RESEARCH ARTICLE

• Arch Hyg Sci 2018;7(4): 303-311
• Journal Homepage: http://jhygiene.muq.ac.ir

Spatial Distribution of Arsenic under the Influence of Chemical Fertilizers Using Geostatistics in Eghlid, Fars, Iran

Parvin Sabet Aghlidi[a], Mehrdad Cheraghi[a]*, Bahareh Lorestani[a], Soheil Sobhan Ardakani[a], Hajar Merrikhpour[b]

[a]Department of the Environment, Hamedan Branch, Islamic Azad University, Hamedan, Iran.
[b]Department of Agriculture, Sayyed Jamaleddin Asadabadi University, Asadabad, Iran.

***Correspondence** should be addressed to Dr Mehrdad Cheraghi, **Email:** cheraghi_md@yahoo.com

A-R-T-I-C-L-EI-N-F-O

Article Notes:
Received: Jun 6, 2018
Received in revised form: Nov 7, 2018
Accepted: Nov 15, 2018
Available Online: Nov 25, 2018

Keywords:
Cokriging,
Geostatistics,
Agricultural Fertilizers,
Arsenic,
Eghlid,
Iran.

A-B-S-T-R-A-C-T

Background & Aims of the Study: The aim of this study is spatial distribution of arsenic (As) under the influence of chemical fertilizers using geostatistics in city of Eghlid, Iran.

Materials & Methods: In this descriptive study, spatial distribution of arsenic was randomly investigated in 100 soil samples and its content was measured by ICP-OES. Spatial distribution of As and geostatistics were studied by ArcGIS software. Data distribution normality was performed by Kolmogorov-Smirnov test; and then Pearson correlation coefficient was used for correlation analysis.

Results: The mean concentration of As was 1.85 mg/kg in the studied area and its change range was 2.08 mg/kg with the minimum and maximum concentration of 0.90 and 2.98 mg/kg respectively. Since the mean concentration of this element was estimated equal to 5 mg/kg in the world's soil, the mean concentration of As was lower than its global value and higher than the qualitative standard in the studied area. Also, the correlation of As with lead (Pb) was 0.406 which was significant at the level of 99%. Therefore, lead was used as the auxiliary data for As zoning. The results of the geostatistics, cokriging method showed that the highest precision due to the lower error of RMSE and RMSS (RMSE = 0.001, RMSS = 1.052), and thus map of spatial distribution of As was provided on this basis.

Conclusions: Results indicated that the dense agricultural soils located in the center of studied area had the highest concentration of As, but the northwestern poor agricultural soils had the highest concentration of As in studied area.

Please cite this article as: Sabet Aghlidi P, Cheraghi M, Lorestani B, Sobhan Ardakani S, Merrikhpour H. Spatial Distribution of Arsenic under the Influence of Chemical Fertilizers Using Geostatistics in Eghlid, Fars, Iran. Arch Hyg Sci 2018;7(4):303-311

