



Pollution assessment and source apportionment of arsenic, lead and copper in selected soils of Khuzestan Province, southwestern Iran

Saeid Hojati¹

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Abstract

Due to the intensified industrial activities and excessive application of agrochemicals and organic waste materials over the last few decades, there is a great concern about the accumulation of potentially toxic elements (PTEs) in soils from north of Khuzestan Province, southwestern Iran. Therefore, a comparative study with a total number of 300 composite soil samples (0–10 cm) from industrial, urban, agricultural, forest, and rangelands; and 26 samples from the major types of soils parent materials was conducted to examine sources, pollution status, and the effects of soil properties, land use types, and the local lithology on the total concentrations of As, Pb, and Cu (measured using atomic absorption spectrometer (AAS) equipped with graphite furnace) in the soils studied. The mean values of Pb and Cu were 12.2 ± 4.6 and 13.5 ± 7.6 mg kg⁻¹, respectively, slightly higher than the background values of the study area, but lower than the guideline values of Iranian Environmental Quality Standard for Soils. However, the mean values of As (1.72 ± 1.15 mg kg⁻¹) were lower than both background values and the guideline values of Iranian Environmental Quality Standard for soils. The greatest values of the geo-accumulation index (I_{geo}), enrichment factor (EF), and the concentrations of Pb, Cu, and As were arranged as industrial > urban > agriculture > rangelands = forest land uses. The results also indicated that concentrations of all PTEs were greater in soils as compared to those in parent materials. Using principal component analysis (PCA), the origin of Cu and Pb with moderate to high enrichments was attributed to the inputs from both natural and anthropogenic sources. However, As was found to be mainly influenced by lithogenic origin.

Keywords Anthropogenic · Geo-accumulation index · Enrichment factor · Multivariate analysis

Introduction

Over the last few decades, increase of industrial activities, excessive application of herbicides and pesticides to control plant diseases, as well as use of chemical fertilizers and industrial organic waste materials, brought about major concerns about accumulation of PTEs, and their potential threat to food safety, human health, and the adverse effects on soils of Khuzestan Province, southwestern Iran (Jiang et al. 2017; Sun et al. 2013).

Natural concentration of PTEs (i.e., As, Pb, Cd, Co, Cr, Ni, and Cu) in soils primarily depends on the geochemistry of

their parent materials (DeTemmerman et al. 2003; Lu et al. 2012). However, numerous studies have shown that pollution sources of PTEs in the environment could derive also from anthropogenic sources (Wei and Yang 2010; Cai et al. 2015; Jiang et al. 2017). The identification of spatial distribution and apportioning of PTEs in soils is necessary for undertaking appropriate action against soil pollution, and exploring locations where remediation efforts should be focused (Maas et al. 2010; Cai et al. 2015). Multivariate statistical analyses (PCA and cluster analysis (CA)) are among the most common used techniques for identification of the source of soils' PTEs (Maas et al. 2010; Li et al. 2013; Viera da Silva et al. 2016). Using multivariate and geostatistical analyses, Sun et al. (2013) suggested that soil Cr, Ni, and Zn had a lithogenic origin in agricultural soils in Dehui, Northeast China. However, they reported the elevated Cu concentrations to be associated with industrial and agronomic practices. Similarly, Kelepertzis (2014) reported that both PCA and CA could

✉ Saeid Hojati
s.hojati@scu.ac.ir

¹ Soil Science Department, College of Agriculture, Shahid Chamran University of Ahvaz, Ahvaz 6135783151, Iran

successfully differentiate the origin of Pb, Cu, Zn, Ni, As, Cd, Co, and Cr into anthropogenic and natural groups. They showed that the distribution of Co, Cr, Fe, and Ni is mainly controlled by lithogenic sources. Whereas, the accumulation of Cu, Zn, Cd, As, and Pb was attributed to prolonged application of large amounts of fertilizers and pesticides-fungicides in agricultural soils of Argolida basin, Greece.

Assessment of soil pollution is usually carried out by comparing metal concentrations with the related environmental guidelines, or by calculating an accumulation factor in comparison to the relevant background values (Mirzaei et al. 2014). Different indices including the geo-accumulation index (I_{geo}) (Muller 1969), the contamination factor and the degree of contamination (Hakanson 1980), the enrichment factor (EF) (Loska et al. 2004), pollution index and the integrated pollution index (Sun et al., 2010), the individual element polluted index (Rashed 2010), and the pollution load index (Muhammad et al. 2011) are commonly used to estimate degree of soils pollution with PTEs. Using I_{geo} , EF, and contamination factor, Marrugo-Negrete et al. (2017) reported that soils of Sinu river basin in Colombia is highly polluted by Ni, but moderately to highly contaminated with Zn and Cu.

Although during the last decades the pollution status of soils has been extensively investigated in many parts of the world, but little information is available about the accumulation of PTEs in soils of different land uses in Mesopotamian countries and in particular of Iran. Therefore, in our study, the EF and I_{geo} indices and multivariate statistical analyses were employed to (i) evaluate the extent and level of soil pollution in the area; (ii) determine effects of land use and parent materials on the mean contents of arsenic (As), lead (Pb), and copper (Cu); and (iii) identify the contribution of lithogenic and anthropogenic sources of selected PTEs in the soils under study.

Materials and methods

Description of study area

The study area is located in Khuzestan Province, southwestern Iran extending from the east 47° 52'00" to 50°24'00" longitudes and the north 31°29'30" to 31°36'54" latitudes (Fig. 1). Several populated cities including Ahvaz, Shoush, Shoushtar, Dezful, Gotvand, Masjed Soleiman, and Izeh are located in the study area. The area is irrigated by the Karoun and Karkheh rivers flowing over the entire territory and contributing to the fertility of the land. The main agricultural products in the study area are wheat and sugar cane, from which Khuzestan takes its name. However, there are some varieties of other agricultural products such as barley, oily seeds, rice, eucalyptus, medicinal herbs; palm and citrus, which all show the great potential of this fertile plain for agricultural activities (Statistical Center of Iran, 2013).

Climatically, the study area is very hot and occasionally humid. Summertime temperatures routinely exceed 45 °C, especially in the south and in the winter the air temperature can drop below freezing, with occasional snowfall in mountainous parts, in northeast of the study area (Statistical Center of Iran, 2013). The area is also the major oil-producing region of Iran. The petrochemical and steel industries, pipe making, the power stations that feed the national electricity grid, and the chemical plants are among the major industrial activities carrying out in north of Khuzestan Province. There are also several cane sugar mills in the study area, among them are Haft Tapeh and Karun Agro Industry near Shushtar city.

