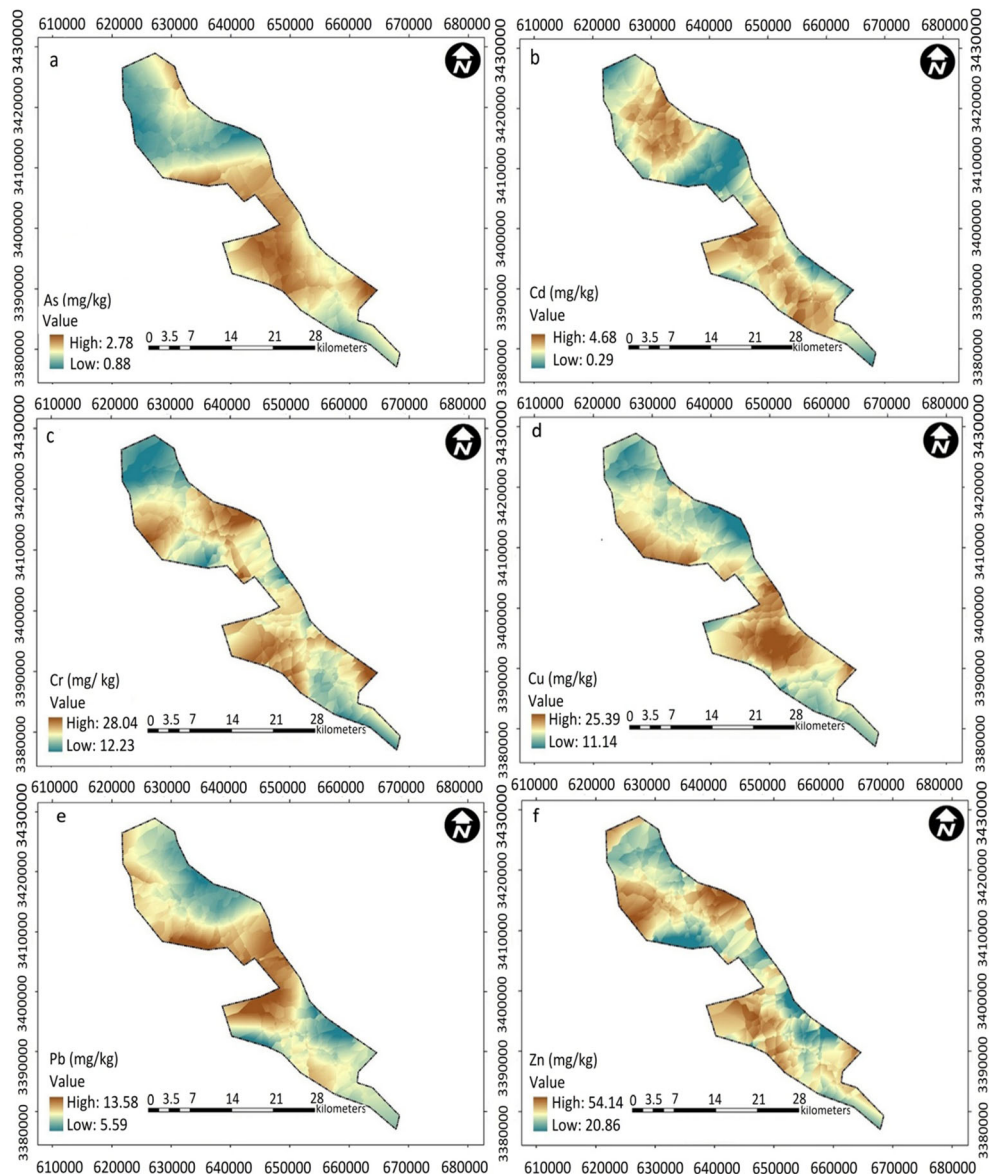


Fig. 5 Spatial distribution of As (a), Cd (b), Cr (c), Cu (d), Pb (e) and Zn (f) content in agricultural soil specimens in Eghlid County



lead and zinc in the analyzed soil samples of Eghlid County are much lower than those determined for soil specimens of Poland in mg/kg (8.84, 34.43, 39.80 and 62.47 for arsenic, chromium, lead and zinc, respectively), while, in comparison the average levels of cadmium and copper are higher than those determined for farming soils collected from Poland (0.8 and 8.47 mg/kg for Cd and Cu, respectively) [32].

