Journal of Himalayan Earth Sciences Volume 56, No. 1, 2023 pp. 33-47

Investigation of the effect of lithological units on the distribution of elements pollution in soils resulting from their erosion (Zozan plain, northeastern Iran)

Shima Raftari[1], Mohammad Javanbakht[2*] and Hanieh Pourjavad[3]

[1]*Department of Geology, Mashhad Branch, Islamic Azad University, Mashhad, Iran*

[2]*Department of Geology, Mashhad Branch, Islamic Azad University, Mashhad, Iran*

[3]*Department of Combat Desertification, Faculty of Desert Studies, Semnan University, Semnan, Iran*

**Corresponding author: mo_ja58@yahoo.com*

Published online: 14/04/2023   Accepted date: 10/04/2023   Submitted date: 04/10/2021

Abstract

The study aimed to investigate the effect of a lithological factor on the distribution of elements in the soil of the surrounding areas. For this purpose, the Zozan plain was selected which is located in the southeastern part of Khorasan Razavi province in the Sangan Khaf region of Iran between 59° 30' to 60° 00' east longitude and 34° 00' to 34° 30' north latitude. Since lithologic and anthropogenic factors control the distribution of elements and soil contamination in a region, this study investigates the effect of these factors, especially lithologic units, on the distribution of pollutants and contamination in the Zuzan Plain. A total of 53 soil samples were taken from the area and analyzed by the inductively coupled plasma method to achieve the research objectives. Investigation of correlations between soil chemical parameters based on Pearson correlation coefficients, cluster analysis, and principal component analysis indicated two main clusters. The results of geochemical studies on the soil of the region showed that the soils of the area have a low enrichment in terms of the mean enrichment factor (EF) compared to calcium elements. The geo-accumulation index (Igeo) indicated that in soils of the Zuzan area, only calcium element in the non-infected class was slightly infected. The soil contamination coefficients showed that the main contamination of the soil was caused by calcium and, to a lesser extent, by chromium and lead. The results of the contamination degree of the samples in the study area indicated that 12 samples were in the acceptable class while the rest of the samples fell in the middle class.

A comparison of the data obtained from the analysis of the rock units around the plain showed that the samples of the Zuzan plain were influenced by natural factors and that the lithogenic units of the area controlled the main distribution of the elements.

Keywords: The Zuzan Plain, Soil pollution, water pollution

1. Introduction

Soil is a mixture of various components including minerals, organic matter, and air (Lao, 1988). The heavy metal pollution of the soil highly depends on human activities such as industrial production, agricultural operations, and the burning of fossil fuels (Pagnanellia et al., 2004). Soil contamination evaluation is far easier than assessing the contamination of water resources due to the soil's relatively stable environment (Meiggs, 1980). Heavy metals in soil usually have complex connections with each other. Important factors such as heavy metal concentrations in rocks and materials, different processes of soil formation, and human factors (e.g., contamination by human activities), determine the relative frequency of heavy metal concentration in the soil (Sun et al., 2010). The Zuzan plain is composed of a variety of rock units with human factors such as rural pollution and agricultural lands being the main causes of soil pollution in this area. Also, in the lack of industrial pollution and other important human factors in this area, we can examine the pattern of lithogenic factors in soil contamination. This plain is located in the east of Iran, in the southeastern part of Khorasan Razavi Province, and between 59° 30' and 60° 00' east longitude and 34° 00' to 34° 34' north latitude. The study area is located 70 km to the west of Khaaf city (the traditional route of Mashhad-Torbat Heydarieh) (Fig. 1).

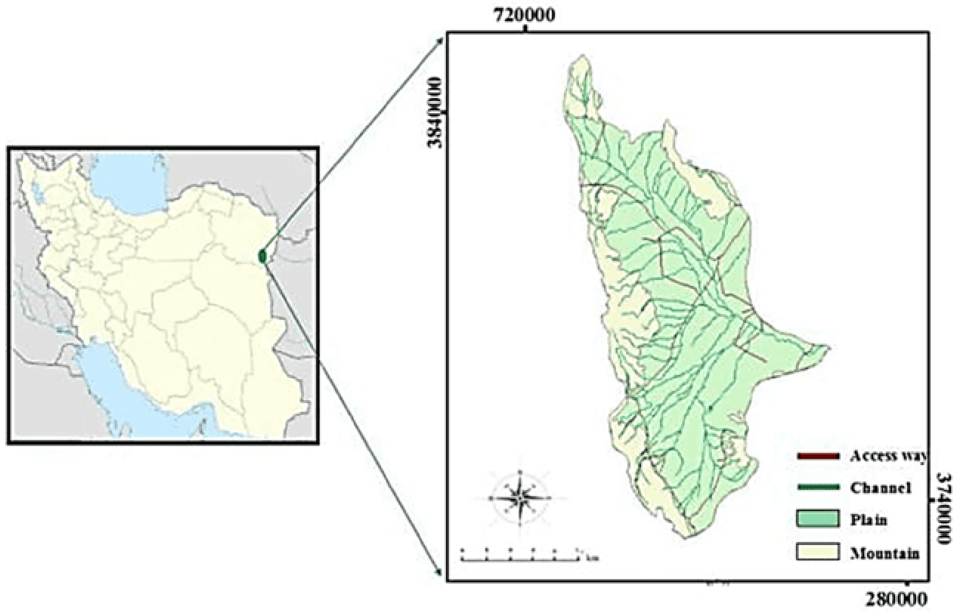

Fig. 1. Geographic location and access routes to the studied area.

2. Geology of the region

The geological map of the Zuzan Plain contains extant outcrops from the Paleozoic to Quaternary, in which there are also some large stratigraphic gaps. All information was provided by the geological map (1:100000) of the Zuzan sheet (Bulorian and Safari, 2005). Regarding the oldest exposed rocks, one can mention the metamorphic complex on the west part of the sheet, which is supposed to be related to the Paleozoic. A small exposure of the Permian limestones can be seen in the north of the sheet. Mesozoic rocks consist of shale and sandstone units of the Upper Triassic to Lower Jurassic and Cretaceous limestones, generally exposed to the northeastern of the sheet. Dispersed exposed segments of dolomites in this period are also seen in the northeast of the sheet. The sandy oosparites, conglomerates and shales, as well as dacite, andesites and basalt outcrops, are seen in the northeastern sheet. In addition, the middle Jurassic conglomerates, biosparites, and cherty limestones with a very limited expansion in the northeast of the Zuzan Plain can be seen. At the beginning of the Tertiary, in the south, central and northern parts of the sheet, volcanic activities begin, which then continue with the volcaniclastic deposits. The chemical composition of the lava is more andesitic with less agglomerate and volcaniclastic deposits. The second volcanic phase of the region is located in the Upper Eocene (southern part of the sheet), which is mostly composed of basalt, basaltic andesite, and andesite. A widespread plutonic phase in the Early Oligocene, or perhaps the Upper Eocene occurred in the northern part of the sheet. In the west and north of the Zuzan Plain, and to a very small extent in the southwest, shale and sandstone plains have also been accompanied by contact metamorphism, which is accompanied by silicification and sericite. The clastic unit (conglomerate and sandstone silt and gypsum with interbeds) belongs to the Late Neogene with a large outcrop in the north and northwest of the region. The Plio-quaternary continental deposits and wind accumulations are other deposits spreading in this sheet. Thus, in summary, based on the geological map, the rock units can be divided into two zones. The first zone consists of units extending from the north to the east, while the second zone consists of units that have begun from the north and continued to the west of the region. Studies show that in the eastern to northeast parts, two major lithological units can be distinguished (Bulorain and Saffari, 2005). Sedimentary deposits include limestone, dolomite, conglomerate, sandstone and shale, which account for about 50% of the units around the study area, and are mostly carbonate, along with the igneous units including dacite, andesite and basalt, accounting for 26% of the unit of the region. From the west to the south, three main ithological main units are mostly expanded. Intermediate to igneous units include andesite and basalt and clastic units containing sandstone and conglomerate with andesitic grains, accounting for about 1.5% of the units, acidic igneous units, including granite and microgranite, which make up about 15.5% of the rock units of the region, along with carbonate sediments, clastic and evaporative deposits, which are 7% abundant.

