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ORIGINAL ARTICLE

Heavy metal pollution assessment in agricultural soils of Kermanshah province, Iran

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Abstract

Heavy metals in agricultural soils are of major environmental concern because of the longstanding toxicity and bioaccumulation of metals. We collected 53 soil samples from agricultural fields in Kermanshah province, Iran. Our results showed average concentrations of Zn, Cu, Ni, Cr, Mn and Fe were 74.6, 41.2, 131.5, 79.2, 559.1, and 25,935 mg kg^{-1}, respectively. The concentrations of Zn (81%), Cu (98%), Ni (100%), Cr (98%) and Mn (79%) were greater than their background values in the world soils. Except for Ni (68%) and Cr (4%), the concentrations of Zn and Cu were lower than the maximum permissible levels suggested by the Iranian Environmental Quality Standard for agricultural soils. Multivariate statistical analyses successfully grouped the metals according to their anthropogenic or natural origins. The anthropogenic activities have resulted in Zn, Cu, and Fe accumulation in the agricultural fields, whereas Ni and Cr amounts are mainly derived from natural, combined with anthropogenic origins. On the other hand, Mn shows evidences of a geogenic source in the soils. The calculated results of enrichment factor (EF) and geo-accumulation index (I_{geo}) of the heavy metals reveal a similar order of Ni > Cu > Cr > Mn > Zn > Fe. The high EF and I_{geo} for Ni and Cu in agricultural soils indicate that there is a considerable Ni and Cu pollution probably. The EF and I_{geo} of Zn and Fe are low and the assessment results indicate an absence of distinct Zn and Fe pollution in agricultural soils. The assessment results of pollution indexes also support serious pollution of agricultural soils by Ni and Cu. In general, the integrated pollution index analysis indicates the agricultural soils in the region as seriously polluted.

Keywords Agricultural soil · Heavy metals · Pollution assessment · Multivariate analysis · Kermanshah

Introduction

Our lives are closely associated with soil quality. However, in recent years, rapid industrialization and urbanization have caused heavy metal contamination to become a serious concern both in developed and developing countries. In particular, agricultural soils can be a long-term sink for heavy metals (Micó et al. 2006).

The accumulation of heavy metals in soils is affected by many environmental factors, including parent material and soil properties, as well as by human activities (Nagajyoti et al. 2010). The pollution sources of heavy metals in environment are mainly derived from anthropogenic sources (Wei and Yang 2010). The main sources of heavy metals in agricultural soils are due to activities such as irrigation using wastewater, application of mineral fertilizers, livestock manure, pesticides, disposal of urban and industrial wastes, mining, smelting processes, and atmospheric pollution from motor vehicles and the combustion of fossil fuels (Alloway 1995; Romic and Romic 2003; Montagne et al. 2007; Qishlaqi and Moore 2007; Sridhara Chary et al. 2008; Li et al. 2008, 2009; Yang et al. 2009; Hani and Pazira 2011; Esmaeili et al. 2014). Heavy metal pollution in soils is a growing risk that is of great concerns due to the potential negative impacts of heavy metals on the environment (Yanez et al. 2002). Moreover, they can be readily transferred to the human body through food chain and affect human health (Lin et al. 2017). Consequently, areas that are polluted by heavy metals and their sources must be identified to develop pollution control practices, and effective soil remediation and management recommendations.

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Kermanshah province is located in the western part of Iran and known as an important agricultural area in the region. With the rapid increases in industrialization, urbanization and intensive agriculture in the last 3 decades, Kermanshah has become one of the most developed areas in Western Iran. Coupled with the lack of pollution controls, human activities associated with these developments have caused significant impacts on the local environment. An increase in contaminant emissions may pose substantial implications on the local agriculture, as heavy metals may enter and accumulate in agricultural soils, which could enhance the risk of metal contamination through the food chains in the region. Therefore, it is important to identify the contaminated soils and the potential pollution sources in Kermanshah to plan management strategies for achieving better environmental quality in similar areas of Iran. No information is available about the pollution level and sources of Zinc (Zn), Copper (Cu), Nickel (Ni), Chromium (Cr), Manganese (Mn), and Iron (Fe) in agricultural soils of the region.

This study is the first detailed report on metal accumulation in agricultural soils of Kermanshah province, and results will promote the care for the environment by monitoring heavy metal levels in receiving soils and controlling the pollutant sources. The present study was performed at a regional scale to (1) determine the contents of Zn, Cu, Ni, Cr, Mn and Fe in agricultural soils; (2) define their natural or anthropic sources using multivariate analysis and to assess their contamination levels; and (3) establish relationships between heavy metals and selected soil properties. Assessment of the heavy metals levels in the agricultural soils using Iranian Environmental Quality Standard (IEQS) guidelines is given in this report.

Materials and methods

Characteristics of the study area

The study area (Fig. 1) is located in Kermanshah province of Iran (33°40′–35°18′N, 45°24′–48°07′E), with a total surface area of 19,243 km^2 (including ten counties) and mean altitude of 1200 m above the sea level. The annual mean precipitation and temperature in the province are 450 mm and 16 °C. The prevailing wind directions are west to east with northwest and southwest fluctuations (IRIMO 2013). The soils of the study area, classified using United States Department of Agriculture (USDA) Soil Taxonomy method, are Entisols, Inceptisols, Vertisols and Mollisols. Based on the results of X-ray diffraction (XRD) of the soil samples in Kermanshah province by Heidari et al. (2008), most of the soils in Kermanshah province are dominated by smectite, with different amounts of vermiculite, illite, chlorite, and kaolinite clay minerals.

