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Contamination assessment and spatial distribution mapping of heavy metals in agricultural soils of south Hossein Abad copper index (Neyriz, Iran)

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Key words: Hossein Abad, Heavy metals, Enrichment factor, Geoaccumulation index, Pollution index, Isograde maps.

Abstract

The scope of the study in this research is a part of agricultural soil of Hossein Abad in the vicinity of Abadehtashk and Neyriz. With regard to the role of heavy elements in causing ecological disorders and their effects on the health of the human beings and other creatures, the study of the destructive effects of the heavy elements and the environmental conditions of the soil of that region is of grave importance. In order to check the distribution and mobility of potentially toxic elements, sampling was done in 16 stations in the region. The fine grain clay sample particles smaller than 0.63 micron were chemically analyzed using ICP-OES technique. The comparison of the results of the analysis of the samples with the field samples and valid global standards showed a high concentration of heavy metals such as: Co, Cr, Cd, Ag, Cu, Pb, Ni and As in some stations of the case study. The results of the study show that in this area the index of geoaccumulation for the above mentioned elements is low, the pollution index for the two elements of Cr and Ag is medium and the enrichment factor for the three elements of Co, Ag and Cd is low and for Cr is medium. Also in this area the geoaccumulation index for the elements of Ni, Cu, Pb and As is low, the pollution index is medium and the enrichment factor for Ni and As is medium and for Cu and Pb is low. In Isograde maps the same trend of pollution can be observed. The polluted areas are clearly shown on these isograde maps.

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Introduction

Environmental pollution with heavy metals due to the effects of toxic elements on living organisms are the World's problem (Mac Farlane and Burchett, 2000). Heavy metals because of high stability and accumulation in the soil and eventually entering the food cycle are very important (Loska and Wiechula, 2003).

Since heavy metals accumulate in soil's high levels, they are good detectors for assessment of environmental pollution (Kelly, 1996). For this reason a lot of researches are done on the role of heavy metals, and environmental pollution has been entering the food cycle (Asadi Kapourchal *et al.*, 2011; Davari *et al.*, 2012; Arabi *et al.*, 2011; Babaeian *et al.*, 2012).

Soil contains live and dead organic and inorganic materials. Soils are in the base of human beings' maintenance because they make the rooted plant's growth possible. As soil is used for farming by human beings it is one of the resources and as it can be protected by careful usage of chemical fertilizers it is renewable. However, though it is possible to fertilize the soils by irrigation and applying fertilizers, they can be damaged or destroyed irreversibly by natural factors or carelessness of human beings (Boekhold *et al.*, 1993).

The aims of this research are surveying the spread and rate of the heavy metals' contamination of Hossein Abad mine index on agricultural soils in the region.

Material and methods

Area under study

The scope of this study includes the high mountains in the north which are a part of the Zagros mountain range (Colin *et al.*, 2006).

The highlands of the scope are the limestones which form Jahrom formation. The ultramaphic rocks also have rough morphology which is covered in most areas by debris of the same material. A large part of the northeast of the region and the border between ultramaphic rocks and limestones are lime debris (Mc Bride, 1999).

In the south, the area is limited to alluvial plains which are full of silt, clay and gravels of ophiolitic rocks. The region under study is covered with mountains which are extended from northwest to southwest with a rough topography of high lands and deep valleys (Al-Khashman and Shawabkeh, 2006). In the lower part of the studied region the inhabitants of Hossein Abad earn their living by farming (Lu *et al.*, 2009; Eby, 2004).

In this study the effect of copper mineralization and paragenetic elements on farming soil in the region is surveyed.

Sampling

The sampling of the soil in 16 stations was done to determine the concentration level of the potentially toxic elements and the factors which controlled the mobility.

To do so, all the samples taken from surface were from 0 to 15 cm depth of the soil. To survey the rate of the elements and clarify the local background, a sample was taken from the upper part which was out of the mineralization area (Krauskopf, 1994). The sampling method was systematic sequential method (Farkas *et al.*, 2007). The position of the sampling stations based on satellite images of Google Earth are shown in Fig. 1.

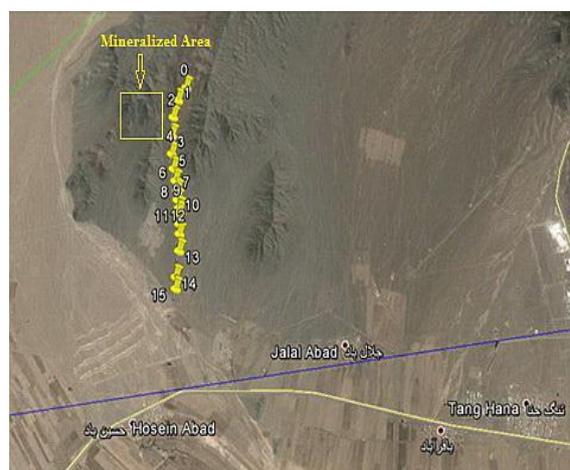


Fig. 1. Location of sampling stations on the Satellite image from Google Earth's output.