3. Materials and methods

3.1. Soil sampling

The outcrops, access routes, and suitable locations for sampling were identified according to the geological map of the region. A total of 53 soil samples were taken from the studied area, from 10 to 30 cm depth (Up to a depth of 10 cm was not investigated due to the possibility of false environmental or human changes) (Fig. 2).

3.2 Preparation of soil samples

To prepare specimens for chemical analysis, each sample was graded using the Folk standard (1974), to determine the concentration of heavy metals in the soil, the comparison of these elements with international standards, as well as the factors of enrichment, pollution factor, accumulation index and pollution load coefficient, were used. The samples were analyzed by inductively coupled plasma (ICP-OES) in Oslo libratory Canada with the minimum, maximum and mean values of the metals reported in Table 1. Element measured in ppm unit. Also, according to the results of cluster analysis, calcium has been studied specifically due to its high frequency.

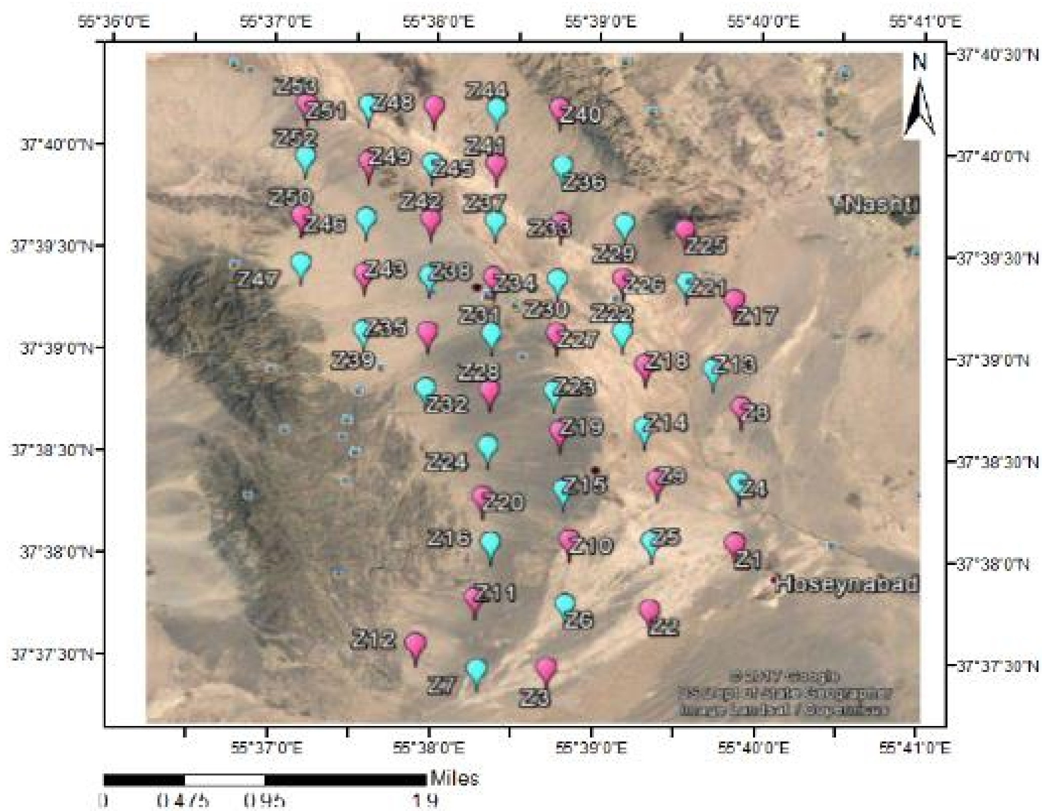

Fig. 2. 53 soil samples from 10 to 30 cm depth

Table 1. Concentration of heavy elements and metals in samples of soils removed from the Zuzan Plain (ppm).

Z	Zn	Pb	Cr	Ni	Cu	As	Co	Sn	Ba	V	Mo	Fe	Al	Ca	K	Mg	S
Minimum	46	10	50	25	17	7	7	1	305	63	0	21000	40100	51800	7450	9920	180
Mean	83	38	327	37	26	11	19	1.5	712	95	1	31200	48900	64600	12200	14000	2330
Maximum	120	64	643	50	35	16	31	2	939	127	2	43500	57100	77300	17200	18400	4310
Crust	130	20	90	68	45	15	19	6	580	130	2.6	48000	80000	32500	26600	15000	2400
World Shale	**48**	**13**	**298**	**43**	**22**	**10**	**12**	**2**	**338**	**100**	**2**	**30900**	**51200**	**71700**	**12200**	**14000**	**470**

3.3 Statistical analysis

Statistical methods were used for the correlation between the element's concentration. The cluster diagram of the elements, main component analysis, and the correlation coefficient was analyzed using SPSS22 software. The Pearson coefficient was employed to examine the relationship between the variables and their relationship with the identification and the origin of the data. Pearson coefficient was employed to examine the relationship between variables. In the discussion, Pearson's coefficient measures the linear correlation between two variables. The value of this coefficient varies between -1 and 1, where "1" means complete positive correlation, "0" means no correlation, and "-1" signifies complete negative correlation.

3. Results

4.1 Cluster Analysis

A cluster analysis chart is a non-controlling classification process that better illustrates the correlation between elements. According to the obtained dendrogram, the two main clusters A and B can be distinguished (Fig. 3). The first cluster (A) includes Vanadium (V), Iron (Fe), Chromium (Cr), Molybdenum (Mo), Nickel (Ni), Magnesium (Mg), Aluminium (Al), Potassium (K), Tin (Sn), and Cobalt (Co), while the second cluster (B) contains Copper (Cu), Arsenic (As), Sulfur (S), Lead (Pb), Barium (Ba), Zinc (Zn), and Calcium (Ca). The study shows that the first cluster consists of 3 sub-clusters of A1 (V, Fe, Cr, Mo), A2 (Ni, Mg, Al, K, Sn), and A3 (Co), while the second cluster consists of two sub-clusters of B1 (Cu, As, S) and B2 (Pb, Ba, Zn, Ca).

This method provides massive information about the basic structure of the data and the possible relationships between them (Golobocanin et al., 2004). Specifically, this method seeks to discover variables in cases where the observed changes can be checked by a far smaller number of variables. The analysis of the main components of the geochemical data of Zuzan Plain shows two main components. The main component of PC1 is the elements (V, Fe, Cr, Mo, Ni, Mg, Al, K, Sn, Co) along with PC2 containing the elements (Cu, As, S, Pb, Ba, Zn, Ca) (Fig. 4). Studies show that the first component consists of 3 sub-components PC1A (V, Fe, Cr, Mo), second PC1B including (Ni, Mg, Al, K, Sn) and PC1C (Co), while the second component of the following two The PC2A component consists of (Cu, As, S) and PC2B (Pb, Ba, Zn, Ca).