Background

Soil stability, fertility and environmental health in conventional agricultural systems have always been the subjects for debate; and researchers have considered the sustainable agriculture and combined use of fertilizers as the most important ways to overcome this problem and the ways to reduce chemical substances. In these systems, a percentage of plants' fertilizer needs are fulfilled by chemical fertilizers and the other percentage by organic fertilizers such as manure or green fertilizer (1). However, in addition to soil fertilization, fertilizers also cause environmental pollution (2) because disposal of urban and industrial waste, car emissions, mining activities and agricultural practices lead to accumulation of metals in soils (3). Unlike organic pollutants, metals are not chemically decomposable. These metals contaminate soil and water resources in various ways such as sewage sludge, chemical fertilizers, and sedimentation of materials resulted from plants and mines, urban wastewater, and solid waste burying in inappropriate areas. Therefore, it takes decades to eliminate accumulation of heavy metals in the soil by existing methods. Despite the fact that these pollutants are not toxic in some places, accumulation of heavy metals in soil and water will be harmful (4). Heavy metal pollution is a serious threat to human health by entering into the food chain and also a threat to environmental security through penetration into the groundwater. In general, sources of heavy metals in soil include natural resources and human input; therefore, researchers have paid attention to effects of agricultural practices on accumulation of elements especially in arable soil due to potential of transferring heavy metals through agricultural products to humans and animals (5). Arsenic is one of these metals as an unnecessary element for plants and animals and it pollutes the environment through natural resources (geological activities, volcanoes) and artificial sources (use of insecticides, herbicides, etc.) (6). Arsenic is one of important environmental pesticides which can be accumulated in plants and animals and is transmitted to humans through the food chain (7). This toxic element causes toxicity if it is transmitted to parts of plants, which are eaten by humans and livestock, through soil at concentrations greater than 10 µg/g (8). As a result, awareness of spatial distribution of this element in agricultural soils and consequently the fertilizer recommendations based on their amounts agricultural lands is a fundamental task in preventing agricultural land pollution through accumulation of these elements as well as correction of existing situation. In fact, a precise and sustainable agricultural system requires creating a database of regional soils in terms of heavy metal concentration and physical and chemical properties of soils to be able to help them with the aim of better crop management and healthier and further agricultural production (9). Therefore, the present study investigated the spatial distribution of As under the influence of chemical fertilizers using geostatistics in Eghlid region.

Data collection is very expensive for production of necessary precision agricultural maps; hence, development of modern interpolation techniques has largely solved this problem. In fact, we can achieve proper and principled cultivation management by creation of spatial distribution maps of concentration based on the accepted standards. Therefore, the interpolation techniques such as directional inverse distance weighting (IDW), Kriging and radial basis functions are widely used in soil research and contamination mapping (10).

Aims of the study:

The purpose of this study was spatial distribution of As under the influence of chemical fertilizers using geostatistics in city of Eghlid. The present study also used various kriging methods with the highest precision under the influence of chemical fertilizers for As spatial distribution.

Materials & Methods

Study area

Eghlid County is one of the northern counties of Fars province of Iran. Eghlid City is the capital of this county. Population of this city was 93763 based on the census of 2016. This county is one of the mountainous and green areas of Fars with cold and winter weather. Eghlid County with an area of 7054 square kilometers accounts for about 7.5% of total soil area of Fars province. This county has two urban regions namely Eghlid and Sedeh, three districts, nine small villages, and eighty villages. 56803 (60%) out of population of

93975 live in urban areas and 35159 people (40%) in rural areas. Eghlid County is at geographic range of longitude of E 52° and 55' and latitude of N 3° and 13'. It is limited to Abadeh County from the north, Marvdasht and Sepidan Counties from the south, Khorrambid County from the east, and Isfahan and Kohgiluyeh and Boyer-Ahmad Provinces from the west (Figure 1). Eghlid County is one of the mountainous regions and highlands of Iran, and Eghlid city is the second highest city in Fars province after Safashahr, and the sixth highest city in Iran. Its highlands are the continuation of Zagros Mountains and its maximum height is 3943 m above sea level namely name of Bell Mount in the south of Eghlid. In addition to production of crops, a variety of horticultural products is produced by farmers in this county and they account for 8581 hectares of cultivation based on the latest statistics. The main horticultural products are apple, almond, grape, and walnut. Other horticultural products such as apricot, cherry, sour cherry, peach, nectarine, peacherine, different types of plum, different types of tomato, quince, pear, persimmon, pomegranate, berry, fig, Russian Olive and saffron are also produced by gardeners.

