Case Study

Potential ecological risk assessment of heavy metals in archaeology on an example of the Tappe Rivi (Iran)

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Abstract

Ancient soils may be highly polluted with heavy metals because of intensive anthropogenic activities over the centuries. Soils in the archaeological site of Rivi are an example of an ancient soil that is exposed to heavy metal pollution. The current study focused on pollution levels of potentially harmful elements (Fe, Co, Cu, Cr, Cd and Pb) using various indices in the soil of Rivi in North Khorasan province, Iran. For this purpose, a total of 93 soil samples were collected from different parts of site (n = 5) and the pollution level of heavy metals were analyzed based on the Geo-accumulation Index (Igeo), contamination factor (CF), Degree of contamination (Cd), the Pollution Load Index (PLI), and the individual potential risk (Eri). Pollution indices were determined based on local geochemical backgrounds. Results showed that: The mean concentrations obtained in mg/kg were Cu (18.88), Pb (36.20), Cr (28.14). Co (21.00) and Cd (5.31). Cr showed a partially moderate pollution level, Pb showed a slight pollution level, and Co and Cd showed no-pollution level, compared to the classification standard. Based on the Risk index values, for heavy metals in the study area was ranked in the order of: Pb > Cu > Cr > Cd > Co. Co and Cd of ancient soils were mainly originated from the soil parent material and topography of the study area. Cu was mainly originated from human activities, and Cr and Pb may be originated from both natural and anthropogenic factors in the study area. Results of this study can reveal a long-term exposure of ancient humans to these elements, via their activities, which may have played particular role in environmental-pollution tolerance. Therefore, studying the effects of these potentially toxic elements on archaeologist's health, the results are crucial to identifying and dealing with risk during their excavations.

Keywords Pollution indices · Heavy metal enrichment · Acient soils · Rivi site

1 Introduction

Human activities are usually identified with pollution on earth, which can make environments a dangerous place to live in. Urbanization and the development of cities over the past centuries would lead to chemical pollution, particularly by reason of their large populations and the inception of the metallurgy industries [17]. Hence, ancient pollution may rely on the main economic development time of the city or a specific district, and the chemical composition of the municipal waste which entered in the soil at that period [23]. The human activities have changed the properties of many natural soils over the centuries. Cultural layer above or between natural horizon is an index of human-origin impacts on the soil environment. It occurs when the natural soil profile is covered by external material [8, 10]. Furthermore, soil material originating investigations from cultural layer enable the reconstruction of anthropogenically impacted pedogenesis histories, an assessment of interaction degree among humans and the environment of soil and an assessment of the soil pollution degree and changes derived from human activity [38].

The heavy metal accumulation is probably a consequence of broadly historical pollution [18]. The pollution

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of heavy metal has been studied over the last 100 years. Heavy metals distribution has been great concern within the soil profile, contamination degree, as well as their origin [34]. Furthermore, they are able to remain in urban soils for long period of time, consequently under specific conditions they can be a further pollution source of urban soil [11]. In addition, long-term accumulation of heavy metals can impact on human health, since they can easily transfer into the trophic chain and thus their capability to end up within the human body in highly concentrated level [30].

Enrichment of soil with heavy metals could represent ancient human activities [24]. Also, heavy metal accumulation could be supported by natural processes. Heavy metals are regarded significant components of the Earth's crust [42]; therefore, the nature of the parent material and process of soil formation at the site can make an appropriate or inappropriate condition for accumulation of heavy metal. Moreover, weathering of the parent material is a natural event which can impact on the heavy metal accumulation [19]. Heavy metal mobilization and arrangement in the soils depends on particular soil processes such as: respiration, runoff or leaching into the soil profile [11].

Identification between anthropogenic activities and natural levels of a given substance could be complicated, particularly when assessing the pollution level of environment [20]. Also, total content of soil heavy metals may not always be an enough assessment method [21]. However, the soil pollution assessment with heavy metals is possible according to use of suitable indices [24]. The indices are help out to assess whether the heavy metal concentration was as a result of natural processes or was due to anthropogenic activities [6]. Many contamination indices have been used to assessment soil conditions. The indices of contamination permit determining the provenance of trace metals accumulated in soils and determining ecological risk [22].

Several researches have established potential risks posed due to contamination using ecological risk indices, but most of them have focused on current anthropogenic sources, hence the data from these investigations are less comparable with those collected from anthropogenic pollution sources in ancient times, which was main aim of this study. To our knowledge, this the first study that attempting to use various pollution indices in order to understanding the features of the pollution in the ancient soils. Assessment of contamination status of ancient sites by using the pollution indices is recommended, whether it was natural or anthropogenic, instead of only content assessing of metals. Due to potential harmful effects of heavy metals, it is necessary to assess the heavy metal contamination level of soils, not only in modern environment but also for historical places. In this study, we provide pollution level, potential ecological risks and the high environmental-risk zone of Fe, Co, Cu, Cr, Cd and Pb, in ancient soil samples collected from archeological sites of Rivi which have been proven to have ancient anthropogenic activities. In order to reach this objective several heavy metals have been determined and geochemically analysed. The results of the research could illustrate the general accumulation and ecological risk features of heavy metal contamination in ancient soil.