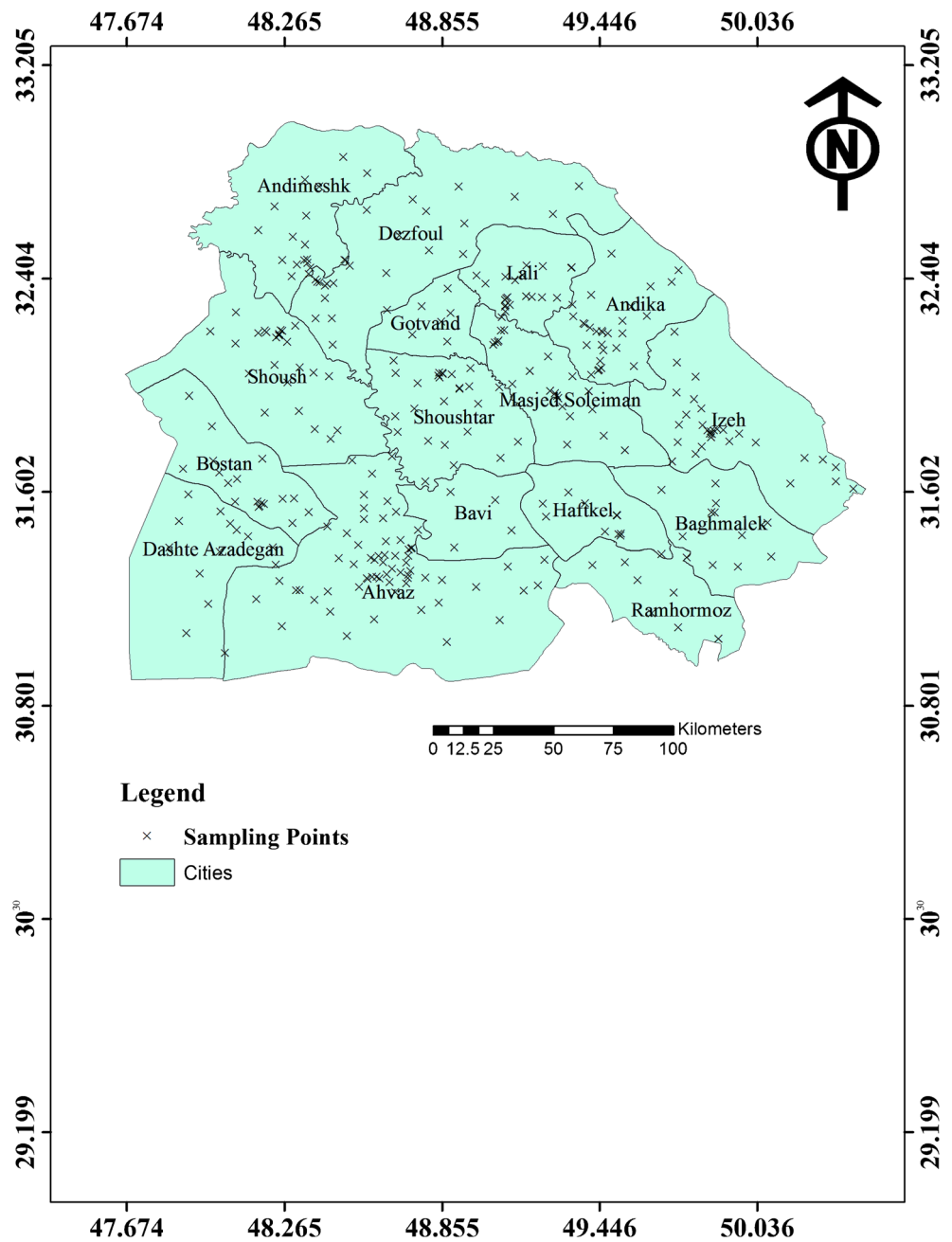
Parent materials in the central part of the study area, including the urban district and agricultural lands, are mainly recent alluvium of Quaternary ages with an approximately flat slope. Mountainous and undulating landforms located in the eastern part mainly include limestones, shale, marls, and sandstones; the landforms in southern and the western parts dominantly include low level piedmont fan and valley terrace deposits (Fig. 2).

Sampling scheme and characterization of samples

A total number of 300 composite samples were taken from surface soils (0–10 cm) in north of Khuzestan Province (Fig. 1). Composite sampling means that in each point five subsamples were taken from the square vertices. Then, these samples were mixed with each other and 1 kg of them were sifted and used in subsequent studies. The location of each sample was distinguished by global positioning system (GPS) and the type of land use in each point was recorded. On this basis, 88 samples from arable lands, 64 samples from urban areas, 55 samples from industrial regions, 60 samples from rangelands, and 33 samples from forest land use systems were collected. In order to study the impact of parent materials on the total concentration of PTEs As, Pb, and Cu in the soils of study area, 26 samples were also collected from the major types of parent materials in the region. All the samples were kept in polyethylene containers and transported to the laboratory. Then, they were air dried for several days and sieved to 2 mm for analysis of soil properties. Soil texture was analyzed using the pipette method following dispersion after 2 h shaking with 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. Soil pH was measured in 1:1 suspension (soil to H₂O) using an Ohaus Starter 3100. The analysis of organic carbon was performed using the Walkley-Black wet oxidation method (Nelson and Sommers 1982). Cation exchange capacity (CEC) was determined by ammonium saturation method at pH 7 (Sparks 1996). Electrical conductivity (EC) was measured in extracts from a 1:1 soil-water suspension using an Ohaus starter 3100 C conductivity meter.

To determine the total concentration of As, Pb, and Cu, 1 g of each sample (soils or parent materials) was mixed with 5 ml concentrated nitric acid (65%), 10 ml hydrogen peroxide (30%), and 20 ml concentrated hydrochloric acid (37%) and

Fig. 1 Map of sampling points in north of Khuzestan Province



then they were melted in a Teflon container in microwave. Afterwards, they were brought to 100 ml volume using hydrochloric acid. Finally, the concentration of PTEs was measured by Varian Atomic Absorption Spectrometer model A240 which was equipped with graphite furnace (Sparks 1996).