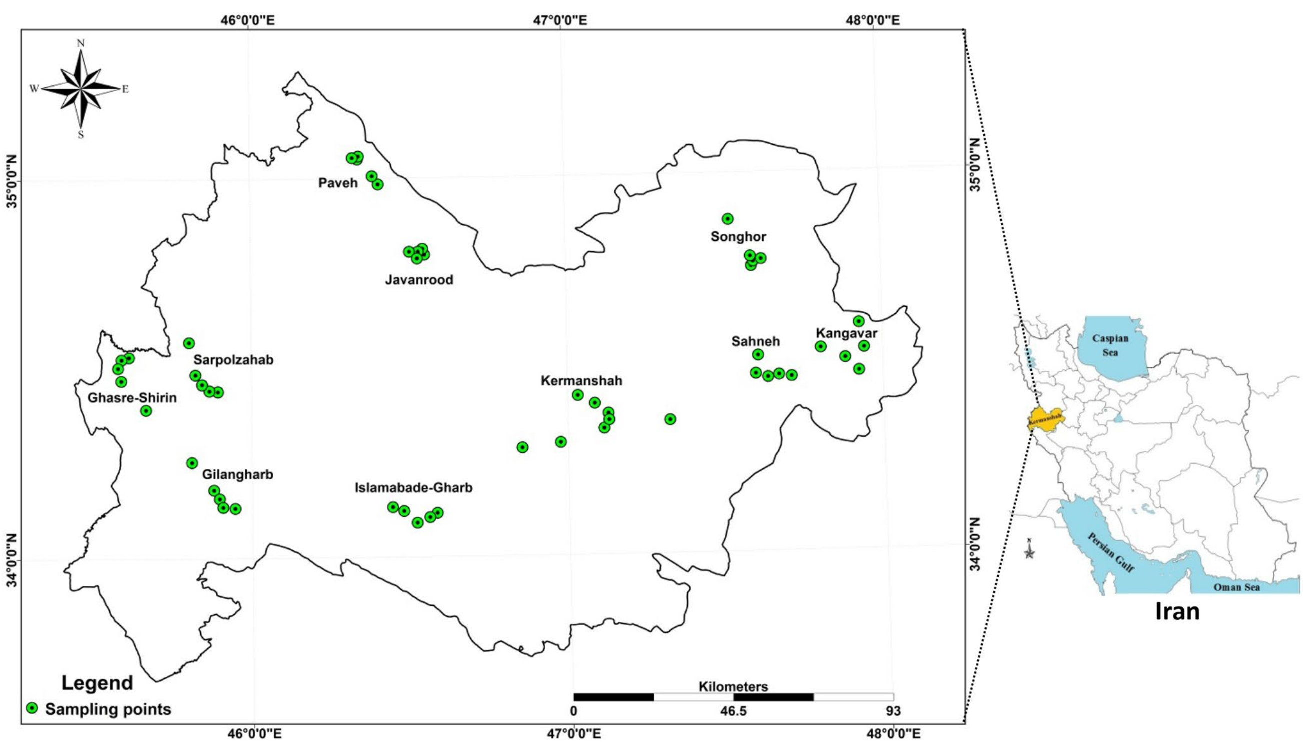

Fig. 1 Study area and sampling points in Kermanshah province

The area has been traditionally associated with agricultural activities favoring mainly the production of wheat (45%), chickpea (17.5%), barley (16.4%), and corn (4.1%) (Ahmadi Doabi et al. 2016). The major sources of pollution in the province are gaseous wastes in the form of automobile exhaust, chemical factory emissions, different kinds of industries (including petrochemical, oil refinery and cement industries) and primitive forms of heating, as well as dust input from Iraq, the neighboring country. In addition to high population growth, the rate of urbanization has also accelerated, and is now one of the highest in Iran.

Soil sampling, preparation and analysis

To assess the heavy metals levels in agricultural soils, 53 topsoil samples (0–20 cm) were collected from agricultural fields across Kermanshah province based on a randomized design in May 2013 (Fig. 1). Sampling points were chosen based on the predominant crop distribution, sizes of agricultural areas, industries distribution, soil type, and irrigation water. The soil samples were taken from the designated locations by a process of composite sampling (quincunx sampling pattern), using a stainless steel auger. Five soil subsamples were taken and mixed together at each sampling point. These composite soil samples each weighing about 0.5 kg were dispatched to a central laboratory for physical and chemical analyses. In laboratory, samples were air-dried, homogenized, sieved through a 0.15-mm (100-mesh) screen for determination of heavy metals (Micó et al. 2006; Lu et al. 2012) and 2-mm screen for the rest of the physicochemical parameters.

Soil pH and electrical conductivity (EC) were determined in aqueous suspensions (1:2.5 soil:water ratios). The soil particle size distribution was measured by the hydrometer method to determine the sand, silt and clay percentages (Gee and Bauder 1986). Soil organic matter (SOM) content was determined by the Walkley–Black method (Jackson 1958; Cai et al. 2012). Cation exchange capacity (CEC) was measured using saturation with sodium acetate solution, replacement of the absorbed sodium with ammonium and determination of displaced sodium by flame photometry (Micó et al. 2006). Calcium carbonate ($CaCO_3$) was analyzed using a manometric measurement of the CO_2 released following acid (HCl) dissolution (Houba et al. 1995). To heavy metal measurement, an accurately weighed 0.5 g of soil was placed in a test tube, 10 ml of a 3:1 concentrated HCl/HNO_3 mixture was added to each test tube, and the mixture was left at room temperature overnight. Each test tube was covered with an air condenser and refluxed gently at 80 °C for 2 h. After cooling, the solution was filtered through a moistened Whatman 42 filter paper and diluted to 50 ml volume with distilled water (Sparks et al. 1996; Karimi et al. 2009). The final solutions were analyzed for their Zn, Cu, Ni, Cr, Mn, and Fe concentrations using an Atomic Absorption Spectrophotometer (AAS: model Perkin Elmer 3030, USA). Detection limits were between 0.01 and 0.02 ppm for all studied elements.

Statistical analysis

To evaluate the analytical data, correlation analysis, principal component analysis (PCA) and cluster analysis (CA) were used. The correlation coefficient measures the strength of a linear relationship between two quantitative variables. PCA and CA are the most common multivariate statistical methods used in environmental studies (Tahri et al. 2005; Yongming et al. 2006).