4.2 Estimation of contamination in the Zuzan area

To evaluate the amount of contamination in the Zuzan area, the factors of enrichment, pollution, accumulation index, and pollution load coefficient were used.

i. Enrichment factor (EF)

The enrichment factor is an appropriate method for separating natural and human-induced pollution. This factor seeks to determine the metal contamination as an anthropogenic or lithogenic source(Adamo et al., 2005) (Equation 1).

$$EF = \frac{\text{Mx XFex}}{\text{Mb XFeb}} \qquad \textit{Eq. 1}$$

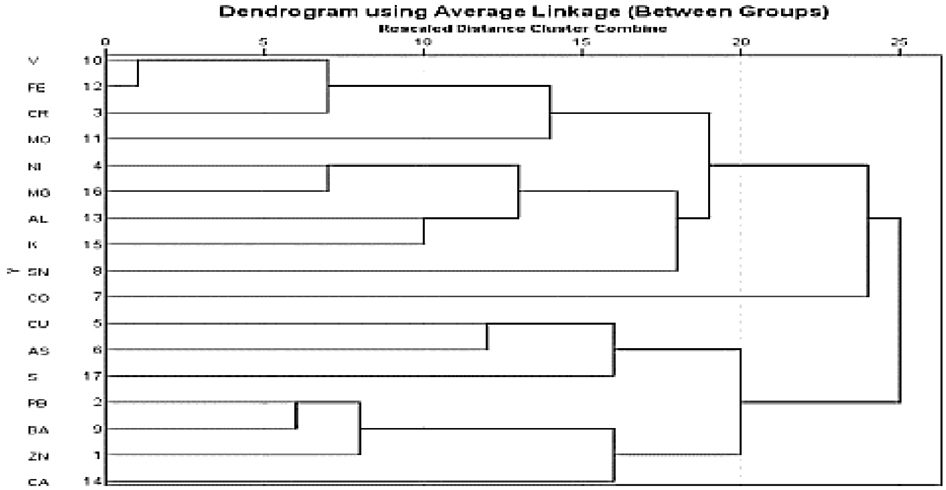

Fig. 3. Dendrogram chart derived from cluster analysis of elements in soil samples of the Zuzan area

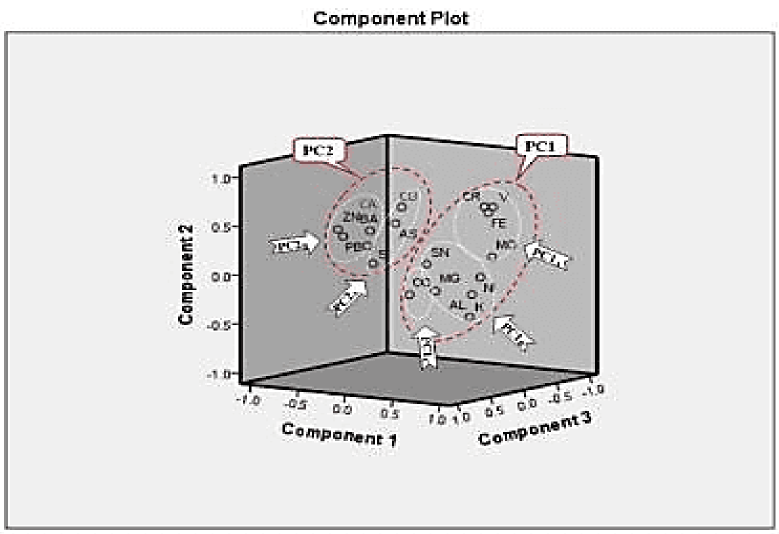

Fig. 2. 53 soil samples from 10 to 30 cm depth

where EF is the enrichment factor, XFeb is the concentration of the studied element, Mx is the concentration of the element (Al), XFex is the concentration of the element in the environment , Mb is the concentration of the element in the erath crust (concentration in global shale). The mean Al is considered as the metal in the environment (global shale) at a concentration of 80000 ppm.

According to the results and its comparison with the standard, only Ca is at the lower level in terms of the intensity of enrichment, while the rest of the elements are in the category without enrichment (Fig. 5)

ii. Geoaccumulation index (Igeo)

It is also called the Muller Index (Muller, 1979). This index is used to evaluate the degree of heavy metal contamination in the soil (Audry et al., 2004; Bermejo Santos, et al., 2003; Munendra et al., 2002).

This index is expressed as follows (Equation 2):

$$Igeo = log^2(\frac{Cn}{1.5\mathrm{Bn}}) \qquad \text{Eq. 2}$$

where Cn is the measured concentration of the element in the sample, and Bn is the concentration of the same element in the base sample (its average concentration in global shale). The coefficient of 1.5 is also applied to eliminate possible changes in the background due to geological impacts (Gonzales et al., 2006; Ghrefat & Yusuf, 2006) (Table 3).

Table 2. Enrichment Factor classification (Chen et al., 2007).

Enrichment intensity	Extremely intense	Very intense	Intense	Fairly intense	Medium	Few	Without enrichment
EF	More than 50	25-50	10-25	5-10	3-5	1-3	Less than 1

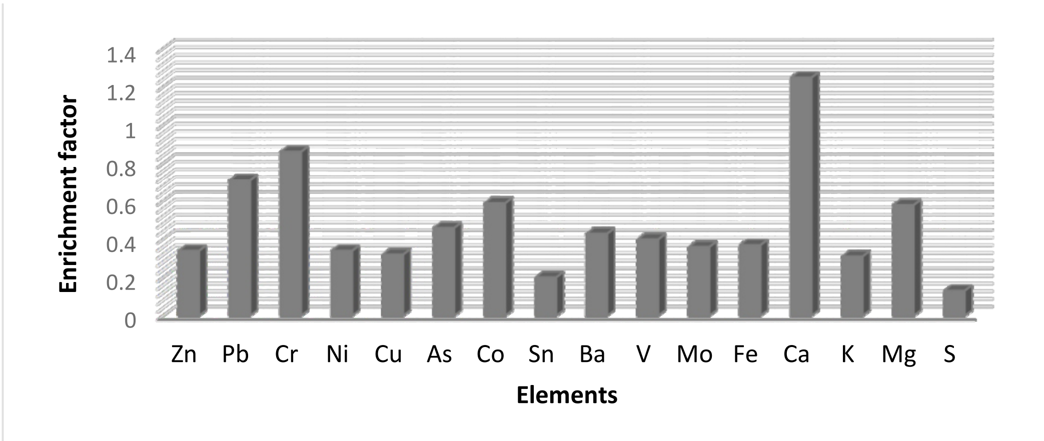

Fig. 5. Average characteristics of the enrichment factor in the Zuzan fields.

