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Spatial Variability of as and Cd Concentrations in Relation to Land Use, Parent Material and Soil Properties in Topsoils of Northern Ghorveh, Kurdistan Province, Iran

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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 agricultural soils. A total of 87 surface (0 to 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).

Key words: Heavy metal · Parent material · Land Use · Soil contamination

INTRODUCTION

Soil pollution is an important environment issue [1, 2]. Among numerous soil pollutants, heavy metals are especially dangerous due to their toxicity and persistence in the environment and public health concerns [3, 2]. Metals can be transferred from soil to the other ecosystem components, such as underground water or crops, and can affect human health through the water supply and food web [2].

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. The main factors affecting As concentration in soils are rock composition and human activities such as mining, smelting, combustion of fossil fuels, pesticides and herbicides applications. The parent material is the most important factor affecting As content. Other factors are soil texture and soil organic matter content [4].

Another toxic heavy metal is Cadmium (Cd) that warning of health risks from Cd pollution were issued initially in the 1970s [5]. 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 [6]. 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 [7].

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 [8]. The methods of geostatistics use the stochastic theory of spatial correlation both for interpolation and for apportioning uncertainty [9]. Moreover, geostatistics has been successfully applied in investigating and mapping soil pollution by heavy metals, in recent years [10-18]. A main contribution of a semivariogram is that it reveals the spatial change properties of sampled values that belong to the regional variables.

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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.

MATERIALS AND METHODS

Study Area: 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 1352 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 to 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 Figure 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 2) 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 [19].

Soil Sampling and Laboratory Analysis: Eighty-seven topsoil samples (0 to 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 far 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

