ISSN: 0067-2904

Effects of Land Use and Land Cover on Concentrations of Heavy Metals in Surface Soils of Lesser Zab River Basin, NE Iraq

Younus I. Al-Saady[1*], Balsam S. Al-Tawash[1], Qusay A. Al-Suhail[2]
[1]College of Science, University of Baghdad, Baghdad, Iraq
[2]College of Science, University of Basra, Basra, Iraq

Abstract

To investigate and assess the effects of land use and land cover (LULC) on concentrations of heavy metals in the surface soils of Lesser Zab River Basin (LZRB), 25 surface soil samples were taken from different LULC classes. Heavy metals concentrations were measured and their enrichment factors were calculated. Most of the LZRB soil samples are moderately alkaline with pH>8 and characterized by low organic content. The average abundance of the major oxides follow the decreasing order of SiO_2 % > CaO % > Al_2O_3 % > Fe_2O_3 %> MgO > K_2O % > TiO_2 % > Na_2O % > SO_3 % > P_2O_5 %. A correlation matrix revealed that clay and feldspar minerals, Fe and Mn oxides / hydroxides are the most important carrier phase for several heavy metals as their correlation of high significant values. The average values of the heavy metal contents are arranged in the following decreasing order: Mn> Cr> Ni>Zn> Cu> Co>Pb>Cd. The LZRB soils exhibits concentration higher than direct geochemical background (DGB), and lower than indirect geochemical background (IGB) and there is a clear difference in the accumulation of heavy metal in soils under different LULC classes. The highest accumulation of heavy metals has been found in agricultural land and next highest concentration in urban and built up land. Assessment of soil contamination is conducted using enrichment factor (Ef), contamination factor (Cf), and contamination degree CD. According to these factors the soils of LZRB showed no or minimal contamination for most metals in different LULC classes.

Keywords: Soil, LULC; Heavy metals; Geochemical background; Multivariate statistic; Enrichment factors

تأثيرات استخدام الأرض و غطاء الأرض على تراكيز الفلزات الثقيلة في التربة السطحية لحوض نهر الزاب الأسفل، شمال شرق العراق

يونس ابراهيم الساعدي[1]*، بلسم سالم الطواش[1]، قصي عبد الوهاب السهيل[2]
[1]كلية العلوم، جامعة بغداد، بغداد، العراق
[2]كلية العلوم، جامعة البصرة، البصرة، العراق

الخلاصة

لبحث وتقييم تأثير غطاء واستخدامات الارض على تراكيز الفلزات الثقيلة في ترب حوض نهر الزاب الأسفل ، تم جمع 25 نموذجاً للتربة من مختلف اصناف غطاء الأرض و استخدامات الأرض (LULC). تم قياس تراكيز الفلزات الثقيلة واحتساب معامل اغنائها. معظم نماذج التربة متوسطة القلوية مع اس هيدوجيني اكبر من 8 وذات محتوى واطئ من المواد العضوية. معدل وفرة الأكاسيد الرئيسية وبترتيب تناقصي هو (SiO_2 % > CaO % > Al_2O_3 % > Fe_2O_3 %> MgO > K_2O % > TiO_2 % > Na_2O % > SO_3 % >

*Email: younusalsaady@yahoo.com

(P2O5%). وكشفت مصفوفة الارتباط بأن المعادن الطينية، معادن الفلدسبار وأكاسيد وهيدروكسيدات الحديد و المنغنيز / هي الطور الرئيسي الحامل للعديد من الفلزات الثقيلة عند قيم الأرتباط العالية. معدل وفرة الفلزات الثقيلة رتبت تنازليا كما يلي (Mn> Cr> Ni>Zn> Cu> Co>Pb>Cd). . أظهرت بعض ترب حوض الزاب الأسفل مستويات مرتفعة من الفلزات الثقيلة، مع تراكيز أعلى من الخلفية الجيوكيميائية المباشرة (DGB) وأقل من الخلفية الجيوكيميائية غير المباشرة (IGB) و أن هناك فرق واضح في تراكم الفلزات الثقيلة في التربة العائدة الى اصناف غطاء وأستخدامات الأرض المختلفة. كما ان الأراضي الزراعية تحتوي على أعلى معدل لتراكم الفلزات الثقيلة ومن ثم المناطق الحضرية. جرى تقييم تلوث التربة باستخدام عامل الأغناء (Ef)، عامل التلوث (Cf)، ودرجة التلوث (CD)، ووفقا لهذه العوامل اظهرت نتائج ترب حوض الزاب الأسفل غياب او وجود الحد الأدنى من التلوث لمعظم الفلزات الثقيلة في اصناف غطاء واستخدامات الأرض.

1. Introduction

Soil is a product of the rock weathering and mineral deposits due to the interaction between the atmosphere, the biosphere, the lithosphere and hydrosphere [1]. The concentrations and distribution of heavy metals in soils depends on the source material and depositional environment, textural characteristics, organic matter content, and mineralogical composition [2-4]. The development and formation of chemical elements in soil are affected not only by parent material, climate, biology, and topology factors, but also by human activities [5]. Human activities resulting in soil contamination by heavy metals include mining, industrialization, waste disposal, and agriculture activity [6]. Under certain circumstances the presence of heavy metals in large amounts in soil could be harmful to plants, animals and people [1,7].

However, parent rocks are the major controlling factor on the concentration of heavy metals. Heavy metals are particularly of environmental concern because of their potential toxicity and their importance as essential nutrient. Background concentrations of heavy metals in soils are, therefore, important due to the recent interest in contamination potential and toxic effects of these elements on humans and the environment [8]. Soil environmental quality directly affects the daily lives of human beings [5]. Therefore, the exploration of spatial distribution characteristics of chemical elements in soil is meaningful for further understanding the surface pollution and degradation, monitoring of the environmental changes, and ensuring the safety of the human environment [9]. Several studies have been conducted to investigate the environmental situation and contaminant levels in surface water, ground water and river sediment of LZRB [10-12];. However, heavy metals assessment and their relation with various land uses has received limited attention.

This study aims (a) to identify the regional geochemistry of the surface soil and describe the factors controlling their geochemical variability (b) to identify the possible sources of contamination that can explain the influence of anthropogenic activities and geogenic origin and their impacts on soils within the Lesser Zab River Basin (LZRB). Hence, the concentrations and the distribution of the heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) and major oxides (SiO2, Fe2O3, Al2O3, TiO2, CaO, MgO, SO3, Na2O, K2O and P2O5), pH and Organic matter (OM) in the soil of different Land use and Land cover (LULC) classes are determined to achieve these aims. Furthermore several procedures have been used to establish the status of selected heavy metals, including multivariate statistical analysis as parson correlation, cluster analysis, as well as contamination factor (CF), enrichment factor (EF), and contamination degree CD. These data also provide further contribution studies in Iraq.

