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ORIGINAL ARTICLE

Evaluation of metals that are potentially toxic to agricultural surface soils, using statistical analysis, in northwestern Saudi Arabia

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Abstract Heavy metals in agricultural soils enter the food chain when taken up by plants. The main purpose of this work is to determine metal contamination in agricultural farms in northwestern Saudi Arabia. Fifty surface soil samples were collected from agricultural areas. The study focuses on the geochemical behavior of As, Cd, Co, Cr, Cu, Hg, Pb and Zn, and determines the enrichment factor and geoaccumulation index. Multivariate statistical analysis, including principle component analysis and cluster analysis, is also applied to the acquired data. The study shows considerable variation in the concentrations of the analyzed metals in the studied soil samples. This variation in concentration is attributed to the intensity of agricultural activities and, possibly, to nearby fossil fuel combustion activities, as well as to traffic flows from highways and local roads. Multivariate analysis suggests that As, Cd, Hg and Pb are associated with anthropogenic activities, whereas Co, Cr, Cu and Zn are mainly controlled by geogenic activities. Hg and Pb show the maximum concentration in the analyzed samples as compared to the background concentration.

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Keywords Metals · Contamination assessment · Multivariate analysis · Agricultural soils · Northwestern Saudi Arabia

Introduction

Metals have been identified as a serious threat to soil quality due to their persistency, toxicity and bioaccumulation (Morton-Bermea et al. 2002; Levia and Morales 2013; Adeyi and Torto 2014; Nazzal et al. 2013a). In contrast to organic pollutants, metals cannot be chemically or biologically degraded (Ayyasamya et al. 2009). The accumulation of metals in soil adversely affects biological activities, reduces the availability of nutrients, and poses a serious threat to environmental and human health by entering into food chains and underground water supplies via the respective plant uptake and leaching processes (Man-Zhi et al. 2006).

In urban areas, the deposition of pollutants emitted to the atmosphere from point sources, such as residential heating and industrial facilities (Sterckeman et al. 2000; Wu et al. 2015; Lu et al. 2012), and mobile sources, such as traffic (Martín et al. 2006; Albanese et al. 2010), is the primary source of soil pollution. Metals such as Pb, Cr, Ba, Zn, V, Co, Cu, Ni and As are easily emitted from fossil fuel combustion (Wong et al. 2003), tyre abrasion (Weckwerth 2001; Iijima et al. 2007), lubricants (Park and Park 2011; Pinedo et al. 2013), industrial and incinerator emissions (Valberg et al. 1996; Wang et al. 2008; Ono 2013) and can accumulate in soil. Trace elements are excellent indicators of the natural variability in soil composition, toxicology, exposure and health risks associated with soil pollution (Adamo et al. 2014; Palma et al. 2015).

Amongst the range of contaminants that may be found in soils, potentially toxic elements or heavy metals are of particular interest for a number of reasons. Firstly, they show a tendency, under normal circumstances, to accumulate in soils and have a long persistence time because of their interactions with particular soil components (Charlesworth and Lees 1999a, b; Chon et al. 1995; Ellis and Revitt 1982; Ghrefat et al. 2014; Nazzal et al. 2013b; Al-Taani 2014a, b). Secondly, they are ubiquitous in soils and arise from both natural and anthropogenic sources, with pathways including inheritance from the parent rocks, application of wastes, and local and long-range atmospheric and fluvial deposition of emissions from industry and mining (Forstner and Wittman 1983; Harrison et al. 1985; Howari and Banat 2001; Abu-Rukah 2001; Howari et al. 2004; Ghrefat et al. 2011; Nazzal et al. 2013a, b, 2014; Batayneh et al. 2014).

Statistical analyses especially principal component analysis has been frequently used in soil studies for identifying the sources of soil pollution and more importantly to distinguish between natural and anthropogenic sources (Facchinelli et al. 2001; Lee et al. 2006; Yang et al. 2011). Multivariate analyses use information arising from relationships between variables in order to improve estimations for variables, and to identify the different causes of variations over different spatial scales (Castrignanò et al. 2009). Some of the factors responsible for the enrichment of a given metal in the soils are likely to have a short-range influence, whereas others operate over longer distances; soil variables are thus expected to be correlated in a scale-dependent way. The scale-dependent correlation structure of some soil variables probably reflects different sources of variability and is crucial in environmental investigations (Borůvka et al. 2005). Investigation into these relationships, however, requires a particular statistical approach combining classic principal component analysis, to describe the correlation structure of multivariate datasets, with geostatistics, in order to take into account the co-regionalized nature of the variables (Sollitto et al. 2010).