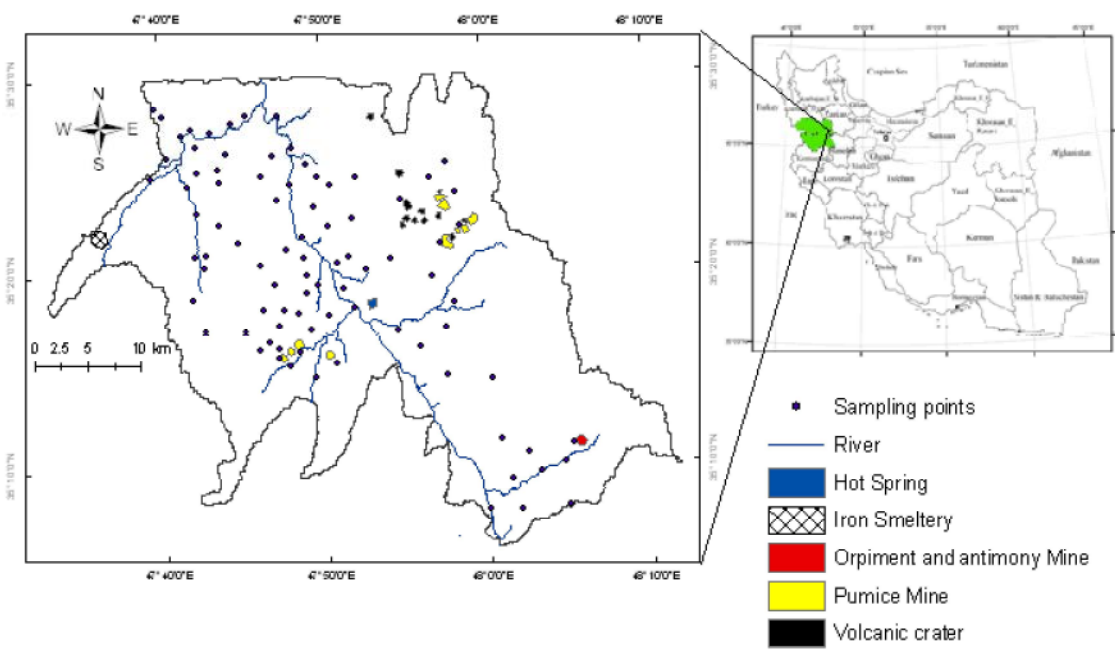

Fig. 1: Location of the study area with the 87 sampling points

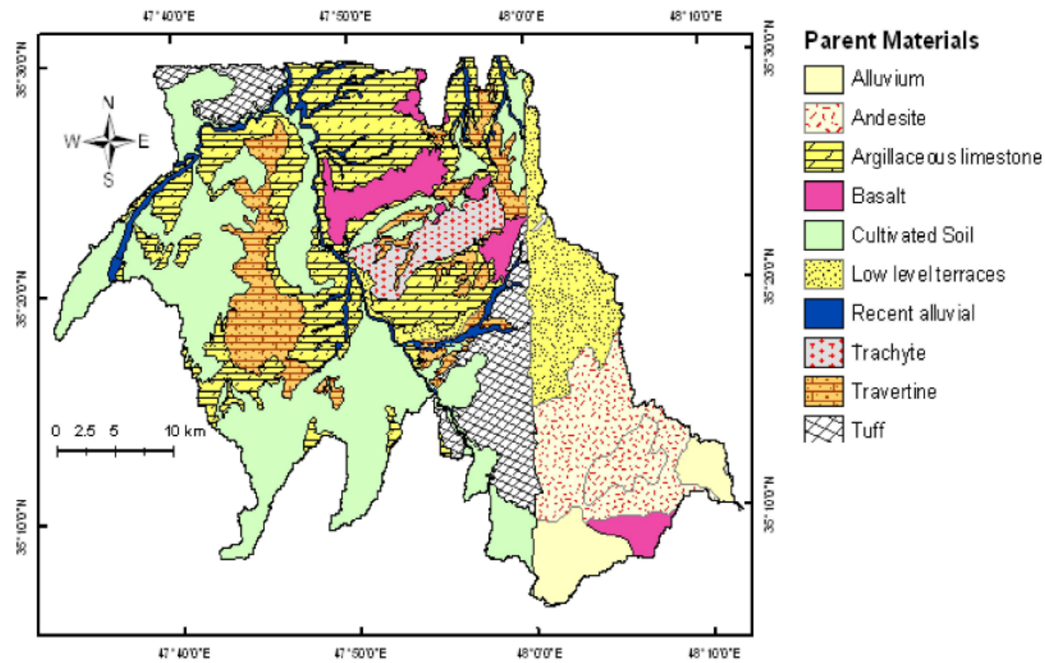

Fig. 2: A simplified geology map of the Northern Ghorveh

were analyzed in triplicate. A global positioning 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 ground 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 [20]. Arsenic and cadmium were measured by graphite furnace atomic absorption spectrometry (VARIAN 220A). The soil organic matter was determined by the Walkey–Black method [21]. The soil pH was determined by a pH meter with a soil/water ratio of 1:2.5. 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 to 106.4% and 89.5 to 107.4%, respectively.

Statistical and Geostatistical Analysis: Some fundamental statistical parameters, which are generally accepted as indicators of the central trend and data spread, were analyzed, including the mean, standard deviation, variance and maximum and minimum values. 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). Often there will be many possible explanatory variables in the data set, and with a stepwise regression method, the explanatory variables can be considered one at a time. The one that explains the most variation in the dependent variable will be added to the model at each step. The process stops when the addition of an extra variable will make no significant improvement in the amount of variation explained.

The regression equation is:

$$Y = b0 + b1\ X1 + b2X2 + ... + bnXn, \quad (1)$$

Where Y represents the dependent variable and X is the independent variable. The values b_0, b_1, b_2 …b_n are called the regression coefficients and are estimated from the collected data by a mathematical process called least squares, explained by [22].

Geostatistics uses the technique of variograms to measure the spatial variability of the recognized variable and to provide the input parameters for the spatial interpolation of kriging [8]. Kriging has been widely used as an important interpolation method at different scales, especially in soil pollution [23]. The semivariogram γ(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 [24]:

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

Where Z(xi) represents the measured value of the soil property at location of xi, 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. By fitting the appropriate variogram model, the distance-dependent coefficients can be estimated and graphically interpreted. 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.

The statistics of the differences between the measured and predicted values at the sampled points is often used as an indicator of the performance of an inexact method [25]. 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) [26].

The statistical analysis was performed using Microsoft Excel (Version 2003) and SPSS (V.15) software package (SPSS Inc., Chicago USA) for Windows. Geostatistical analysis and spatial distribution using ordinary kriging were performed with GIS software ArcGIS V.9.2 (ESRI Co, Redlands USA).