2. Materials and methods

2.1. Site Characterization

The Lesser Zab Basin (LZRB) is located in the northeast of Iraq between latitudes of 35° 10´ - 36° 55´ N and longitudes of 43° 25'- 46° 20' E covering an area of about 19860.65 km^2. The catchment area extends partly into Iran (5813.88 km^2, i.e., 29.27% of the total area), while the major portion (14046.77 km^2, i.e., 70.73% of the total area) is in Iraq [13]. The LZRB is a part of the Zagros orogenic belt. It is a mountainous region, encompassing the Zagros mountains which extend to the northeastern of Iraq. Iraqi portion of the LZRB passes through all of the divisions of the Western Zagros Fold-Thrust Belt (Thrust Belt, Suture Zone, Imbricate Zone, High Folded Zone, and Low Folded Zone) [14-16]. Most of the Iranian portion of the LZRB is located in the Sanandaj-Sirjan zone, and Zagros Fold-Thrust Belt [17, 14]. The LZRB consists of wide range of different lithostratigraphic units. The stratigraphic units of the LZRB that date from the Precambrian to the Recent include sedimentary, metamorphic, igneous rocks and Quaternary sediments [18-21]. There are important topographic variations within landforms of the basin which influence on both soil moisture and chemistry. The climate of the LZRB is defined by significant seasonal variations in precipitation, humidity, temperature, and evaporation, with dry and hot summers and cold, wet, and sometimes snowy winters. According to the Köppen Geiger climate classification system [22], the climate is classified as warm temperate with a dry and hot summer (Csa) in the middle and upper part of the LZRB and arid with dry and hot summer (Bsh) in the lower part of the basin with short spring and autumn seasons compared to summer and winter. The LZRB can be subdivided into six main LULC classes involving; barren land, agricultural land, natural vegetation (Forest), urban and built-up land, burned land and water, reflecting a broad spectrum of chemical and ecological variation from the upstream of the LZR to the confluence with the Tigris River [13].

2.2 Sampling and analytical methods

The sampling sites Figure-1 distributed in a way to cover the entire LZRB basin, in which the collected samples can reflect the regional soil geochemistry of the drainage basin. Soil samples were collected in April 2014 at 25 sites representing different LULC classes Table-1. Approximately 2-3 kg of surface soil was collected with a stainless steel tool at depth between 0 and 20 cm below the surface, and stored in plastic bags. All samples were air-dried and sieved to obtain soil fraction less than 2 mm for chemical analysis. The soil samples were sieved to remove large debris, stones and pebbles.

Surface soil (0-20 cm) samples, included 3 samples of forest, 7 samples of urban and built up land, 10 samples of agriculture land, 3 samples of virgin soil, 1 sample of bare soil and 1 sample from mixed barren land. The samples from sites Zs10, Zs28 and Zs29 are selected as baseline sites since they are taken from the areas undisturbed by direct human activities. These three samples collected from virgin or unused soil from the upper, middle and lower part of the main basin to utilize it in environmental assessments as direct geochemical background (DGB).

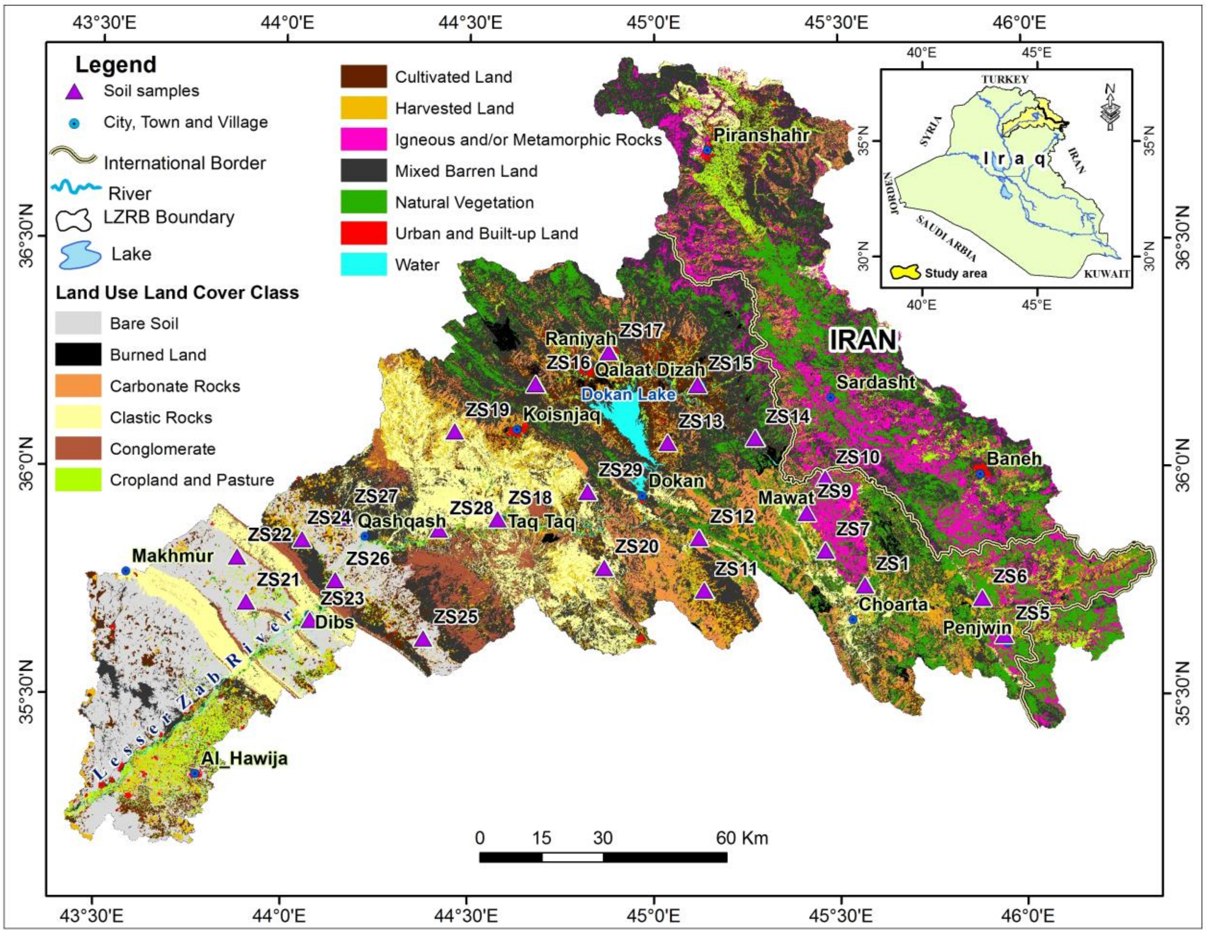


Figure 1-Soil sampling locations, and LULC map of the LZRB after Al-Saady et al. [13].

Each collected soil sample was analyzed for the major oxides and heavy metals. 100 g of soil from the above bulk samples was analyzed by x ray florescence in the laboratory of Iraq Geological Survey (Geosurv-Iraq) to determine the major oxides contents. A 0.1 g of soil sample was digested by Aqua regia according to the TU Bergakademie Freiberg method to determine metals concentration. Heavy metals concentrations in digested solutions were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with the protocols specified by the supplier. Soil pH was determined by soil/water suspensions and the organic carbon was determined by the standard method of Geosurv-Iraq Lab. For quality assurance and control (QA/QC), reagent blanks, soil standard reference materials obtained from the lab of TU Bergakademie Freiberg, and triplicate samples were simultaneously performed and analyzed with the same procedure to assess the precision.