Analytical methods

To obtain the pollution rate, some samples were taken from the soil of the area. To prepare the soil samples, the soil was dried at 25-30°C and then sieved. The particles which passed through 230 mesh sieves were sent to the laboratory and ICP-OES analysis method

was done on the samples (Krauskopf, 1994; Farkas *et al.*, 2007).

Results and discussion

The results of the sample soil analysis along with the average and clarke of the elements are shown in table 1.

Table 1. Concentrations of Co, Cr, Cd, Ag Cu, Pb, Ni, As in agricultural soils of southern Hossein Abad copper index (ppm).

Element	Cu	Pb	Ni	As	Co	Cr	Cd	Ag	Zr
Local background	35	16	47	2.8	27	100	0.17	0.25	95
SHA-01	43	15	48	3.3	30	148	0.18	0.24	77
SHA-02	45	19	64	6.6	25	193	0.17	0.25	91
SHA-03	50	18	60	4.6	27	210	0.17	0.24	87
SHA-04	68	22	74	7.2	28	177	0.19	0.36	80
SHA-05	70	21	77	4.7	28	213	0.17	0.2	79
SHA-06	58	19	68	4	28	237	0.16	0.26	74
SHA-07	51	15	86	5.4	25	234	0.16	0.21	77
SHA-08	49	19	84	6.8	25	247	0.17	0.2	81
SHA-09	51	17	73	3.8	27	246	0.16	0.25	80
SHA-10	45	10	93	5.5	24	217	0.16	0.27	83
SHA-11	46	14	89	4.7	24	198	0.17	0.2	77
SHA-12	52	18	87	3.6	26	218	0.17	0.2	79
SHA-13	44	11	93	5	22	214	0.17	0.21	72
SHA-14	47	14	93	4	23	214	0.17	0.21	70
SHA-15	50	12	103	5.7	20	194	0.18	0.27	69
Average	50.25	16.25	77.44	4.86	25.56	203.75	0.17	0.24	79.44
Max	70	22	103	7.2	30	247	0.19	0.36	95
Clarke	70	12.5	75	1.8	7.1	100	0.2	0.07	165
Min	35	10	47	2.8	20	100	0.16	0.2	69

The rate of enrichment and the percentage of the effect of non-natural factors on the distribution of polluting elements in soil is based on the comparison of the concentration of these elements with non-polluted ones from the upper parts (Guo *et al.*, 2012; Papadopoulos and Rowell, 1988). Based on the above measurement the Ag element in stations 4,10 and15 shows the highest concentration which has increased comparing to upper crust of the earth. The highest concentration of Cd is observed in stations 1,4 and 15 which shows an increase comparing to Clarke average and upper crust. The highest rate of Cr is observed in stations 8 and 9. The highest rate of Co is seen in

stations 1,5 and 6. As has the highest concentration in stations 2,4 and 8 which shows an increase comparing to the upper crust of the earth.

The highest concentration of Ni is in stations 10,13,14 and 15 which shows an increase comparing to the clarke average and the upper crust. The highest rate of Pb and Cu was seen in stations 4 and 5. Fig. 2 shows the rate of the changes of the elements under study in the soil of the region. The increase in the concentration of polluting elements in the farming soil of the south of the Hossein Abad copper index (according to the local background) shows the effect of human factors on the

existing pollution in the soil of the region under study (Turekian and Wedepohl, 1961).

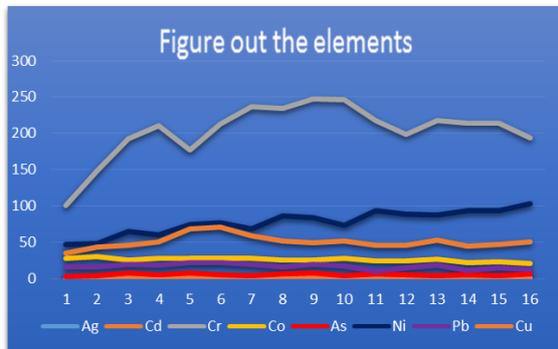


Fig. 2. Line chart elements studied in agricultural soils south of Hossein Abad copper index relative to the local background.