The Kolmogorov–Smirnov test (K–S) was applied to investigate the normality of soil properties and heavy metal content distributions. The K–S test confirmed that soil Zn, Cu and Fe contents, SOM and $CaCO_3$ distributions are normal ($P > 0.05$), while Ni and Cr concentrations, pH, EC, CEC, clay, slit and sand variables are not normally distributed ($P < 0.05$), as may be also inferred by the values of skewness and kurtosis obtained. Since multivariate analysis is sensitive to outliers and non-normality of geochemical data sets (Chen et al. 2008; Hani and Pazira 2011; Niu et al. 2013), Ni and Cr concentrations, CEC and sand variables were normalized by logarithmic transformation (natural logarithms), Mn content, EC and silt properties by Box–Cox transformation, and pH by Johnson-transformation method (unbounded system distribution) prior to implementation of correlation analysis, PCA and CA. Clay distribution was found to be still non-normal, despite applying the above transformations.

Assessment of the contamination levels

Enrichment factor

Enrichment factor (EF) of an element is calculated based on the standardization of a measured element in samples against a reference element. A reference element is often the one characterized by low occurrence variability, such as the most commonly used elements Fe and Al (Chandrasekaran et al. 2015). The enrichment factor was calculated using the following equation:

$$EF = (C_x/C_{ref})_{sample}/(C_x/C_{ref})_{background}, \quad (1)$$

where C_x is the concentration of the element of interest and C_{ref} is the concentration of the proxy or normalizing element, Fe, because of the following reasons: (1) Fe is associated with fine solid surfaces; (2) its geochemistry is similar to that of many heavy metals and (3) its natural concentration tends to be uniform (Chandrasekaran et al. 2015). The world average elemental concentrations reported by

Alloway (2010) in the soils were used as background in this study because regional geochemical background values for these elements are not available. The categories for evaluating EFs were considered as follows: EF < 2 indicates deficiently to minimal enrichment, 2 ≤ EF < 5 indicates moderate enrichment, 5 ≤ EF < 20 indicates a significant enrichment, 20 ≤ EF < 40 indicates very high enrichment, and EF ≥ 40 indicates extremely high enrichment (Sezgin et al. 2004; Kartal et al. 2006; Yongming et al. 2006; Duzgoren-Aydin et al. 2006).

Geo-accumulation index

The index of geo-accumulation (I_{geo}) enables the assessment of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediments (Müller 1969). It could also been applied to assess the contamination of different environments. Mathematically, I_{geo} is given as (Bhuiyan et al. 2010)

$$I_{geo} = \log_2(C_n/\mathrm{kB}_n), \quad (2)$$

where C_n is the concentration of the potentially hazardous heavy metals in the soil sample, B_n is the geochemical background value of the heavy metal (n) in world soils (Alloway 2010) and $k = 1.5$ is the background matrix correction factor introduced to account for possible differences in the background values due to lithospheric effects. The geo-accumulation index consists of seven grades or classes (Müller 1969; Bhuiyan et al. 2010). $I_{geo} \le 0$, class 0)practically unpolluted(; $0 < I_{geo} \le 1$, class 1) unpolluted to moderately polluted(; $1 < I_{geo} \le 2$, class 2)moderately polluted(; $2 < I_{geo} \le 3$, class 3)moderately to heavily polluted(; $3 < I_{geo} \le 4$, class 4) heavily polluted(; $4 < I_{geo} \le 5$, class 5) heavily to extremely polluted(; and $I_{geo} > 5$, class 6)extremely polluted(. Class 6 is an open class and comprises all values of the index higher than Class 5. The elemental concentrations in Class 6 may be 100-fold greater than the geochemical background value.

Integrated pollution index

Pollution index (PI) and integrated pollution index (IPI) are also commonly used to assess the environment quality (Chen et al. 2005). The PI is defined as the ratio of element concentration in the study to the background content of the corresponding element of world soils (Alloway 2010), and is calculated using the following equation:

$$\mathrm{PI}_n = C_n/B_n, \quad (3)$$

where C_n is the concentration of element in environment and B_n is the background value (Alloway 2010). The PI of each element is calculated and classified as either low (PI ≤ 1), moderate (1 < PI ≤ 3) or high (PI > 3). The IPI of all measured elements for each sample is defined as the mean value of the element's PI, and is then classified as low (IPI ≤ 1), moderate (1 < IPI ≤ 2) or high (IPI > 2) (Chen et al. 2005).

Results and discussion

Soil physicochemical properties and heavy metal concentrations

The descriptive statistic of heavy metal concentrations and soil physicochemical characteristics in agricultural soils of Kermanshah province are listed in Table 1. The soil

Table 1 Descriptive statistic of heavy metal concentrations and soil physicochemical properties in agricultural soil samples collected from Kermanshah province ($n = 53$, except for CEC with $n = 28$)

Parameter	Units	Minimum	Maximum	Mean	Median	S.D.	C.V.	Skewness	Kurtosis	K–S test
Zn	mg kg^{-1}	40	113	74.62	72	16.24	21.76	0.14	– 0.44	0.200
Cu	mg kg^{-1}	10	83	41.21	41	12.09	29.33	0.68	2.48	0.200
Ni	mg kg^{-1}	48	306	131.46	125	47.17	35.88	1.73	4.74	0.002
Cr	mg kg^{-1}	32	235	79.21	76	28.73	36.27	3.30	16.57	0.001
Mn	mg kg^{-1}	298	1240	559.06	535	188.98	33.80	1.83	3.95	0.000
Fe	mg kg^{-1}	14,300	35,150	25,935.85	26,650	5358.35	20.66	– 0.38	– 0.49	0.200
pH	–	7.65	8.75	8.10	8.05	0.25	3.04	1.11	1.07	0.000
EC	ds m^{-1}	0.12	2.31	0.28	0.20	0.40	140.51	4.84	22.85	0.000
CEC	meq 100 g^{-1}	12.76	72.38	32.82	31.30	14.80	45.09	1.11	1.12	0.025
SOM	%	0.48	2.81	1.68	1.63	0.48	28.89	– 0.22	– 0.11	0.200
$CaCO_3$	%	4.25	66.75	30.54	29.75	14.37	47.05	0.33	– 0.36	0.200
Clay	%	1.9	27.9	3.41	1.9	3.68	107.86	5.91	39.35	0.000
Silt	%	40	92	74.34	76	12.04	16.20	– 0.98	0.73	0.001
Sand	%	6.10	56.10	22.25	22.10	10.88	48.88	0.97	0.94	0.005