Contamination assessment

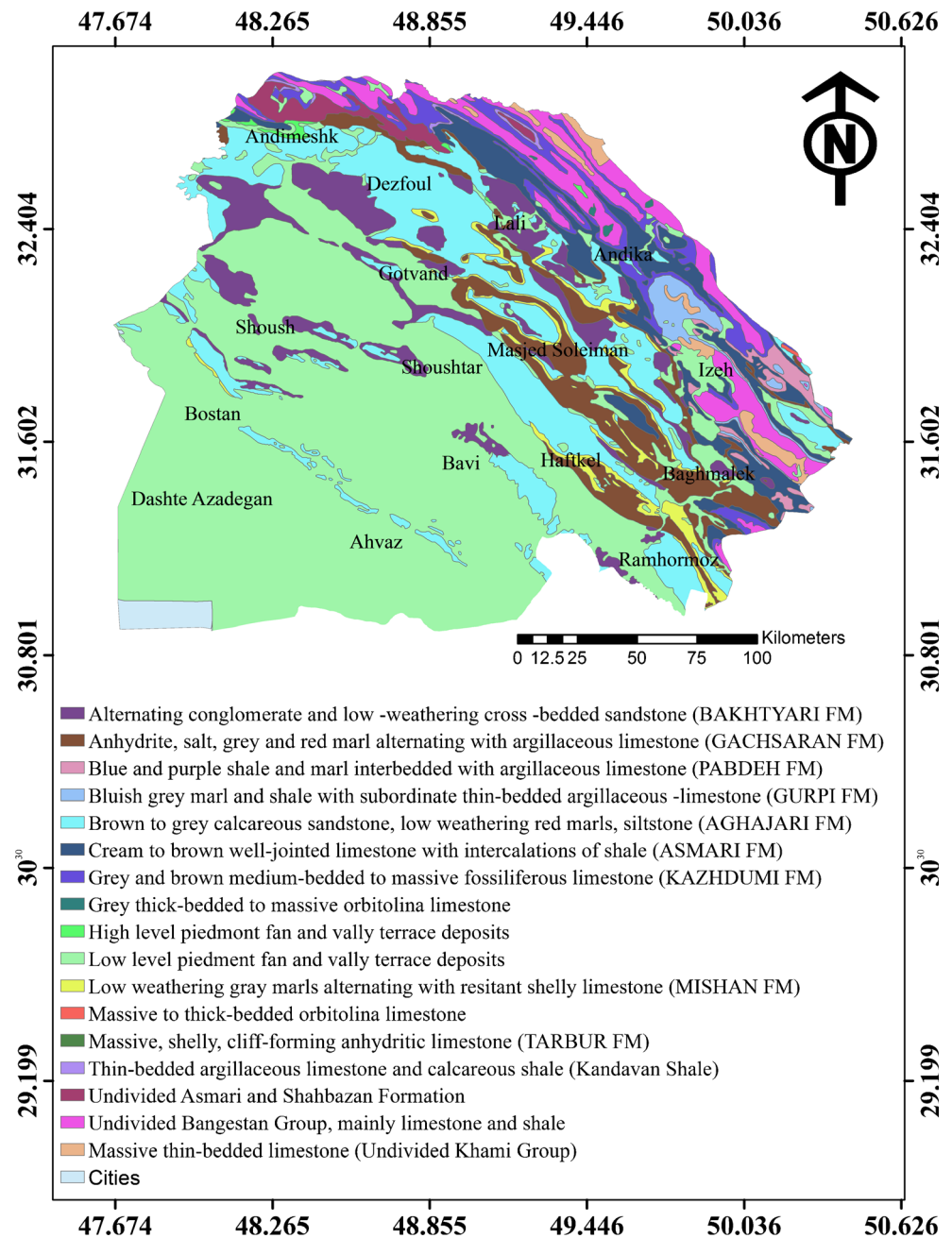
To assess the magnitude of PTEs pollution in soils of study area, the geo-accumulation index (I_{geo}), and enrichment factor (EF) of As, Pb, and Cu were calculated.

The index of geo-accumulation (I_{geo}) was originally defined by Müller (1969). This index could be used in order to determine and define metal contamination in soils and sediments (Banat et al. 2005), by comparing current concentrations of PTEs with pre-industrial levels. It can be calculated by the following equation (Eq. 1):

$$I_{geo} = \log_2 [C_i / (1.5C_{ri})] \tag{1}$$

where C_i is the measured concentration of the examined metal in soil samples, and C_{ri} is the geochemical background concentration or reference value of the metal i . The constant 1.5 is introduced to minimize the effect of possible variations in the

Fig. 2 Geological map of study area in north of Khuzestan Province



background values, which may be attributed to anthropogenic influences or lithologic variations in the soils (Tang et al. 2013).

Due to a more meaningful basis and for better estimation, local background soil values of the study area rather than the average earth's crust values were used as the background. Accordingly, to determine the background concentration of selected PTEs, 42 samples were taken from areas which were away from human activities (Cabrera et al. 1999; Bhuiyan et al. 2010) and geometric mean of them was considered as the background concentration of PTEs. The geo-accumulation index (I_{geo}) was distinguished into seven classes (Buccolieri

et al. 2006) including the following: $I_{geo} \leq 0$, class 0, unpolluted; $0 < I_{geo} \leq 1$, class 1, from unpolluted to moderately polluted; $1 < I_{geo} \leq 2$, class 2, moderately polluted; $2 < I_{geo} \leq 3$, class 3, from moderately to strongly polluted; $3 < I_{geo} \leq 4$, class 4, strongly polluted; $4 < I_{geo} \leq 5$, class 5, from strongly to extremely polluted; and $I_{geo} > 5$, class 6, extremely polluted.

Enrichment factor (EF) can be utilized to evaluate the degree of anthropogenic influence on soil contamination by PTEs, and to differentiate the metals originating mainly from human activities and those from natural sources (Sakan et al. 2009; Ye et al. 2011). Because Fe is abundant in soils, it was

used for normalization purpose. The EF of each heavy metal relative to the background using Fe as the reference metal was calculated by the ratios of element concentration (mg kg^{-1}) (Eq. 2):

$$EF = [Ci/Fe]_{\text{sample}} / [Ci/Fe]_{\text{background}} \quad (2)$$

The $EF < 1.5$ point to mainly crustal origin or natural weathering, while $EF > 1.5$ is indicative of anthropogenic contamination and $EF > 10$ is assumed to imply significant enrichment (Ye et al. 2011).

Data analysis

Descriptive statistics including determination of minimum, maximum, mean, standard deviation, skewness, and kurtosis was carried out with SPSS 20.0 software. Since PCA is sensitive to outliers and non-normality of geochemical data sets (Zhang and McGrath 2004), and to avoid distortions and low significance of the results, logarithmic transformation which is widely applied in other studies (Chen et al. 2008; Tang et al. 2013), was used to obtain the normality of the soil data. Eventually, the normality of data was checked by the Kolmogorov–Smirnov (K–S) test. The test calculates the probability (p value) that the samples were drawn from a normal population. The lower this value, the smaller the chance. Typically, a value of 0.05 is used as a cutoff, so when the p value is lower than 0.05, it can be concluded that the sample deviates from normality (Heumann et al. 2016).

Pearson correlation analysis and PCA were also used to evaluate the relationship between PTEs and the characteristics of soils and parent materials and to identify the origin of PTEs in soils of the study area (Facchinelli et al. 2001; Rodriguez et al. 2008; Chabukdhara and Nema 2012).