2 Materials and methods

2.1 Study area

The ancient settlement area of "Tappe Rivi" is located in Samalghan Plain in the Northeastern of Iran and lies within the geographical coordinates of 56° 32′–56° 49′ E and 37° 27′–37° 37′ N (Fig. 1). The Samalghan Plain is embedded in two mountain ranges, Allah Dagh (in the south) and Gochangochang (in the north). The Tappe Rivi consists at least four settlement mounds (A, B, C and D) and covers more than 110 ha. Five major periods can be described, dating from the Early Iron Age to the Early Islamic period. It has been inhabited by about 2900 years ago until the end of the Sasanid era (1500 years ago) and it was a large village during the Middle Islamic ages (1000 years ago). In general, it has been inhabited during the Iron, Achaemenid, Parthian, Sasanian, and Islamic eras [15].

2.2 Soil sampling

Ancient soil samples (n = 93) were carefully collected (by a hand-driven stainless steel) from four historic mounds in Ancient Rivi under the supervision of archeologists. Depending on the site conditions, soil sampling was carried out in depth. The distribution of the sampling sites was as follows: (1) Twenty-three of samples were taken (0–8 m) from Tappe Rivi A. It is located in the south of the historical occupied area (with a height of approx. 8 m). (2) Twenty-one soil samples were collected from Tappe Rivi B (0–7 m). Rivi B with a height of approx. 5 m is located 600 m to the north. (3) Fifteen soil samples were collected from Tappe Rivi D (0–4 m). Rivi D is located at the center of site, between Rivi A and Rivi B. (4) eighteen soil samples were collected from a Great pit next to Rivi D (E-Rivi D) which it is located on-site. In addition, seventeen samples were taken as control (0–400 cm) from off-site which located outside of the historical site. The aim of collecting control samples was to compare the variations of the elements in the anthrosols samples with the control and to measure the elemental changes outside and inside the ancient site. The samples were

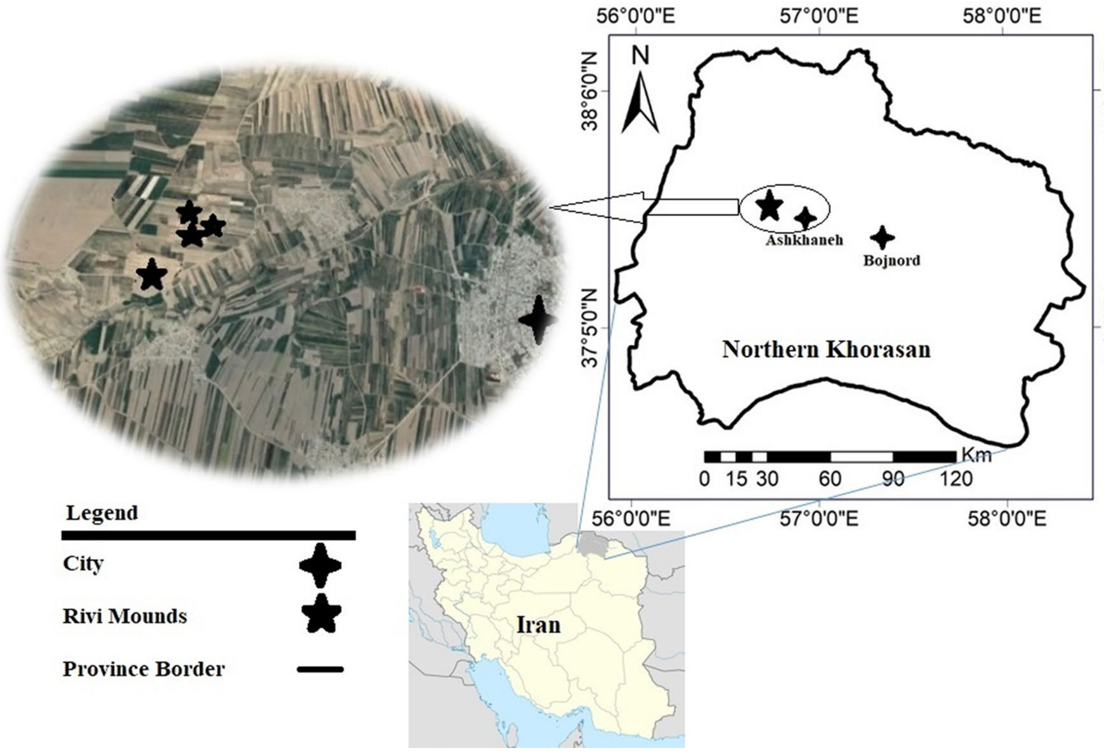

Fig. 1 Location of the study area

placed in a clean Polypropylene Tubes and were properly labeled and carried to laboratory for further processing. The stones or debris were taken by hand and air dried in room temperature.

2.3 Content of heavy metals

For total concentrations of potentially harmful heavy metals, the soil samples were digested with strong acids (HCL and HNO3) using the standard ISO_11466, 1995 method. The concentrations of Fe Cd, Cr, Cu, Co and Pb, were determined by using Atomic Absorption Spectroscopy (AAS, model 350, Analytical Jena, Germany).

2.4 Statistical analyses

In order to describe the analysed content of heavy metals, descriptive statistics were calculated. Statistical comparison of heavy metal content in different sampling locations within the study area were computed by the one-way ANOVA using the IBM SPSS Statistics version 20. In addition, in order to evaluate the relationship between content of heavy metals, the Pearson's correlation coefficients was conducted.