pH ranged from 7.65 to 8.75. The fact that soil pH was higher than 8 in 60% of the samples indicates that these soils are predominated by basic conditions, mainly due to the high carbonate content of the parent rocks. The alkaline substrates tend to be weathered, releasing calcium, and in dry conditions, this is responsible for cementation at soil surface, creating an impermeable crust (Amjadian et al. 2016). In such alkaline soils, most heavy metals are likely to be in a less mobile form (Škrbic and Durisic-Mladenovic 2002), because the mobility and retention of heavy metals are strongly affected by soil pH (Esmaeili et al. 2014). Agricultural soils of the study area had low organic matter content. The mean SOM value in the agricultural soils is 1.68%. Organic matter has also been found to influence heavy metal absorption in soils; this effect is probably due to the high CEC of organic material (Martin and Kaplan 1998; Romic and Romic 2003). However, the influence of SOM on total metal content should be low since the SOM percentage is above 2% for only 28% of soil samples in this study. Calcium carbonate contents of the analyzed soils vary from 4.25 to 66.75%, with an average value of 30.54%, which is extremely calcareous according to Avery classification (Avery 1980). Most of soil samples are not saline (96% of the samples) with an electrical conductivity in the saturation paste extract less than 2 dS m^{-1}. Cation exchange capacity varied from 12.8 to 72.4 meq 100 g^{-1}, with a mean value of 32.8 meq 100 g^{-1} comparable to that of soils from temperate regions (Wilcke et al. 1998). Mean clay, silt, and sand contents in Kermanshah agricultural soils were 3.41, 74.34, and 22.25%, respectively. Soil particle size distributions are related with the content of metals in soil (Nanos and Martin 2012). Clay is the main soil constituent relating to heavy metals owing to their high affinity for clay minerals (Alloway 1995; Rodriguez et al. 2008). Clay fraction percentage in agricultural soils of the study area ranges from 1.9 to 27.9%. Regarding soil texture, most of samples fall in the silt loam (50.9%) and silt (43.4%) categories. The other soil textural classes are loam, clayey loam, and sandy loam, based on the USDA soil texture classification system.

Compared with the background values of world soils (from the considered localities of the world) (Alloway 2010) presented in Table 2, the concentrations of Zn (81%), Cu (98%), Ni (100%), Cr (98%) and Mn (79%) in agricultural soils are greater than their background values, while the concentration of Fe (100%) is lower than its background value. Application of the K–S test showed that concentrations of Ni, Cr, and Mn are not normally distributed; while Zn, Cu, and Fe followed a normal distribution. Skewness values of heavy metals are positive except for Fe, showing that mean concentrations are higher than their median concentrations. The skewness values for Cr were 3.30 (maximum value among all the elements), which indicate the existence of highly contaminated spots. Moreover, the kurtoses of Cr were very sharp because the majority of the samples were clustered at the relatively lower values. In addition, the high coefficients of variation (CV) (especially for Ni, Cr, and

Table 2 Comparison of the heavy metal concentrations (mg kg^{-1}) in the agricultural soils of Kermanshah province with background soils of the considered localities (of the world), reported values for other cities in previous studies and the Iranian Environmental Quality Standard (IEQS) for agricultural soils

Location	Zn	Cu	Ni	Cr	Mn	Fe	Reference
Kermanshah	74.62	41.21	131.46	79.21	559.06	25,936	Present study
Background values	62	14	18	42	418	47,000	Alloway (2010)
IEQS	500	200	110	110	–	–	Environmental Protection Organization of the Islamic Republic of Iran (2013)
Tehran (Iran)	217.9	36.1	36.9	67.9	–	–	Hani and Pazira (2011)
Isfahan (Iran)	111.5	35.7	66.2	85.9	649.9	28,000	Esmaeili et al. (2014)
Isfahan (Iran)	23.8	7	13.4	–	95.7	1240	Jalali and Hemati (2013)
Shiraz (Iran)	117	96.9	171.4	124.5	–	–	Qishlaqi and Moore (2007)
Argolida basin (Greece)	74.9	74.7	146.8	83.1	1020.5	–	Kelepertzis (2014)
Thiva (Greece)	67	32	1591	277	1010	–	Antibachi et al. (2012)
Dehui (China)	58.9	18.9	20.8	49.7	–	–	Sun et al. (2013)
Huizhou (China)	57.2	16.7	14.9	27.6	–	–	Cai et al. (2012)
Almería (Spain)	65.7	25.7	26.9	29.6	–	–	Martin et al. (2013)
Murcia (Spain)*	18.4	11	13.5	17.6	152	–	Acosta et al. (2011)
Alicante (Spain)	52.8	22.5	20.9	26.5	295	–	Micó et al. (2006)
Zagreb (Croatia)	77.9	20.8	49.5	–	613	–	Romic and Romic (2003)
Piemonte (Italy)	62.7	58.3	83.2	46.2	–	–	Facchinelli et al. (2001)

* Medians

Mn) suggest that considerable variabilities exist in the heavy metal data and the spatial distributions of heavy metals in this area are not homogeneous.