The PCA is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components (Jolliffe, 2002). The number of principal components is less than or equal to the number of original variables. This transformation is defined in such a way that the first principal component has the largest possible variance (that is, accounts for as much of the variability in the data as possible), and each succeeding component in turn has the highest variance possible under the constraint that it is orthogonal to the preceding components. The resulting vectors are an uncorrelated orthogonal basis set. The PCA is usually performed by eigenvalue decomposition of a data correlation matrix or singular value decomposition of a data matrix, after mean centering and normalizing the data matrix for each attribute (Abdi and Williams 2010). The results of a PCA are usually discussed in terms of component scores, the transformed variable values corresponding to a particular data point; and loadings, the weight by which each standardized

original variable should be multiplied to get the component score (Shaw 2009). In this study, the principal components were selected for eigenvalues > 1 (Swan and Sandilands 1995). Varimax rotation with Kaiser normalization was also used as the rotation method in PCA analysis, since orthogonal rotation minimizes the number of variables with high loading on each component and makes data interpretation easier (Shaw 2009).

Results and discussion

Summary statistics of soil properties

Descriptive statistics of PTEs concentration and the physico-chemical characteristics of soils are given in Table 1. Soil pH range is limited and varies from 7.11 to 8.93 with a mean value of 7.72 ± 0.25 . Such neutral soil reaction would limit metal mobility in soils. The electrical conductivity in the area ranges from 0.06 (mostly in east and northeast parts) to 85.37 dS m^{-1} with a mean of 9.01 dS m^{-1} . Regarding OC contents of the soils, the mean of OC in the area was 14.62 g kg^{-1} with a range between 5.5 to 36.7 g kg^{-1} . The highest amounts of OC were found within forest and agricultural land uses (Table 2). The cation exchange capacity (CEC) in the area was in the range of $6.50\text{--}104 \text{ cmol}^+ \text{ kg}^{-1}$ with the mean of $26.57 \text{ cmol}^+ \text{ kg}^{-1}$. Again, forest land uses scored the highest mean of cation exchange capacity ($32.99 \text{ cmol}^+/\text{kg}$) and the second highest mean was related to agricultural land uses ($29.58 \text{ cmol}^+/\text{kg}$). Similar pattern was also observed for clay contents of the soils with the highest amounts of clay particles in soils of forest (319.7 g kg^{-1}) and agricultural (318.3 g kg^{-1}) land uses. Accordingly, it seems that the increased CEC values in forest and agricultural land uses are related to their high amounts of organic carbon and clay particles.

Results obtained from K-S test showed that all parameters other than CEC, and OC contents of the soils and the Pb, Cu, and As concentrations of the soils followed a normal distribution pattern. The kurtosis and skewness, which are two measures of the degree of asymmetry in relation to the normal distribution (Liu et al. 2017), also confirmed the above observation. Therefore, in case of these parameters, a common logarithmic transformation was applied to achieve the normal distribution pattern for the data (Table 1).

The mean of the total concentration of As, Pb, and Cu were 1.72, 13.50, and 12.2 mg/kg , respectively. Although the mean concentrations of all metals did not exceed the criteria of the Iranian Environmental Quality Standard for Soils (2014), their mean concentrations were higher than their local background values (Table 3). This indicates the existence of anthropogenic sources along with that of lithogenic inputs for increasing the concentrations of the all PTEs in the study area. Similarly, Li et al. (2015) suggested the existence of an anthropogenic input

Table 1 Descriptive statistics of physicochemical properties and total concentrations of heavy metals in the soils studied ($N = 300$)

| Parameters | pH | EC (dSm^{-1}) | CEC (Cmol kg^{-1}) | SOC (g kg^{-1}) | CCE | Gypsum | Sand | Silt | Clay | Pb (mg kg^{-1}) | Cu | As |
|--------------------------------|-------|-----------------------------|----------------------------------|-------------------------------|-------|--------|-------|-------|-------|-------------------------------|-------|-------|
| Minimum | 7.11 | 0.06 | 6.5 | 5.5 | 18.0 | 0.0 | 20.0 | 20.0 | 45.0 | 1.0 | 2.2 | 0.50 |
| Maximum | 8.93 | 85.37 | 104.0 | 36.7 | 500.0 | 160.0 | 7950 | 910.0 | 605.0 | 86.0 | 117.2 | 2.65 |
| Mean | 7.72 | 9.01 | 26.6 | 14.6 | 404.7 | 8.4 | 262.0 | 437.6 | 300.8 | 12.2 | 13.5 | 1.72 |
| Median | 7.66 | 3.88 | 24.1 | 13.3 | 385.0 | 1.5 | 265.0 | 430.0 | 315.0 | 8.1 | 7.4 | 1.48 |
| Mode | 7.55 | 4.09 | 18.5 | 13.5 | 380.0 | 0.0 | 255.0 | 440.0 | 330.0 | 2.0 | 3.1 | 0.70 |
| Skewness | 1.03 | 2.84 | 0.97 | 0.97 | -0.38 | 4.34 | 0.54 | 0.45 | -0.04 | 2.5 | 3.7 | 8.31 |
| Kurtosis | 2.41 | 8.09 | 2.24 | 2.24 | 1.36 | 20.9 | 1.87 | 2.10 | -0.43 | 8.6 | 18.2 | 85.63 |
| Variance | 0.06 | 242.3 | 219.3 | 37.7 | 31.6 | 5.2 | 139.1 | 143.1 | 101.1 | 175.1 | 255.0 | 4.56 |
| (K-S) test | 0.195 | 0.000 | 0.000 | 0.051 | 0.064 | 0.000 | 0.483 | 0.072 | 0.117 | 0.000 | 0.000 | 0.000 |
| (K-S) test on logarithmic data | - | 0.209 | 0.123 | 0.325 | - | 0.168 | - | - | - | 0.085 | 0.137 | 0.119 |

EC electrical conductivity; CEC cation exchange capacity; CCE calcium carbonate equivalent; S.D. standard deviation; CV coefficient of variation; K-S Kolmogorov–Smirnov

for the higher concentrations of As, Hg, and Ni in the soils of Xiandao District in China. The results also indicated more variation for Cu and Pb than As. This implies the more heterogeneity of the sources for Pb and Cu rather than As. Considering their low concentrations and small variation, the possibility of human input of As seems to be lower than Cu and Pb, which means that distribution of this element may be mainly controlled by lithogenic factors. On this basis, Cu and Pb might be mainly originated from anthropogenic sources. Similarly, Chen et al. (2016b), considering highly elevated Zn, Hg, Cr, and Cu concentrations coupled with high CV values, reported that anthropogenic inputs is the primary source of these elements in northwest of China. However, As and Mn with lower CV values reported to be less influenced from human activities.

Effects of land use on PTEs distribution

The effect of land use on the total concentration of selected PTEs is presented in Table 3. Accordingly, the highest concentrations of Pb, Cu, and As are related to industrial and urban land uses. Arable, rangelands, and forest land uses placed in next orders, respectively. Li et al. (2015) also

reported higher concentrations of As, Mn, and Ni in construction lands than those of farm lands, and forest lands in Xiandao District of China.