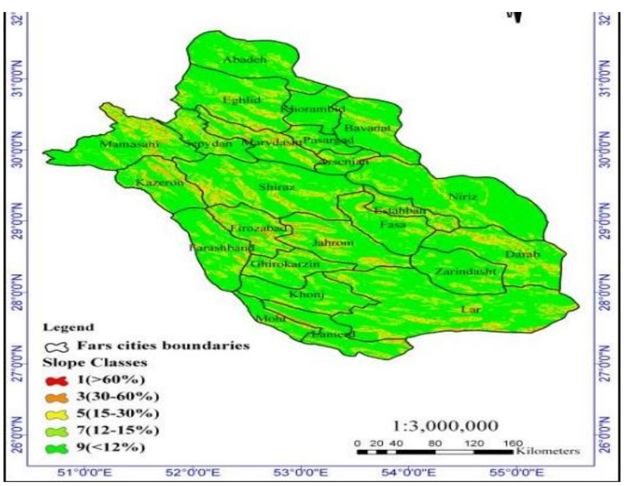


Figure 1) Location of studied area

Chemical analysis

100 air-dried soil samples were passed through a 2-mm sieve. Extraction was done to determine the total concentration of heavy metals in the soil by HNO_3 (10). Total concentration of metals was measured by ICP-OES (ES-710, Varian, Australia). Soil texture was measured by hydrometric method, calcium carbonate and organic matter through titration laboratory method. pH of samples in the saturated soil was measured by pH meter 774; and percentages of sand, silt and clay were measured by hydrometry method for all samples. (11)

Statistical description

Descriptive statistics of data were taken to examine how they were distributed and to obtain a summary of necessary data. Frequency distribution of data is significantly important due to its impact on estimation by geostatistical methods. The presents study investigated frequency distribution by indices namely the mean, median, standard deviation, skewness and kurtosis. In order to perform statistical analyses, samples should follow a normal distribution. Kolmogorov-Smirnov test was done to verify normal distribution of data. Pearson correlation coefficient was used to analyze correlation between heavy metals and physical and chemical parameters in the surface soil.

Geostatistical analysis

Unlike classical methods, geostatistical methods consider location of regions and their relationships and have higher effectiveness in analyzing distribution of heavy metals. These methods are able to perform timely and spatial modeling to describe regional variables by taking into account structural and random variability components. These methods are based on estimation of unknown amount of spatial variable z as a random number with a certain probability distribution at a desired studied region. In the geostatistical method, structure analysis of spatial variations of variables is carried out using a variogram. Variogram shows distance variation or variation structure of a particular variable and is among basic Geostatistical tools for investigating spatial variation of soil properties. Variogram can be calculated by Equation (1).

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

where

$\gamma_i(h)$: Semivariogram

N(h): Number of pairs of samples that are separated by distance h.

Z(Xi): z point in location x

Z(Xi+ h): Location of z point in distance h

Spatial correlation analysis is based on the variogram structure which determines existence of spatial dependence among soil variables. Variograms are used to determine degrees of correlation and range of spatial dependencies. Each variogram can be described with three parameters namely Nugget effect, ceiling and domain (12,13).

The present study used different methods of Kriging in ArcGIS software in order to study spatial variations and estimate concentration of heavy metals. Consideration of higher weighting to the nearest sample and allocation of smaller weights to samples with greater distance from estimation site is one of the ways for correction of identical sample weighting. Statistical expression of such weighting approach covers weighting based on the inverse distance to estimation point according to the following Equation.

$$Z^*(X_0) = \frac{\sum_{i=1}^{n} \frac{1}{d1} z(x1)}{\sum_{i=1}^{n} \frac{1}{d1}} \quad (2)$$

Where d1 is distance between estimation point and each of its neighboring samples. $z(x1)$ is values of samples located in the neighborhood of estimation site. Radial basis functions are a set of precision interpolation techniques and they are among the nonparametric methods. Radial basis function equation is as follows (14).

$$Z^* = Mean \sum_{i=1}^{N} wi \times \emptyset_i \quad (3)$$

where

$\emptyset_i$: Variable value at the point i

wi: Sample weight at the point i

Precision of methods was measured by Mean Absolute Error (MAE) and Mean Bias Error (MBE) as follows.

$$\text{MAE} = \frac{1}{n} \sum_{i=1}^{n} \{|z^*(Xi) - Z(Xi)|\} \quad (4)$$

$$\text{MBE} = \frac{1}{n} \sum_{i=1}^{n} \{z^*(Xi) - Z(Xi)\} \quad (5)$$

In Equations 4 and 5:

$z^*(X_0)$: Estimated value of quantity at an unknown point

λ_i : Weight or importance of sample i

$z^*(X_i)$: Quantity in sample i

Results

Descriptive statistics of studied heavy metals and parameters are presented in Table 1. Mean concentration of As was 1.85 mg/kg with a range of 2.08 mg/kg from maximum concentration of 2.98 mg/kg. The mean concentration of this element was estimated equal to 5 mg/kg in the world's soils. Therefore, the mean concentration of As in the studied area was below its global value and higher than the quality standards. Mean lead concentration was 8.77 mg/kg and its variation range was from maximum concentration of 12.9888 to minimum concentration of 5.11 and 7.77 mg/kg in studied area. Organic matter had a mean concentration of 2.13 mg/kg with a maximum concentration of 2.77 and a minimum concentration of 1.77. Calcium carbonate concentration was 73.05 with a range of 44.02 mg/kg. Other descriptive statistics are also presented in Table 1 indicating that pH of studied soil had a mean of 8.27 and range of variation from 7.21 to 8.99 with about 1.78 lowest variations along with organic matter among the soil parameters. Soil of studied area was neutral to slightly alkaline. Mean percentage of clay in soil was 18.98; mean percentage of Silt was 15.97 and mean percentage of sand was 53.65.

Table 1)Descriptive statistics of soil parameters and heavy metals

Soil factor	Unit	Range	Minimum	Maximum	Mean	Standard	Skewness	Kurtosis
Arsenic	mg/kg	2.08	0.90	2.98	1.85	0.59	0.200	-0.928
Lead	mg/kg	7.77	5.11	12.88	8.77	2.42	0.240	-1.312
Organic matter	%	1.77	1.00	2.77	2.13	0.48	-0.593	-0.642
Calcium carbonate	%	44.02	45.23	89.25	73.05	7.98	-0.017	0.362
pH	-	1.78	7.21	8.99	8.27	0.37	-0.165	-0.069
EC	ds/m	753.00	201.00	954.00	427.15	168.52	1.214	0.907
Sand	%	19.00	58.40	77.40	65.53	4.38	1.034	1.668
Clay	%	12.00	11.20	23.20	18.98	3.72	-0.584	-0.819
Silt	%	8.00	11.40	19.40	15.97	2.19	-0.302	-0.914

Geostatistical analysis

Data with a normal distribution should be used to perform interpolation by ordinary kriging. Therefore, we used Kolmogorov-Smirnov test and presented indicated normality of data. As a result, Pearson correlation analysis was used to examine correlation between studied elements as shown in Table 2. Based on the presented results in Table 2, arsenic and lead have a relatively high correlation at the level of 99 percent; and lead can be used as auxiliary data for zoning of As in Cokriging method.

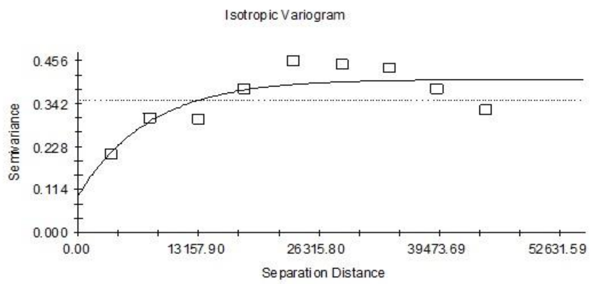
Table 2) Correlation coefficients between studied parameters

		As	Pb	Organic	Ph	$CaCO_3$	EC
As	Pearson Correlation	1					
	Sig (2-tailed)						
Pb	Pearson Correlation	0.406**	1				
	Sig (2-tailed)	0.000					
Organic	Pearson Correlation	-0.115	-	1			
	Sig (2-tailed)	0.254	0.594				
Ph	Pearson Correlation	-0.002	0.068	0.063	1		
	Sig (2-tailed)	0.980	0.504	0.531			
$CaCO_3$	Pearson Correlation	0.067	0.167	-0.004	-0.078	1	
	Sig (2-tailed)	0.505	0.097	0.967	0.439		
EC	Pearson Correlation	-0.169	-	0.195	-0.003	0.017	1
	Sig (2-tailed)	0.092	0.729	0.052	0.977	0.866	

** **Correlation is significant at level of 0.01 (2-tailed).**

Results of isotropic variogram and the best fitted model along with its parameters are presented in Table 3. Figure 2 shows the isotropic variogram of arsenic. Table 4 presents results of evaluated specific and geostatistical methods of Kriging based on R, MAE and RMSE criteria.