2.5 Pollution indices

The use of pollution indices are key method to the effective assessment of soil pollution with heavy metals [18, 24]. On the basis of soil samples from the ancient settlement area of "Tappe Rivi", five indices: Geoaccumulation Index (I_{geo}), The Pollution Load Index (PLI), Risk factor level, Contamination factor (CF) and Degree of contamination (Cd) were calculated. We decided to evaluate the pollution state of the Rivi by using local geochemical background value. To this aim, the soil samples were collected as reported by Bhuiyan et al. [2] from outside the archaeological site. Various sources indicated that the content of local geochemical background was used as a source for the assessing of pollution degree [3, 41].

2.5.1 Geo-accumulation index (I_{geo})

The geo-accumulation index (Igeo) provides a direct evaluation of the degree of heavy metal enrichment in soil. Igeo values are helpful to quantifying the degree of anthropogenically or geogenically accumulated contaminants and divide soil classes based on quality in study area [25, 28]. This index presented by Müller [25] was determined based on background levels by using the following formula:

$$Igeo = log_2 \left[\frac{Cn}{1.5\ Bn} \right] \quad (1)$$

where Cn is the metal accumulation evaluated in each soil and for each metal, Bn is the background level for individual metal and the value of 1.5 is expresses to correct any possible lithological changes. In this study Fe was used because of its high abundance in the crust, high stability, resistance to migration and leaching, low bioavailability and low solubility in neutral and alkaline environments. The seven classes of geo-accumulation index and respective description are listed in Table 1.

2.5.2 Contamination factor (CF)

The contamination factor (CF) was used by Hakanson [12], which obtained by dividing the accumulation of each heavy metal in the soil based on reference or background level. It is calculated as (Eq. 2):

$$CF_i = \frac{C_{metal}}{C_{background}} \quad (2)$$

where C_{metal} is the concentration of each metal in soil sample and $C_{background}$ is the geochemical background values. Hakanson [12] presented four classes of CF to determine the metal pollution levels (Table 2).

2.5.3 Degree of contamination (C_d)

As reported by Hakanson [12], the evaluation of pollution can be obtained by using the degree of contamination index (Cd) which is the sum of all CF and was calculated as follows:

$$C_d = \sum_{i=1}^{n} C_f^i \quad (3)$$

where Cd is the degree of contamination, CF is the contamination factor and n is the number of analyzed heavy metals. C_d is presented into four groups as given in Table 3.

Table 1 Classification of geo-accumulation index and respective description

Geo-accumulation index level	I_{geo} class	I_{geo} value
Uncontaminated	0	I geo ≤ 0
Uncontaminated/moderately contaminated	1	0 < I geo < 1
Moderately contaminated	2	1 < I geo < 2
Moderately/strongly contaminated	3	2 < I geo < 3
Strongly contaminated	4	3 < I geo < 4
Strongly/extremely contaminated	5	4 < I geo < 5
Extremely contaminated	6	5 < I geo

Table 2 Different Contamination factor (CF) for soil

Contamination factor level	CF value
Low contamination factor indicating low contamination	CF < 1
Moderate contamination factor	1 ≤ CF < 3
Considerable contamination factor	3 ≤ CF < 6
Very high contamination factor	6 ≤ CF

2.5.4 The Pollution Load Index (PLI)

The Pollution Load Index (PLI) is also used for the total assessment of the degree of contamination in soil. The PLI has been determined as a concentration factor of each heavy metal with regard to the background level in the soil. Tomlinson et al. [36] proposed PLI for detecting contamination which allows a comparison of contamination levels among sites and at different periods. PLI is calculated based on the following equation:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \cdots \times CF_n} \quad (4)$$

where CF is the contamination factor of a single heavy metal; n indicates the number of analyzed heavy metals. The contamination level of PLI can be ordered as: no-pollution (PLI ≤ 1), moderate pollution (1 < PLI ≤ 2), heavy pollution (2 < PLI ≤ 3), or extremely heavy pollution (3 < PLI). A PLI value close to 1 indicates heavy metals load near the background level, while values >1 indicate pollution [4].

2.5.5 Risk factor level

The potential ecological risk index (Eri) is used to assess the contamination degree in soil [12]. The Eri was calculated by the values of the CF and the toxic-response factor of heavy metals in accordance with the following formula:

$$E_r^i = C_f^i \times T_f^i \quad (5)$$

where T_f is the toxic-response factor of every single metals and C_f is the contamination factor. The Toxic-response values for heavy metals were was Cd = 30, As = 10, Co = 5, Cu = 5, Ni = 5, Pb = 5, Cr = 2, Zn = 1, and Mn = 1 [7, 33]. According to Hakanson [12], E_r values are listed in Table 4.

Table 3 Different degree of contamination (C_d) for soil

Degree of contamination level	C_d value
Low degree of contamination	$C_d < 6$
Moderate degree of contamination	$6 \le C_d < 12$
Considerable degree of contamination	$12 \le C_d < 24$
Very high degree of contamination	$24 \le C_d$

3 Results

3.1 Heavy metal concentration of ancient soils

Table 5 summarizes the concentrations of five elements in the soils of selected areas and a distinct variation has noted in their accumulations. The minimum, maximum and average value of heavy metal values were determined. The results of this study revealed that Cu, Pb and Cr had the highest concentration in the ancient soils.