Geoaccumulation index (Igeo)

To better survey the elements, pollution rate in the soil and sediment, the index of geoaccumulation was used. The formula is as follows:

$$I_{geo} = \log_2(C_n \div 1.5B_n)$$

Where C_n is the concentration of element in the samples, B_n is the background value of the element, and the factor 1.5 is used to take into account the

possible lithological variability. The Muller index has seven classes depending on its value (Müller, 1969).

This index is basically used for the soil samples of a place or area. The classification of the sample's limit of the geoaccumulation index is given in table 2 (Müller, 1969). In table 3 the average of the index of geoaccumulation for Co, Cr, Cd, Ag, Cu, Pb, Ni, As is given.

Table 2. The guide to use the index of geoaccumulation according to Muller's classification (Müller, 1969).

I_{geo} Range	I_{geo} Value	I_{geo} Class	Designation of Sediment Quality
$I_{geo} > 5$	>5	6	Highly Contaminated
$3 < I_{geo} < 5$	4-5	5	Most heavily Contaminated
	3-4	4	Pollution Moderateto
$1 < I_{geo} < 3$	2-3	3	severe infections
	1-2	2	Moderate pollution
$I_{geo} < 1$	0-1	1	To moderate noninfectious
	0	0	Non-infected

Table 3. Average of geoaccumulation index for the heavy metals studied in agricultural soils of southern Hossein Abad copper index.

Elements	Cu	Pb	Ni	As	Co	Cr	Cd	Ag
Average I_{geo}	-0.17	-0.6	-0.13	-0.17	-0.68	-0.47	-0.54	-0.67
Commentary	Reduce pollution							

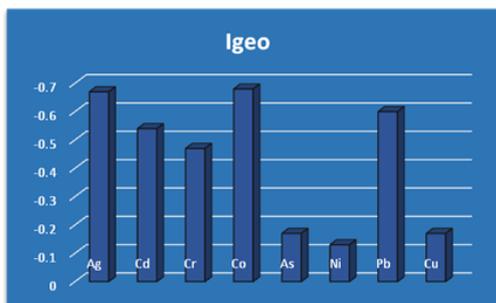


Fig. 3. Column chart of geoaccumulation index for studied heavy metals in agricultural soils in south of Hossein Abad copper Index.

The Pollution Index (PI)

To estimate the essence of an environment the pollution index coefficient is used. The pollution index is shown as the ratio of the concentration of an element in the soil samples to the background rate or the standard rate (control) of the same element in the soil of the region under study (Bloomfield and Pruden, 1980). According to the pollution index three kinds of pollution that is low $PI < 1$, medium $PI < 3 > 1$ and high $PI > 3$ can be observed. In table 4 the pollution index average of Co, Cr, Cd, Ag, Cu, Pb, Ni

and As is given (Müller, 1969; Bloomfield and Pruden, 1980).

Table 4. Pollution index for the studied heavy metals in agricultural soils of southern Hossein Abad Copper index.

Elements	Cu	Pb	Ni	As	Co	Cr	Cd	Ag
Average PI	1.45	1.01	1.68	1.77	0.93	2.1	0.93	1
Commentary	Moderate pollution	Moderate pollution	Moderate pollution	Moderate pollution	Reduce pollution	Moderate pollution	Reduce pollution	Moderate pollution

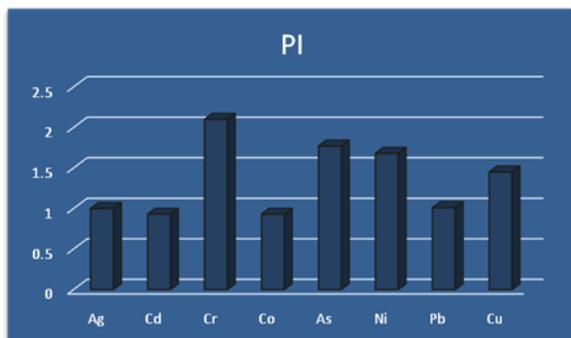


Fig. 4. Pollution Index column chart of studied heavy metals in agricultural soils of southern Hossein Abad copper index.

The Enrichment Factor (EF)

The analysis of the enrichment factor in environmental analyses is one of the important coefficient in the concentration rate of the element under the influence of human and natural factors. The enrichment factor of a certain element in a certain sample is the ratio of the concentration of that element in that sample to the background or standard concentration of the same element which in this research it is calculated based on the background rate. The concentration rate of the background is a certain rate of an element in the soil which is not considered as contamination in the region. The reference element that determines the enrichment factor, is an element with completely geological origins and its rate of distribution in the region is unique (Abraham *et al*, 2008; Eby, 2004). To do so, Alvarez-Ioso suggested non-soluble elements like Ti, Zr, Al and Fe (Semhi and Al-Khirabash, 2010).