2.3 Theoretical background

2.3.1 Geochemical background

Background is defined as: ‘‘a relative measure to distinguish between natural element or compound concentrations and anthropologically influenced concentrations in real sample collectives which may be determined with direct, indirect, and integrated methods [23, 24]. Background value for any element may subjected to wide variations between different regions and even within a specified region due to such factors as source-rock geology and weathering conditions [25]. Several methods can be used to calculate the geochemical background value, including direct geochemical and indirect statistical methods [23, 26, 27]. The integrated use of geochemical and statistical methods have been demonstrated to be useful for reliably determining background levels, and this integration of methods has allowed the validation of each other as well. All of the methods have advantages and disadvantages, more than one method is applied in this research. For the estimation of geochemical background values of the present study direct geochemical method and a statistical analysis are applied. Direct geochemical background method (DGB) is estimated based on determining the average value of heavy metal concentration in three samples of virgin soil which are measured and considered as DGB for the soil of LZRB. Among the statistical methods, two methods are chosen; the first includes the boxplot representations proposed by Tukey [28] and adopted by de Lima Rodrigues et al. [29] where the background value was considered as the upper limit given by the following equation;

$$[UL = Q_3 + 0.5(1.5IQ_3 - IQ_1] \quad \textbf{(Eq. 1)}$$

Where; UL = upper limit, IQ_1 lower quartile and IQ_3 = upper quartile.

The second statistical method is iterative 2 standard deviation (SD) method. The iterative 2 SD technique [average ± 2SD] is mainly used to define background values because it approximates the original data set to a normal distribution [29]. This technique, which presented in detail by Matschullat et al. [23] is based on the assumption that all values in a dataset beyond the average ±2 SD are iteratively omitted until all the values lie within this range (approaching a normal distribution). The average values of both statistical methods have been defined as indirect geochemical background (IGB).

2.3.2 Statistical analysis

Multivariate statistical analysis such as cluster analysis and correlation analysis have been increasingly in use for environmental studies on measurements and monitoring, particularly assessing large and complex geochemical datasets. These methods are powerful tools for a meaningful data reduction and interpretation [29, 30]. In order to investigate the elemental associations among the analyzed elements in the soil a Pearson R correlation and hierarchical analyses were applied. Critical values of the correlation coefficients ($r = 0.38$ at $p = 0.05$); are considered to be statistically significant. The basic statistical parameters for each element and the statistical processing are calculated using the SPSS statistical software (SPSS, V. 17.0). The cluster analysis is applied to the same set of data, in order to find similarities among groups of samples within a population of data described by a multivariate structure.

2.3.3 Assessment of soil contamination

The assessment of soil contamination was conducted using the contamination factor and degree.

2.3.3.1 Enrichment factor (Ef)

Enrichment factor (Ef) is considered as an effective tool to evaluate the magnitude of contaminants in the environment [31, 32]. Enrichment Factor (Ef) is calculated for individual metal in soils to evaluate anthropogenic influences on the accumulation of heavy metals in the soils [32, 33]:

$$Ef = \frac{(C_M/C_{Al})\ sample}{(C_M/C_{Al})\ reference} \quad \text{(Eq. 2)}$$

Where, (C_M/C_{Al}) is the ratio of concentration of heavy metals of the sample (C_M) to that of aluminum (C_{Al}) in the soil sample, and (C_M/C_{Al}) reference is the same reference ratio in the background. In this factor, the concentration of metal M is normalized to the iron. In this study, Al is used as a reference element for geochemical normalization because of the following reasons: (1) Al is associated with fine solid surfaces; (2) its geochemistry is similar to that of many heavy metals and (3) its natural concentration tends to be uniform [34]. Increasing in EF value indicate increasing metals supply from anthropogenic activity [35]. There are five contamination categories are recognized on the basis of the enrichment factor values based on the enrichment ratio methodology [36]: (1) Ef<2 depletion to minimal enrichment indicating of no or minimal pollution, (2) Ef 2-5 moderate enrichment, indicating of moderate pollution, (3) Ef 5-20 significant enrichment, indicating of a significant pollution, (4) Ef 20-40 very highly enriched, indicating a very strong pollution (5) Ef>40 extremely enriched, indicating an extreme pollution.

2.3.3.2 Contamination factor (Cf)

The contamination factor is used to determine the contamination status of the LZRB soils. The Cf is the ratio obtained by dividing the concentration of each metal in the soil (C_M) by the background (C_B) value [37]. Hence, Cf values can evaluate the enrichment of one given metal in the soils over a period of time. In this study, average shale according to Turekian & Wedepohl [38] is considered as background concentration:

$$Cf = \frac{C_M}{C_B} \quad \textbf{(Eq. 3)}$$

Where, C_M is concentration of an individual metal in soil and C_B is the background concentration of the individual metal.

The contamination levels have been classified based into four categories [39], where: Cf < 1 indicates low degree of contamination, 1 < Cf < 3 is moderate degree of contamination, 3 < Cf < 6 is considerable degree of contamination, and Cf > 6 is very high degree of contamination.

2.3.3.3 Contamination degree (CD)

The sum of Cf for all examined heavy metals represents the integrated contamination degree (CD) of the environment [31, 40]. Hakanson [39], defines four categories of CD, on a scale ranging from 6 to 24: low degree (CD<6), moderate degree (6 ≤ CD <12), considerable degree (12 ≤ CD<24), and very high degree (CD ≥ 24).

$$C_{D=\sum Cf} \quad \textbf{(Eq. 4)}$$

Where, $\sum C_f$ is the sum of contamination factor for all metals.

3 Results and discussion

3.2 Geochemistry of soil

The geochemistry of surface soils from the LZRB is studied in order to assess the environmental impact of LULC classes on the environmental geochemical characteristics of the LZRB soil.

3.2.1 pH and organic mater

Soil pH is ranged from 7 to 8.7 with an average of 8.3, Table-1. All soil samples are moderately alkaline with pH>8 except sample Zs6 which was neutral and sample Zs5 which was slightly alkaline. As soil pH increases, the solubility and availability of these heavy metals decreases [41]. The organic matter content of soil sample is ranged between 0.05 and1.38 percent with an average of 0.58 % Table-1. The maximum value was measured in sample Zs5 from urban area of Penjwin city in the southeastern part of the LZRB, while the minimum value in virgin sample Zs29 from the middle part of the main basin south Dokan Lake. The low organic matter content of the soils is perhaps due to the sparse vegetation cover of the area, which is further exacerbated by burning agricultural land and overgrazing.

Table 1- pH, organic matter (OM) and major oxide of LZRB soil compared with the average of these oxides in the upper earth crust [43] and shale [38].

