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ORIGINAL ARTICLE

Assessment of As and Cd contamination in topsoils of Northern Ghorveh (Western Iran): role of parent material, land use and soil properties

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Abstract The aim of this study was to investigate the influences of land use, parent materials (rock types) and soil properties on total arsenic and cadmium concentrations in the agricultural soils. A total of 87 surface (0–20 cm) soil samples were collected from four types of land use: irrigated farming, rangeland, dry farming and orchard. The average concentrations of the analyzed elements in topsoil were 84.426 mg As/kg and 3.289 mg Cd/kg. In addition, the pH, organic matter (OM), cation exchange capacity (CEC), soil grain sizes and $CaCO_3$ were measured for each sample. The results indicated that land use had no significant effect on As and Cd concentrations. Our findings indicated that the Cd concentrations were influenced by bedrock composition, but for As there were no significant differences between various soil parent materials (bedrocks). Soil pollution was assessed on the basis of pollution index (PI), comprehensive pollution index (P_n) and geoaccumulation index (I_{geo}). Calculated indices showed high-pollution levels for As and low- to moderate-pollution levels for Cd.

Keywords Spatial variability · Heavy metals · Soil contamination · Risk assessment · Contamination index

Introduction

Soil is one of the most important but also endangered compartments of the environment, because emitted, persistent pollutants have accumulated in it over a long period of time (Einax and Soldt 1998). If the buffer capacity of soil is exhausted, other parts of the environment, such as groundwater or the biosphere, become endangered due to the transfer of pollutants. For this reason, it is inevitably necessary to carry out a general chemical analysis of a contaminated area, to characterize the pollution state, and to detect potential emission sources (Einax and Soldt 1998).

Soil pollution results from the buildup of contaminants, toxic compounds, radioactive materials, salts, chemicals and cancer-causing agents. The most common soil pollutants are hydrocarbons, heavy metals (cadmium, lead, chromium, copper, zinc, mercury and arsenic), herbicides, pesticides, oils, tars and dioxins. Among these pollutants, heavy metals are of particular concern due to their long residence time in soils and their toxicity to humans (Kabata-Pendias and Pendias 1992; Alloway 1995).

One of the important toxic elements is arsenic (As). It is a ubiquitous element in the environment and may be mobilized through a combination of natural processes, such as weathering and erosion, biological activity, and volcanic emissions, as well as through the activities of man (Smedley and Kinniburgh 2005). The main factors

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affecting As concentration in soils are: rock composition and human activities, such as mining, smelting, combustion of fossil fuels, and pesticide and herbicide applications. Other factors are soil texture and soil organic matter content (Chen et al. 2002). Another toxic heavy metal is cadmium (Cd). Warnings of health risks from Cd pollution were issued initially in the 1970s (Nordberg et al. 1997). Cadmium is water soluble and can be transferred efficiently from soil to plants, which may affect human health if there is excessive intake from a contaminated food source (Satarug et al. 2003).

Understanding the spatial distribution of heavy metals in topsoil is critical for environmental management and agricultural production. It is widely recognized that spatial distributions of geochemical variables are not homogeneous due to complex processes related to multiple factors such as geology, soil, climate, vegetation, elevation, natural mineralization and human activity. These processes affect geochemical variables at different spatial scales, ranging from micro-scale mineral composition to macro-scale geochemical provinces (Zhang et al. 2007).

Heavy metals pollution in soil is commonly estimated by interpolating concentrations of heavy metals sampled at point locations, so that each heavy metal is represented in a separate map (Webster and Oliver 2001). The methods of geostatistics use the stochastic theory of spatial correlation both for interpolation and for apportioning uncertainty (Goovaerts 1997). Moreover, geostatistics has been successfully applied in investigating and mapping soil pollution by heavy metals, in the recent years (Otte et al. 1993; Markus and McBratney 1996; Goovaerts 2001; Guo et al. 2001; Romic and Romic 2003; Rebecca and Anna 2006; Hu et al. 2006; Liu et al. 2006; Moyano et al. 2008). A main contribution of a semivariogram is that it reveals that the spatial change properties of sampled values that is to the regional variables.

This study was conducted in agricultural lands of northern Ghorveh to (1) assess the spatial distribution patterns of As and Cd in the study area (2) evaluate the effects of different land uses on the concentration of As and Cd (3) evaluate the effect of soil properties on the concentrations of As and Cd on a regional scale, and (4) assess the soil environmental quality.

Materials and methods

Study area

Location and land use

The study area is located between 47°32′ and 48°11′E in longitude and between 35°05′ and 35°30′N in latitude and situated 6 km from Northern Ghorveh county in Kurdistan province, Western Iran; the total area is 1,352 km^2. This area is characterized by cold, snowy winters and a Mediterranean climate with an average annual rainfall of 480 mm (for the period 1993–2003 at Ghorveh Station), and the average annual temperature is about 6.13°C. The land is traditionally associated with agriculture and residential uses (of the total area: orchard: 2.15%; irrigated farming: 1.1%; dry farming: 83.1%; rangeland: 13.25%; and residential: 0.389%). The agricultural lands North of Ghorveh are well known for wheat production. The study area map and sampling sites are shown in Fig. 1.