The average concentration of Cu, Fe, Pb, Co, Cr and Cd in the soils of study area were found to be 18.88, 15,118.66, 36.20, 21.00, 28.14 and 8.76 mg/kg, respectively. Data listed in Table 5 are presented that the higher concentrations of heavy metals were detected at Rivi B while the lower concentrations of heavy metals have been found at control area. The highest concentrations of Cu (24.31 mg/kg), Co (25.45 mg/kg), Cr (32.89 mg/kg), Cd (10.00 mg/kg) and Pb (49.87 mg/kg) were found in the soil samples collected from Rivi B. The high concentrations of heavy metals in the soil samples might have come from anthropogenic activities in ancient times. The local geochemical background values for the standard of heavy metals in soil were determined as follows: Cd (4.09), Cu (10.25), Pb (19.36), Co (16.91) and Cr (15.66). At all sites, Cd, Cu and Cr levels exceeded the background contents (Table 5), but Pb and Co showed an inverted pattern which their contents were lower compared to the background values. Cu, Pb, Cr and Co were expected to exhibit an insignificant difference in the mean concentrations between the five sites. However, the contrasting results obtained from this study holds for lack of significant difference in mean concentrations of Fe and Cd between the five sites.

Table 5 Descriptive statistics of heavy metal concentrations in Rivi site

Sampling zone	Heavy metal (mg/kg)				
	Cd	Cu	Pb	Co	Cr
Rivi A					
Minimum value	4.49	12.40	18.22	16.68	19.03
Maximum value	11.19	21.50	38.47	27.38	36.50
Mean	8.99	16.86	29.65	23.49	26.80
SD	1.51	2.07	4.76	3.07	3.48
Rivi B					
Minimum value	8.38	19.58	44.07	20.52	27.81
Maximum value	10.93	28.91	54.47	29.67	37.10
Mean	10.00	24.31	49.87	25.45	32.89
SD	0.58	2.40	3.02	2.50	2.49
Rivi D					
Minimum value	8.35	18.08	36.68	9.44	23.01
Maximum value	10.18	23.96	47.16	14.60	31.99
Mean	9.38	21.36	41.62	12.95	28.67
SD	0.54	1.70	2.37	1.71	2.70
E-Rivi D					
Minimum value	8.18	15.79	35.73	19.04	23.51
Maximum value	11.35	22.06	145.30	41.17	24.29
Mean	9.28	18.90	112.37	38.15	21.36
SD	0.71	1.74	20.18	1.34	1.32
Control					
Minimum value	4.91	10.25	95.78	19.37	16.92
Maximum value	7.08	14.26	135.38	23.40	21.53
Mean	5.64	12.57	108.14	21.23	18.39
SD	0.50	1.18	9.46	1.37	1.19

3.2 Correlation analysis

The identification of the sources of heavy metals in soils is very beneficial for identifying contamination hot spots and the potential provenances of contaminants [1, 14]. High correlations between heavy metals may have common contamination sources [35, 40]. The results of the Pearson correlation analysis are provided in Table 6, and reveal that complex correlations exist between the five heavy metals in the soils of the ancient settlement area of "Tappe Rivi". The significance level ($p \leq 0.05$ and $p \leq 0.01$) of multi-element correlation for soil samples was determined and the results depicted a high strong positive correlation between Pb and Cu (0.930**). The significant correlations reported that they may have been derived from common sources, possibly from ancient human activities. A strong

Table 4 Classification of the risk factor (E_r^i) for soil

Risk factor level	Er value
Low potential ecological risk	Er < 40
Moderate potential ecological risk	40 ≤ Er < 80
Considerable potential ecological risk	80 ≤ Er < 160
High potential ecological risk	160 ≤ Er < 320
Very high potential ecological risk	320 ≤ Er

Table 6 Correlation coefficients of heavy metals in ancient soils of study area

Metals	Cd	Cu	Pb	Co	Cr
Cd	1				
Cu	0.746**	1			
Ni	0.127	−0.125			
Pb	0.781**	0.930**	1		
Co	0.364**	0.215*	0.227*	1	
Cr	0.773**	0.766**	0.784**	0.410**	1

**$P < 0.01$; *$P < 0.05$

positive correlation was observed between Cu–Cd, Pb–Cd, Cr–Cd, Cr–Cu and Cr–Pb, and these metals may have been originated from anthropogenic sources. The correlation coefficients for the pairs Cu–Cd, Pb–Cd, Cr–Cd, Cr–Cu and Cr–Pb were calculated to be 0.746**, 0.781**, 0.773**, 0.766**and 0.784**, respectively. The correlation Co-Pb and Co–Cu were 0.227*and 0.215*, respectively, which were also significant correlations. Corrections coefficients among Ni–Cu was negative (− 0.125) which suggested that these metal pairs probably originated from different sources.

3.3 Pollution assessment of ancient soils

3.3.1 Geo-accumulation index (I_{geo})

Geo-accumulation formula suggested by Muller [26] was further used to know about the possible metal pollution in the ancient soil of the archaeological site in Rivi. A reported values of the geo-accumulation index was described in Table 7. The results indicated that the values of I_{geo} decreased in the order of Cu > Pb > Cr > Cd > Co for soils. I_{geo} was distinctly variable and suggested that the soil in Rivi ranged from uncontaminated to moderately contaminated. I_{geo} revealed that all the samples examined in Rivi in respect of Co, Cd (Except Rivi D), Cu (Except Control), Cr (Control), and Pb (Except Rivi A and Control) fell into class 0-uncontaminated. I_{geo} values for Pb ranged from − 0.02 to 0.77 with a mean value of 0.24 and most of the samples fell into class 1 of uncontaminated to moderately contaminated. Cu and Cr showed a moderately contaminated states, but uncontaminated in the Control areas (Fig. 2).