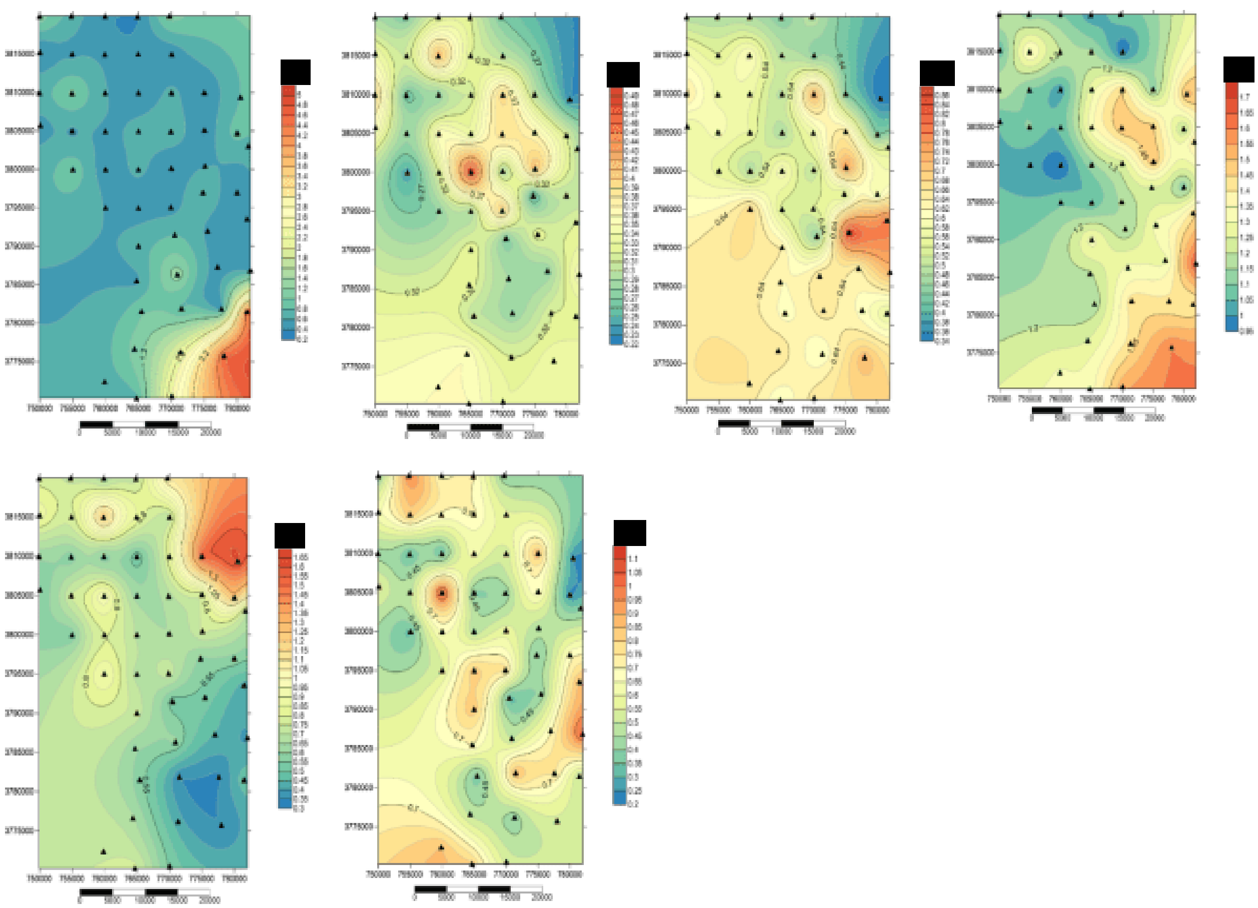

Fig. 6 Zoning map for enrichment factor in the Zuzan plain (ppm). Elements showing an increase in concentration towards the following directions of chromium in the southeast, magnesium and calcium in the east and south-east, copper in the center, cobalt from northwest to east of the region and lead in the northeast.

Based on the results and comparison with the standard, only the element of calcium is in terms of the severity of contamination in the non-contaminated to a slightly contaminated category, while the rest of the elements fall in the non-contaminated category (Fig. 7).

iii. Contamination degree

The concentration of elements in the sample is divided into the concentration of the element in the sample and indicates the amount of contamination of the sediments with heavier elements (Abrahim & Parke 2008; Adomako. et al, 2008).The contamination degree is calculated from Equation 3:

$$CF = \frac{\text{Csamplee}}{\text{C background}} \quad \text{Eq. 3}$$

where contamination factor, C is the sample concentration of the element in the sample and C background is the concentration of the element in the base sample (its concentration in global shale).

Based on the comparison of the results of the standard contamination factor (Satyanarayana et al., 1994) (Table 4), it can be concluded that the element of Ca with the content of (1.94), Cr (1.34) and Pb (1.12) are in the middle class while the remaining elements in the pollution category are small (Fig 9).

iv. Contamination degree (Cd)

The total contamination coefficients of the pollutants indicate the total degree of sediment contamination, which is called the Hackenson contamination degree (1980) (Equation 4).

$$Cd = \sum_{i=0}^{n} \text{Cf} \quad \text{Eq. 4}$$

Where Σcf is the total contamination factor

Based on the results and their comparison with the Hankonson standard (1980) (Table 5), the samples of the study area are in low pollution and medium pollution (Fig. 11 and 12).

v. Modified Contamination degree (mCd)

Due to the limitations in the index of the degree of contamination, presented by Hackson (1980), corrected correlation was presented by Abraham (2005) (Equation 5).

$$mCd = \frac{\sum cf}{\text{n}} \quad \text{Eq 5}$$

Where Σcf is the total contamination factor, n is the number of elements to calculate. According to Abrahim and Parker (2008), the qualitative soil classification is presented in the table (Table 6).

Based on the results and comparison with Table 7, the samples of the studied area are in low pollution and low contamination level (Fig. 13 and 14).

Table 3. Geoaccumulation index classification (Igeo) adapted from(Muller,1979).

Severity of pollution	**Very polluted so severely polluted**	**So polluted**	**Slightly polluted until very polluted**	**Slightly polluted**	**Non-polluting to slightly polluted**	**Non-pollute**
Igeo	4-5	3-4	2-3	1-2	0-1	Less than zero

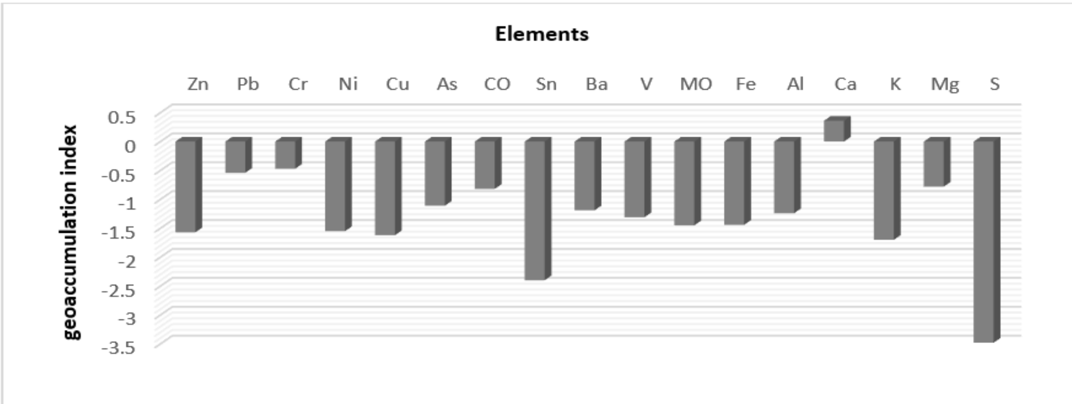

Fig 7. Average Characteristics of the Geoaccumulation index (Igeo) in the Zuzan Fields