In the region under study Zr was chosen as the reference element because of its geochemical essence and minute change and mobility in the geochemical environment (Poppe, 2001; Semhi and Al-Khirabash, 2010).

$$EF = \frac{[Cx \div Cref]_{sample}}{[Cx \div Cref]_{background}}$$

In this case, Cx is the concentration of the element and Cref is the concentration in the reference sample. sample refers to the amount and concentration of the element in the sample and background refers to the concentration of the element in the base. The classification of the enrichment factor limit is given in table 5 (Guo *et al.*, 2012; Papadopoulos and Rowell, 1988).

In table 6 the average of enrichment factor for Co, Cr, Cd, Ag, Cu, Pb, Ni and As is shown.

Table 5. Enrichment factor classification (Müller, 1969).

Commentary	Enriched factor
There has enriched the few	EF < 2
Enriched medium	2 < EF < 5
High enriched	5 < EF < 20
Highly enriched	20 < EF < 40
Enriched extra	EF > 40

Table 6. Average of enrichment factor for the elements studied in Hossein Abad village agricultural soils.

Elements	Cu	Pb	Ni	As	Co	Cr	Cd	Ag
Average EF	1.83	1.28	2.08	3.03	1.07	2.56	1.2	1.15
Commentary	Reduce pollution	Reduce pollution	Moderate pollution	Moderate pollution	Reduce pollution	Moderate pollution	Reduce pollution	Reduce pollution

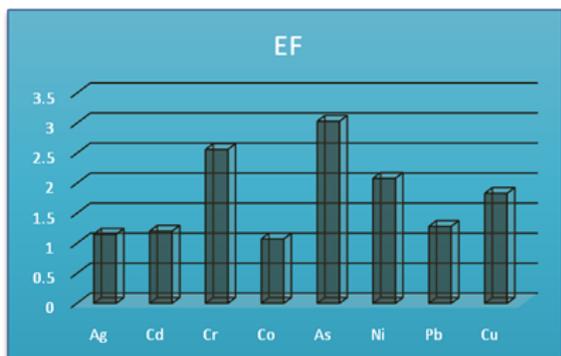


Fig. 5. Column diagram of enriched factors studied in agricultural soils of southern Hossein Abad copper index.

The percentage of Antropogenic Factors (An)

The percentage of Antropogenic Factor in a sample means the percent that the people have been responsible for the introduction of the element in the sample. In environmental analyses antropogenic factors stand the second after enrichment factor in evaluating the rate of concentration of element under

the influence of human beings (Turekian and Wedepohl, 1961). Its formula is as follows:

$$An(\%) = \frac{Mt - \left[M.s \times \frac{Mr}{M.r} \right]}{Mt} \times 100$$

In this formula:

An: The percentage of endogenous human (anthropogenic). **Mt**: The amount of element in the sample. **M.s**: Content reference element in the sample. **Mr**: the element in the reference. **M.r**: the amount of reference element in the reference environment (Chen *et al.*, 2001). According to the caculated Figs. of chemical analysis of farming soil samples in the south of Hossien Abad copper index, the antropogenic factor average of the elements is given in table 7.

Table 7. Average of antropogenic factors for the studied elements in agricultural soils in south of Hossein Abad Copper Index (%).

Elements	Cu	Pb	Ni	As	Co	Cr	Cd	Ag
Average An	43%	-3.83%	51%	68%	11%	58.00%	17%	16%
Commentary	Reduce pollution	Reduce pollution	Moderate pollution	Moderate pollution	Reduce pollution	Moderate pollution	Reduce pollution	Reduce pollution

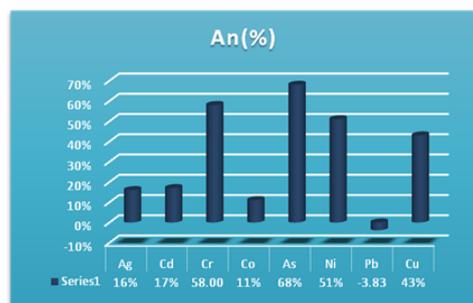


Fig. 6. Antropogenic factors Column Chart of studied elements in agricultural soils of south Hossein Abad copper Index.

Distribution Mapping of elements

After assessing the pollution by caculating geological measures in agricultural soils of Hossein Abad village, it was known that the 8 elements of Co, Cr, Cd, Ag, Cu, Pb, Ni, As had low or medium pollution that shows the pollution potential of these elements in the study region. The distribution of these elements in the study area can be observed by using Isochemical maps. To do so, in this part the Isochemical maps were drawn for these elements and polluted areas or

the areas that could be polluted were determined (Krauskopf, 1994; Farkas *et al.*, 2007).