Geology of the study area

The studied area belongs to the Sanandaj–Sirjan geological zone. The area is made up of the following formations:

Quaternary sedimentary-igneous rocks: consisting of alluvial sediments, travertines, poorly consolidated conglomerates, basanites and basalts.

Miocene–pliocene sedimentary-igneous rocks: composed of argillaceous limestones, marls, sandy marls, conglomerates, lahars, tuffs, lapilly tuffs, pumiceous tuff breccias, latites and dacites.

Eocene sediments: they include conglomerates and calcareous sandstones.

Triassic–jurassic sedimentary-metamorphic rocks: composed of quartzites, micaschists, phyllites, slates, crystalline limestones, breccias, marbles and limestones.

Triassic metamorphic rocks. They include a variety of metamorphosed rocks such as meta andesites, amphibolites, black schists, phyllites, meta gabbros and scapolite marbles.

Major geological features are shown (Fig. 3) in a simplified geological map of the Kurdistan province which is based on the 1:100,000 geology map of the Geological Survey of Iran (GSI 1999).

Soil sampling and laboratory analysis

Eighty-seven topsoil samples (0–20 cm in depth) were collected from the study area in September 2008 at intervals of 3 km. During the soil sampling, the planned regular sampling of 3 × 3 km was not possible to be followed accurately because of topographical problems and mountainous terrain of the study area, but care was taken to preserve a uniform distribution of sampling sites as possible. At each sampling point, five subsamples were taken from the four corners and the center of a rectangular block and mixed to achieve a composite soil sample. The subsamples were mixed into one composite sample for each soil and were analyzed in triplicate. A global positioning

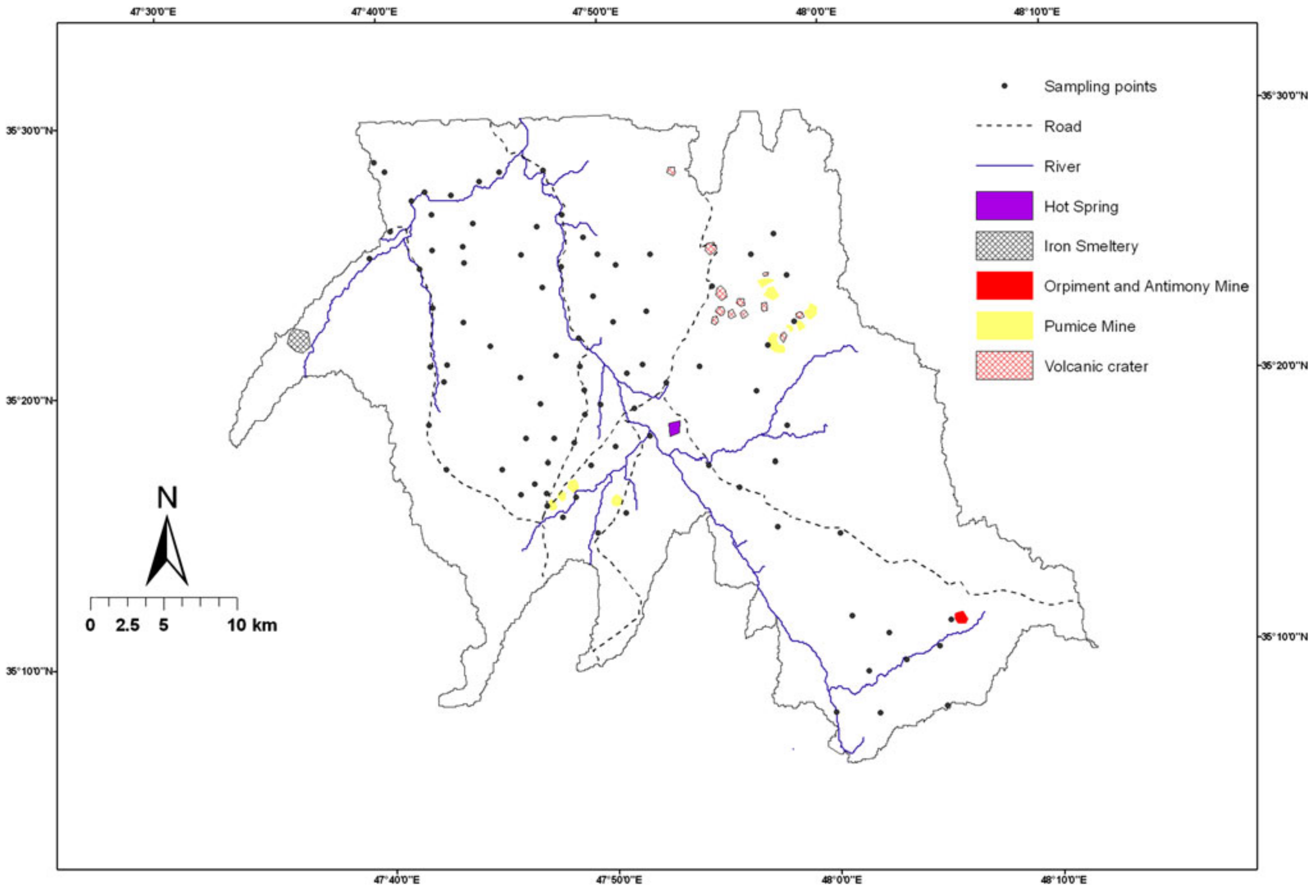

Fig. 1 Location of the study area with the 87 sampling points

system (GPS) was used to precisely locate every sampling site (latitude and longitude). About 1.5 kg of each sample was stored in a polyethylene package and transported to the laboratory.