The present study deals with the assessment of metal contamination in surface soils, addressing general geochemical trends, enrichment factors and geoaccumulation indices. Efforts have also been made to identify the genesis of the contamination using standard statistical and GIS techniques.

Study area descriptions

Physiography and climate

The present study encompasses parts of the provincial boundaries of Ha'il, Al Jawf and Tabuk regions (Fig. 1).

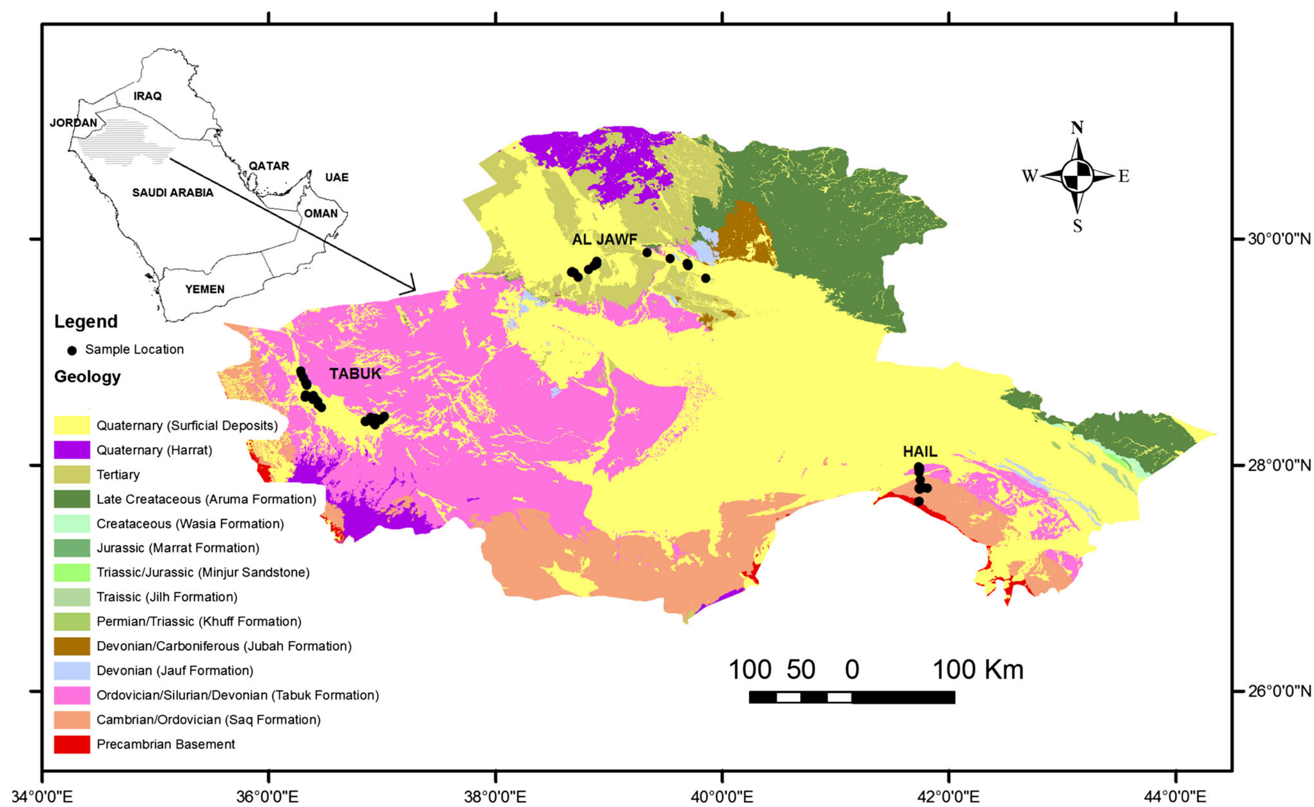

Fig. 1 Geology of the study area and the location of collected soil samples

The Ha'il region lies between approximately 40°E–42°30″E and 26°50″–28°33″N. This is a predominately flat region having no drainage network with general slope toward the southeast. The Al Jawf region lies to the north of Tabuk and Ha'il regions, lying between approx. 38°E–42°E and 28°20″N–31°50″N. The region is characterized by a low relief with mean average elevation of 700 m above mean sea level (amsl). The Tabuk region lies approximately between 36°E–40°E and 26°50″N–28°58″N. Physiographically, this region has significant drainage network draining to the southeast. The maximum elevation is approximately 1500 m amsl along its north-western periphery.

The Ha'il region experiences a continental desert type of climate with hot summers and cool winters with temperature ranging from a high of 45–27 °C and a low of 23–3 °C (Almazroui 2012). The average annual rainfall in the Ha'il region ranges from 100 to 120 mm. Annual evaporation rates in the central part of Saudi Arabia, including Ha'il, approach 3480 mm (Edgell 2006). Al Jawf province falls in dry, arid to extremely arid region. The mean annual temperature is about 23 °C, with summer temperatures reaching more than 40 °C and winter temperature falling up to 9 °C during January and February. The annual mean precipitation is about 60–70 mm. The climate in the Tabuk area is of the continental type but is influenced occasionally by its proximity to the Mediterranean Sea (ŞEN 1983). The maximum and minimum temperatures are about 47 °C in summer and −2 °C in winter, respectively (Al Sharhan et al. 2001). The average annual rainfall ranges between 50 to 100 mm.

Geological and hydrogeology

The Arabian Peninsula can be divided into two main geologic units, a western part comprising of Precambrian basement rocks known as the Arabian shield and an eastern part consisting of gradually thickening Phanerozoic sedimentary sequence from west to east known as the Arabian Platform (Seber and Mitchel 1992; Rodgers et al. 1999). The western boundary of the area (Fig. 1) is marked by the contact between Precambrian basement and the overlying sedimentary rocks of the Arabian Shelf. The Precambrian basement rock comprises of felsic and intermediate igneous and metamorphic rocks. The sedimentary sequence comprises mainly of sandstone and limestone ranging from Cambrian-Ordovician to Quaternary age (Laboun 2013).