The important points about isochemical maps in the project are as follow:

1. North is in the top of the maps.
2. The isochemical lines on the maps are in ppm.

3. The concentration limit for the mentioned elements are shown in different colors. In all isochemical maps the pollution will be interpreted as follows: purple and blue shows little or no pollution. Stronger colors show more pollution so that red shows the highest pollution rate.

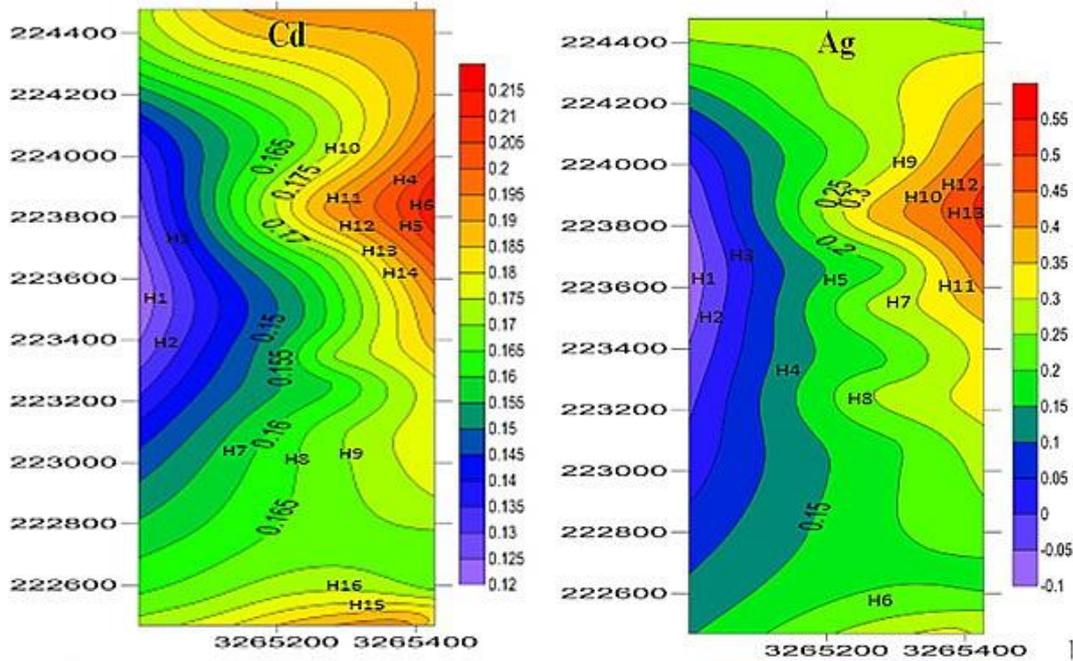


Fig. 7. Distribution maps of Cd, Ag concentration in the studied area.