LULC	Name	pH	OM	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	SO_3	L O I	Na_2O	K_2O	P_2O_5	Total
Bare soil	ZS21	8.4	1.05	35.3	5.39	11.92	0.43	19.01	4.45	0.09	21.64	0.25	1.4	0.11	99.99
Agriculture land	ZS6	7	0.35	59.36	9.83	14.96	0.74	1.72	2.84	0.04	7.12	0.53	2.72	0.14	100
	ZS13	8.2	0.71	44.47	7.73	11.96	0.57	11.73	4.1	0.05	17.75	0.16	1.35	0.14	100.01
	ZS16	8.1	0.9	53.95	9.47	12.91	0.68	3.98	4.46	0.06	12.42	0.19	1.72	0.15	99.99
	ZS19	8.4	0.54	40.95	5.78	9.69	0.43	16.49	5.12	0.09	19.08	0.38	1.85	0.15	100.01
	ZS22	8.5	0.66	37.23	5.66	9.22	0.49	20.26	4.26	0.07	20.34	0.39	1.44	0.11	99.47
	ZS27	8.5	0.51	35.12	5.66	8.99	0.47	22.6	3.91	0.05	21.66	0.16	1.23	0.13	99.98
	ZS9	8.4	0.88	43.78	7.68	9.76	0.51	15.4	4.5	0.08	15.44	0.66	1.94	0.29	100.04
	ZS14	8.2	0.95	57.52	8.15	12.58	0.57	4.52	4.5	0.08	9.47	0.32	2.14	0.15	100
	ZS25	8.5	0.91	33.56	5.24	10.46	0.39	22.5	3.99	0.08	22.28	0.21	1.21	0.12	100.04
	ZS24	8.5	0.82	33.96	5.28	12.2	0.41	20.2	4.08	0.07	22.19	0.22	1.28	0.11	100
Forest	ZS1	8.16	0.67	45.71	7.91	12.59	0.57	11.7	3.8	0.05	15.61	0.22	1.69	0.12	99.97
	ZS7	8.3	1.05	49.52	6.96	12.68	0.53	9.25	3.31	0.07	14.75	0.51	2.28	0.15	100.01
	ZS12	8.3	0.27	58.68	6.54	8.43	0.37	6.89	3.99	0.06	12.7	0.21	2.01	0.12	100
Mixed land	ZS20	8.5	0.05	50.57	6.9	12.75	0.47	9.3	3.74	0.03	13.2	0.8	2.15	0.09	100
Urban and Built up land	ZS5	7.4	1.38	50.32	12.2	5.42	0.28	2.23	17.13	0.08	10.89	0.21	1.02	0.21	99.99
	ZS11	8.6	0.14	21.23	4.04	8.4	0.28	31.5	2.93	0.05	30.62	0.09	0.81	0.07	100.02
	ZS15	8.5	0.47	46.33	6.53	12.37	0.49	11.3	3.48	0.12	16.93	0.3	1.97	0.17	99.99
	ZS17	8.4	0.54	34.89	5.99	12.67	0.45	17.6	4.12	0.06	22.6	0.16	1.32	0.13	99.99
	ZS18	8.6	0.21	50.13	6.61	11.19	0.42	10.6	6.14	0.11	12.2	0.35	2.1	0.13	99.98
	ZS23	8.1	0.46	36.85	5.81	9.07	0.42	20.3	5.01	2.26	18.54	0.33	1.37	0.1	100.06
	ZS26	8.5	0.28	41.52	5.81	9.3	0.44	16.9	5.02	0.42	18.5	0.45	1.59	0.12	100.07
Virgin soil	ZS28	8.22	0.41	40.85	6.48	10.64	0.44	16.5	5.73	0.06	17.01	0.41	1.75	0.1	99.97
	ZS10	8.22	0.41	48.63	12.75	13.94	0.76	3.77	8.62	0.03	8.2	1.42	1.73	0.16	100.01
	ZS29	8.6	0.07	47	7.6	14.13	0.52	8.65	4.08	0.04	14.61	0.57	2.68	0.12	100
Min.		7	0.05	21.23	4.04	5.42	0.28	1.72	2.84	0.03	7.12	0.09	0.81	0.07	
Max.		8.7	1.38	59.36	12.75	14.96	0.76	31.46	17.13	2.26	30.62	1.42	2.72	0.29	
Average		8.3	0.57	43.9	7.12	11.13	0.49	13.39	4.93	0.17	16.63	0.38	1.71	0.14	
SD[a]		0.38	0.36	9.15	2.09	2.22	0.12	7.52	2.79	0.44	5.37	0.28	0.48	0.04	
Average upper earth crust[b]		7.00	0.05	21.23	4.04	5.42	0.28	1.72	2.84	0.03	7.12	0.09	0.81	0.07	
Average shale[c]				58.5	4.72	15	0.77	3.1	2.5	0.65		1.3	3.1	0.16	
SD,[a]: Standard deviation; [b]Average upper earth crust (Wedepohl 1995); [c]Average shale, after (Turekian & Wedepohl 1961)															

3.2.2 Major oxide

The average abundance of major oxide follow the decreasing order of SiO_2 % > CaO % > Al_2O_3 % > Fe_2O_3 %> MgO > K_2O % > TiO_2 % > Na_2O % > SO_3 % > P_2O_5 %. The spatial distribution patterns of major oxides are shown in Figure-2. SiO_2 ranges from 21.23 to 59.36 % with an average of 43.63 %. The lowest value is measured in sample Zs11 which has the highest CaO % and this reflects high carbonate content. Even though SiO_2 is the most predominant oxide, it is still lower than the average in upper earth crust in all the studied samples as well as lower than average shale except in sample Zs6 Table-1. High SiO_2 contents, coupled with depletion in alumina and the alkalis, relative to the upper continental crust, is a reflection of the preponderance of quartz relative to feldspar, carbonate and clay minerals in the soils. The high values of SiO_2 > 50% are restricted in the middle and upper parts of the main basin Figure-2. Al_2O_3 ranges from 5.42 to 14.96 % with an average of 11.13 % Table-1. All samples have Al_2O_3 percent lower than the average percent of earth crust and the average in the shale Table-1. The highest Al_2O_3 content are mainly recorded in the soil samples located in the northeastern and southeastern parts of the main basin while the lowest in northwestern and south western parts. The Fe_2O_3 content of the soils is variable, ranging from 4.04 % to 12.75 % with an average of 7.12 %. This may represent crystalline Fe oxides and the Fe in primary silicate minerals. All samples except Zs11 are higher than average shale and fifteen samples were higher than the average of the upper earth crust with respect to Fe_2O_3 content Table-1. Consequently, there is enrichment in the Fe_2O_3 content in the soils of LZRB. Most of the iron combined with clay minerals [42].