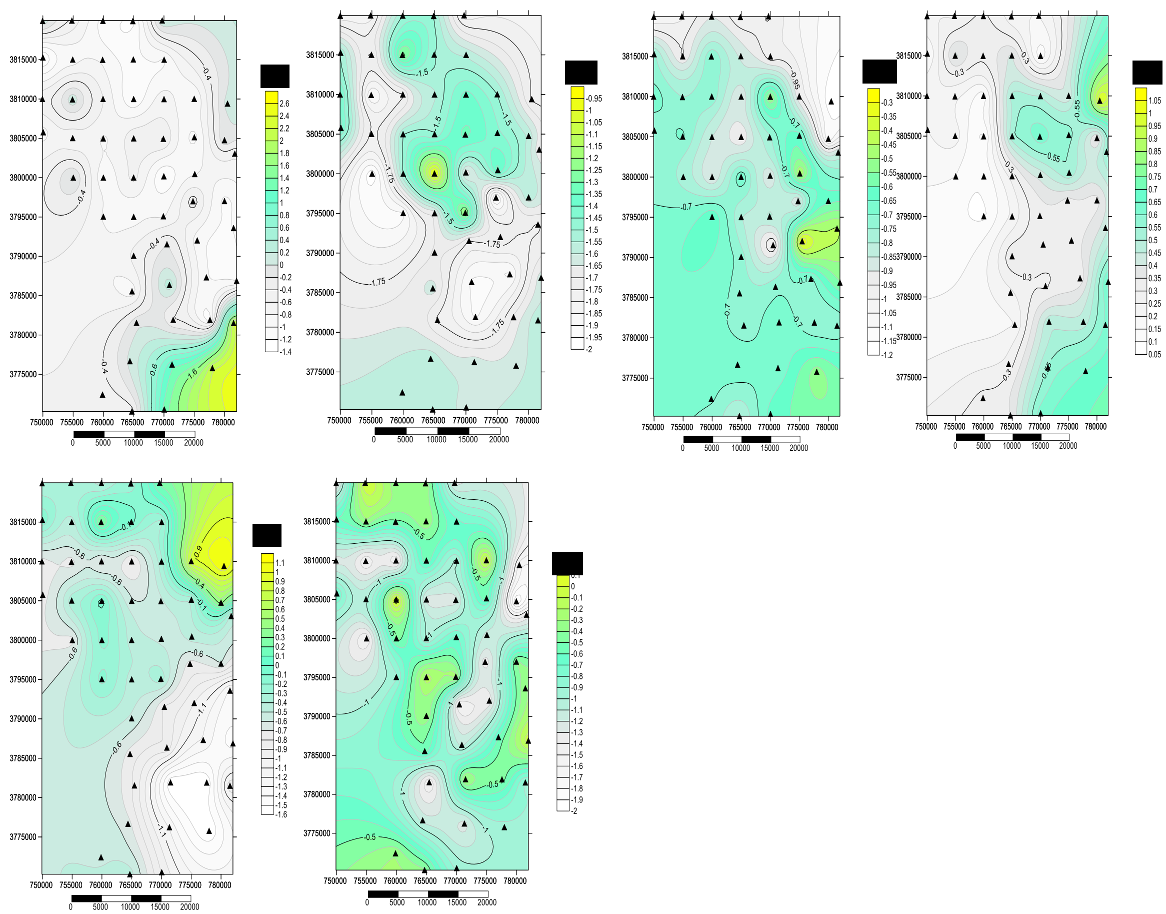

Fig. 8 Geoaccumulation index zoning map (Igeo) elements in the plain area of the Zuzan (ppm). According to the zoning map, the chromium element in the southeast shows magnesium and calcium in the northeast, copper in the center, cobalt from the northeast to the east, and lead in the northeast.

Table 4. Contribution coefficient factor (CF) classification (after Satyanarayana et al., 1994)

Severity of pollution	Very high pollution	Acceptable pollution	Medium pollution	Little pollution
CF	More than 6	3-6	1-3	Less than 1

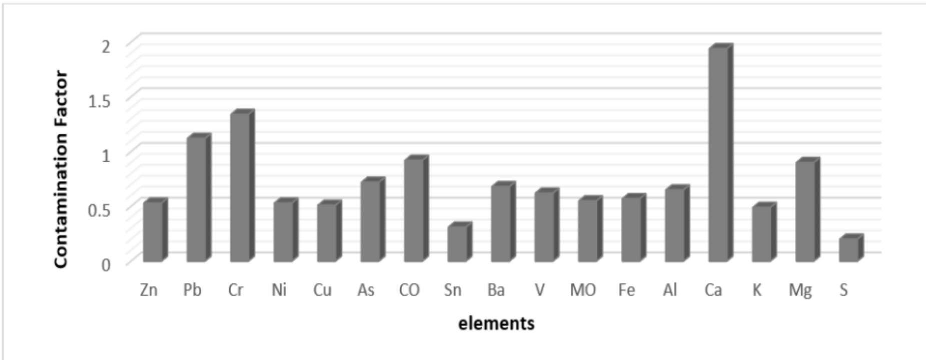

Fig. 9 Contamination Factor (CF) in soils of the Zuzan area (ppm unit)