3.3.2 Contamination factor (CF)

The level of heavy metal pollution can be represented by the contamination factor (CF). CF is the ratio between the heavy metal amount in the soil to the background value of the metal [37]. Calculated CF values and their proportions for individual heavy metals in ancient soil samples were presented in Fig. 3 and Table 8, respectively. The pollution order of CF for six elements in the study area was found to be in the order of Pb > Cu > Ni > Cd > Co (Table 8). The average values of CF for Cd, Cu, Ni and Pb fell into the moderate contamination factor and For Co and all stations posed the moderate contamination factor, except for Rivi D, which posed the low contamination factor.

Table 7 Average I geo and contamination levels of soil in Rivi site

Area	Cd	Cu	Pb	Co	Cr
Rivi A	− 0.35	0.1	− 0.02	− 0.1	0.16
Rivi B	− 0.3	0.65	0.77	− 0.002	0.48
Rivi D	0.61	0.47	0.51	− 0.99	0.29
E-Rivi D	− 0.4	0.3	0.4	− 0.25	0.32
Control	− 0.12	− 0.3	− 0.45	− 0.46	− 0.12

3.3.3 Degree of contamination (C_d)

The degree of contamination of heavy metals in this study was ordered as following: Pb > Cu > Cr > Cd > Co. C_d values for all heavy metals were below 12 which were classified as having a low degree of pollution (Table 9; Fig. 4).

3.3.4 Pollution load index (PLI)

Pollution load index was computed for the better representation of spatial distribution of pollutions in the study area. The Pollution Load Index (PLI) of heavy metals in the ancient soil varied from 1.28 to 1.77, with an average value of 1.55, at the moderate pollution level. All of the soil samples fell into moderate pollution level (Table 10). The moderately polluted of this site in this study may be due to the anthropogenic activities (Fig. 5).

3.3.5 Risk factor (Er)

The ecological risk assessment results of toxic heavy metals in soils of Rivi were summarized in Table 11. It was found that the risk indices (E_r) of heavy metals were ranked in the order of Cr < Cu < Pb < Cd. The ecological risk of Cd in the Rivi D and Control areas indicating that Cd posed Moderate ecological risk to archaeological site. The monomial ecological risk of Cd in Rivi A, Rivi B and E-Rivi D indicated low ecological risk to the environment. E_r^i values for Cu, Pb and Cr from all sampling zones were below 40, thereby indicating low risk (Fig. 6).

4 Discussion

Numerous investigations have been undertaken to establish potential risks due to pollution using ecological risk indices [24]. However, wide variety of these studies mainly concerned on modern anthropogenic sources. Consequently, the results of other studies are less comparable with those obtained from anthropogenic pollution sources in ancient times, as was the case here. In this study, the multivariate statistical analysis revealed that heavy metals Cd, Cu, and Cr had high contents in the site and the correlations between Cu–Cd, Pb–Cd, Cr–Cd, Cr–Cu and Cr–Pb were strong, and the assessments revealed that soil samples that contained high levels were found at Rivi B while the lower heavy metal concentrations have been found