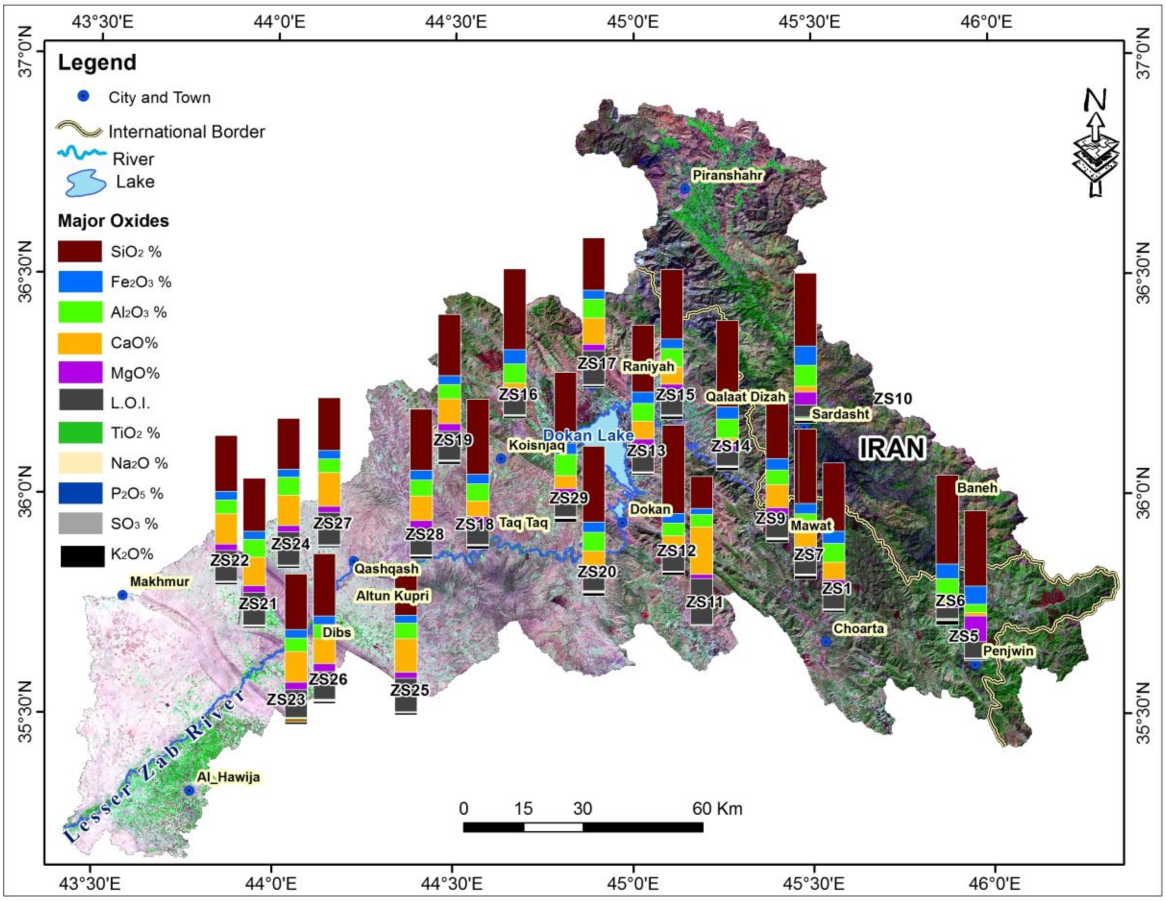


Figure 2- Spatial distribution patterns of the major oxides in soil.

The alkali contents of Na_2O and K_2O were low, where the Na_2O contents varied from 0.09 to 1.42 % with an average of 0.38 %, and K_2O ranged between 0.81 and 2.72 % with an average of 1.71 %. Na_2O and K_2O content are lower than average in shale and lower than average upper earth crust in all samples except of samples Zs6 and Zs29 which have K_2O % slightly higher than average upper earth crust Table-1. The TiO_2 is ranged from 0.28 to 0.76 % with an average of 0.49 %. All samples except of Zs6 and Zs10 are lower than average upper earth crust, and average shale, with respect to TiO_2 Table-1. The alkali-earth oxides (MgO and CaO) are high in the most samples relative to the average upper earth crust and average shale. CaO content of samples range from 1.72 -31.46 % with an average of 13.39 %. The wide range of CaO is probably due to predominance of carbonate formations in the area. The highest Ca concentration is measured in Zs11 at the vicinity of limestone bedrock. High Ca and Mg concentrations in the LZRB soils are due to the dominance of limestone and in less extent dolomite rocks which contribute in the soil constituents. There is appreciable accumulation, of alkali-earth oxides in the soil samples of the LZRB that lead to somewhat deplete in SiO_2 and Fe_2O_3. MgO range from 2.84 - 17.13 % with an average of 4.93 %. The highest content of MgO is recorded in Zs5 from Penjwin city, which is also has high Fe_2O_3. The highest content of MgO and Fe_2O_3 may be attributed to the wide distribution and occurrence of ultramafic and mafic rocks in the parent rocks from which soil is derived. SO_3 ranges from 0.03 % to 2.26 % with an average of 0.17. The highest values of SO_3 are measured in Zs23 and Zs15 which are 2.26 and 0.12, respectively. These relatively high values of these samples are interpreted as partly due to the presence of sulfate mineral as gypsum. The P_2O_5 contents are very low and in the range of 0.07- 0.29 % with an average of 0.14 %. The depletion of P_2O_5 could be due to the low abundance of accessory phases, such as apatite and monazite, where the main source of P_2O_5 could be from phosphate fertilizer.

3.2.3 Heavy metals

Heavy metals concentrations showed rather large variation in the spatial distribution of Mn, Cr, Ni, Zn, Cu, Co, Pb and Cd in the soils of different LULC classes, Table-2 and Figure-3. Heavy metals concentrations from the soil samples of LZRB are compared with direct geochemical background (DGB) and indirect geochemical background (IGB) Table-2. The average abundance of heavy metals in soil samples follows the order of Mn>Cr>Ni>Zn>Cu>Co>Pb>Cd.

Chromium (Cr): Chromium concentrations vary from 13.72 ppm to 1041.4 ppm with an average of 79.84 ppm Table-2. The anomalous value of Cr in soil sample Zs5 is eliminated from graph to highlight variation in Cr concentrations between other soil sampling sites. All soil samples except Zs5 are lower than IGB and most of samples from agriculture soil are higher than the DGB Figure-4a. The highest average concentrations of Cr were in urban and built up land and if the anomalous value of Zs5 is eliminate the highest average will be in the agriculture land Table-2 and Figure-3. Cr shows relatively intense enrichment in agricultural soil and some urban and built up areas when compared to DGB indicating influx of Cr from agriculture and other anthropogenic sources.

Manganese (Mn): Manganese is present in soil as a result of mineral weathering and atmospheric deposition, originating from both natural and anthropogenic sources [44]. The major source of manganese in soils originates from earth's crust, while the major anthropogenic sources of environmental manganese include municipal wastewater discharges, sewage sludge, and combustion of fossil fuels, mining and mineral processing [45]. Manganese mobility in soil is extremely sensitive to soil conditions such as acidity, wetness, organic matter content, biological activity etc [44]. Manganese concentration range from 90.27 to 1523.9 ppm with an average of 556.52 ppm Table-2. There are large differences between the maximum and minimum content of Mn. The maximum value of Mn is found in soil sample Zs6 (1523.9 ppm) which is taken from agricultural land. There are two soil samples Zs5, and Zs15 from urban and built up land and one soil sample Zs6 from agriculture land concentrations are higher than IGB and more than half of the samples collected from different LULC classes are higher than DGB Figure-4b.