The analysis of the computed values for PI, IPI and PLI indices indicates that based on site category, the Eghlid County region is moderately affected by agricultural activities especially the excessive use of metal-containing pesticides, phosphate-based fertilizers and other inorganic fertilizers. Namely, agricultural soils of Eghlid County are particularly affected by Cd contamination arising from anthropogenic (human) activities. On the whole, the IPI and PLI confirm the results achieved applying the Igeo index. Similarly,

Curran-Courmane et al. (2015) reported that the mean PI value of Cd of 4.8 indicates that 62% of the soil samples collected from green spaces of New Zealand were highly contaminated by this element. Mirzaei et al. (2014) also reported similar results by studying the soil samples of Golestan Province, Iran.

Based on the results of correlation coefficient analysis, Pb's correlations with the other elements were relatively weak especially inversely correlated with As ($r = -0.054$); this, coupled with the mean content lower than the reference value, demonstrate that Pb probably originates from natural sources. Also, although very low correlation coefficients between Cd and the other elements is observed, specially the negative correlation with chromium ($r = -0.048$), copper ($r = -0.038$) and lead ($r = -0.084$), its average content is higher than the reference value indicating that in the study area this element

may have a different pollution source in comparison with the other elements that delivers the soils with Cd balanced to Cr, Cu and Pb.

The results of element source identification indicated that Cd could have an anthropogenic origin. In this regard, industrial activities and agronomic practices such as the use of live-stock manures and notably phosphorus fertilizers which clearly cause increases in the Cd contents in the agricultural soil [4] are the main sources of cadmium contamination. Similar results have also been reported in studies on the contents of Cd in the soil samples of agricultural regions in Shunde, China and industrial district of Wuhan, China [9, 63]. Generally, PCA results have been consistent with Igeo, potential ecological risk, PI, IPI, PLI and correlations matrices. This can be taken to mean that arsenic, chromium, copper, lead and zinc variability in the agricultural soil specimens of Eghlid County may be caused by natural sources, while the contamination of topsoil by cadmium may be the result of the anthropogenic activities. Also, the results of PCA agree well with that of the HCA and indicate that As, Pb and Zn can be associated with lithogenic components. Therefore, it can be concluded that these elements originate from natural sources. On the other hand, cadmium might be resulted from human interventions in the study region.

Conclusions

The present investigation was conducted as a pioneer study for the assessment of the agricultural soil contamination with As, Cd, Cr, Cu, Pb and Zn in the Eghlid County, Iran. The study revealed that the median value for Cd is higher than the background concentration reported by Azimzadeh and Khademi (2013). These findings have serious implications for the public health. Also, the results indicated that both anthropogenic and geogenic factors have their own respective loadings on the elements content in the agricultural soil specimens. The values of Igeo indicated that Cd with average index value of 3.02 is significantly accumulated in the soils. In contrast, the Igeo value of other elements suggested that the study area is not contaminated by these elements. The mean PI value of Cd showed that 80% of topsoil specimens are highly contaminated by this element. The IPIs indicate that 62% of the soil samples have high contamination, while the PLI indicated moderate levels (65%) of soil contamination. The results of PCA, HCA and also spatial distribution patterns of elements suggested that human impacts (anthropogenic activities) are the most important sources of Cd pollution; whereas, other element contents have a lithogenic origin. All of the above results indicate that agricultural practices and probably environmental deterioration are the main parameters which cause soil contamination by cadmium. Therefore, while it is expected that the metal inputs may increase in the future, it is

recommended to include plant analyses in the future studies for determining the impact of the amount of bioavailable metals.

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Authors' contributions All authors had equal role in design, work and manuscript writing. All authors read and approved the final manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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