The Cambrian-Ordovician Saq Sandstone is found at the base of the sedimentary sequence. Moving away from the contact with the basement toward the east, the overlying formations appear one after the other in chronological order (Power et al. 1966).

The study area is represented a typical multilayered aquifer system with the Saq formation being the most prolific source of large-scale water supply, though it is not the only aquifer which is exploited in the region. Depending upon the thickness, hydraulic characteristics, water quality and aquifer type (confined or unconfined), other aquifer units exposed in the area are also exploited. The main hydrogeological units in the present study as inferred from the geological mapping, well lithologs and aquifer tests can be classified into five aquifers or aquifer groups and one aquitard (MoWE 2008). From bottom to top, they include:

- Saq Sandstone
- Sarah sandstones (Tabuk Formation)
- Jubah sandstone
- Khuff limestone
- Secondary (Mesozoic)–Tertiary–Quaternary (STQ) sandstone and limestone.

The Jawf limestone and sandstone which lie between the Tabuk and Jubah formation act regionally as an aquitard, but it contains units that are locally exploited as aquifer. The Cambro-Ordovician Saq formation comprising mainly of medium-to-coarse sandstones and ranging in thickness from 400 to 928 m forms the major aquifer system in northern Saudi Arabia (Al Sharhan et al. 2001) and covers the entire study area.

Materials and methods

Sampling and analysis

A total of 50 soil samples were collected during August 2013. The samples were collected from agricultural farms situated along the main highways. The sample locations have been shown in Fig. 1. The samples were collected from the upper 10 cm section in labeled polyethylene bags. After grinding and sieving through 2 mm mesh in the laboratory, these samples were stored in plastic bags. Specimens were prepared by weighed around 200 mg of sieved materials into dry and clean Teflon digestion beakers. Following this, all specimens were digested by adding 6 ml HNO_3, 2 ml HCl and 2 ml HF. The digested samples were then heated on a hot plate at 120–150 °C for about 40 min. The samples were filtered through Whatman filter paper No. 42. Following this, the filtered digest was transferred to a 50-ml plastic volumetric flask and filled up to the mark by deionized water. The selected metals were measured using a ICP-MS (Inductively Coupled Plasma-Mass Spectrometer): NexION 300D (Perkin Elmer, USA).