Table 2-The concentrations of heavy metals (ppm) in surface soils from different LULC classes of LZRB

LULC	S.NO.	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Bare soil	ZS21	54.96	270.01	7.33	53.8	10.52	25.22	0.13	4.41
Agriculture land	ZS6	101.89	1523.90	26.61	104.89	36.62	82.75	0.30	13.96
	ZS13	112.31	708.95	16.61	108.86	21.87	53.66	0.33	9.17
	ZS16	118.98	918.20	19.30	134.08	25.19	58.69	0.37	10.09
	ZS19	107.66	321.67	11.36	78.43	14.07	32.71	0.19	5.43
	ZS22	96.11	515.16	10.95	75.07	14.12	34.57	0.19	5.47
	ZS27	64.28	350.71	9.44	60.71	11.60	36.24	0.15	4.98
	ZS9	117.36	614.73	13.07	72.35	24	50.04	0.16	8.80
	ZS14	107.25	961.16	17.61	108.75	29.7	58.56	0.23	11.58
	ZS25	51.53	295.08	8.11	50.27	11.38	28.17	0.16	7.45
	ZS24	92.62	514.47	11.49	76.68	17.03	39.81	0.22	6.16
	Average	97	672.4	14.45	87.01	20.56	47.52	0.23	8.31
Forest	ZS1	13.72	90.27	1.94	12.46	2.52	5.88	0.03	1.03
	ZS7	47.78	662.19	10.08	53.19	19.06	43.23	0.13	8.12
	ZS12	80.18	826.48	16.44	114.73	30.54	36.13	0.07	5.77
	Average	47.22	526.32	9.49	60.13	17.37	28.42	0.08	4.97
Mixed [2]	ZS20	55.3	505.03	9.67	33.33	14.41	43.27	0.08	6.06
Urban and Built up land	ZS5[1]	1041.4	1026.6	76.59	1438.22	16.31	52.35	0.19	4.83
	ZS11	33.82	177.25	5.17	34.09	8.02	25.27	0.15	3.31
	ZS15	125.07	1018.16	21.71	116.27	35.12	86.04	0.32	19.73
	ZS17	66.58	310.33	10.76	73.54	17.55	42.35	0.35	18.48
	ZS18	120.66	669.23	15.73	115.27	20.89	43.65	0.13	7.73
	ZS23	87.09	344.09	9.51	67.37	12.38	29.44	0.12	10.33
	ZS26	56.59	290.59	6.83	46.51	8.31	22.76	0.09	3.71
	Average	81.64	468.28	11.62	75.51	17.04	41.59	0.19	10.55
Virgin soil	ZS28	70.15	520.52	11.01	80.18	15.88	33.21	0.1	5.26
	ZS10	74.77	321.86	12.14	79	18.54	27.06	0.07	2.49
	ZS29	59.59	626.41	12.90	56.67	18.77	48.14	0.09	8.3
	Average	68.17	489.6	12.02	71.95	17.73	36.14	0.09	5.35
Minimum		13.72	90.27	1.94	12.46	2.52	5.88	0.03	1.03
Maximum		1041.4	1523.9	76.59	1438.22	36.62	86.04	0.37	19.73
Average of all samples		79.84	556.52	12.32	75.27	18.25	41.12	0.17	7.83
SD[3]		194.6	331.16	13.92	274.26	8.43	17.79	0.1	4.52
IGB[4]		143.1	1014.0	20.2	141.0	28.7	64.5	0.3	11.5
DGB[5]		68.2	489.6	12.0	71.9	17.7	36.1	0.1	5.4

[1] Zs5 of anomalous value and is eliminated from calculating average of all samples and also from average of urban and built up land, [2]Mixed barren land, [3]SD; standard deviation, [4]IGB; indirect geochemical background, [5]DGB; direct geochemical background is considered as local geochemical background in this research instead of global references.

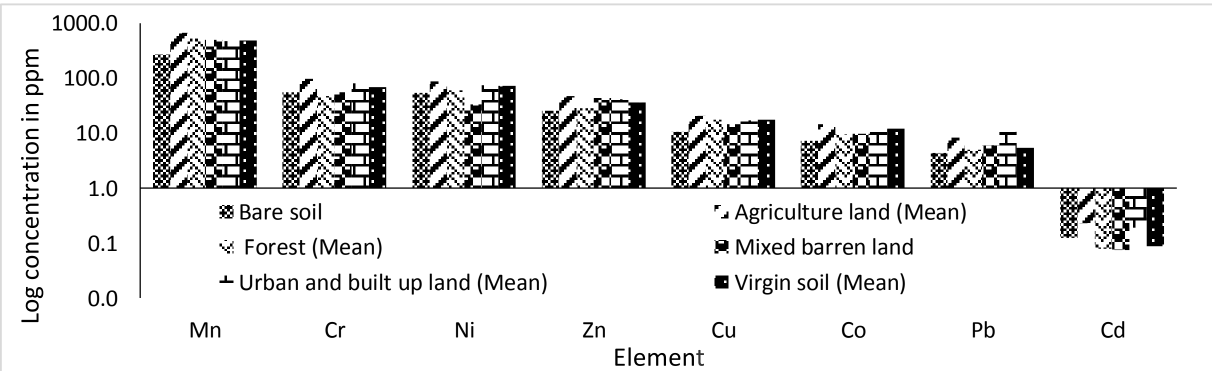


Figure 3- Levels of Heavy metals content in the surface soils from lands of different types, Zs5 of anomalous value and is eliminated from calculating average of urban and built up land.

All of these three samples located in the area dominant by exposures of igneous and metamorphic rocks in the upper part of the LZRB. Because there is no an appreciable source for Mn flux to the environments at these sites Therefore, the parent rocks are expected as the main source of Mn than anthropogenic effects.

Furthermore, high value of Mn from different LULC classes confirm that the geogenic origin is the main factor controlling the enrichment of Mn. pH of the LZRB soils is also influence on Mn content. At soil pH above 6, manganese forms bonds with organic matter, oxides and silicates whereby its solubility decreases [44]. According to classification of soil sample based on LULC map the highest average concentration of Mn content 672.4 ppm is measured in the agriculture land class Table-2 and Figure-3.