Based on results of spatial analysis of obtained variogram (Table 3), it was found that the fitted model to experimental model of As was exponential and had higher R and lower RSS than other fitted models.



Exponential model (Co = 0.0951; Co + C = 0.4082; Ao = 7700.00; r2 = 0.688; RSS = 0.0171)

Figure 2) Isotropic variogram of arsenic in Eghlid

Radius of influence of As variogram (Table 3) indicated that MF index had a spatial correlation to radius of 23,000 km.

Table 4 presents an analysis of spatial correlation of the kriging method by different models (exponential and spherical) for arsenic.

Based on the existing theories, MBE should be close to ideal value of zero and RMSS close to ideal value of 1. Furthermore, the more the RMSE and MAE values are reduced, the more the precision of Kriging method is increased (15). Based on the presented results, among all applied methods for As, the simple Cokriging with exponential model has the lowest values of RMSE (0.001) and RMSS (1.052).

In general, the exponential model in cokriging method had the highest precision due to the lower RMSE and RMSS error values than other models, and thus it was used in drawing a spatial distribution map of arsenic.

Table 4) Isotropic variogram parameters

Model	Nugget Co	Sill Co+C	Range Parameter AO	Effective Range	Proportion C/(Co+C)	R^2	RSS
☐Spherical	0.26630	0.53360	97100.000	97100.00	0.501	0.346	0.0359
☑Exponential	0.09510	0.40820	7700.00	23100.00	0.767	0.688	0.0171
☐ Linear	0.28256	0.42882	44449.6354	4449.6354	0.341	0.318	0.109
☐ Linear to sill	0.28400	0.62600	105400.00	05400.00	0.546	0.318	0.0372
☐Gaussian	0.31700	0.63500	68500.000	18645.4803	0.501	0.172	0.0453

Table 5) Spatial correlation analysis of kriging methods by different models

Name of method	Interpolation method	Mean e	RMSE	Mean Standardized	Root-Mean-Square Standardized	Average Standard Error
Inverse Distance Weighting (IDW)	Spherical	0.005454	0.480423			
Radial Basis Functions (RBF)	Spherical	0.003831	0.480389			
Ordinary kriging	Exponential function	0.006549	0.487434	0.011608008	1.087221058	0.440338697
Universal kriging	Exponential function	0.006549	0.487434	0.011608008	1.087221058	0.440338697
Simple kriging.	Exponential function	0.004385	0.472295	0.011971115	0.948768529	0.495975343
Ordinary cokriging	Exponential function	0.002202	0.464261	0.003430603	1.054638159	0.434212223
Universal cokriging	Exponential function	0.002202	0.464261	0.003430603	1.054638159	0.434212223
Simple cokriging	Exponential function	0.001272	0.445237	-0.005355523	1.052278964	0.424727148

Spatial distribution of arsenic concentration

A cokriging method based on exponential function was chosen as a final method based on the obtained results in preparation of a spatial distribution map of arsenic. The results showed that, arsenic levels in the northwest had the lowest value, but the center to the southeast of studied area had higher As values.

Figures 3, 4, 5, 6, 7, 8 and 9 shows that the spatial distribution of As affected by chemical fertilizers, the land use of studied area, the land use map, the base preparation map, and the climate, erosion, vegetation, and shape maps.

Combination of geological and land use maps of Eghlid indicates that the central dense agricultural lands have the highest concentration of arsenic. However, poor agricultural lands have the lowest concentration of As in studied area.