The accuracy and precision of the analytical method applied for the multielement determination of soil samples were evaluated by the analysis of a Certified Reference Material (CRM), namely IAEA SOIL-7, which was obtained from the International Atomic Energy Agency (IAEA), Vienna, Austria. The recovery ranged between 97 and 109 %, indicating the accuracy of the method used in this study.

Enrichment factor (EF)

The enrichment factor (EF) was used to determine the level of metal contamination in the study area and to assess the influence of anthropogenic factors if any. For calculating the EF, the concentration of a given element in the soil is compared with a conservative element such as Al, Fe or Si. Fe has been frequently used by many workers as a conservative element to differentiate between the natural and anthropogenic components of other elements (Cevik et al. 2009; Bhuiyan et al. 2010; Esen et al. 2010). The EF is calculated as follows (Ergin et al. 1991):

$$\mathrm{EF} = (\mathrm{M/Fe})_{\mathrm{sample}}/(\mathrm{M/Fe})_{\mathrm{background}}$$

where $(\mathrm{M/Fe})_{\mathrm{sample}}$ is the ratio of metal and Fe concentrations of the sample, and $(\mathrm{M/Fe})_{\mathrm{background}}$ is the ratio of metal and Fe concentrations of the background. In the present study, the background concentrations of the various elements in average shale obtained from Turekian and Wedepohl (1961) has been used.

Index of geoaccumulation

The Geoaccumulation Index (I_{geo}) has been frequently used in soil studies (Loska et al. 2004; Yaqin et al. 2008; Wei and Yang 2010; Nazzal et al. 2013a) and helps in the assessment of heavy metal contamination in the soils by comparing the present and preindustrial metal concentration. The following formula is used to calculate the index of geoaccumulation (I_{geo}) values:

$$I_{\mathrm{geo}} = \mathrm{Log}_2(C_n)/(1.5B_n)$$

where $\mathrm{C_n}$ is the metal content in the soil and $\mathrm{B_n}$ is the geochemical background value in shale (Turekian and Wedepohl 1961), and the factor 1.5 is used for possible changes in the background data due to lithological variations.

Statistical analysis

Pearson's correlation coefficient, principal component analysis (PCA), and cluster analysis were carried out using Statistical Package for the Social Sciences (SPSS) software, package 20, for Windows.

Pearson's correlation coefficient shows the linear relationship between two sets of data. Their value ranges from +1 to −1 with 0 indicating the absence of a relationship between two variables.

PCA is a widely used data reduction technique (Loska and Wiechuła 2003) where a large number of measured parameters/variables can be transformed to a smaller number of latent factors also known as principal components which can then be used for analyzing relationships among the measured variables (Yongming et al. 2006). PCA results show significant variations depending on whether correlation or covariance matrix has been used. In the present study, the correlation matrix is used. Varimax rotation is generally applied to all the extracted principal components to reduce the contribution of the variables which are not significant. The principal components having eigenvalues greater than 1 based on the Kaiser criterion (Kaiser 1960) was used in this study.

Hierarchical cluster analysis is a widely used data tool which is used for making a binary tree of the available data that merges similar groups of points in a way that variables/points within a given cluster are more closely related to one another that those falling outside the cluster.

Results and discussion

General trend

The minimum, maximum and average concentrations in the various sampling sites of the metals surveyed in this study, in relation to the background values, are presented in Table 1, which shows the wide range of values found for each metal. The statistical analysis indicates that the concentration of metals varied across all the study samples. The average values (in ppm) of As, Hg and Pb in the study area are above the background values found in shale (Turekian and Wedepohl 1961).