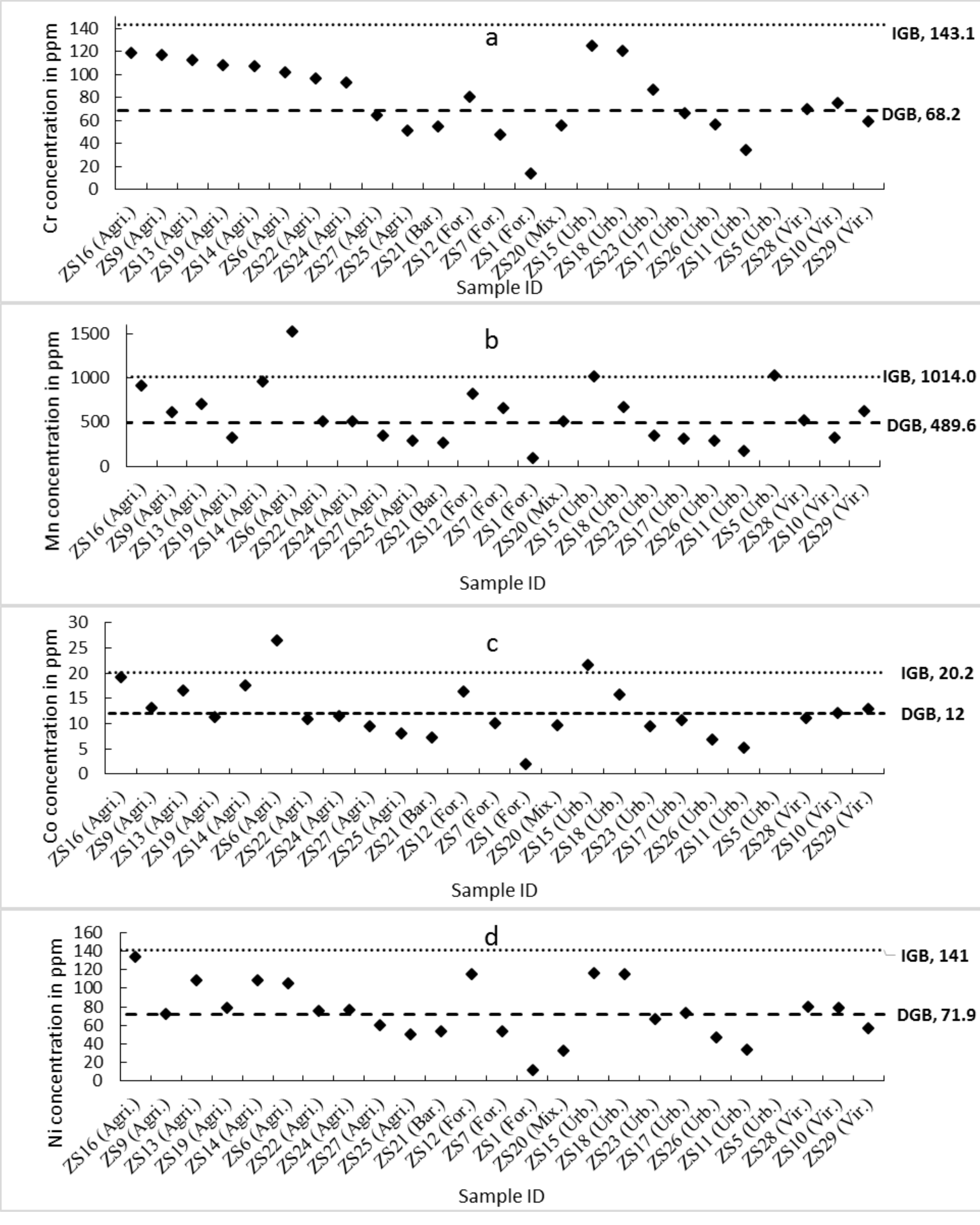
Cobalt (Co): Cobalt content of the LZRB soil samples are in the range of 1.94 ppm - 76.59 ppm with an average of 12.32 ppm Table-2. Eleven samples are higher than DGB and only sample Zs5 is higher than IGB therefore, Figure-4c. The application of cobalt-containing sludge or phosphate fertilizers to soil, the disposal of cobalt-containing wastes, and atmospheric deposition from activities such as the burning of fossil fuels and forest fires may be result in elevated levels of cobalt in soil [46, 47]. Agriculture land class has the highest average concentration and urban and built up land has the second the highest Table-2 and Figure-3. The presence of Co above the background value of different LULC classes suggest that the natural origin is the main source of this element aside from anthropogenic source.

Nickel (Ni): Nickel occurs naturally in soils as a result of the weathering of the parent as ultramafic igneous rocks, the underlying geology and soil-forming processes strongly influence the amount of Ni in soils [48]. Ni concentrations in samples of the LZRB range from 12.46 to 1438.22 ppm with an average of 75.27 ppm Table-2. Sample Zs5 has anomalous value excessively higher than IGB and more than half of the present samples are higher than DGB Figure-4 d. The anomalous value of Zs5 is eliminated from the graph. Surface soil of the LZRB is characterized by relatively high level of Ni. The high content of Ni is probably due to the parent material, i.e. ultramafic rocks present in the upper part of the main basin.

The upper part of the main basin also comprises different types of igneous and metamorphic rocks such as mafic and/or basaltic lava, andalusite schist, gneiss, phyllites, serpentinite, quartzite, recrystallized and massive metamorphosed limestone, andesites, diorite, granodiorite, syenite and nepheline syenite [49, 21, 13]. The samples of the upper and middle parts of the main basin are rich in Ni than lower part indicating that lithogenic origin is the main source of Ni, even though the anthropogenic sources cannot be ignored especially of agriculture and urban and built up lands. According to the classification of soil with respect to LULC map and excluding the anomalous value of Zs5, the highest average of Ni is in the agriculture land class Figure-3.

Copper (Cu): Copper content of soils ranges from 2.52 to 36.62 ppm, with an average of 18.25 ppm Table-2. The minimum value of Cu is recorded in the sample Zs1 from forest land, while the maximum is in sample Zs6 from the agricultural land. Variation of Cu content in soils of LZRB is due to many factors, such as mineralogical composition and grain size of the soil, bedrock origin, and anthropogenic activities. There are only five samples Zs6, Zs12, Zs14 and Zs15 are higher than IGB and eleven samples are higher than DGB Figure-4 e. According to the LULC map the agriculture land class has the highest average concentration of Cu Table-2 and Figure-3.

Zinc (Zn): Zinc content in soils of LZRB ranges from 5.88 to 86.04 ppm with an average of 41.12 ppm Table-2. The highest value of Zn 86.04 ppm is in the sample Zs15 from urban and built up land of Qalaat Dizah city and the second highest value 82.75 ppm is in the sample Zs6 from agriculture land. Zn concentrations in more than half of samples are higher than DGB and only two soil samples higher than IGB Figure-4f. Regarding to LULC map, the highest average of Zn content where measured in agriculture land class Table-2 and Figure-3. Distribution of high Zn content within different LULC classes suggests that the geogenic origin is the dominant source of Zn nonetheless the agriculture activities (fertilizer) is also important source. The highest concentration of Zn among soil samples 86.042 ppm is measured in soil of the Urban and Built up land class from Qalaat Dizah city (sample Zs15).