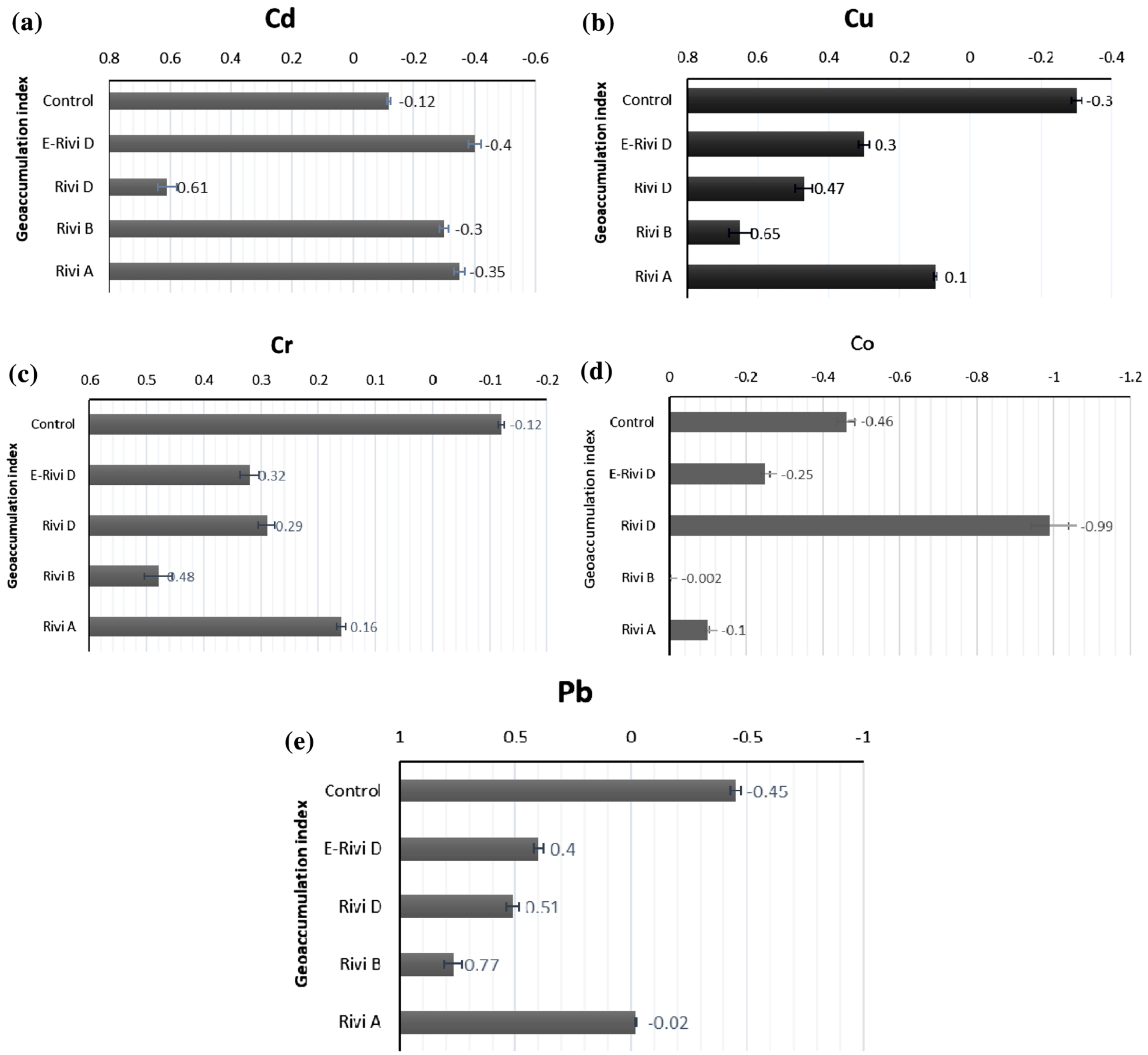

Fig. 2 **a** I_{geo} value for Cd; **b** I_{geo} value for Cu; **c** I_{geo} value for Cr; **d** I_{geo} value for Co; **e** I_{geo} value for Pb

at control area. The average concentrations of Cd, Cu and Cr in all samples significantly exceeded the background values present in Rivi. Previous investigations [27, 39] revealed Cu was an enriched chemical element in ashes from fires. Oonk et al. [29] have been reported that Cu is one of the most promising anthropogenic indexs, because of its stability in soils and sediments [9]. Hence, the concentration of Cu in Rivi probably related to the evidence of the usage of fire at the site.

According to calculated I_{geo}, it could be mentioned that, the entire site was categorized as uncontaminated or moderately contaminated. The case of Co geo-accumulation indices, we found that the whole site was characterized by Uncontaminated, which is class 0 (zero, no contamination), hence it means that Rivi site is not contaminated by cobalt. The highest degree of pollution that we measured in Rivi was indicated for Cu and Cr which is class 1 (Table 7). Similar results concerning I_{geo} of Cu is reported by Rachwal et al. [32] studying assessment of heavy metal contamination of Saxonian soil [32]. Pb and Cd displayed Uncontaminated to moderately contaminated. It can be thought that content of Cd and Pb were from natural sources or non-anthropogenic contamination. In the case of Cr and Cu our results are consistent with those reported by Jena et al. [16] regarding the elemental concentrations in very less degree of pollution and the contamination level.