The concentration of Arsenic in the investigated soils ranged from 8.10 to 33.60 ppm with an average value of 18.206 ppm which is higher than the background concentration of 13 ppm. Since all the soil samples were collected from agricultural farms, the high values of As may attribute the application of pesticides and fertilizers in the farms. Use of pesticides and fertilizers are the major sources of As in soils (Jiang and Singh 1994).

The concentrations of Mercury in the studied soils were in the range of 1.90–3.40 ppm, against a background concentration value of 0.4 ppm. All the soil samples from the study area showed higher values (2.56 ppm) than the background value. The accumulation of Hg in soils is controlled by organic complexes and rainfall. Mercury is derived mainly from natural sources, although Hg concentrations in the environment can be influenced by human activities. Those activities include the combustion of fossil fuels, mining, smelting and solid waste

Table 1 Descriptive statistics summary of chemical composition ($N = 50$)

Descriptive statistics (all values in ppm)						
Element	Range	Minimum	Maximum	Mean	SD	Background concentration[a]
As	25.5	8.1	33.6	18.206	6.9383	13
Cd	0.69	0.09	0.78	0.2328	0.1699	0.3
Co	4	0.9	4.9	2.152	1.1763	19
Cr	22.8	14.8	37.6	26.328	7.4945	90
Cu	37	5.8	42.8	18.934	11.83	45
Hg	1.5	1.9	3.4	2.564	0.4467	0.4
Pb	46.5	15.9	62.4	29.508	9.0329	20
Zn	31.6	20.6	52.2	33.946	7.7259	95

[a] Background concentration has been taken from the average shale concentration as given by Turekian and Wedepohl (1961)

combustion (Li and Feng 2012). The combustion of fossil fuels for running the pumping units and oil leakages from the pumping units and the leakages from in situ oil storage tanks is the source of high Hg concentration in the analyzed soils.

In the study area, the average concentration of lead ranged between 15.90 and 62.40 ppm, with majority of the samples showing concentrations higher than the background values of 20 ppm. Proximity of the agricultural farms to roads having high density of traffic can be a potential source of Pb in the analyzed soils as vehicular fumes have high Pb content (Micó et al. 2006).

The average concentration of Cd (0.233 ppm) in the analyzed samples is less than the background values (0.3 ppm), and some samples show higher concentrations with values reaching up to 0.8 ppm. The use of phosphate fertilizers is one of the main sources of elevated Cd concentration (Chien et al. 2011) and is believed to be the main source of Cd in the study area as well.

Overall, the field investigations and observations support the idea that the higher concentrations of metals (higher than the background concentrations) in the study area, especially As, Hg, Pb and Cd, are primarily due to anthropogenic activities such as fossil fuel combustion, the use of insecticides and fertilizers in farming activity.

Assessment of soil pollution

Enrichment factor (Efc)

The enrichment factor (Efc) is used here to assess the level of metal contamination and their possible impact on soil quality in the northwestern part of Saudi Arabia. In this study, the world averages for metals in shale (Turekian and Wedepohl 1961) are used to determine of level of background metals, which in turn are used to calculate the Efc. According to Zhang and Liu (2002), Efc values of between 0.5 and 1.5 have been entirely linked to crustal materials and natural processes as sources of metals in soils, whereas values > 1.5 have been attributed to anthropogenic activities. According to the classification of Chen et al. (2007), meanwhile, an Efc < 1 corresponds to no enrichment, Efc = 1–3 to minor enrichment, Efc = 3–5 to moderate enrichment, Efc = 5–10 to moderate-to-severe enrichment, Efc = 10–25 to severe enrichment, Efc = 25–50 to very severe enrichment, and Efc > 50 to extremely severe enrichment. The average Efc values of As, Cd, Co, Cr, Cu, Hg, Pb and Zn are 8.03, 4.08, 0.65, 2.12, 3.04, 46.35, 10.67 and 2.58, respectively. Except for cobalt, all the other elements show enrichment factor values of greater than 1.5 which can be attributed to anthropogenic activities. Table 2 shows the enrichment values for the analyzed heavy metals and the degree of enrichment. Hg shows very severe enrichment, whereas Pb shows severe enrichment. The high enrichment showed by Hg and Pb in the study area is mainly due to the use of chemical and organic fertilizers and pesticides in agriculture activities. Groundwater extraction pumps and in situ fuel storage tanks may cause oil spills, which could also be a source of Hg and Pb. Fuel combustion as a result of traffic flow in the area probably also contributes to high Hg and Pb concentrations, since these samples were collected