Moreover, the higher concentration of Cu in agricultural soils of our study area rather than forest and rangelands could be ascribed to the use of commercial fertilizers, as well as the long-term application of Cu-based pesticides and fungicides on agricultural crops (Acosta et al. 2011; Kelepertzis 2014). Mico et al. (2006) also reported that elevated concentrations of Pb in the soils of the Segura river valley (Alicante, Spain) were the result of industrial emissions, application of agrochemicals, and reuse of wastewaters in irrigation of agricultural fields. On this basis, the high amount of Pb, Cu, and As concentrations in industrial, urban, and agricultural land uses could be attributed to the role of human activities.

Effects of parent materials on PTEs distribution

The range of values for heavy metal concentrations in the major rock types in the study area are given in Table 4. Accordingly, the highest concentration of Pb, Cu, and As could be seen in shale rocks, which suggests the greater role of shale rocks in increasing concentrations of these metals in

Table 2 Effects of different land use systems on physical and chemical characteristics of the soils ($N = 300$)

| Land uses | EC | pH | CCE | CEC | OC | Sand | Silt | Clay | Gypsum |
|-------------|---------------|---------------|------------------|----------------|----------------|------------------|------------------|------------------|----------------|
| Industrial | 5.9 ± 1.1 | 7.6 ± 0.2 | 405.4 ± 6.7 | 19.5 ± 3.7 | 14.5 ± 2.4 | 367.8 ± 5.5 | 401.8 ± 8.6 | 230.4 ± 4.4 | 73.0 ± 3.1 |
| Urban | 8.9 ± 0.6 | 7.7 ± 0.2 | 383.8 ± 5.9 | 27.4 ± 5.1 | 14.9 ± 3.3 | 282.0 ± 9.3 | 424.2 ± 10.1 | 295.7 ± 7.1 | 29.0 ± 0.8 |
| Agriculture | 2.9 ± 0.4 | 7.7 ± 0.1 | 395.9 ± 14.3 | 26.5 ± 3.9 | 15.5 ± 9.5 | 276.0 ± 6.6 | 429.2 ± 8.5 | 294.7 ± 6.5 | 24.0 ± 1.1 |
| Rangelands | 3.4 ± 0.3 | 7.8 ± 0.1 | 419.0 ± 20.5 | 29.6 ± 4.2 | 14.6 ± 6.7 | 234.2 ± 7.0 | 447.4 ± 11.2 | 318.3 ± 9.0 | 56.8 ± 4.3 |
| Forests | 2.3 ± 0.2 | 7.8 ± 0.1 | 395.9 ± 16.8 | 33.0 ± 6.6 | 17.8 ± 7.3 | 198.3 ± 11.9 | 481.9 ± 21.2 | 319.7 ± 11.2 | 16.1 ± 1.5 |

Table 3 The total concentrations of Pb, Cu, and As in soils of different land uses

| Land use | Pb (mg kg ⁻¹) | Cu | As | Fe |
|---|------------------------------|---------------|--------------|-----------------|
| Industrial | 60.21 ± 12.84 | 74.75 ± 18.42 | 13.07 ± 8.21 | 24,367 ± 69.80 |
| Urban | 22.81 ± 9.09 | 24.48 ± 10.85 | 3.41 ± 0.77 | 23,995 ± 194.10 |
| Agriculture | 12.20 ± 3.45 | 13.64 ± 2.61 | 2.77 ± 0.32 | 23,589 ± 112.50 |
| Rangelands | 2.02 ± 0.02 | 3.28 ± 1.03 | 0.76 ± 0.09 | 24,221 ± 109.60 |
| Forests | 1.93 ± 0.10 | 3.04 ± 0.24 | 0.74 ± 0.05 | 24,854 ± 169.30 |
| Iranian Environmental Quality Standard for Soils | 300.00 | 63.00 | 17.00 | – |
| Background values | 4.98 ± 0.66 | 8.73 ± 0.22 | 2.59 ± 0.38 | 23,659 ± 55.40 |

soils of the study area. Nael et al. (2009) also drew the same conclusion and suggested that differences between the concentrations of heavy metals in some soils from north of Iran are relatively attributed to the differences in lithology of their parent materials. They showed that soils developed from shale rocks contained considerable amounts of Pb and Zn. Among the other parent materials, the concentration of Pb, Cu, and As showed a decreasing order of marl > non-segregated sediments > sandstones > limestones. Similarly, Taghipour et al. (2011) reported the highest concentration of Cr, Cu, Pb, Ni, Zn, and Co in shale and schist rock types of Hamadan Province in west of Iran. They showed that the lowest concentrations of these PTEs could be found in felsic igneous (granite-granodiorite) and other sedimentary rocks such as limestones and sandstones.

The results also illustrated that the concentration of Pb, Cu, and As in the soils of study area was significantly higher than their parent materials (Table 4). This suggests that there are factors other than that of parent materials which control distribution of these elements in the soils.

Besides, the correlation coefficients between the total concentrations of Pb ($r = 0.75^{**}$) and Cu ($r = 0.76^{**}$) in soils and their corresponding parent materials was lower than that of As ($r = 0.88^{**}$) (Fig. 3). This clearly proposes less contribution of

parent materials to the distribution of Pb and Cu as compared to that of As in soils of the study area.

Pollution status of soils

Index of geo-accumulation (I_{geo})

The range of I_{geo} values for Pb, Cu, and As were (–0.80 to 3.22), (–0.78 to 3.17), and (–0.82 to 3.13), respectively; indicating unpolluted to highly polluted status of the soils in the area under study. Besides, the mean of I_{geo} values for Pb, Cu, and As followed a decreasing order as Pb (0.77) > Cu (0.51) > As (0.2). The highest mean of I_{geo} values for Pb, Cu, and As were found in industrial (3.01, 2.69, 2.20) and urban (1.93, 1.49, 0.69) land uses, and the next ranks belonged to arable (1.35, 0.78, 0.41), rangelands (–0.40, –0.40, –0.42), and forest (–0.44, –0.46, –0.42) land uses, respectively. Accordingly, the industrial, urban, and agricultural land uses were moderately to strongly contaminated with respect to As, Cu, and Pb. Similarly, Huang et al. (2016) reported higher values of I_{geo} index for Pb than Cu and As in soils near smelting area in Qingjiang county, China. Wei and Yang (2010) also compared PTEs pollution in urban and