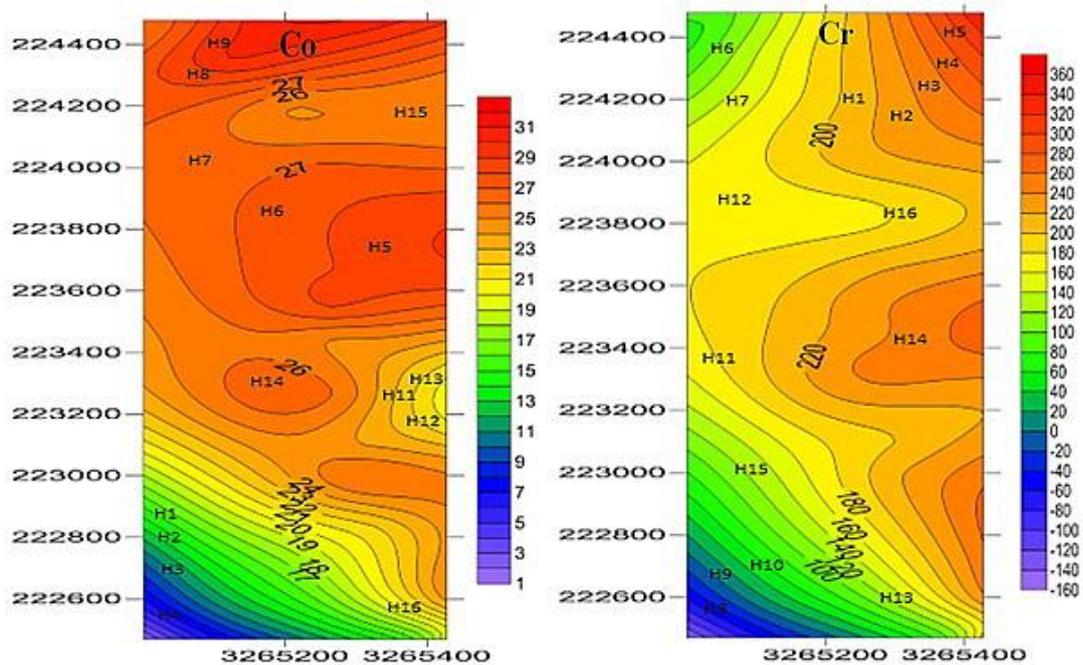


Fig. 8. Distribution maps of Co, Cr concentration in the studied area.

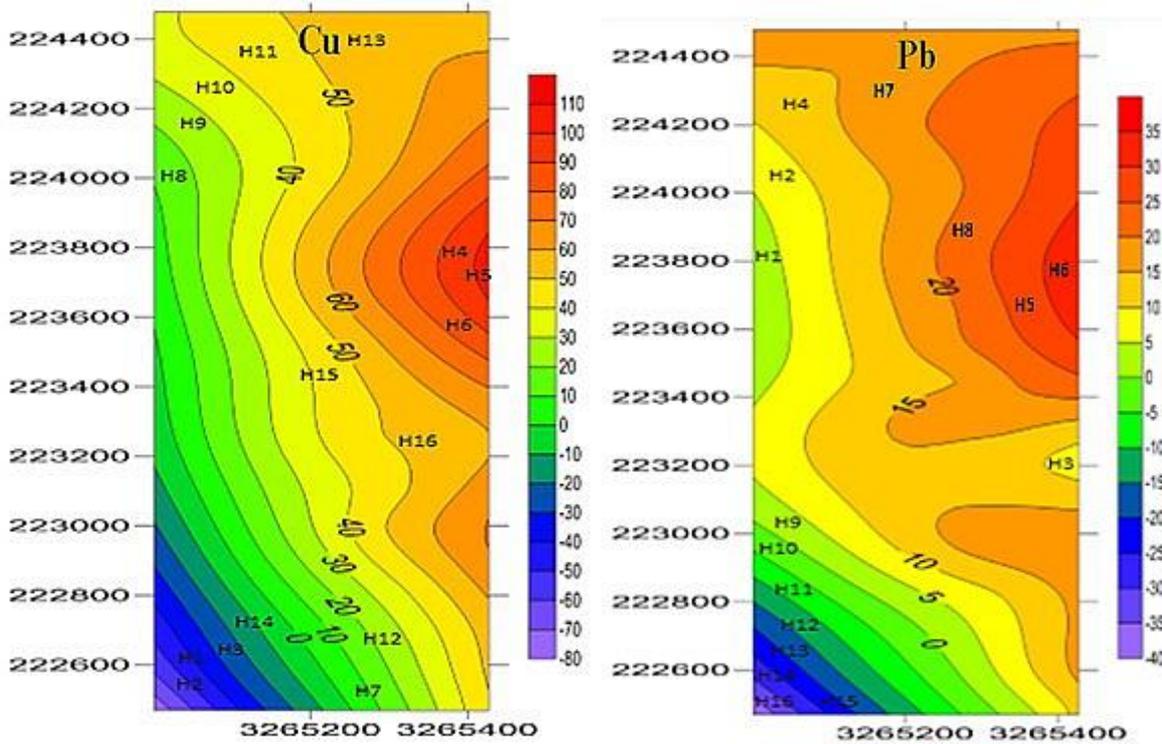


Fig. 9. Distribution maps of Cu, Pb concentration in the studied area.