Table 2 Average enrichment factor for the analyzed soil samples

Element	Average enrichment factor	Degree of enrichment (after Chen et al. 2007)
As	8.03	Moderate-to-severe enrichment
Cd	4.08	Moderate enrichment
Co	0.65	No enrichment
Cr	2.12	Minor enrichment
Cu	3.04	Minor enrichment
Hg	46.35	Very severe enrichment
Pb	10.67	Severe enrichment
Zn	2.58	Minor enrichment

from farms lying adjacent to major traffic highways. Overall, the mean Efc decreases in the order Hg > Pb > As > Cd > Cu > Zn > Cr > Co which can also be seen as the decreasing order of their overall contamination of soils in the northwestern of Saudi Arabia. In this study, the Efc values represent an effective tool to differentiate between the natural origins of metal contaminants from anthropogenic sources.

Index of geoaccumulation (I_{geo})

I_{geo} is classified into seven grades, the highest of which (grade 6) reflects 100-fold enrichment above the background values (Table 3). The I_{geo} values calculated on the basis of metal concentrations in the analyzed soils reveal no real sign of contamination with almost all the samples showing a lack of contamination for all metals except Hg, which shows a moderate level of contamination due to anthropogenic sources (Table 4). Both the I_{geo} and Efc values depend on the background data, grain size, and bonding of metals (Rubio et al. 2000). However, the results of metal contamination obtained from calculation of enrichment factor and index of geoaccumulation do not confirm with each other. In terms of E_{fc} only cobalt shows no enrichment, whereas in terms of I_{geo} only Hg shows moderate contamination, while all the other metals show no contamination. The possible differences in the level of contamination as obtained from E_{fc} and I_{geo} may be due to the fact that the calculation of the later depends on the concentration of a given metal in the analyzed sample to its background concentration without involving the use of a conservative element.

Table 3 Different contamination levels (adapted from Muller 1981)

I_{geo} class	I_{geo} value	Contamination level
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated/moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately/strongly contaminated
4	$3 < I_{geo} < 4$	Strongly contaminated
5	$4 < I_{geo} < 5$	Strongly/extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

Table 4 Geoaccumulation index (I_{geo}) and contamination levels (in parentheses) for selected metals in the soil samples of study area

Element	I_{geo} value	Contamination level (after Muller 1981)
As	−0.2	Uncontaminated
Cd	−1.2	Uncontaminated
Co	−4.1	Uncontaminated
Cr	−2.4	Uncontaminated
Cu	−2.1	Uncontaminated
Hg	2.1	Moderately to heavily contaminated
Pb	−0.1	Uncontaminated
Zn	−2.1	Uncontaminated

Multivariate statistical result analysis

Principal component analysis (PCA)

Generally, metals in soils are characterized by complicated relationships. PCA has previously been shown to be an effective method to determine human impacts on the level of metals in soil on a spatial scale (Li and Feng 2012). Theoretically, the number of principal components (PC) extracted is the same as the number of parameters involved in PCA; however, only those PC which have eigenvalues of greater than one are taken into consideration as they account for the maximum data variance. In the present study, PCA resulted in the extraction of three principal components which accounted for 66.5 % of the total data variability. Varimax rotation was then applied to the extracted components to reduce the contribution of variables that are not significant. Table 5 shows the eigenvalues and the respective variance shown by the extracted PC. Table 6 shows the three extracted PC with the factor loadings for each parameter based on Varimax rotation with Kaiser normalization. The PC 1 accounts for 23.02 % of the total data variability and shows significant factor loadings of Cd (0.850) and Pb (0.764). As shown in earlier section, Cd values in some samples and the average Pb values are higher than the average background concentrations and may be related to anthropogenic influences. The origin of Cd is mainly related to the use of phosphate fertilizers in the agricultural farms, whereas the source of Pb is mainly linked with aerial deposition from the use of leaded gasoline (all the farms were located along the major roads with frequent vehicular traffic). PC 2 accounted for 20.92 % of the total data variance and was represented by significant factor loadings of Co (0.745), Cu (0.917) and Hg (−0.569). Co and Cu do not show significant enrichment, and their presence is mainly related to the natural crustal weathering processes. Hg which is represented by a negative factor loading shows high average values in the collected soil samples and also shows high enrichment and is mainly enriched due to anthropogenic activities. PC 3 accounts for 17.75 % of the total data variability and is represented by high factor loadings of As (0.778) and Cr (−0.918). The presence of As which shows higher values in the analyzed soil samples is associated with the agricultural activities mainly through the use of fertilizers and pesticides on the farms and is linked to anthropogenic sources, whereas the high factor loadings of Cr are mainly associated with geogenic sources related to the crustal weathering.