All of the samples were air-dried and grounded to pass through a 2 mm sieve. The soil samples were digested by aqua regia with a mixture of nitric and hydrochloric acids according to the 3050B method of the United States Environmental Protection Agency (USEPA 1996). Arsenic and cadmium were measured by graphite furnace atomic absorption spectrometry (VARIAN 220A). The soil organic matter was determined by the Walkey–Black method (Schnitzer 1982). The soil pH was determined by a pH meter with a soil/water ratio of 1:2.5 (Allen et al. 1974). The cation exchange capacity (CEC) was measured using 1 mol/L ammonium acetate solution. Soil grain sizes (sand, silt and clay) were measured by hydrometric method. Standard reference material (GBW-07401) of soils was applied for quality assurance and control (QA/QC). The quality control performed included a daily analysis of a standard and replicate analysis of samples and blanks. The satisfactory recovery rates for As and Cd were 92.7–106.4% and 89.5–107.4%, respectively.

Statistical and geostatistical analysis

The Kolmogrov–Smirnov (K-S) test, skewness and kurtosis were applied to assess normality of the data set. Stepwise regression analysis was also used to select the main factors affecting soil heavy metals (As and Cd).

Geostatistics uses the technique of variograms to measure the spatial variability of the recognized variable and providing the input parameters for the spatial interpolation of kriging (Webster and Oliver 2001). Kriging has been widely used as an important interpolation method at different scales, especially in soil pollution (Chen et al. 2008). The semivariogram $\gamma(h)$ measures the mean variability between the two points x and $x + h$, as a function of their distance h, for data located at discrete sampling locations. The semivariogram is an autocorrelation statistic defined as follows (Isaaks and Srivastava 1989):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2, \qquad (1)$$

where $Z(x_i)$ represents the measured value of the soil property at location of x_i, $r(h)$ is the variogram for a lag distance h between observations $Z(x_i)$ and $Z(x_i + h)$, and

$N(h)$ is the number of data pairs separated by h. The variogram model is chosen from a set of mathematical functions that describe spatial relationships. The appropriate model is chosen by matching the shape of the curve of the experimental variogram to the shape of the curve of the mathematical function.

The fitted model provides information about the spatial structure as well as the input parameters such as nugget, sill and range for kriging interpolation. In this study, to make distribution maps, several spatial interpolation techniques, such as kriging, global/local polynomial interpolation (G/LPI), inverse distance weighting (IDW) and radial basis functions (RBF), were evaluated for the best results. We used kriging (ordinary kriging) as a spatial interpolation technique to make distribution maps, because it is very flexible and allows users to investigate graphs of spatial autocorrelation. It also allows for prediction, prediction standard error, and probability maps, and at the same time, it minimizes the error of predicted values.

For the evaluation of the simulation quality and the model-experiment comparison of the different model approaches, cross-validation indicators and additional model parameters can be used. In this paper, to compare these models, cross validation was performed using the statistical parameters of mean error (ME), root mean square error (RMSE), average standard error (ASE), mean standard error (MSE), and root mean squared standardized error (RMSSE) (Robinson and Metternicht 2006).

Coefficient of variation

Coefficient of variation (CV), usually presented as a form of percentage, can be used to compare the variability of same property under similar values of variances and different means situations in relative terms (Wu et al. 2008). To compare the variable of As and Cd concentrations in each of land use and geology map units, heavy metal concentrations data were divided into four and eight classes based on land use and geology map units, respectively. All the coefficients of variation (CVs) of As and Cd in map unit classes were calculated.

Methods to assess soil pollution

Soil pollution factors

Soil quality of the study area was assessed by single factor-pollution index (PI) (Huang 1987) and comprehensive pollution index (Nemero index) (Li et al. 2003). The PI of arsenic and cadmium was calculated by Eq. (2):

$$\mathrm{PI}_i = \frac{C_i}{S_i} \qquad (2)$$

And the formula of the comprehensive pollution index (P_n) is:

$$\mathrm{P}_n = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n}\mathrm{PI}_i\right)^2 + [\max(\mathrm{PI})]^2}{2}} \qquad (3)$$

where, C_i is the measured value of element i at each sampling site, and S_i is the criteria value or guideline of the heavy metal i; max (PI) is the maximum value of the pollution indices of the heavy metal. In the same way, the comprehensive pollution index (Nemero index), was classified as single-factor pollution index. PI and P_n classifications (Bai et al. 2010) are shown in Table 1.

Index of geo-accumulation

The geo-accumulation index (I_{geo}) introduced by Muller (1969) was used to assess heavy metal contamination in agricultural soils of the study area. It was computed by the following equation:

$$I_{\mathrm{geo}} = \log_2 \frac{C_n}{1.5B_n} \qquad (4)$$

where, C_n is the concentration of the element in the soil and B_n is the concentration of element in the Earth's crust. The constant 1.5, takes account the variation of the element in the environment due to lithogenic effects. I_{geo} classifications according to Muller (1969) are shown in Table 1.