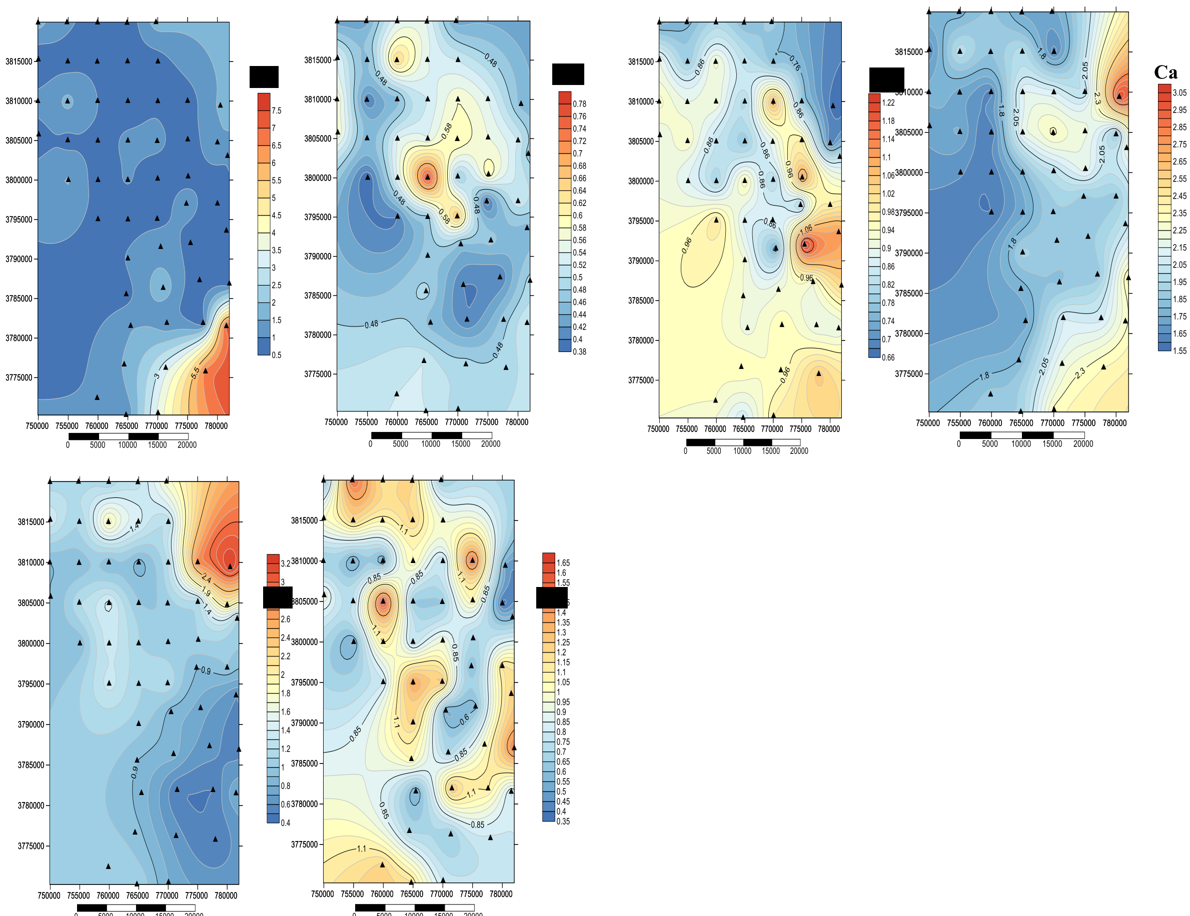

Fig. 10 Contamination Factor zoning map (CF) Elements in the plain area of the Zuzan (Unit of measurement ppm). Based on the chromium zoning map in the southeast, magnesium and calcium in the northeast, center copper, cobalt from northwest to east of the region, and lead in the northeast increase.

Table 5. Classification of Contamination Degree (Cd) Adapted from (Hakanson 1980).

The quality of the environment examined	Very high pollution	Acceptable pollution	Medium pollution	Low pollution
Cd	Cd>24	12<Cd<24	6<Cd<12	Cd<6

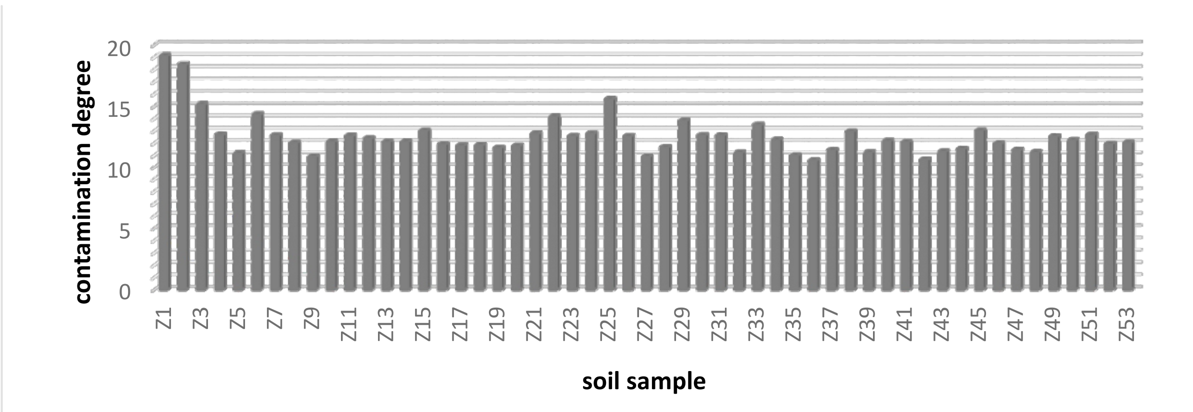

Fig. 11. Degree of contamination degree (Cd) in soils of the Zuzan area (ppm unit)

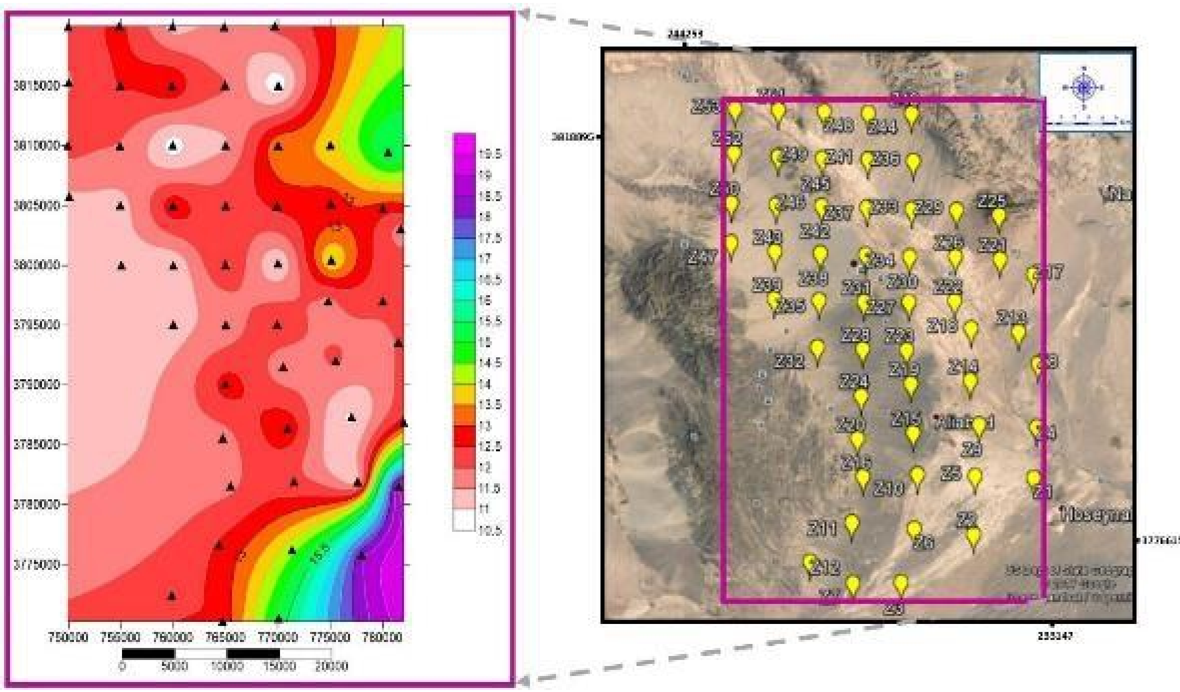

Fig. 12. Mapping the degree of contamination (Cd) in the plain of the Zuzan (ppm unit)

Table 6. Classification of the modified contamination degree (mCd) (after Abrahim and Parker, 2008)

The quality of the environment examined	Our pollution is too high	Severe pollution	Very high pollution	High pollution	Medium pollution	Low pollution	Very low pollution
mCd	mCd>32	16<mCd<32	6<mCd<16	4<mCd<8	2<mCd<4	1.5<mCd<2	mCd<1.5

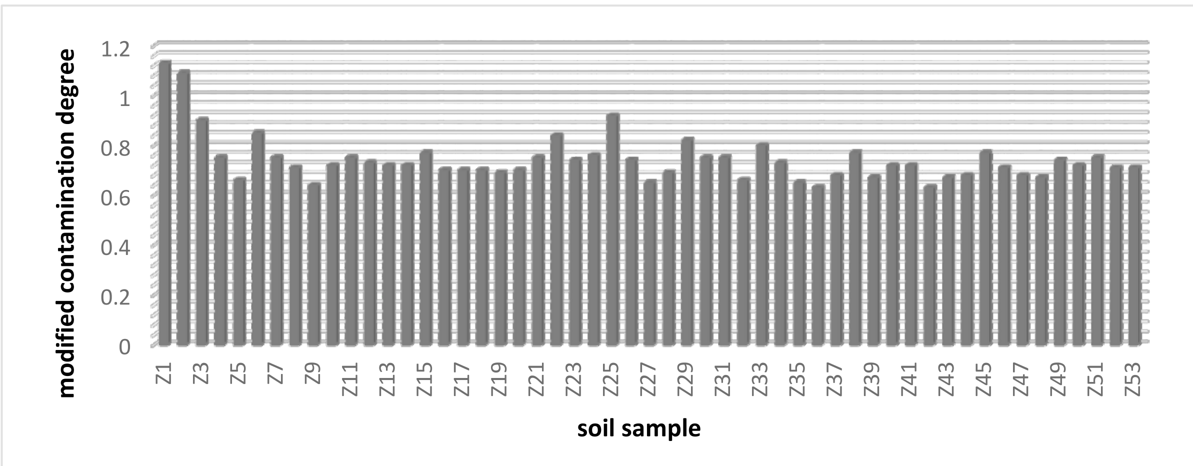

Fig. 13 Degree of contamination degree (mCd) in soils of the Zuzan area (ppm unit)