In Table 2, the metal concentrations obtained in this study are compared with data reported for the other areas of the world and Iran, and the Iranian Environmental Quality Standard (EQS) for agricultural soils. Comparing with the results of the previous studies in Iran, average Zn and Cu contents in soil samples of the study area are lower than those in agricultural soils of Khoshk River banks in Shiraz reported by Qishlaqi and Moore (2007), and Zn in agricultural soil of industrial zone of Isfahan province, and also agricultural soils of southern Tehran reported by Esmaeili et al. (2014), and Hani and Pazira (2011), respectively. According to Jalali and Hemati (2013), the mean Zn and Cu contents in paddy soils of Isfahan province are 23.8 and 7 mg kg^{-1}, respectively, which are lower than the corresponding concentrations in agricultural soil samples in the study area. Also, the mean concentration of Ni is higher than the Ni concentration reported by Jalali and Hemati (2013) in paddy soils (13.4 mg kg^{-1}) and by Esmaeili et al. (2014) in agricultural soils of industrial zone (66.2 mg kg^{-1}) of Isfahan province. However, it was lower than the mean concentration reported by Qishlaqi and Moore (2007) in agricultural soils (171.4 mg kg^{-1}) of Khoshk River banks in Shiraz. According to Hani and Pazira (2011), the mean Ni and Cr contents in agricultural soils of southern Tehran are 36.9 and 67.9 mg kg^{-1}, respectively, which are lower than the corresponding concentrations in agricultural soil samples of the present study. Manganese content of Kermanshah agricultural soils is within the lowest found in the literature, whereas the mean concentration of Zn is similar to those obtained in Argolida basin (Greece) and higher than other cities except for Zagreb (Croatia). The mean concentration of Cu for agricultural soils in Kermanshah is greater than other compared cites except for Argolida basin and Piemonte (Italy). Table 2 reveals a significant enrichment of Ni and Cr in agricultural soils of Kermanshah since the mean concentrations of these metals are substantially higher than values determined in most of the other areas. Only, agricultural soils in Thiva (central Greece) and Argolida basin display greater Ni and Cr mean values that have been ascribed to local parent materials enriched with these specific metals.

Except for Fe, all the other heavy metal mean concentrations were greater than concentrations in the background values of the world soils, probably suggesting the existence of contamination and likely from anthropogenic sources. The mean heavy metal concentrations in the 53 soil samples collected in Kermanshah province were all below the values in the IEQS for agricultural soils (Environmental Protection Organization of the Islamic Republic of Iran 2013) except for Ni. However, some of the maximum values (Table 1) greatly exceeded the values in the IEQS (e.g., 306 versus 110 mg kg^{-1} for Ni, and 235 versus 110 mg kg^{-1} for Cr), and these maximum values were mainly related to the soil samples from the Islamabade-Gharb city sites.

Correlation coefficient analysis results

The Pearson (for all variables except for clay) and Spearman (only for clay) correlation coefficients were calculated between six elements and other soil characteristics, and the results are shown in Table 3.

Table 3 Correlation coefficients[a] matrix among heavy metals and soil physicochemical properties in the agricultural soils of Kermanshah ($n = 53$, except for CEC with $n = 28$)

	pH	EC	CEC	SOM	$CaCO_3$	Clay	Silt	Sand	Zn	Cu	Ni	Cr	Mn
EC	0.23												
CEC	0.10	0.30											
SOM	− 0.04	− 0.01	0.18										
CaCO3	0.23	− 0.05	0.53**	− 0.24									
Clay	− 0.32*	− 0.32*	0.44*	0.19	0.02								
Silt	0.41**	− 0.07	− 0.39*	0.01	0.16	− 0.42**							
Sand	− 0.38**	0.12	0.36	− 0.06	− 0.12	0.29*	− 0.96**						
Zn	0.16	0.09	− 0.14	0.24	− 0.51**	− 0.08	0.19	− 0.22					
Cu	− 0.12	0.20	− 0.27	0.30*	− 0.68**	− 0.14	− 0.05	− 0.03	0.65**				
Ni	0.42**	0.15	− 0.32	0.16	0.10	− 0.25	0.43**	− 0.41**	0.13	− 0.06			
Cr	0.45**	0.29*	− 0.31	0.27	− 0.15	− 0.21	0.23	− 0.22	0.33*	0.16	0.80**		
Mn	0.19	− 0.11	0.36	− 0.24	0.84**	0.01	0.16	− 0.12	− 0.60**	− 0.87**	0.16	− 0.17	
Fe	0.13	0.25	− 0.23	0.20	− 0.69**	− 0.08	0.07	− 0.09	0.82**	0.72**	0.22	0.52**	− 0.76**

Levels of significance: *$P < 0.05$; **$P < 0.01$

[a]Pearson's correlation coefficients were used for all variables except for clay, and Spearman correlation coefficients were used for clay

Nickel and Cr display significant correlation with pH, probably reflecting the low variability of pH (3.04%) in the studied agricultural soils. The medium correlations of CEC with clay ($r=0.44$) and $CaCO_3$ ($r=0.53$) at $P<0.05$ and $P<0.01$, respectively, showed that these two parameters were the main factors determining the soil CEC. Sand and clay fractions are found to be negatively correlated with heavy metal concentrations, whereas positive correlation exists between some heavy metals with pH, SOM and silt fractions. This shows that heavy metals are slightly distributed over clay minerals and mainly distributed over silt and SOM. Significant although weak correlation was observed between Cu and SOM, confirming the affinity of this metal for organic compounds and possible strong complex formation (Marchand et al. 2011). The results indicate that Zn, Cu and Fe positively correlate with each other ($r=0.65$–0.82) at $P<0.01$. The correlations between heavy metals in soil may reflect similar contamination levels and/or discharge from similar pollution sources, interdependence, and same behavior during their transport in the system (Li et al. 2013; Ali et al. 2016). Zinc and Fe also show significant correlations with Cr ($r=0.33$ and $r=0.52$) at $P<0.05$ and $P<0.01$, respectively, indicating common influential factors affecting on their concentrations. Chromium also significantly correlates with Ni ($r=0.80$) at $P<0.01$. The positive correlations among Ni, Cr and Fe is likely due to the degradation of parent rocks, suggesting their geogenic association. Mn did not show significant positive correlation with any of studied metals indicating that this element was mainly derived from lithogenic sources.