Results and discussion

Descriptive statistics

The main soil properties and heavy metals (As and Cd) in the soil are summarized in Table 2. The average values for the seven soil properties were 22.197, 0.928, 8.379, 46.172, 42.152, and 11.68%, and 11.084 cmol+/kg for $CaCO_3$%, OM%, pH, sand%, silt%, clay% and CEC, respectively. The mean value for As was 84.426 mg/kg, and the mean value for Cd was 3.289 mg/kg.

Table 2 presents the summary statistics of the datasets for soil properties, including the As and Cd concentrations. The analysis showed that $CaCO_3$, OM, pH, sand and CEC passed the Kolmogorov–Smirnov normality test (K-S $P < 0.05$), but As, Cd, silt and clay did not pass. Because further geostatistic analysis would need data to follow a normal distribution, data transformation was carried out on the As and Cd data prior to the next analysis. In our study, the log transformation was used to make the data more normal and less skewed (Webster and Oliver 2001).

Table 1 Classifications of soil contamination indices

Single-factor pollution index (PI)[a]			Comprehensive pollution index (P_n)[b]			Geo-accumulation index[c]		
Class	Value	Contamination level	Class	Value	Contamination level	Class	Value	Contamination level
1	$PI \leq 1$	No	1	$P_n \leq 1$	No	0	A	$I_{geo} \leq 0$
2	$1 < PI \leq 2$	Low	2	$1 < P_n \leq 2$	Low	1	B	$0 < I_{geo} \leq 1$
3	$2 < PI \leq 3$	Moderate	3	$2 < P_n \leq 3$	Moderate	2	C	$1 < I_{geo} \leq 2$
4	$PI > 3$	High	4	$P_n > 3$	High	3	D	$2 < I_{geo} \leq 3$
						4	E	$3 < I_{geo} \leq 4$
						5	F	$4 < I_{geo} \leq 5$
						6	G	$I_{geo} \geq 5$

A uncontaminated, *B* uncontaminated to moderately contaminated, *C* moderately contaminated, *D* moderately to heavily contaminated, *E* heavily contaminated, *F* heavily to extremely contaminated, *G* extremely contaminated

[a] Single-factor pollution index (Bai et al. 2010)

[b] Comprehensive pollution index (Bai et al. 2010)

[c] Geo-accumulation index (Muller 1969)

Table 2 Statistical summary of heavy metals concentrations (mg/kg) and soil properties

	As	Cd	$CaCO_3$ (%)	OM (%)	pH	Sand (%)	Silt (%)	Clay (%)	CEC[d]
Mean	84.4261	3.28897	22.19684	0.92760	8.3795	46.172	42.152	11.68	11.0844
Std. deviation	52.2291	2.051233	11.041341	0.416159	0.16985	13.9102	10.3468	7.071	2.65140
Minimum	21.539	1.059	0.625	0.033	7.80	11.4	13.4	2	3.880
Maximum	247.225	9.415	48.375	2.129	8.98	82.0	65.6	45	15.758
Skewness	1.498	1.187	−0.036	0.175	−0.148	0.346	−0.362	1.770	−0.340
Kurtosis	1.526	0.002	−0.194	−0.039	3.385	−0.112	0.206	4.862	−0.233
K-S *p*[a]	0.002	0.000	0.958	0.930	0.214	0.827	0.045	0.042	0.851
K-S *p* log[b]	0.157	0.052							
CV (%)	61.86	63.44	49.74	44.86	2.02	30.13	24.54	60.54	23.92
Guide value[c]	12	1.4	–	–	–	–	–	–	–
Conc. in Earth's crust[e]	0.5–2.5	0.1–0.2	–	–	–	–	–	–	–

[a] Kolmogrov-Smirnov test

[b] Kolmogrov-Smirnov test of lognormal transformed data

[c] Canadian soil quality guidelines for the protection of environmental and human health

[d] CEC: Cation Exchange Capacity(cmol(+)/kg)

[e] Concentration in Earth's crust (mg/kg) (Kabata-Pendias and Pendias 1999, 2001)

Correlation analysis

To understand the effect of soil properties on As and Cd concentrations, the correlations between As, Cd and soil properties (grain size, $CaCO_3$, pH, OM, CEC) were analyzed (Table 3). The results showed that As content was positively correlated with silt and clay ($P < 0.05$) and negatively correlated with sand ($P < 0.01$). The correlation coefficient *r* between As and sand was the highest among all soil properties, with a value of −0.324. Cadmium was significantly positively correlated with sand ($P < 0.01$) and negatively correlated with $CaCO_3$ ($P < 0.01$), silt ($P < 0.01$), clay ($P < 0.05$) and CEC ($P < 0.01$). A strong negative correlation was found between As and Cd, probably indicating, they came from different origins.