Table 4 The total concentrations of Pb, Cu, and As in the major types of parent materials and soils developed on them

| Parent materials (PM) | Number of samples | Pb (mg Kg ⁻¹) | Cu | As |
|--------------------------|-------------------|------------------------------|--------------|-------------|
| Sandstones | Soils = 23 | 18.20 ± 0.48 | 20.90 ± 0.67 | 1.10 ± 0.17 |
| | PM = 3 | 13.20 ± 0.65 | 12.50 ± 0.51 | 1.43 ± 0.11 |
| Limestones | Soils = 66 | 10.60 ± 0.48 | 11.80 ± 0.40 | 0.98 ± 0.10 |
| | PM = 6 | 9.00 ± 0.21 | 6.10 ± 0.28 | 0.95 ± 0.12 |
| Marls | Soils = 56 | 22.30 ± 0.95 | 17.70 ± 0.53 | 1.38 ± 0.23 |
| | PM = 6 | 16.80 ± 0.35 | 13.90 ± 0.59 | 1.60 ± 0.29 |
| Shales | Soils = 37 | 32.70 ± 1.36 | 41.20 ± 0.39 | 1.61 ± 0.25 |
| | PM = 5 | 19.50 ± 0.42 | 34.10 ± 0.86 | 1.93 ± 0.18 |
| Non-segregated sediments | Soils = 118 | 17.60 ± 0.91 | 16.30 ± 0.57 | 1.06 ± 0.14 |
| | PM = 6 | 13.90 ± 0.55 | 12.80 ± 0.71 | 0.84 ± 0.21 |

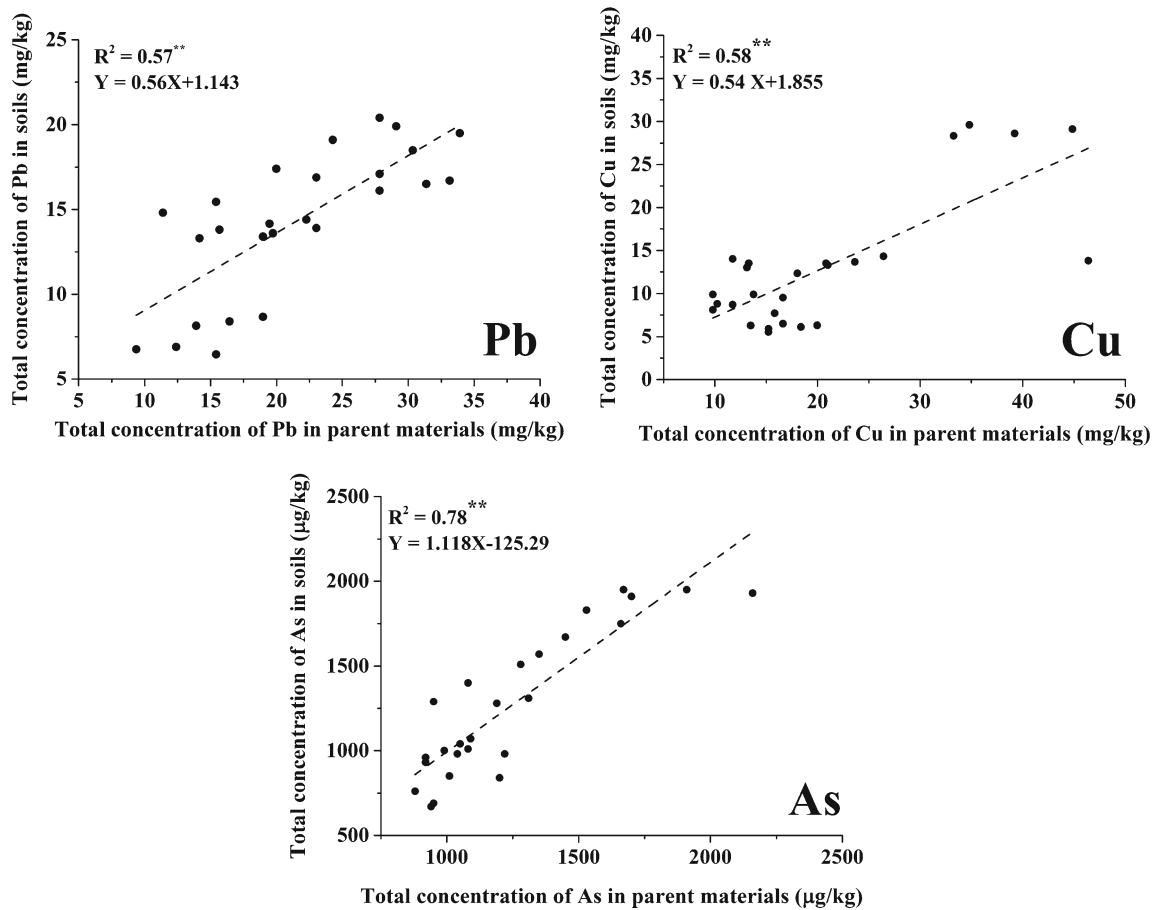


Fig. 3 Relationships between the total concentration of Pb, Cu, and As in soils and associated parent materials

agricultural soils of China and reported that soils in urban areas are more contaminated by Cr, Pb, Cu, Ni, Zn, and As.

The high amount of the I_{geo} values in industrial and urban areas rather than other land uses (Table 5) could be attributed as a result of industrial activities such as oil and gas exploration projects, combustion of fossil fuels, mining, petrochemical and steel industries, pipe making, and urban development issues (Taghipour et al. 2011; Wei and Yang 2010). The

positive I_{geo} values of arable lands (Table 6) also can be related to the use of chemical fertilizers, reuse of industrial wastewaters in irrigation of farmlands, and application of a variety of pesticides and herbicides for pest and weed control in them. The negative I_{geo} values of rangelands and forest land uses also suggest that they could be classified in the category of non-polluted areas.

Table 5 Mean of EF and I_{geo} values in soils taken from different land uses

| Land use | Pb | | Cu | | As | |
|-------------|-------|-----------|------|-----------|------|-----------|
| | EF | I_{geo} | EF | I_{geo} | EF | I_{geo} |
| Industrial | 11.73 | 3.01 | 8.31 | 2.69 | 4.89 | 2.20 |
| Urban | 4.51 | 1.93 | 2.76 | 1.49 | 1.29 | 0.69 |
| Agriculture | 2.45 | 1.35 | 1.57 | 0.78 | 1.07 | 0.41 |
| Rangelands | 0.40 | -0.40 | 0.37 | -0.40 | 0.29 | -0.42 |
| Forests | 0.37 | -0.44 | 0.33 | -0.46 | 0.27 | -0.42 |
| Min | 0.19 | -0.80 | 0.20 | -0.78 | 0.05 | -0.82 |
| Max | 13.68 | 3.22 | 8.61 | 3.17 | 5.05 | 3.13 |
| Mean | 3.90 | 0.77 | 2.69 | 0.51 | 1.58 | 0.20 |