RESULTS AND DISCUSSION

Descriptive Statistics: The main soil properties and heavy metals (As and Cd) in the soil are summarized in Table 1. The average values for the seven soil properties were 22.197%, 0.928%, 8.379, 46.172%, 42.152%, 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 1 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. The As and Cd concentrations were normally distributed after log normal transformation.

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 2). 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 represented in Equations 3 and 4 indicate that the As was mainly affected by soil sand percentage, and Cd was mainly affected by soil silt percentage.

$$Y_{AS(mg/kg)} = 140.564 - 1.216 X_{Sand(\%)} \quad (3)$$

$$Y_{cd(mg/kg)} = 8.232 - 0.117 X_{Silt(\%)} \quad (4)$$

Table 1: Statistical summary of heavy metals concentrations (mg/kg) and soil properties

	As	*Cd*	*$CaCO_3$%*	*OM%*	*pH*	*Sand%*	*Silt%*	*Clay%*	*CEC[b]*
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
CV(%)	61.86	63.44	49.74	44.86	2.02	30.13	24.54	60.54	23.92
Guide Value[a]	12	1.4	-	-	-	-	-	-	-

a Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health

b CEC: Cation Exchange Capacity(cmol+/kg)

Table 2: 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							
CaCO3%	-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

*p<0.05; ** p<0.01; OM: organic matter; CEC: Cation Exchange Capacity(cmol+/kg)

Table 3: 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

Geostatistical Analysis: The attributes of the semivariograms for each heavy metal in the soil are summarized in Table 3. The experimental semivariogram depicts the variance of the sample values at 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 [27]. 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 Figure 3. As and Cd concentrations in the four land uses were compared using one-way ANOVA (Table 4). 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 highest in irrigated farming, followed by dry farming and rangeland, and they were

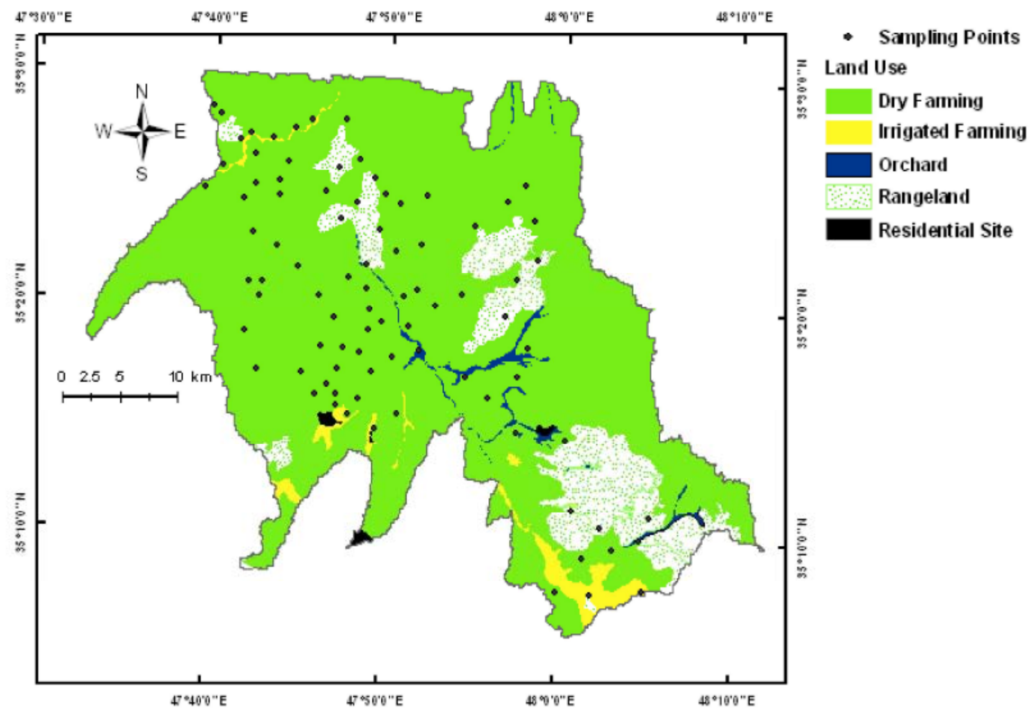

Fig. 3: Land use map of the study area

Table 4: 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 $p<0.05$

Table 5: ANOVA statistical results of the As and Cd concentrations among the eight parent materials Means with the same letter are not significantly different at $p<0.05$

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		

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 [28]. 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. Because As and Cd concentrations are high regardless of the land use, the As and Cd are likely of geological origin.