Stepwise regression analysis

For As and Cd, sand, silt, clay, $CaCO_3$ and CEC were selected as independent variables to perform the stepwise regression analysis. The results for As and Cd represented in Eqs. 5 and 6, respectively.

$$Y_{As(mg/kg)} = 140.564 - 1.216X_{Sand(\%)} \tag{5}$$

$$Y_{Cd(mg/kg)} = 8.232 - 0.117X_{Silt(\%)} \tag{6}$$

Geostatistical analysis

The attributes of the semivariograms for each heavy metal in the soil are summarized in Table 4. The experimental semivariogram depicts the variance of the sample values at

Table 3 Pearson correlation coefficients of heavy metals and soil properties

	As	Cd	$CaCO_3$ (%)	OM (%)	pH	Sand (%)	Silt (%)	Clay (%)	CEC
As	1								
Cd	−0.373**	1							
$CaCO_3$%	−0.017	−0.332**	1						
OM%	−0.085	−0.096	0.207	1					
pH	0.033	0.156	0.124	−0.237*	1				
Sand (%)	−0.324**	0.528**	−0.461**	−0.193	0.036	1			
Silt (%)	0.274*	−0.564**	0.405**	0.346**	−0.153	−0.87**	1		
Clay (%)	0.235*	−0.214*	0.314**	−0.126	0.154	−0.694**	0.249*	1	
CEC	0.141	−0.385**	0.425**	0.796**	−0.179	−0.747**	0.760**	0.358**	1

OM organic matter, *CEC* cation exchange capacity (cmol + /kg)

* $P < 0.05$

** $P < 0.01$

Table 4 The best fitted semivariogram models and their parameters for soil heavy metals

Metal	Semivariogram model	Nugget (C_0)	Sill ($C + C_0$)	$C_0/C + C_0$	Range	RMSE	Anisotropy angle
As	Rational quadratic	0.11836	0.27059	0.437	8850	43.33	37.1
Cd	Rational quadratic	0.06232	0.09253	0.673	68210	1.106	33.8

various distances of separation. Nugget variance represents the experimental error and field variation within the minimum sampling spacing. The ratio of nugget to sill (nugget/sill) can be used to express the extent of spatial autocorrelations of environmental factors: if the ratio is less than 25%, the variable has strong spatial dependence; between 25 and 75%, the variable has moderate spatial dependence; and greater than 75%, the variable shows only weak spatial dependence. The spatial variability of the soil properties may be affected by intrinsic (soil formation factors, such as soil parent materials) and extrinsic factors (soil management practices, such as fertilization). Usually, strong spatial dependence of soil properties can be attributed to intrinsic factors, and weak spatial dependence can be attributed to extrinsic factors (Cambardella et al. 1994). The semivariograms showed that the soil As and Cd were fitted a Rational Quadratic model. The nugget/sill ratios of As and Cd were 43.7 and 67.3%, respectively; they have moderate spatial dependence on the large scale of the study area, indicating that intrinsic and extrinsic factors such as agricultural practice, parent material and topography changed their spatial correlations.

Spatial variation of soil heavy metals and land use

The study area contains about 86.35% cultivated soil. The soil sample data over different land uses are illustrated in Fig. 2. As and Cd concentrations in the four land uses were compared using one-way ANOVA (Table 5). The two significance values for the *F* test were higher than the significance level of 0.05, indicating that land use has no significant effect on the As and Cd concentrations.

Although there was no significant difference between As and Cd concentrations among the various land uses, As concentrations were the highest in irrigated farming, followed by dry farming and rangeland, and they were the lowest in orchard. The higher concentration of As in the agricultural area is mainly caused by the application of manure, compost, sewage sludge, pesticides, and fertilizers. To obtain high production, farmers apply many agrochemicals to the soils (Camelo et al. 1997). However, different agricultural land uses need different kinds and amounts of agrochemicals. Like As, the highest concentrations of Cd found in irrigated farming was caused by agrochemical application.

Heavy metals variations among rock types

Samples were classified based on their underlying rock types (Fig. 3), and the mean comparison of As and Cd concentrations in topsoils in each rock-type area was performed using one-way ANOVA (Table 6). The mean comparison showed that rock type had no significant effect on As concentrations, but there was a significant difference between Cd concentrations among rock types. Among all of the rock types, soils from the alluvium area displayed the highest Cd concentrations, followed by tuff and andesite areas. Soils from the argillaceous limestone and alluvial deposit areas