Table 5 Extracted principal components showing the eigenvalues and percentage of data variability

Total variance explained						
Component	Initial eigenvalues			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	2.226	27.831	27.831	1.842	23.029	23.029
2	1.674	20.924	48.754	1.822	22.777	45.807
3	1.42	17.748	66.503	1.656	20.696	66.503
4	0.998	12.472	78.974			
5	0.729	9.109	88.083			
6	0.665	8.318	96.401			
7	0.148	1.849	98.25			
8	0.14	1.75	100			

Extraction method: principal component analysis

Table 6 Extracted principal components showing the factor loadings of the different elements

	Components		
	1	2	3
As	0.054	0.237	**0.778**
Cd	**0.85**	0.143	−0.166
Co	0.345	**0.745**	0.324
Cr	0.162	0.097	**−0.918**
Cu	0.17	**0.917**	0.06
Hg	0.476	**−0.569**	0.214
Pb	**0.764**	−0.025	0.14
Zn	0.364	0.124	−0.077

Values in bold represents significant factor loadings

Extraction method: principal component analysis

Rotation method: Varimax with Kaiser normalization

Rotation converged in seven iterations

Correlation analysis (CA)

The Pearson correlation coefficients for the metals in the studied soil samples are summarized in Table 7. A significant positive correlation is found between Cu and Co ($r = 0.73$) and Pb and Cd ($r = 0.55$). Cr, meanwhile, shows a negative correlation with As. The correlation (positive and negative) found between the studied metals may reflect nearly similar levels and sources of contamination in the study area.

The data on metal concentrations were standardized by means of a Z-score before cluster analysis, and Euclidean distances for similarities in the variables were calculated. Hierarchical cluster analysis (HCA) (Fig. 2) was performed on the resulting standardized data using the Ward's method (Hervada-Sala, and Jarauta-Bragulat 2004). Two distinct clusters were observed, with cluster 1 containing Co–Hg–Cd; where Hg and Cd show a high concentration compared with background values in the studied area. Cluster 2 contains As–Cu–Pb–Zn–Cr (divided into two subclusters: As–Cu and Pb–Zn-Cr) with As and Pb showing higher values than the background concentrations.

Conclusions

The soils studied in the study area were compared with the background values of Hg, Pb, Co, Zn, Cd, As, Cr and Cu. Results of chemical analysis of soils suggested the presence of both anthropogenic and natural sources for metal contamination. Possible anthropogenic sources of contamination were identified as agricultural activities in the form of fertilizers (both organic and chemical), pesticides, and seepage from oil tanks and groundwater pumps, oil combustion and traffic effluents. Natural sources of contamination are related to the local geology, which shows the presence of metal-bearing parent rocks, including basalt, phosphate and bituminous limestone.

Arsenic was also found in study area soils at levels within the permissible limits, but the concentration closed to the critical level. Sources of As in the environment are both natural and anthropogenic. The levels of As in soils of various countries have been found to range from 0.1 to 40 mg/kg (Mandal and Suzuki 2002), but these levels vary considerably between the different geologic regions in the present study. As was also found to be negatively correlated with Cr. Negative coefficients indicate that the source of As and Cr is not same as the cluster of Cu, Pb and Zn. Although the results of the present study provide a preliminary conclusion regarding the origin of each metal, further studies are necessary in order to gain a better understanding of the sources of pollution affecting the soils of northwestern Saudi Arabia.