Multivariate analysis of the sources of soil heavy metal variations

PCA is widely used to reduce data and to extract a small number of latent factors for analyzing relationships among the observed variables (Yongming et al. 2006). Varimax rotation with Kaiser normalization was applied because orthogonal rotation minimizes the number of variables with a high loading on each component and facilitates the interpretation of results. The results of PCA, as well as the eigenvalues and communalities for elemental concentrations in agricultural soils are shown in Table 4. Three principal components (PC) with eigenvalues greater than 1 (before and after rotation) were extracted. In other word, the PCA resulted in a reduction of the initial dimension of the data set to three components explaining about 81.47% of the data variation. The graphic representation of these components is shown in Fig. 2, depicting the association between the elements and other soil properties. The rotated component matrix demonstrated that Zn, Cu, and Fe were involved in the first component (PC1), Ni and Cr in the second component (PC2), and pH, CEC and SOM in the third component (PC3), with higher loading plots observed for PC3 (0.19) compared to PC1 (−0.92) and PC2 (−0.07). Manganese was the only metal that did not demonstrate a clear association with either the first to the third component.

Table 4 Rotated component matrix for normalized elemental concentrations and selected properties of agricultural soils in Kermanshah province (significant loading factors are marked in bold)

Element	Rotated component matrix			Communalities
	PC1	PC2	PC3	
Zn	**0.87**	0.21	0.23	0.84
Cu	**0.93**	0.23	0.08	0.92
Ni	0.15	**0.94**	− 0.08	0.90
Cr	**0.64**	**0.67**	0.02	0.88
Mn	− 0.92	− 0.07	0.19	0.89
Fe	**0.95**	0.15	0.01	0.92
pH	0.42	0.09	**0.59**	0.52
CEC	− 0.26	− 0.35	**0.74**	0.74
SOM	0.04	**0.55**	**0.64**	0.72
Eigenvalue	4.03	1.90	1.40	
% Variance explained	44.76	21.13	15.58	
Cumulative % variance	44.76	65.89	81.47	

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser normalization. Rotation converged in five iterations

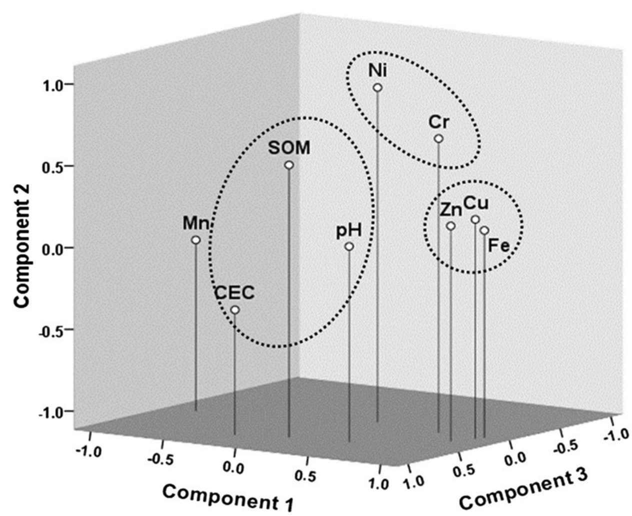

Fig. 2 Principal component analysis loading plots for the three rotated components

CA classifies a set of observations into two or more mutually exclusive unknown groups based on a combination of internal variables (Facchinelli et al. 2001; Lu et al. 2010; Chandrasekaran et al. 2015). A dendrogram is the most commonly used method of summarizing hierarchical clustering (Lu et al. 2010). The heavy metal concentration data and soil properties (the variables) were standardized by means of z-scores before CA and then Squared Euclidean distances for similarities in the variables were calculated. Then hierarchical clustering by applying Ward's method was performed on the standardized data set (Yongming et al. 2006). The results of CA are illustrated in Fig. 3 as a dendrogram that enabled the identification of three major groups of elements describing the geochemical complexity of the study area. Group I is comprised of Zn, Cu, and Fe. Group II included Ni and Cr, and was clearly distinguished from group III that consisted of Mn.

The PC1 explained 44.76% of the total variance and can be considered to be an anthropogenic component related to the agricultural activities taking place in the area for a long period of time in agreement with the clustering of variables in Group I. Except for Fe, Zn and Cu were also found to be present in greater amounts in the agricultural soils than the background soils confirming the interpretation of their anthropogenic origin. The Cr loading (0.64) is not as high as the Zn, Cu, and Fe loadings (0.87, 0.93 and 0.95, respectively), which may imply quasi-independent behavior within the group (Lu et al. 2010). Ahmadi Doabi et al. (2016) studied the heavy metal mass balance modeling in Kermanshah agricultural soils and reported that the long agricultural history combined with the excess use of fertilizers and pesticides has resulted in Cu accumulation in agricultural soils of this region. They estimated that livestock manure, mineral fertilizers, municipal waste compost and atmospheric deposition contribute to 55, 24, 19, and 2%, and 56, 4, 38, and 2% of total Zn and Cu inputs into agricultural soils in Kermanshah province, respectively (Ahmadi Doabi et al. 2016). The association of Fe with Zn and Cu as revealed by the CA (Fig. 3) may point out that the application of fertilizers, pesticides and animal manures is the important sources for Fe in the studied agricultural soils.