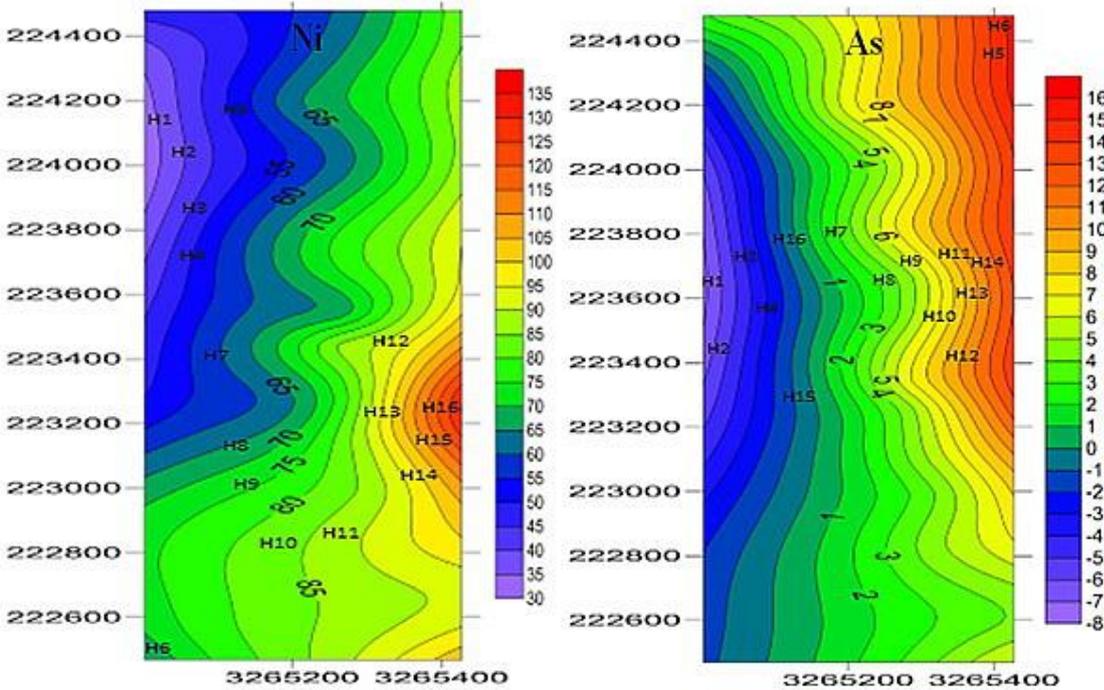


Fig. 10. Distribution maps of Ni, As concentration in the studied area.

The Frequency diagrams

Some antropogenic and geogenic factors have caused an increase in the concentration of the elements in some of the samples. The histogram of the elements

also confirm our claim. So the histograms for each element are surveyed (Lu *et al.*,2009; Eby, 2004).

The abundance distribution curve histograms of elements such as copper, cobalt and chromium are negative and skewness to some extent means that the variation of copper in most of the samples is more than average. The abundance distribution curve histograms for elements such as copper, silver and

cadmium is to some extent positive and their skewness means that the variation of copper in a lot of samples is lower than average. The abundance distribution histograms of nickel and arsenic are normal and their skewness means that the variation of nickel in most of the samples is average.

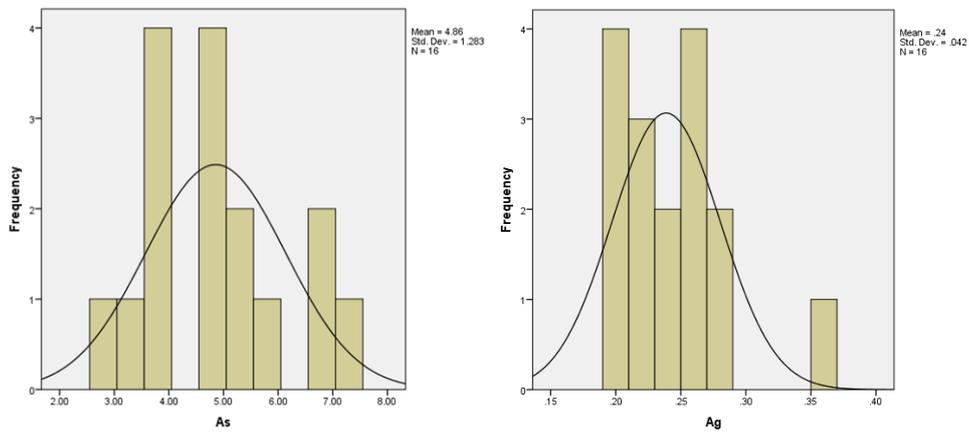


Fig. 11. Frequency distribution histogram for elements of silver and arsenic (ppm).

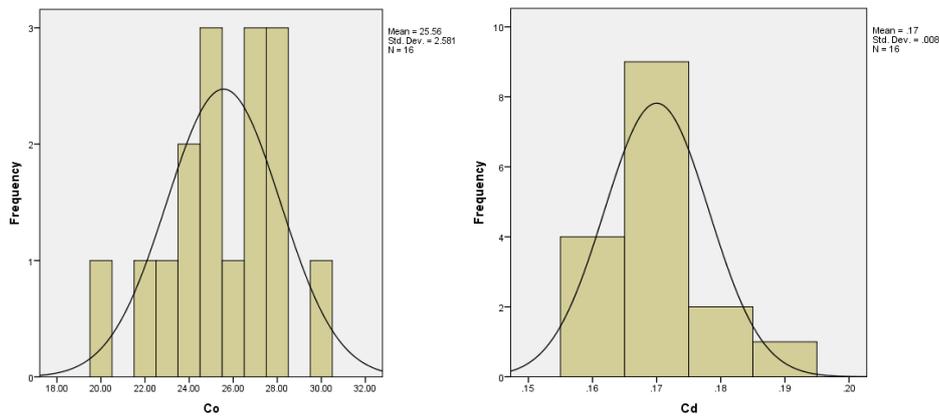


Fig. 12. Frequency distribution histogram for the elements cobalt and cadmium (ppm).