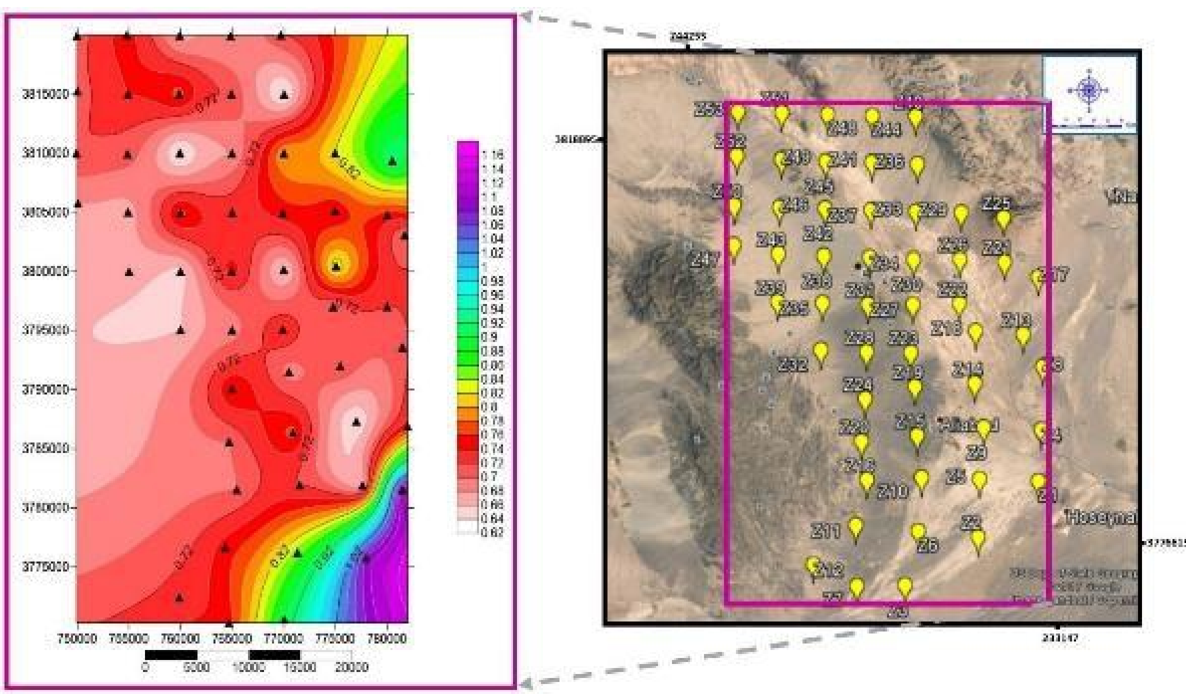

Fig. 14. Mapping the modified contamination degree (mCd) in the plain of the Zuzan (ppm unit)

The presence of sedimentary rocks (mostly carbonate) and acidic igneous to basic rocks caused the separation of two subgroups in the first group and carbonate and clastic units (sedimentary rocks), plutonic igneous rocks, and sedimentary-igneous rock divided into three subgroups, in The second group have been made. On the other hand, the map of the dispersion of the elements shows, that the dispersion of Fe, Zn, Cur and Ni in the northwest, center, and south of the plain does not follow the anomalies of the surrounding rocks. Other elements have a great on the natural factors of the region. Finally, it can be noted that the changes in soil contamination in the region are more pseudosclerotic and only in areas where the focus of human activities (northwest and center, villages of the Zuzan and the Qasim Abad and agricultural land in these regions and the south and southeast Hussein Abad village and its agricultural land), some of the elements show an increase. Since there are no factories or industrial plants contaminated in this plain, this is an acceptable result. Soil contamination coefficients indicated that calcium and a lower amount of chromium and lead are the main soil pollutants in the area, all of which are based on ground-based zoning maps.

According to the results, the highest positive correlation was found between vanadium and chromium with a value of 0.701, and the highest negative correlation was observed between aluminum and lead with a value of -0.582 (Table 7).

Table 7. The Pearson correlation (r) of elements in soils of the Zuzan area

	Zn	Pb	Cr	Ni	Cu	As	Co	Sn	Ba	V	Mo	Fe	Al	Ca	K	Mg	S
Zn	1																
Pb	672**	1															
Cr	-.146	-.194	1														
Ni	-.402**	-.498**	.505**	1													
Cu	.419**	.168	-.094	-.061	1												
As	.336*	-.062	.207	.110	.448**	1											
Co	-.049	.012	-.276*	.047	.156	.052	1										
Sn	-.037	-.106	.112	.320*	.200	.154	-.028	1									
Ba	.508**	.687**	-.038	-.539**	-.109	-.101	-.335*	-.310*	1								
V	-.105	-.238	.701**	.256	-.055	.240	-.078	.085	-.143	1							
Mo	-.394**	-.443**	.316*	.208	-.093	-.002	-.061	.078	-.151	.399**	1						
Fe	-.136	-.133	.598**	.206	.043	.152	-.023	.193	-.187	.902**	.392**	1					
Al	-.232	-.582**	.055	.423**	-.166	.157	.017	.128	-.397**	.275*	.337*	.172	1				
Ca	.260	.147	.354**	-.007	.061	.401**	-.114	-.044	.424**	.197	.151	.010	-.105	1			
K	-.243	-.445**	-.025	.279*	-.235	-.145	-.010	-.019	-.236	.013	.304*	-.030	.538**	-.319*	1		
Mg	-.140	-.497**	.110	.625**	.144	.246	-.015	.336*	-.453**	.024	.137	-.050	.609**	.052	.329*	1	
S	.232	-.031	-.098	-.011	.248	.354**	-.104	.149	-.074	-.110	-.144	-.145	.154	.205	-.154	.512**	1

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

*.Correlation is significant at the 0.05 level (2-tailed)