The second principal component (PC2) accounting for 21.13% of the total variability can be presumed to represent a lithogenic component as may also be inferred by the clustering of Ni and Cr in group II of CA. A clear subgroup of pH and SOM is evident inspecting the dendrogram produced

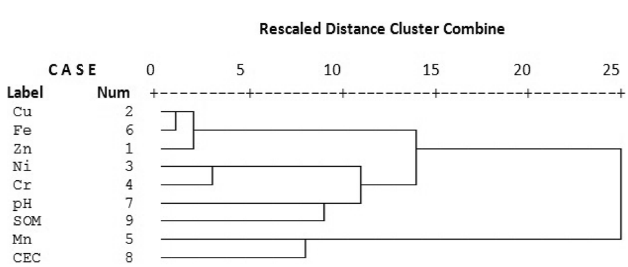

Fig. 3 Dendrogram results from Ward's method of hierarchical cluster analysis for eight studied variables. Similarities have been calculated from Euclidean distance

by CA (Fig. 3), followed by Ni and Cr that form another subgroup. Ahmadi Doabi et al. (2016) reported that annual Ni inputs into agricultural soils of Kermanshah province were 67, 14, 15, and 4% of total inputs, by livestock manure, mineral fertilizers, municipal waste compost and atmospheric deposition, respectively, neglecting weathering process and the role of parent materials.

The third component (PC3), which explains 15.58% of total variance, shows high positive factor loadings on pH, CEC and SOM (Fig. 2). The attribute of SOM was ambiguous, given the loading values of 0.55 and 0.64 in PC2 and PC3, respectively (Fig. 2). High negative loading factor on PC1 for Mn suggest that the origin of this metal was completely different from the source of Zn, Cu, and Fe in PC1 (Fig. 2).

It seems reasonable to conclude that Zn, Cu, and Fe constitute an anthropogenic component related to specific human activities, whereas the metal Mn appear to be associated with parent rocks. In the case of Ni and Cr, these elements display a combined relationship with both groups and seem to have both natural and anthropic origins. However, this still need further research because of lacking adequate understanding of the soil parent materials in the study area.

Assessment of the heavy metal contamination in agricultural soils

Enrichment factor analysis

Enrichment factor values between 0 and 1.5 indicate the metal is entirely from crustal materials or natural origin, while an EF > 1.5 suggests that the sources are more likely to be anthropogenic. EFs greater than 10 are considered to be non-crusted source (Zhang and Liu 2002).

The EF ranges for Zn, Cu, Ni, Cr, and Mn are 1.58–2.79, 2.26–9.06, 5.20–45.61, 1.48–8.57, and 1.84–5.76, with the means of 2.20, 5.31, 13.77, 3.46, and 2.43, respectively (Fig. 4a). The mean EF of Cu, Ni, and Cr is higher than 3, while the mean EF of Zn and Mn is less than 3. On the other hand, maximum EF of Cu, Ni, and Cr is close to or higher than 10, which shows that these elements in agricultural soils mainly originate from anthropogenic sources (Liu et al. 2003). The mean and percentage of EF for Zn, Mn, and Cr show that most of agricultural soil samples were moderately enriched with Zn, Mn, and Fe. For element Cu, the mean EF (5.31) and occurrence of 68% of EF values in 5–20 range indicate that agricultural soils are mainly in level of significant contamination, while about 32% of samples belong to moderate enrichment. For element Ni, 89% of EF values are in the range of 5–20, and 9% of them in the range of 20–40, with mean EF higher than 5, reflecting that soils are in significant contamination level. Soil contamination was

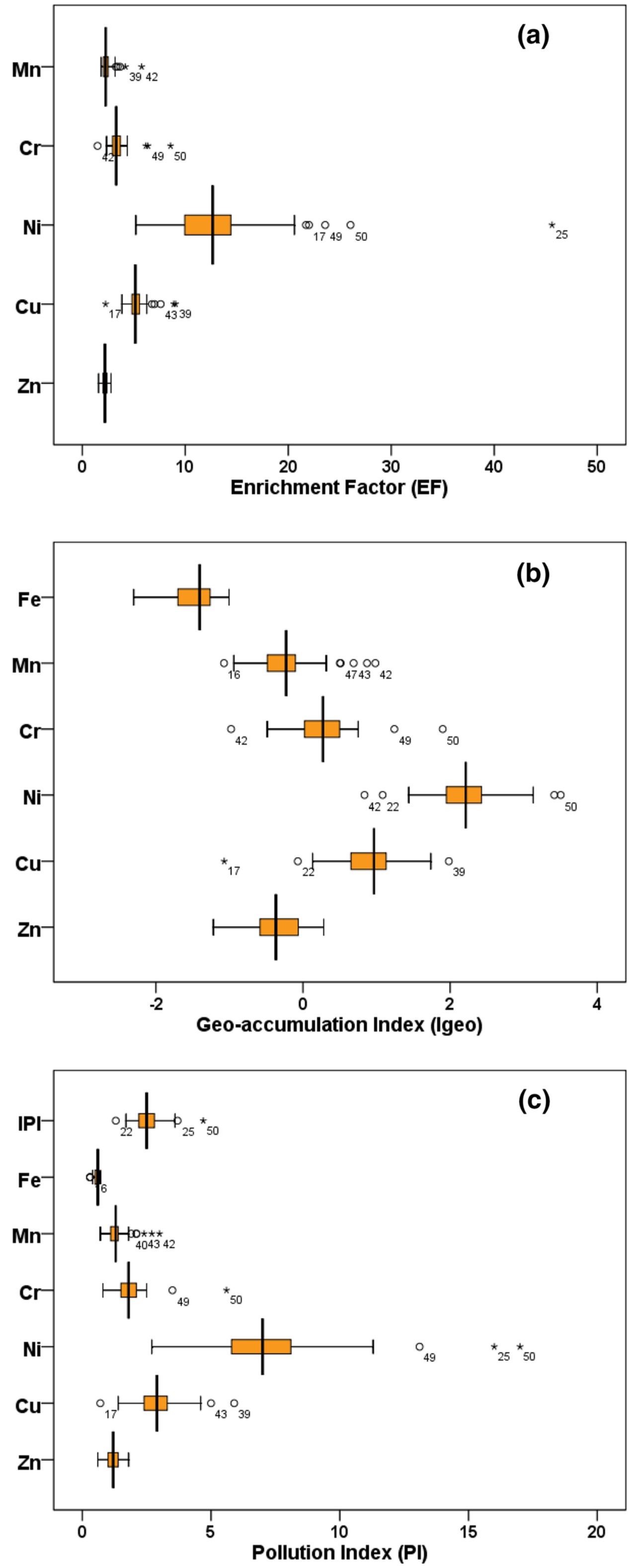

Fig. 4 Boxplots of EF (**a**), I_{geo} (**b**), PI (**c**), and IPI (**c**) for heavy metals in the agricultural soil samples of Kermanshah province