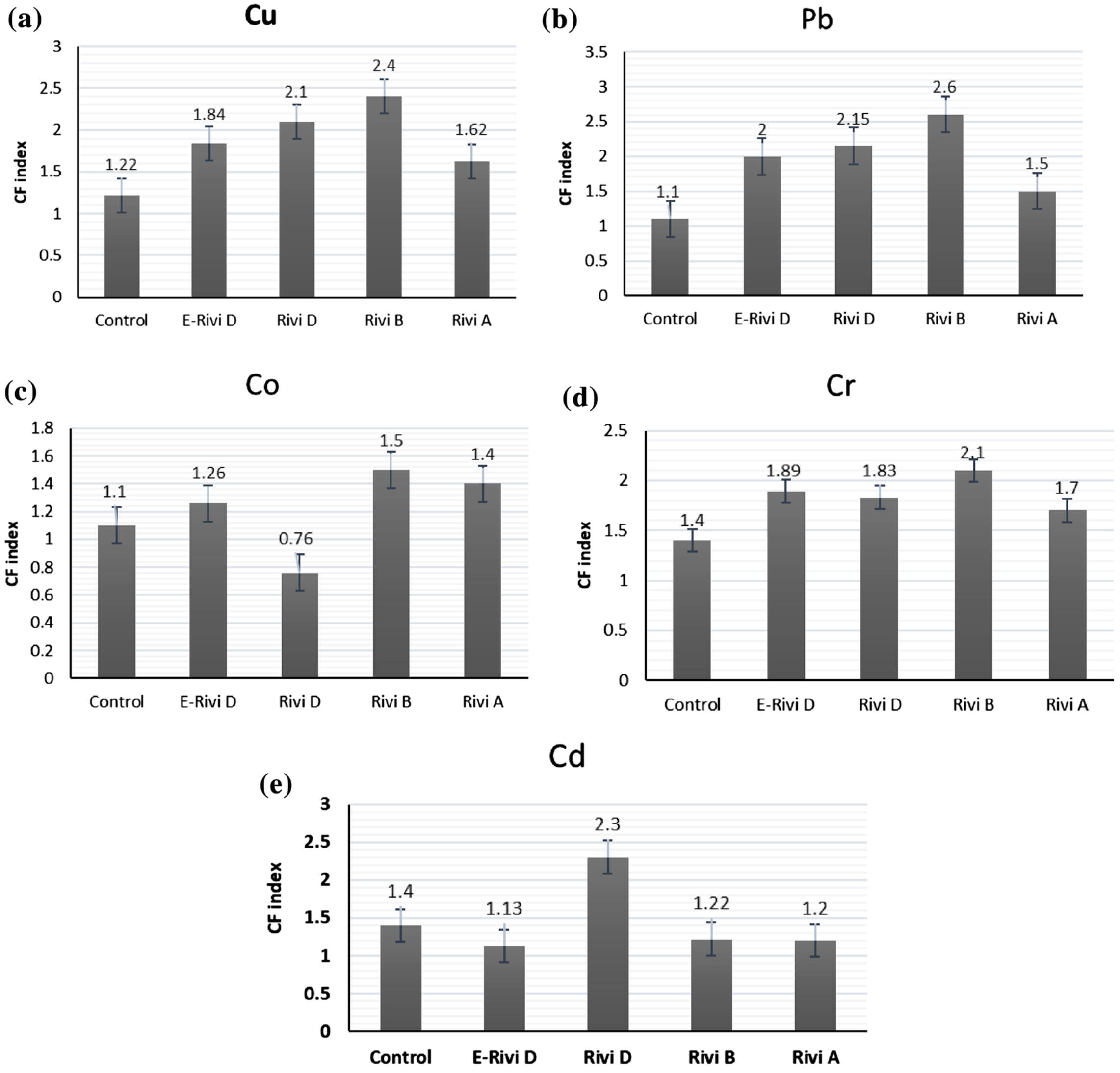

Fig. 3 **a** CF value for Cu; **b** CF value for Pb; **c** CF value for Co; **d** CF value for Co; **e** Cr value for Cu

Table 8 Average contamination factor and contamination levels of soil in Rivi site

Area	Cd	Cu	Ni	Pb	Co
Rivi A	1.2	1.62	1.61	1.5	1.4
Rivi B	1.22	2.4	1.27	2.6	1.5
Rivi D	2.3	2.1	1.44	2.15	0.76
Control	1.4	1.22	1.5	1.1	1.1

Table 9 Average degree of contamination of soil in Rivi site

Metals	Cd	Cu	Pb	Co	Cr
Values	7.25	9.18	9.35	6.02	8.92

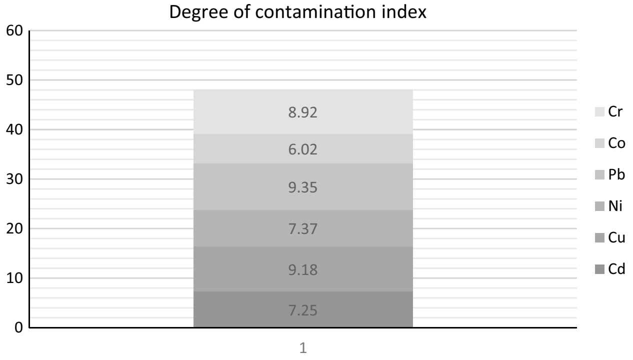

Fig. 4 Representation of C_d of different metals

Table 10 Average Pollution Load Index (PLI) of soil in Rivi site

Areas	Rivi A	Rivi B	Rivi D	E-Rivi D	Control
Values	1.5	1.77	1.66	1.58	1.28

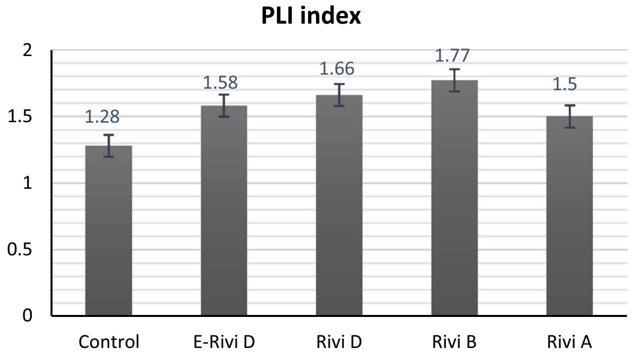

Fig. 5 Representation of PLI of metals at different sampling zones

Table 11 Average Risk factor and contamination levels of soil in Rivi site

Area	Cd	Cu	Pb	Cr
Rivi A	36	8.1	7.5	3.4
Rivi B	36.6	12	13	4.2
Rivi D	69	10.5	10.75	3.66
E-Rivi D	33.9	9.2	10	3.78
Control	42	6.1	5.5	2.8

Based on CF values, the content of elements in soils indicates Moderate levels of pollution. Graphical representation of CF levels are exhibited in Fig. 3. The results indicated Low contamination factor of Co at Rivi D and other elements showed moderately contaminated in the entire areas of archaeological site of Rivi. Similar results denoting the Saxonian soil (Germany) as low and moderate contamination factors were reported by Rachwal et al. [32]. Also, in the case of Cd of forested lands Rachwal et al. [32] revealed a moderate level of contamination ($1 \leq CF < 3$).

The results (Table 9) revealed Low degree of contamination (C_d) for all heavy metals (Cd, Cu, Pb, Co, Cr) at the ancient settlement area of "Tappe Rivi". C_d values for Cd, Co, Cr, Pb, and Cu were 7.25, 6.02, 8.92, 9.35, and 9.18, respectively (Table 9).

The PLI [36] enables the comparison among different geographic sites and for different periods [5, 31]. The PLI is a simple and comparative method that provides the level of trace metal pollution [13]. According to the results of this index the entire site was categorized as moderate pollution (Table 10). In other words the rest of the ancient soils implied moderate pollution ($1 < PLI \leq 2$).