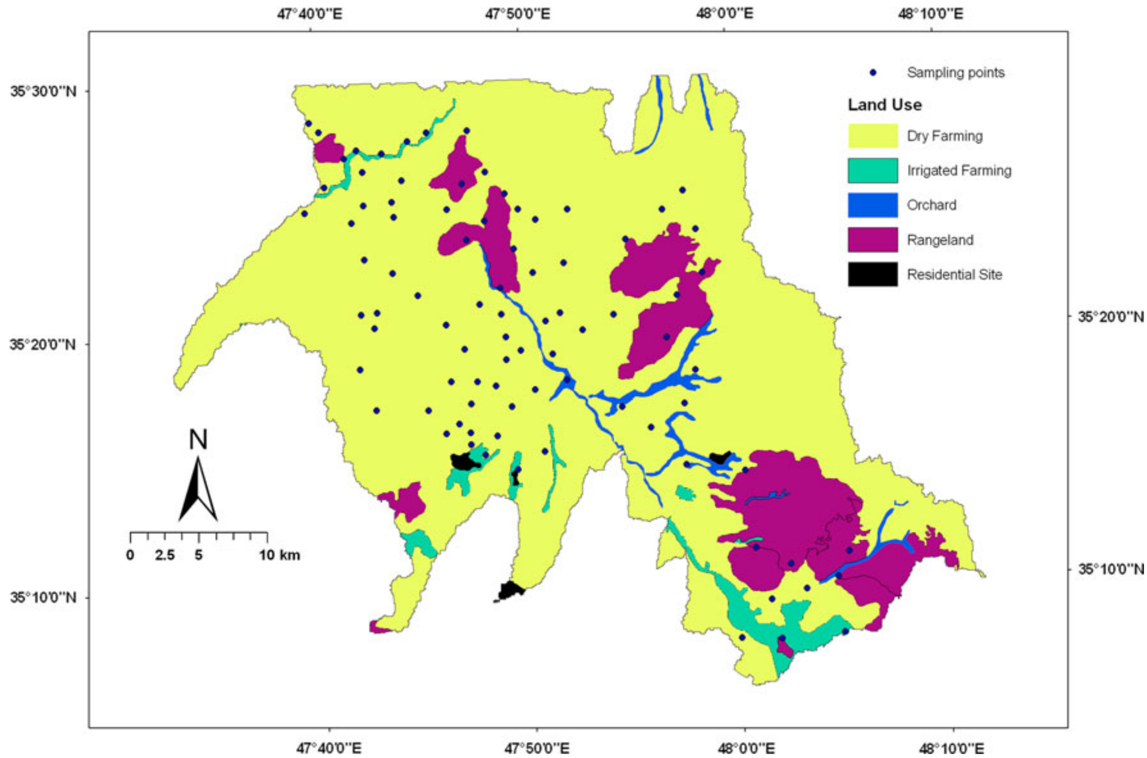

Fig. 2 Land use map of the study area

Table 5 ANOVA statistical results of the As and Cd concentrations under the four land uses

Land use (sample numbers)		Irrigated farming (6)	Rangeland (11)	Dry farming (67)	Orchard (3)	*F*	Sig.
As (mg/kg)	Mean	84.14400[a]	67.98783[a]	86.53551[a]	54.0065[a]	0.457	0.713
	CV	0.6559	0.5180	0.6226	0.5141	–	–
Cd (mg/kg)	Mean	5.03933[a]	4.63233[a]	3.08033[a]	4.56150[a]	1.979	0.123
	CV	0.5708	0.5311	0.6571	0.9107	–	–

Means with the same letter are not significantly different at $P < 0.05$

generally had low Cd concentrations. This result may relate to the development history of soils. In the primary stage, pedogenesis is mainly controlled by parent material, but in the subsequent long-term evolution of soil, the effect of other factors (such as climate, organisms, etc.) on soil-forming processes may exceed that of parent material (Birkeland 1984; Li et al. 2004). In other words, soils originating from different parent materials can have similar chemical composition, when they have evolved for long period under similar climate conditions (Wu et al. 2010).

As shown in Table 6, the CV of soil As from each rock-type area varied from 0.3375 to 1.022, indicating that there were significant variations in As concentrations within each rock-type area. Andesite and travertine areas showed the highest CV values. Soils from basalt as well as alluvium areas had the lowest CV values, indicating that the soils from these areas were more homogenous than those from the other rock-type areas. For Cd, the highest value belonged to argillaceous limestone area, and the lowest one belonged to alluvium.

Spatial distributions of heavy metals

The variogram models were used as input to ordinary kriging, and the resulting contour maps are shown in Fig. 4. The contour maps illustrate that several relatively high-concentration 'hotspots' exist for As in the study area. The high concentrations of As were mainly located in the eastern, central and northwestern parts of the study area. According to the study area map (Fig. 1), there is an orpiment and antimony mine in the eastern part of the study area.

The geological map shows that As hotspots coincide with the occurrence of travertine and argillaceous limestone rocks in the region. Travertines, particularly those forming around hot springs, are sometimes associated with diverse hydrothermally deposited minerals containing a