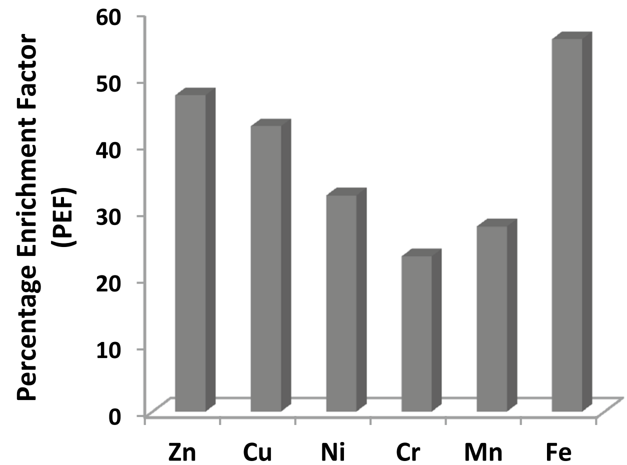

Fig. 5 Percentage enrichment factor (PEF) of heavy metals (mg kg^{-1}) in agricultural soils of Kermanshah province

also evaluated using the percentage enrichment factor (PEF) (Zonta et al. 1994; Loska and Wiechula 2003), as following:

$$\%\mathrm{EF} = \frac{C - C_{\min}}{C_{\max} - C_{\min}} \times 100, \quad (4)$$

where C is the mean total concentration, C_{min} is the minimum concentration and C_{max} is the maximum concentration of the metal in soil. Figure 5 gives the calculated percentage of enrichment factor (EF %) values of heavy metals. The percentage of enrichment factor for Fe was 55.81% which is greater than the other studied heavy metals. The lower PEF was observed for Cr (23.25%), Mn (27.72%), and Ni (32.36%) due to the natural origin, whereas higher PEF was found for Zn (47.40%) and Cu (42.74%) that might be due to the anthropogenic sources.

Geo-accumulation index analysis

The calculated results of I_{geo} for heavy metals in Kermanshah agricultural soils are presented in Fig. 4b. The I_{geo} ranges from − 1.22 to 0.28, − 1.07 to 1.98, 0.84 to 3.50, − 0.98 to 1.90, − 1.07 to 0.98, and − 2.30 to − 1.00 with a mean value of − 0.35, 0.91, 2.20, 0.26, − 0.23, and − 1.48 for Zn, Cu, Ni, Cr, Mn, and Fe, respectively. The order of mean I_{geo} values is Ni > Cu > Cr > Mn > Zn > Fe, similar to the order of EF, which can also be seen as the decreasing order of their overall contamination degrees in agricultural soils of Kermanshah. The mean and percentage of I_{geo} for Zn, Mn, and Fe show that most agricultural soil samples were practically unpolluted and unpolluted to moderately polluted with Zn, Mn, and Fe. For Cu, the mean I_{geo} and 58% of I_{geo} values falling into class 1 indicate unpolluted to moderately polluted status of the most studied soils, while

38% of I_{geo} were between 1 and 2 revealing moderately polluted status of the soil samples. The mean I_{geo} was obtained for Ni points from moderately to heavily polluted levels. Also, 34% and 58% of I_{geo} values for Ni mainly fall into class 2 (moderately polluted) and class 3 (moderately to heavily polluted), respectively, showing that the majority of the agricultural soils in the study area were polluted by Ni. The mean and percentage of I_{geo} values for Cr reveal practically unpolluted and unpolluted to moderately polluted status of the agricultural soils. In general, the analytical results of I_{geo} were similar to the analytical results of EF.

Integrated pollution index analysis

The PIs, calculated according to the background concentration of heavy metals in world soil, vary greatly among different metals (Fig. 4c). Iron, Zn, Mn, and Cr exhibit lower values, ranging from 0.30 to 0.75, 0.65 to 1.82, 0.71 to 2.97, and 0.76 to 5.60, respectively. For Fe, the mean PI is 0.55 and all of the samples have low PIs, indicating that the concentration of Fe in the agricultural soil samples is comparable with the background concentration of world soil and there is no pollution of Fe in Kermanshah agricultural soil samples. The mean PIs for Zn, Mn, and Cr are 1.20, 1.34, and 1.89, and 68%, 77%, and 94% of samples are classified as middle PI, for these elements, respectively, indicating an absence of problematic Zn, Mn, and Cr pollution of agricultural soils in the study area. The PIs of Cu and Ni are much higher, ranging from 0.71 to 5.93 and 2.68 to 17.01, with mean values of 2.94 and 7.30 for Cu and Ni, respectively. These results indicate that Cu and Ni (especially Ni) are in the level of serious pollution in the agricultural soils of the study area. The IPIs of agricultural soil samples vary from 1.27 to 4.74 with an average of 2.54, indicating that all studied samples were polluted by heavy metals.

Conclusion

Although the mean concentrations of Zn, Cu, Ni, Cr, and Mn in the agricultural soils of the study area were greater than their values in soils of the considered localities of the world (as background values), they (except for Ni) were lower than the maximum permissible concentrations in the IEQS for agricultural soils. Results of the multivariate statistical analyses suggested that among the metals considered, soil Mn might be mainly derived from the soil parent materials, while Ni and Cr probably have mixed sources of both natural and anthropogenic (with less traces of influence); however, there are still some uncertainties that need further research due to the lacking of adequate and precise understanding regarding the soil parent materials in the study area. In contrast, human activities might play the most important role in Zn, Cu, and Fe, and also to a lesser extent in Ni and Cr accumulation in the soils of this region.

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