Enrichment factor

Enrichment factor is a useful tool to discriminate between natural and anthropogenic sources and to reflect the status of heavy metal pollution (Sakan et al. 2009). The results from our study area showed that the EF of Cu ranges from 0.33 to 8.31, the EF of Pb ranges from 0.37 to 11.73, and the EF of As ranges from 0.27 to 4.89 (Table 5). Taking as a whole, the mean EF values of Pb, Cu, and As suggested their enrichments in surface soils of the study area. Besides, for most of the land uses except those of forest and rangelands, the EF values of Pb and Cu were higher than 1.5 (Table 5) indicating an anthropogenic source of them, mainly from activities such as oil and gas exploration projects, traffic, deposition of industrial wastes, reuse of wastewaters in irrigation of

Table 6 Pearson correlation matrix of the relationships between soil properties and the total concentrations of PTEs

| | EC | pH | CCE | CEC | OC | Sand | Silt | Clay | Gypsum | Pb | Cu | As |
|--------|--------------------|---------|---------------------|---------------------|---------------------|---------|--------------------|--------------------|--------------------|--------|--------|----|
| EC | 1 | | | | | | | | | | | |
| pH | 0.68** | 1 | | | | | | | | | | |
| CCE | -0.52** | -0.27** | 1 | | | | | | | | | |
| CEC | -0.42** | -0.31** | 0.14* | 1 | | | | | | | | |
| OC | -0.27** | -0.27** | 0.30** | 0.26** | 1 | | | | | | | |
| Sand | -0.17** | -0.13* | 0.04 ^{ns} | -0.12* | 0.02 ^{ns} | 1 | | | | | | |
| Silt | 0.15** | 0.10 | -0.07 ^{ns} | -0.14* | -0.06 ^{ns} | -0.63** | 1 | | | | | |
| Clay | 0.02 ^{ns} | 0.04 | 0.04 ^{ns} | 0.30** | 0.05 ^{ns} | -0.41** | -0.44** | 1 | | | | |
| Gypsum | 0.32** | 0.17** | -0.18** | -0.25** | -0.14* | -0.19** | 0.16** | 0.02 ^{ns} | 1 | | | |
| Pb | 0.22** | 0.25** | -0.12* | -0.08 ^{ns} | 0.20** | -0.19** | 0.07 ^{ns} | 0.14* | 0.11 ^{ns} | 1 | | |
| Cu | 0.18** | 0.23** | -0.13* | -0.07 ^{ns} | 0.15** | -0.16** | 0.05 ^{ns} | 0.12* | 0.05 ^{ns} | 0.95** | 1 | |
| As | 0.35** | 0.34** | -0.25** | 0.07 ^{ns} | 0.35** | -0.37** | 0.06 ^{ns} | 0.34** | 0.08 ^{ns} | 0.84** | 0.85** | 1 |

* Significant at $P < 0.05$; ** Significant at $P < 0.01$; ^{ns} Not significant

farmlands, pesticides and herbicides application, and so on. However, except for industrial areas, the average EF values of As were less than 1.5, indicating that this metal derived from the crustal materials. Similarly, Chen et al. (2016a) showed that the surface soils in Beijing city in China were moderately contaminated by Cd, Pb, Cu, As, and Hg. Combining the results obtained from pollution indices and multivariate curve resolution-weighted alternating least square analyses, both natural and anthropogenic sources were responsible to release the aforesaid metals in the soils.

Correlation matrix

The correlation between PTEs content and physicochemical characteristics of soils is given in Table 6. The results indicate a positive correlation between soil pH and EC with the concentrations of each of Pb, Cu, and As. This suggests that distribution of both pH and EC likely exert some level of control on the distribution of Pb, Cu, and As in the soils. Accordingly, it can be concluded that saline-alkaline soils in the study area have a relatively higher concentration of Pb, Cu, and As rather than those of alkaline-not saline, saline-not alkaline, and not saline-not alkaline soils. Khaledian et al. (2017) also reported a positive correlation between pH and concentration of exchangeable Pb, Cu, Cd, and Zn in Lithuanian Podzols.

The results also showed a significant positive correlation between the total concentrations of each of the PTEs (Pb, Cu, and As) and organic carbon contents of the soils. This suggests that at least part of Pb, Cu and As concentrations in the soils under study are linked with organic matter. Indeed, organic materials with functional groups such as hydroxyls, carboxyls, and phenols play a key role in controlling PTEs activity, and the absorption and bonding of them with soil particles (Alloway 1990). Similarly, Rodriguez-Martin et al. (2006)

and Mico et al. (2006) reported a positive correlation between PTEs and organic matter content and pointed out that soil organic matter could be an important sink for the PTEs.

Results of correlation analysis between each of the PTEs contents of the soils and the particle size distribution showed that fine-grained soils exhibit higher tendency for heavy metal adsorption than coarse-grained soils. This could be ascribed to the fact that heavy-textured soils contain particles with larger surface areas (i.e., clay minerals, iron, and manganese oxy-hydroxides) which creates more active sites for the absorption of PTEs by soil particles (Bradl, 2004). Dragovic et al. (2008) also reported that the PTEs content of the soils in Zlatibor mountainous area in Serbia are significantly correlated with particle size distribution and soil organic matter parameters.

Interestingly, no significant correlation was observed between CEC contents of the soils and each of the PTEs. The most plausible explanation for this finding could be the absence of As, Pb, and Cu in exchangeable phase of the soils. On the other hand, since the concentrations of major cations in the soils are normally much greater than PTEs, then it seems that CEC tends to be more affected by those metals than PTEs studied (Hafezi Moghaddas et al. 2013).

The results also implied that there is a significant correlation between As and selected soil properties such as OC, CCE, and clay contents demonstrating important interactions among them. On the other hand, Pb and Cu showed a less significant correlation with soil properties. Similarly, Mico et al. (2006) reported that concentrations of Pb, Cu, and Cd are less associated than Co, Cr, Ni, and Zn with some soil properties (i.e., OC, clay, and carbonates). Accordingly, they suggested that PTEs such as Pb, Cu, and Cd are mainly affected by human activities. On this basis, it seems that sources of Pb and Cu are different with that of As in soils of the study area. To shed more light on this, the interrelationships between PTEs were calculated. Metal-metal relationships have been suggested to

Table 7 The total variance explained by PCA of the data matrix

| Components | Initial eigenvalues | | | Rotation sums of squared loadings | | |
|------------|---------------------|---------------------|-------------|-----------------------------------|---------------------|-------------|
| | Total | Percent of variance | Cumulative% | Total | Percent of variance | Cumulative% |
| 1 | 5.71 | 47.57 | 47.57 | 5.62 | 46.80 | 46.80 |
| 2 | 2.11 | 17.54 | 65.11 | 2.12 | 17.68 | 64.47 |
| 3 | 1.39 | 12.64 | 76.73 | 1.47 | 12.26 | 76.73 |
| 4 | 0.89 | 7.42 | 84.15 | | | |
| 5 | 0.68 | 5.65 | 89.80 | | | |
| 6 | 0.58 | 4.80 | 94.61 | | | |
| 7 | 0.26 | 2.20 | 96.80 | | | |
| 8 | 0.15 | 1.29 | 98.09 | | | |
| 9 | 0.09 | 0.73 | 98.81 | | | |
| 10 | 0.08 | 0.69 | 99.49 | | | |
| 11 | 0.04 | 0.34 | 99.83 | | | |
| 12 | 0.02 | 0.17 | 100.00 | | | |

provide valuable information on pathways and sources of PTEs in the soils (Kelepertzis 2014; Pan et al. 2016). According to the values of Pearson correlation coefficient there were significant positive correlations among the PTEs studied. However, a stronger correlation was found between Pb and Cu than those calculated between Cu and As, and between Pb and As. This clearly suggests that factors controlling inputs of Pb and Cu in the soils of study area are the same, but to some extent different in case of As.