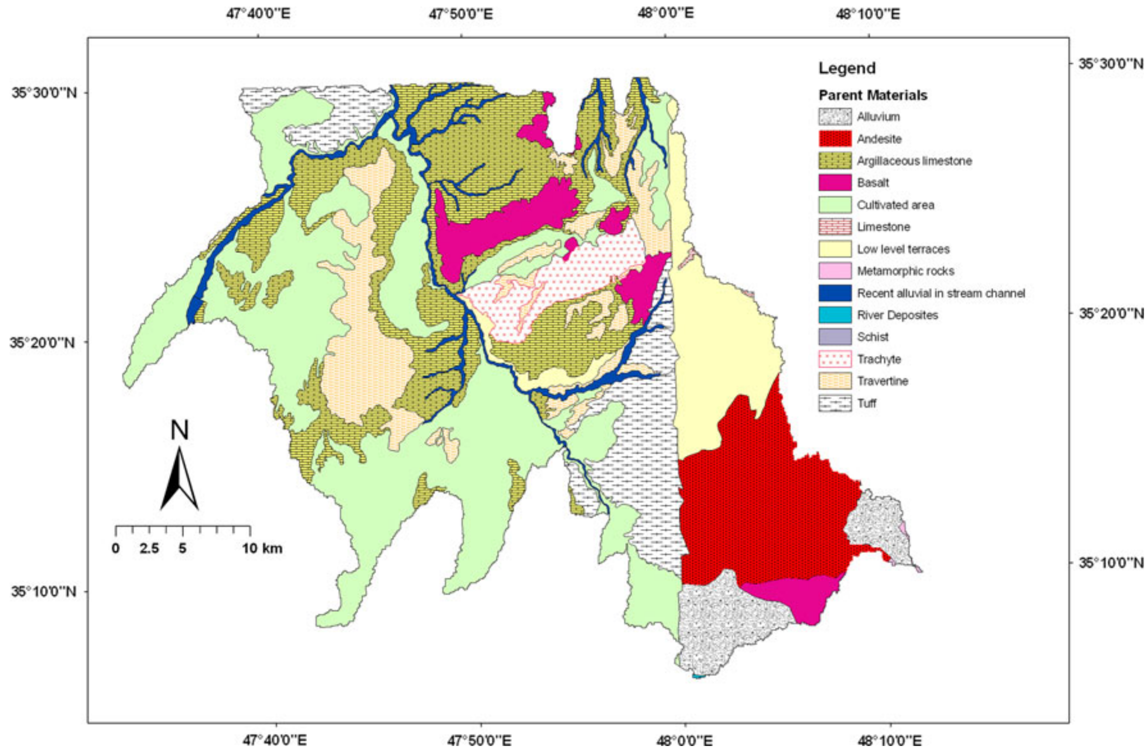

Fig. 3 A simplified geology map of the Northern Ghorveh

Table 6 ANOVA statistical results of the As and Cd concentrations among the eight parent materials

Rock type or parent material (sample numbers)		Tuff (3)	Travertine (12)	Recent alluvial in stream channel (7)	Argillaceous limestone (24)	Basalt (5)	Alluvium (4)	Andesite (5)	Trachyte (3)	*F*	Sig.
As (mg/kg)	Mean	66.215[a]	96.475[a]	90.747[a]	97.622[a]	67.718[a]	45.589[a]	84.516[a]	47.632[a]	0.807	0.585
	CV	0.4528	0.6810	0.4110	0.6327	0.3375	0.2194	1.022	0.6407		
Cd (mg/kg)	Mean	5.101[bc]	3.126[ab]	1.572[a]	3.232[ab]	4.066[abc]	6.446[c]	5.035[bc]	5.050[bc]	2.918	0.012
	CV	0.6190	0.5927	0.1091	0.7099	0.6773	0.0884	0.4947	0.4821		

Means with the same letter are not significantly different at $P < 0.05$

wide range of elements. Many geothermal areas are associated with volcanic activity and many of the hot springs actively precipitate arsenic, antimony, mercury, and thallium, whereas some geothermal waters contain very high concentrations of boron (Selinus 2005). Arsenic is an important component of the heavily mineralized travertines in western Turkey (Bernasconi et al. 1980), where it is associated with several oxides and sulphides of antimony, e.g., scorodite and stibnite. Average sediments are enriched in arsenic relative to igneous and metamorphic rocks, because they contain greater quantities of minerals with high-adsorbed arsenic loads (Selinus 2005). Argillaceous deposits have a broad range of As concentrations with a typical average of around 13 mg/kg (Ure and Berrow 1982). The higher values reflect the larger proportion of sulfide minerals, oxides, organic matter, and clays present.

The spatial variability of As coincided with the soil parent materials, which indicated that the As concentration was mostly determined by natural factors.

High Cd concentrations were mainly located in the eastern part of the study area that coincides with the results on Table 6. Comparison of the means indicated that soils from alluvium, andesite and tuff areas have the highest Cd concentrations among all rock types, and these rocks are mainly distributed in the eastern belt of the study area (see Fig. 3).

Soil quality assessment based on pollution indices

Evaluation of soil quality was performed for 87 soil samples according to Canadian soil quality guidelines for the protection of environmental and human health (CCME (Canadian Council of Ministers of the Environment) 1999).