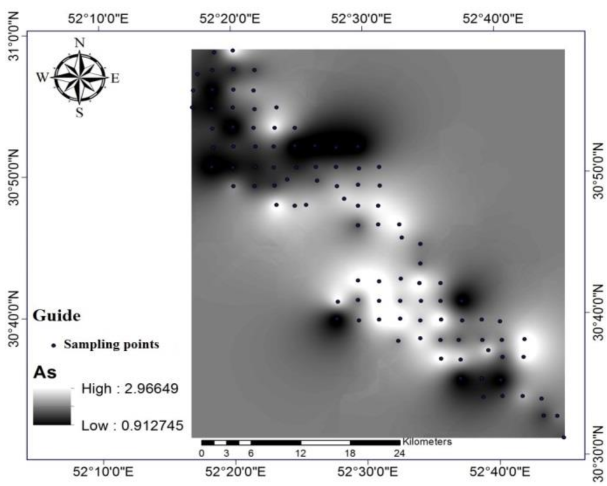


Figure 3) Spatial distribution of arsenic under influence of chemical fertilizers

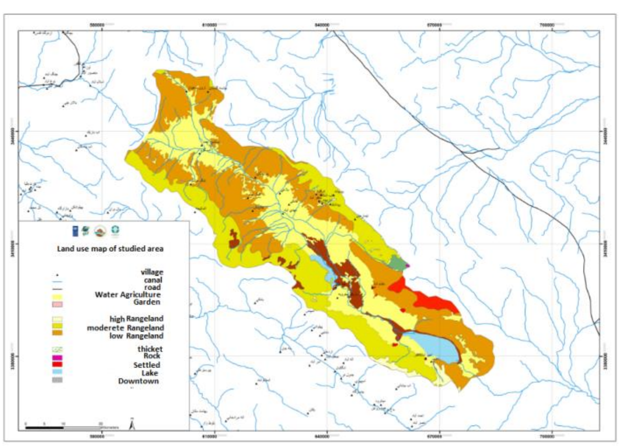


Figure 4) Land use map of studied area

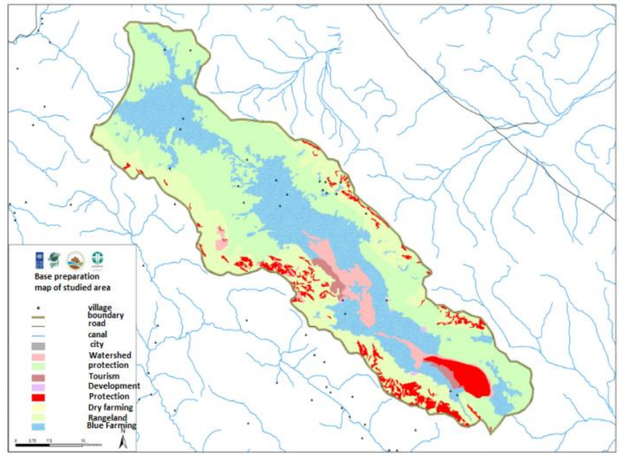


Figure 5) Base preparation map of studied area

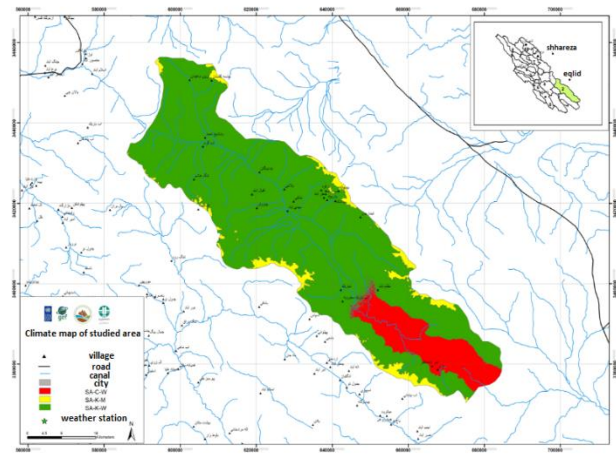


Figure 6) Climate map of studied area

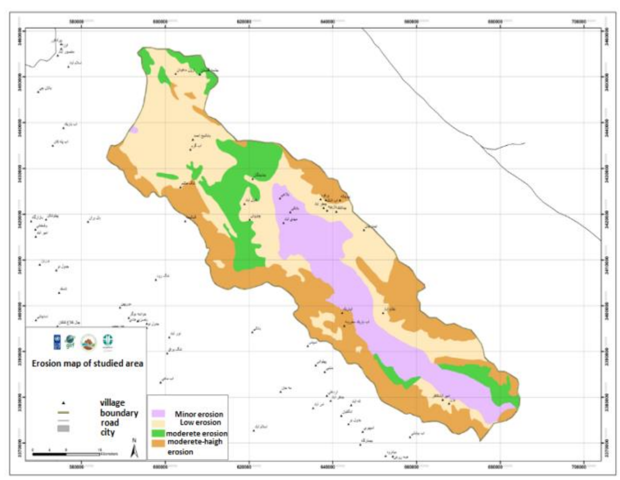


Figure 7) Erosion map of studied area

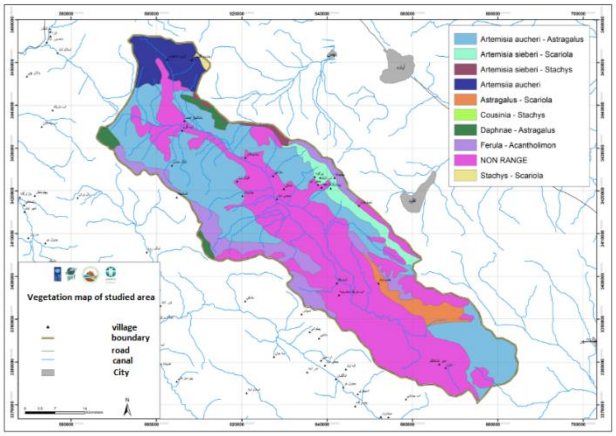


Figure 8) Vegetation map of studied area

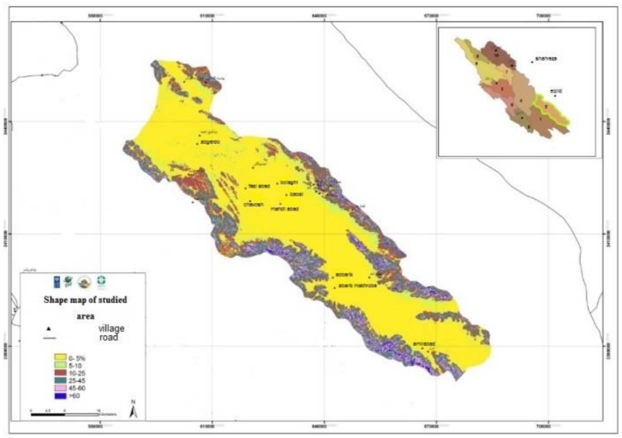


Figure 9) Shape map of studied area

Discussion

The present study investigated the spatial distribution of As affected by chemical fertilizers in Eghlid. Therefore, Kolmogorov-Smirnov test was used to examine normal distribution of data, and then Pearson correlation coefficient was used to analyze correlation after confirmed data normality.

Based on the results of descriptive statistics, the mean concentration of As was 1.85 mg/kg and the range of its changes was equal to 2.08 mg/kg with minimum and maximum concentration of 0.90 and 2.98 mg/kg respectively in the studied area. Since the mean concentration of this element in the world's soil was obtained equal to 5 mg/kg, the mean concentration of As was lower than its global value and above the qualitative standard in the studied area. In the study area, the mean Pb concentration was equal to 8.78 mg/kg and the range of its changes was equal to 7.77 mg/kg with minimum and maximum concentration of 5.11 and 12.99 mg/kg respectively. Furthermore, the results indicated that the correlation of As with lead was equal to 0.406 which was significant at the level of 99%. Therefore, we can use lead as an auxiliary data for As zoning in the Cokriging method due to the relatively significant high correlation between arsenic and Lead.

The results of the geostatistical statistics showed that, among all applied methods, Cokriging method had the highest precision due to lower RMSE and RMSS error than other models, and thus it was used for mapping the spatial distribution of arsenic. Based on the results of compared land use and spatial distribution of arsenic, dense agricultural lands located in the center of studied area had the highest concentration of arsenic, but poor agricultural lands of northwest had the lowest concentration of As in studied area. Based on the zoning of As in the present study, the concentration of As is worrisome in studied area and it is necessary to prevent pollution of surrounding farmlands by prioritization of contaminated areas and cleaning and refining using modern methods such as soil washing and green refinement. Based on the results of the present study, the central and south east of region and then the central regions of northwest are in the priorities of refinement.