Heavy Metals Variations among Rock Types: Samples were classified based on their underlying rock types (Figure 2), and the mean comparison of As and Cd concentrations in topsoils in each rock-type area was performed using one-way ANOVA (Table 5). 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

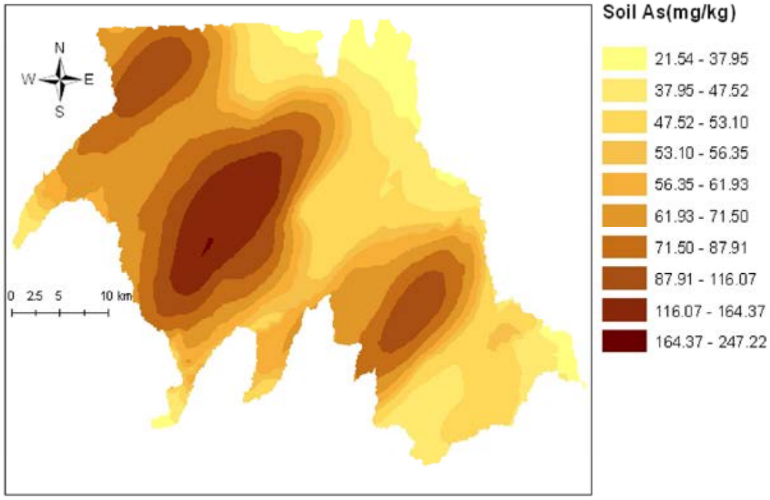

Fig. 4a: Filled contour map of soil As

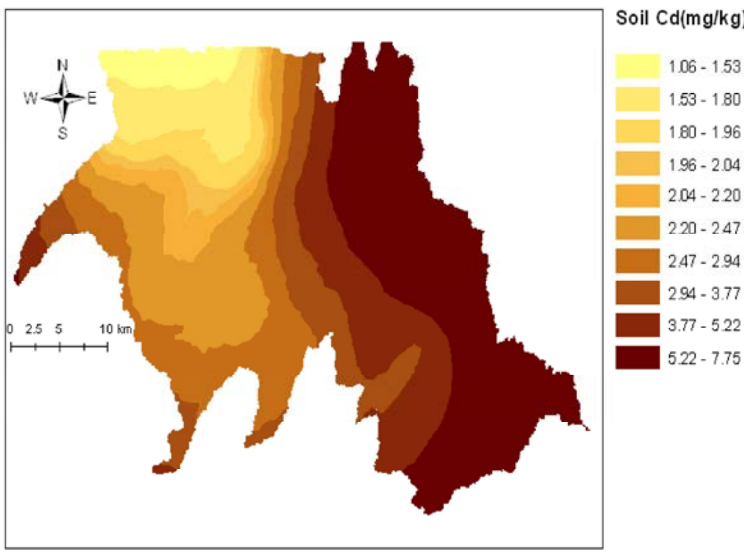

Fig. 4b: Filled contour map of soil Cd

and alluvial deposit areas 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 [29, 30]. 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 [31].

As shown in Table 5, 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 and 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 Figure 4a and 4b. 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 (Figure 1), there is an orpiment and antimony mine in the eastern part of the study area. Orpiment (As_2S_3) is a common monoclinic arsenic sulfide mineral that is found worldwide. It occurs as a sublimation product in volcanic fumaroles, low temperature hydrothermal veins and hot springs and as a byproduct of the decay of another arsenic mineral, realgar.

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 wide range of elements. Arsenic is often a significant component in deposits from hot springs [32]. Arsenic is an important component of the heavily mineralized travertines in western Turkey [33], where it is associated with several oxides and sulphides of antimony, e.g., scorodite and stibnite. 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 coincide with the results on Table 5. 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 Figure 2).

CONCLUSIONS

This study evaluated the effects of land use, rock type and soil properties on soil As and Cd concentrations, 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. It can be assumed therefore that there is a strong relationship with the mineralogical structure of the study area. It is expected that other factors may also have influenced soil geochemistry, such as different degrees of mineralization and metamorphic processes of bedrocks.

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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