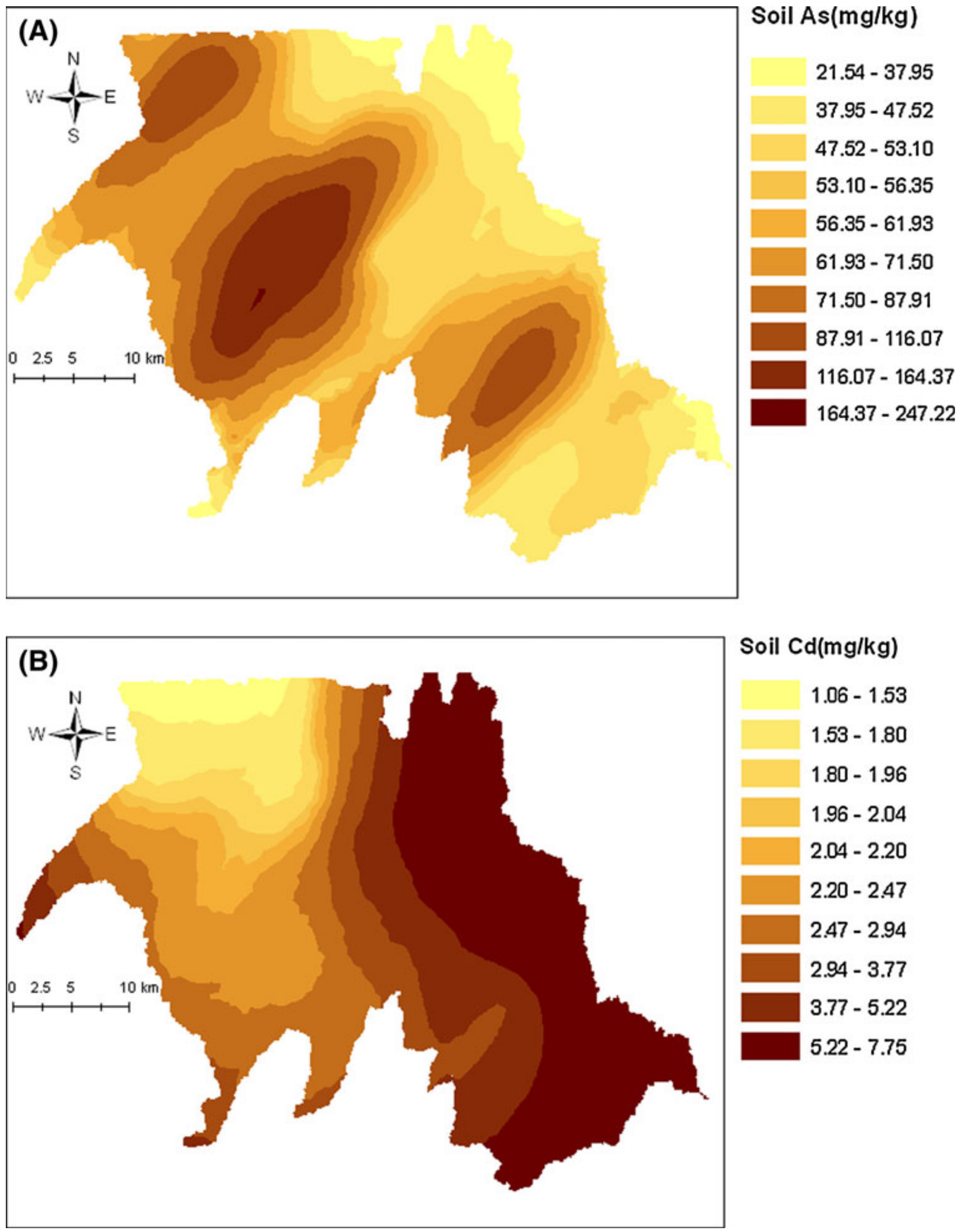

Fig. 4 Filled contour maps of soil heavy metals (As and Cd)

Table 7 Descriptive statistics of the soil contamination indices

Heavy metal	PI-mean	PI-Std.	PI-Max.	PI-Min.	Single-factor pollution index (% of total area)				Comprehensive pollution index (P_n)	Geo-accumulation index		
					No	Low	Moderate	High		Min.	Mean	Max.
As	7.035	4.352	20.602	1.795	0	0.58	3.17	96.24	15.394	6.780	5.008	3.259
Cd	2.349	1.536	6.725	0.756	4.13	38.48	18.53	38.85	1.896	5.387	3.613	2.235

According to Canadian standard, PIs of As and Cd were more than 1. It is notable that 96% of the total area were highly contaminated by As. The PI value of Cd ranged from 0.756 to 6.725 and 57% of the area in the studied region were moderately or heavily contaminated by Cd (Table 7). The minimum, maximum and mean values of I_{geo} for each element were shown in Table 7. The average I_{geo} indicated that the pollution degree of arsenic was higher than cadmium. The mean I_{geo} (5.008) obtained for As was more than 5 and suggested that tested soils fell into class 6 (extremely contaminated). The cadmium I_{geo} showed heavily contaminated with a mean of 3.613, revealed that nearly all the samples examined fell into class 4, ranging from 2.235 to 5.387(heavily contaminated).

The Nemero's pollution index (P_n) for all the soil sampling points was calculated (Table 7) to show the relative magnitudes of soil pollution. Higher value for P_n, indicates more serious pollution. The P_n value obtained for arsenic was 15.394, revealed that pollution degree fell into class 4 pointing to heavily contaminated area. For cadmium, calculated P_n (1.896) fell into class 2 showing the tested soils are low contaminated by Cd. Since the concentrations of elements (As and Cd) in the majority of the samples were higher than their standard values, this can be a harmful health risk to local residents. In a previous study, arsenic-related health symptoms such as skin lesions and keratosis were demonstrated among residents of polluted villages in the Kurdistan province (Mosaferi et al. 2008).

Conclusions

This study evaluated the effects of land use, rock type and soil properties on As and Cd concentrations in soils, using correlation and ANOVA analysis. The analysis showed that land use had no significant effect on As and Cd concentrations. It revealed that rock type has no significant effect on As concentrations, but there is significant difference between Cd concentrations among rock types. The results show a high correlation of As and Cd with the percentage of soil granulometric fraction. So, there is a strong relationship with the mineralogical structure of the study area. Other factors may also have influenced soil geochemistry, such as different rock types, climate, etc.

The studied heavy metal (As and Cd) concentrations are higher than guideline values. Thus, these elements can threaten food safety and human health. These results can be helpful for improving agriculture and the natural ecosystem in the region. As shown in this study, it is still a challenging task in environmental geochemistry to separate all of the factors controlling soil geochemistry and to investigate their influences on the regional scale.

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