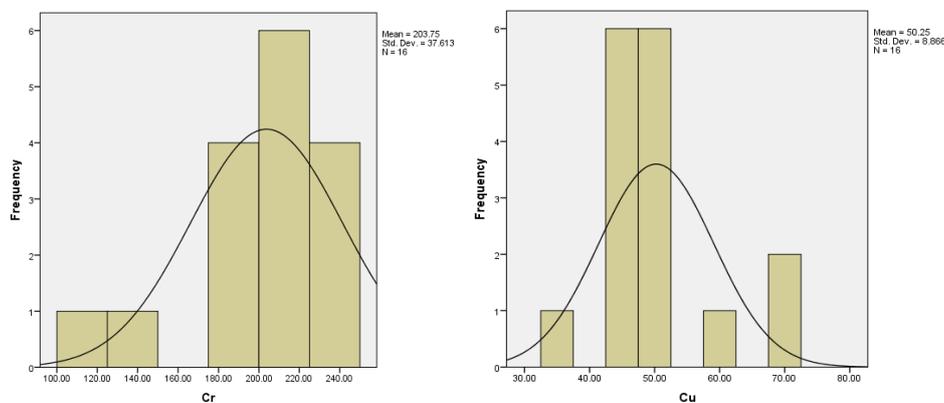


Fig. 13. Frequency distribution histogram for the elements chromium and copper (ppm).

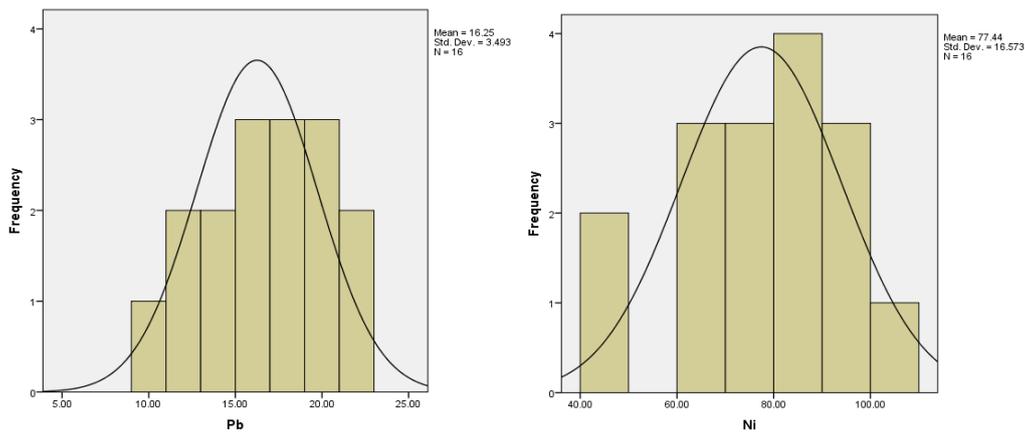


Fig. 14. Frequency distribution histogram for elements of lead and nickel (ppm).

Conclusion

To survey the effect of copper index of Hossein Abad on the agricultural soil of that region the geoaccumulation, pollution and enrichment indicators and antropogenic factor were used. The results show that in this region the geoaccumulation index for the elements Co, Cr, Cd, Ag is low, the pollution index for the elements Cr, Ag is medium and the enrichment factor for three elements of Co, Ag, Cd is low and for Cr is medium. In distribution maps the same pollution trend can be observed, in these maps the position of pollution is completely clarified. In this region the geoaccumulation index for Pb, Cu, Ni, As is low, the pollution index is medium and the enrichment factor for Ni, As is medium and for Cu, Pb is low. The pollution of cobalt, cadmium, chromium and silver is because of their concentration in ultrabasic rocks in the region. They have geological origin (geogenic) and are not under the influence of mining activities at present. As the pollution is low or medium at the moment and there are no mining activities and they are just exploring, the start of the operation of mining can aggravate the pollution by heavy metals in the region. So following environmental standards is necessary.

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