Overall, this study reveals a considerable variation in the concentration of the various metals in the soils samples, a

Table 7 Correlation matrix of the investigated metals

	As	Cd	Co	Cr	Cu	Hg	Pb	Zn
As	1							
Cd	0.125	1						
Co	0.259	0.209	1					
Cr	−0.531	0.341	−0.199	1				
Cu	0.261	0.256	0.736	0.084	1			
Hg	0.011	0.193	−0.062	−0.09	−0.276	1		
Pb	0.001	0.55	0.288	−0.105	0.049	0.139	1	
Zn	0.011	0.174	0.198	0.09	0.092	0.118	0.05	1

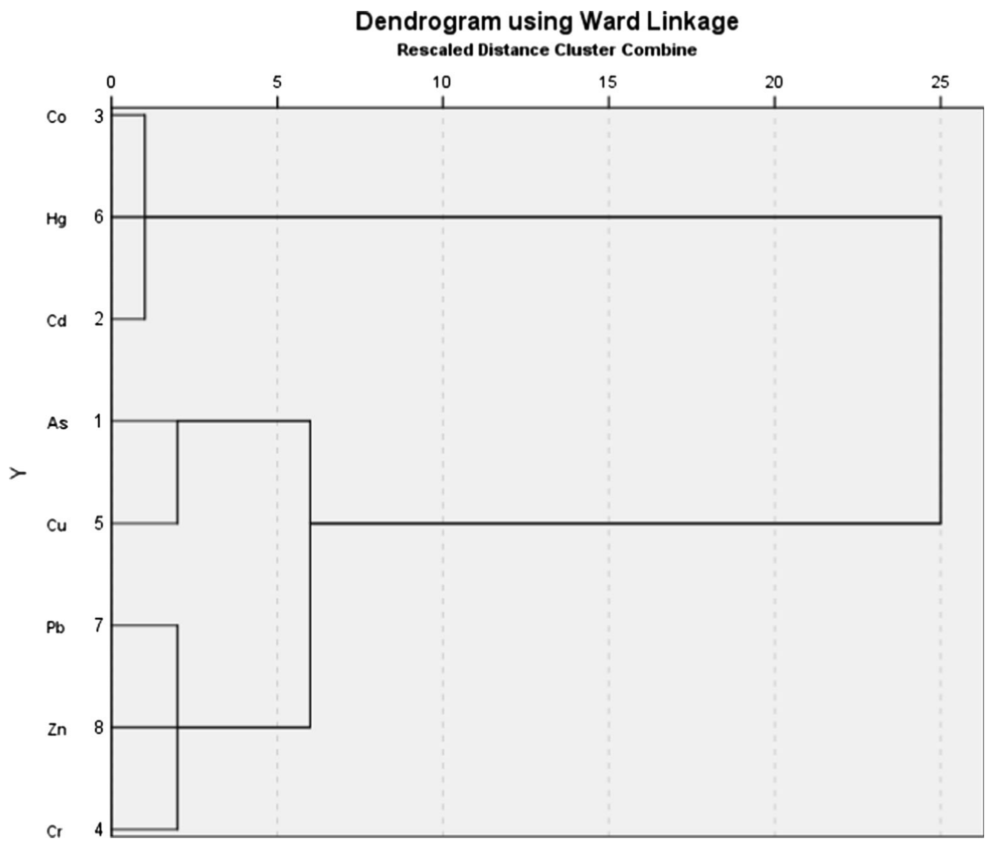

Fig. 2 Cluster analysis of the investigated sites

variation which can be ascribed to the intensity of agricultural activity, fossil fuel combustion and traffic. The multivariate statistical methods helped in identifying the potential sources of metals and also helped to assess soil environment quality in northwestern Saudi Arabia. Geostatistical analysis and multivariate statistical analysis showed distinctly different associations between the studies metals, suggesting that As, Cd, Hg and Pb were associated with anthropogenic activities, whereas Cr, Cu Co and Zn in the study area were mainly controlled by parent materials and, therefore, had commonalities with natural and anthropogenic metal concentrations in the surface soils. The reported findings have the potential to help decision-makers to put in place effective approaches to reduce contamination, lessen human exposure and protect populations at risk.

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