Principal component analysis (PCA)

The silt, gypsum, and CEC contents of the samples were not included in the PCA as they were not correlated with Pb, Cu, and As. The results of PCA are presented in Tables 7 and 8. Three principal components with eigenvalues greater than one

Table 8 Component matrix and rotated component matrix of the parameters studied

| Parameters | Component matrix | | | Rotated component matrix | | |
|------------|------------------|---------------|---------------|--------------------------|----------------------------|---------------|
| | PC1 | PC2 | PC3 | PC1 | PC2 | PC3 |
| pH | -0.092 | 0.846 | 0.018 | 0.189 | -0.829 ^a | 0.022 |
| CCE | 0.278 | -0.511 | 0.284 | 0.231 | 0.586 | 0.150 |
| Sand | 0.142 | -0.238 | -0.765 | 0.046 | 0.092 | -0.807 |
| Clay | -0.202 | 0.069 | 0.803 | -0.124 | 0.074 | 0.818 |
| OC | -0.121 | 0.851 | 0.040 | -0.004 | -0.833 | 0.216 |
| EC | 0.033 | -0.546 | 0.273 | -0.017 | 0.591 | 0.158 |
| Total Pb | 0.970 | 0.040 | 0.046 | 0.967 | 0.080 | -0.052 |
| Total Cu | 0.970 | 0.044 | 0.055 | 0.966 | 0.127 | -0.054 |
| Total As | -0.654 | -0.798 | -0.028 | -0.710 | -0.958 | 0.056 |

^a Significant factor loadings are bold faced

(before and after rotation) were extracted. The graphic representation of the three components is depicted in Fig. 4, where the associations between metals and soil properties can be seen. Accordingly, PCA reduced the initial dimension of the dataset to three components which accounted for about 77% of the total variance in this study. The remaining 23% was not explained by the factors used in this study. The bold values in Table 8 are the loadings greater than 0.5, which were taken in the determination of principal components. The underlying common factors represented by the principal components may not be readily obvious, but the results provide a basis for speculation (Taghipour et al. 2011). The rotated component matrix showed that Pb and Cu were associated with the

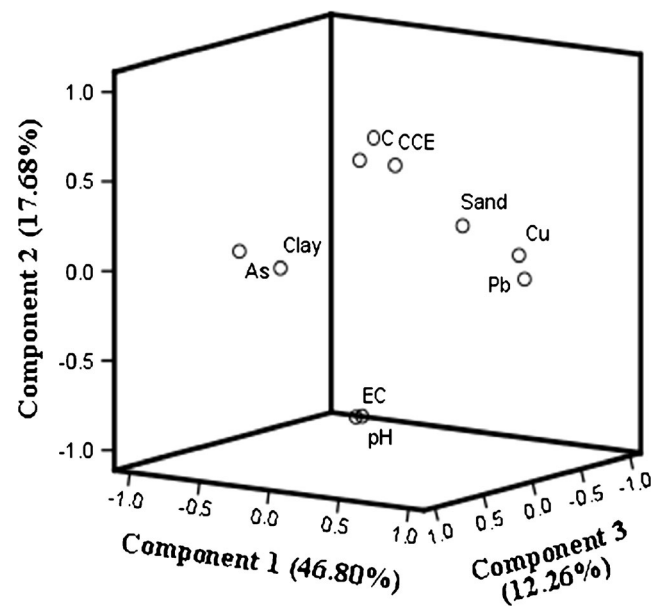


Fig. 4 Principal component analysis (PCA) loading plot of heavy metal concentrations and associated soil properties

first component (PC1) which explained 47% of the total variance (Table 8). This suggests that these metals may have similar sources of natural and/or anthropogenic origins. Regarding the results obtained from the EF values and the impacts of parent materials and land uses on PTEs concentration of the soils, this component could be considered as a mixed of anthropogenic and lithogenic sources in distribution of Pb and Cu in the soils studied.

The second component (PC2), explaining 17.7% of the total variance, has relatively high loadings on As, EC, pH, CCE, and OC contents of the soils (Table 8). Moreover, since As-salts are used in only special applications such as in fungicides and pesticides, a non-point source contamination could not be considered for this element. Thus, it could be concluded that distribution of As in soils of the study area is mainly due to the lithogenic origin. Similarly, Lu et al. (2012) considering the results of PCA reported that As distribution in agricultural soils from Shunyi, Beijing, China mainly come from lithogenic sources.

The third component (PC3) which accounted for 12.26% of the total variance showed high loadings with clay and sand contents of soils.

Conclusion

Pollution status, relationships with soil properties, and the main sources of As, Pb, and Cu in topsoils from different land uses in North of Khuzestan Province, southwestern Iran were studied. Compared with their local soil background values, higher concentrations of Pb, Cu, and As were observed to different extents. Accordingly, industrial and urban soils showed higher concentrations and enrichments of Pb, Cu, and As rather than other land uses. Results from EF analysis of the soils implied that the mean of EF values for Cu and Pb was greater than 1.5. This is clearly indicative of metals enrichment in the soils from anthropogenic sources, particularly in industrial, urban, and agricultural soils.

The higher concentrations of soils Pb, Cu, and As than their corresponding parent materials further confirms contributions from both natural and anthropogenic sources, controlling the distribution of these elements in the soils studied. The greatest concentrations of selected PTEs were found in soils developed on shales and marls.

Results obtained from multivariate PCA analysis also indicated that both Pb and Cu originated from similar mixed sources of industrial activities and natural parent materials, while As mainly came from the contribution of lithogenic processes. On a whole, it can be concluded that for monitoring the PTEs content of the soils and developing suitable remediation strategies, special attention must be given to soil parent material and land use systems in the study area. Such results could be used for providing essential information about soil

quality status in soils of Iran, and a basis for effective protection of them against long-term accumulation of PTEs.

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