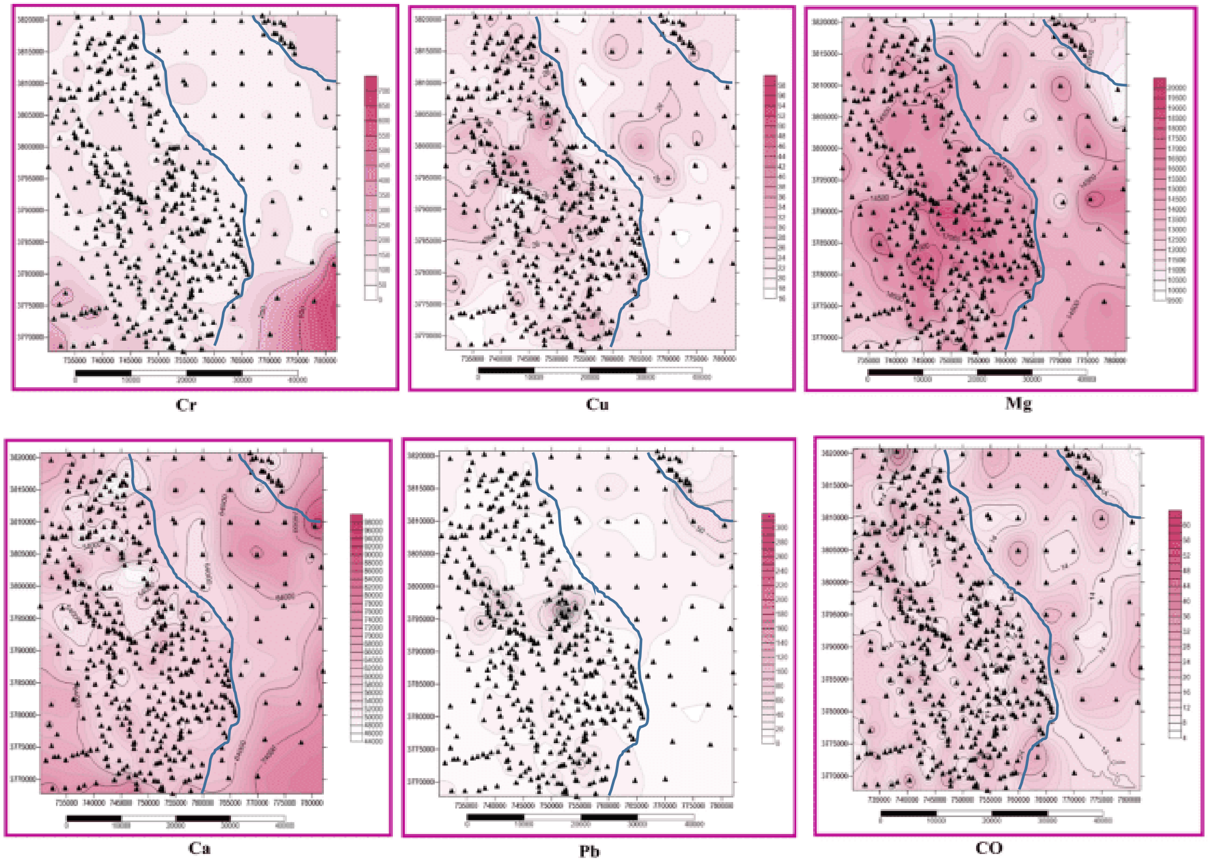

Fig. 15. Geochemical data of the drainage tracks collected by the Geological Survey and Mineral Exploration, along with data from soil samples from the Zuzan region (ppm unit)

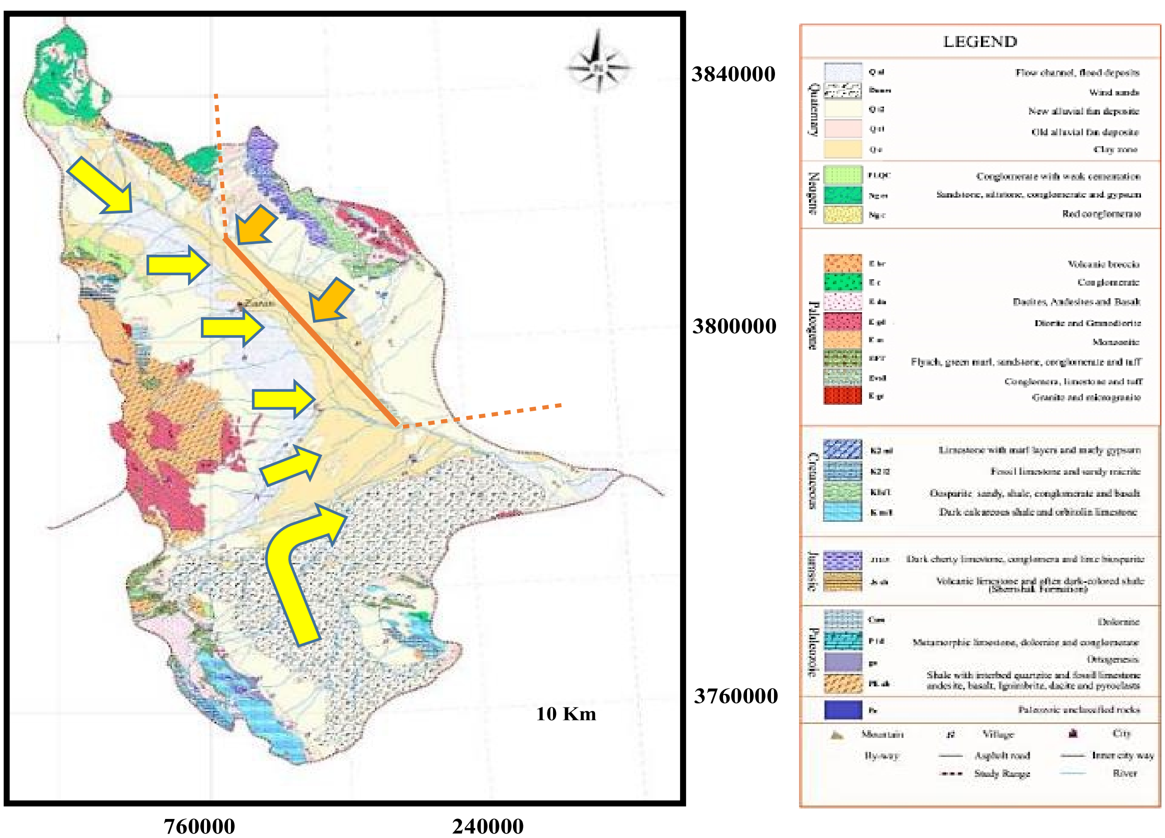

Fig. 16. Geological map of the Zuzan plain, the trend of the impact of rock units on each zone.

5. Conclusions

Based on the results of the elements arsenic, magnesium, sulfur and aluminum in the East; Iron, nickel, vanadium, molybdenum, tin and chromium in the southeast; Lead, barium, calcium and zinc in the Northeast; Copper is most abundant in the center of the plain and cobalt and potassium are in the northwest. Based on statistical analysis in the soil samples of Zozan plain, the two main clusters A and B, can be distinguished. The first cluster (A) includes V, Fe, Cr, Mo, Ni, Mg, Al, K, Sn, Co and the second cluster (B), includes Cu, As, S, Pb, Ba, Zn, Ca, are elements. Studies show that its first cluster consists of 3 sub-clusters A1 (V, Fe, Cr, Mo), A2 contains Ni, Mg, Al, K, Sn) (and A3 contains (Co) and its second cluster consists of 2 sub-clusters. B1 consists of Cu, As, S) and B2 consists of (Pb, Ba, Zn, Ca). West, southwest and southeast of the region, while the second group is more affected than the northeastern units of the region, so studies show that most of the elements in the soil of Zozan plain are affected by rock units around the plain.

Authors' Contribution

Mohammad Javanbakht, proposed the main concept and involved in write up and assisted in making the complete manuscript. Shima Raftari, collected field data. Hanieh Pourjavad, did provision of relevant literature, and technical review and proof read of the manuscript before submission.

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