Conclusion

Finally, the results showed that the dense agricultural soils located in the center of studied area had the highest concentration of arsenic, but the northwestern poor agricultural soils had the highest concentration of As in studied area. It is suggested performing mine extraction and processing based on the relevant standards and based on organizations' view such as

Environmental Protection Agency in order to prevent further contamination.

Footnotes

Conflict of Interest:

The authors declared no conflict of interest.

References

1. Faraji, S., Rafiei-Al-Hosseini; M., Abbasi-Souraki, A. Impact of individual and combined use of organic, biological and chemical fertilizers on quantitative and qualitative traits of sugar beet. Agricultural Crop Management 2015;17(3):789-800. (Full Text in Persian) Link
2. Kelly JJ, Häggblom MM, Tate RL. Effects of heavy metal contamination and remediation on soil microbial communities in the vicinity of a zinc smelter as indicated by analysis of microbial community phospholipid fatty acid profiles. Biol Fertil Soils 2003 Jul 1;38(2):65-71. Link
3. Atafar Z, Mesdaghinia A, Nouri J, Homaee M, Yunesian M, Ahmadimoghaddam M, Mahvi AH. Effect of fertilizer application on soil heavy metal concentration. Environ Monit Assess 2010 Jan 1;160(1-4):83. Link
4. Yari Y, Momtaz HR, Taheri M. Spatial distribution of some heavy metals in industrial soils of Zanjan. J Water Soil Sci 2016;26(4.1):223-236. Link
5. Shahbazi, A., Soffianian, AR., Afraz, R., Khodakarami, L. Study on spatial distribution of heavy metals namely Cadmium, Copper and Lead in soil and determination of origin of these metals (case study: Nahavand County). J Remote Sens GIS Applicat Natural Resour Sci 2011;2(2):97-108. (Full Text in Persian) Link
6. Gunes A, Pilbeam DJ, Inal A. Effect of arsenic–phosphorus interaction on arsenic-induced oxidative stress in chickpea plants. Plant Soil 2009 Jan 1;314(1-2):211-20. Link
7. Roy P, Saha A. Metabolism and toxicity of arsenic: A human carcinogen. Curr Sci 2002 Jan 10:38-45. Link
8. Karimi, N., Souri, Z. Study on interaction of Arsenic and phosphorus on chlorophyll content and accumulation of Malondialdehyde (MDA) in Isatis cappadocica plant. Plant Physiol 2015;4(11):1-12. (Full Text in Persian) Link
9. Rahimpour F, Abbaspour RA. Zoning the pollution of heavy metal of soil through kriging and radial basis functions (case study: Heris County). Q Geogr Inform 2014;23(91). (Full Text in Persian) Link
10. Journel AG, Kyriakidis PC, Mao S. Correcting the smoothing effect of estimators: a spectral postprocessor. Math Geol 2000 Oct 1;32(7):787-813. Link
11. Farzaneh P, Soffianian AR, Moattar F. Zoning lead, chromium, cobalt, copper and nickel in surface soil of Hamadan city by GIS and geostatistics. Q Human Environ 2011; 9(4):39-48. (Full Text in Persian) Link
12. Cao HF, Chang AC, Page AL. Heavy Metal Contents of Sludge-Treated Soils as Determined by Three Extraction Procedures 1. J Environ Qual 1984;13(4):632-4. Link
13. Weaver RW, Angle JS, Bottomley PS. Methods of soil analysis, microbiological and biochemical properties, part II, Soil Science of America. USA: Wisconsia; 1994. p. 1097.
14. Shi J, Wang H, Xu J, Wu J, Liu X, Zhu H, Yu C. Spatial distribution of heavy metals in soils: a case study of Changxing, China. Environ Geol 2007 Mar 1;52(1):1-0. Link
15. Mohammadi J. Pedometery (Spatial statistics). Iran: Pelk Publications; 2006. (Persian)