The ER_i values for Cd exhibited the Moderate potential ecological risk at Rivi D, while Cu, Cr and Pb displayed Low potential ecological risk in the entire site. A larger range was observed for the ERi values, 3.4–69. Two areas were identified as significantly involved in value of the ER_i: Cd-Rivi D and Cd-Control area, their values were 69 and 42, respectively.

There wasn't any significant pollution level in the study area and the majority of pollution indices that we assessed in this study showed a moderate pollution level.

5 Conclusion

The aim of this study was to identify possible features and risks of heavy metal variation which can be associated to natural occurring accumulations in soils or to ancient anthropogenic inputs, with regard to detect the content of elements affected by ancient human activities in the archaeological site of Rivi. This study provided a new, description of the overall pollution levels posed by heavy metals in ancient soils in an archaeological site in Iran.

The concentrations and potential ecological risk assessment of heavy metals (Co, Pb, Cr, Cd and Cu) in ancient soil from four mounds in Rivi were investigated. Descriptive statistics analysis showed that Cu, Pb and Cr had the highest content of heavy metals in the ancient soils and the higher accumulation of heavy metals were found at Rivi B. Ancient soil values, indicating that this contamination could be resulted from anthropogenic inputs. Geo-accumulation Index (Igeo), contamination factor (CF), Degree of contamination (Cd), the Pollution Load Index (PLI), and the individual potential risk (Eri) showed that the soils are not polluted by Cd and Co but slightly enriched with Cr, Pb and Cu due to anthropogenic activities. The highest concentrations of metals were found in soils samples at the Rivi B due to anthropogenic activities and the lowest concentrations of metals were found in Control area. In comparison with the concentrations of selected metals in modern anthropogenic sources such as cities, the heavy metals concentrations in ancient Rivi were generally at uncontaminated or moderate levels. The use of pollution indices when studying the contamination degree of ancient sites) is suggested to enable a worldwide comparison.

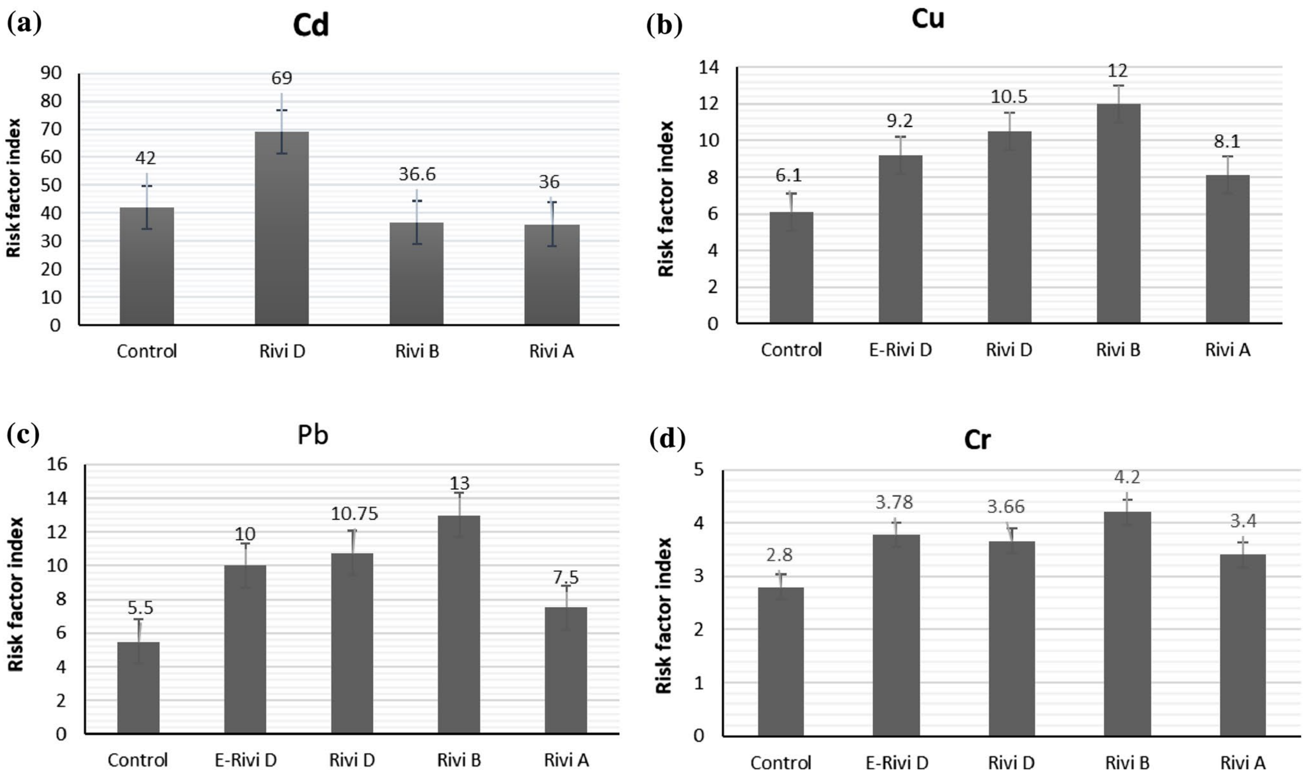

Fig. 6 **a** E_r value for Cd; **b** E_r value for Cu; **c** E_r value for Pb; **d** E_r value for Cr

Compliancer with ethical standards

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

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