Continued Figure-4

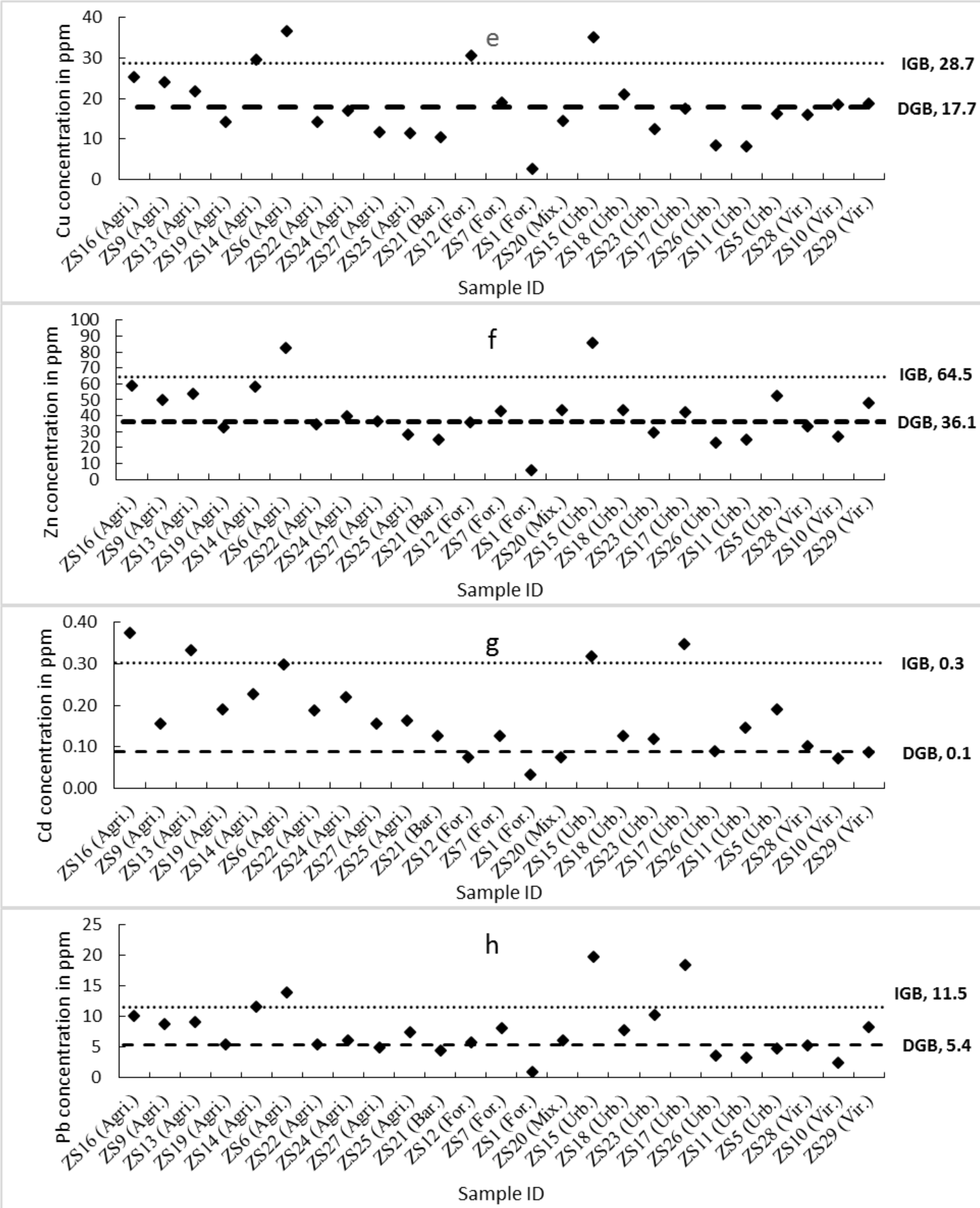


Figure 4- a, b, c, d, e, f, g and h: Heavy metals in the soil of LZRB comparing to direct (DGB) and indirect geochemical background (IGB), the anomalous values are eliminated from figure.

Cadmium (Cd): Cadmium occurs naturally in the soil as a result of weathering the parent rocks. Although most natural soils contain less than 1 ppm Cd from the weathering of parent materials, those developed on shale or associated with mineral deposits can have higher levels [50]. Cadmium strongly adsorbs to organic matter in soils. Cd of LZRB samples ranges from 0.03 to 0.37 ppm with an average of 0.17 ppm Table-2. More than two third of the samples are higher than DGB and only four soil samples are higher than IGB.

All of these samples belong to agriculture land and urban and built up land classes Figure-4g. Classification of soil samples according to LULC map shows that the highest average concentration 0.23 ppm of Cd is detected in the agriculture land and the second highest average concentration 0.19 ppm is in the urban and built up land Table-2 and Figure-3. This in turn, refers to the fertilizers effects especially for the area near Dokan Lake , whereas the Cd may enter agricultural soils through the use of phosphate fertilizers and sewage sludge [51]. Hence, anthropogenic sources of cadmium are much more significant than natural one to accumulate of Cd in soil.

Lead (Pb): Lead concentrations of the present samples range from 1.03 to 19.73 ppm with an average of 7.83 ppm Table-2. Seventeen soil samples out of twenty five are higher than DGB and only four samples were higher than IGB Table-2 Figure-4h. Pb is considered as a good indicator of pollution by urban run-off water. The leaded gasoline is responsible for the Pb pollution during the 20th century in urban area [52, 53]. According to LULC classification map urban and built up land class has the highest average of Pb and agriculture land has the second highest one Figure-3. This confirms that the sources of Pb in soils are mainly from atmospheric deposition. Soil samples Zs15 from Qalaat Dizah city and Zs17 from Raniyah city have the highest Pb contents 19.73 ppm and 18.48 ppm respectively. Urban environments in general have received higher depositions of Pb from vehicles emissions than have rural areas. When Pb is deposited in soil from fertilizer and anthropogenic sources, it does not biodegrade or decay and is not rapidly absorbed by plants, so it remains in the soil at elevated levels.

3.2.4 Multivariate Analysis

3.2.4.1 Correlation matrix:

Results of correlation analysis for soil samples show that there are positive correlation of SiO_2 with Fe_2O_3, TiO_2, K_2O, Mn, Co, Cu and Zn and also between some major oxides and heavy metals (e.g. TiO_2, MgO, Na_2O, P_2O_5, Cr and Ni) with Fe_2O_3 as well as Al_2O_3 with Na_2O and K_2O indicate that weathering of clays, iron oxy-hydroxyls and feldspar minerals play an important role in soil formation of LZRB. Na_2O also positively correlate with Fe_2O_3, Al_2O_3 and TiO_2 indicate that these elements are associated entirely with detrital phases of different types of accessory minerals and can be attribute mainly to the fine fraction of feldspar and clay minerals. CaO and LOI are closely correlated to each other and negatively correlate with most of major oxides and heavy metals. Negative correlation of CaO and LOI with major oxide confirms that they are derived from carbonate rocks, representing the decreasing amount of silicate minerals at increasing of carbonate minerals in soil.

Cr, Mn, Co and Ni are positively correlated with the Fe_2O_3. In addition, all heavy metal except Cr are strongly correlate to Mn. This could be explain by the heavy metals adsorption on Fe and Mn oxide/hydroxide. The close correlation of Cu, Zn, Cd and Pb with Al_2O_3 are also indicative of adsorption of these heavy metals on clay minerals. Cr, Co, Ni are strongly correlate with MgO which reflect the “ultramafic” source of the soils. They are derived from direct weathering of ultramafic rocks particular ophiolitic sequences and from the recycling of sedimentary rocks enriched in ultramafic debris, which occurs as outcrops in the northern eastern and south eastern parts of the main basin. Meanwhile Cr content is strongly correlated with Ni and Co due to their typical mineralogical association in mafic minerals; moreover, Cr and Ni are positively correlated with Fe_2O_3, as expected for metallic elements having geochemical affinity. Positive correlated between MgO and P_2O_5 refers to the tendency of MgO to form in the structure of phosphate minerals. OM, Cr, Co, Ni, Cu and Zn are positively correlated with P_2O_5 is a good indicator of the anthropogenic pollution from agriculture and urban areas. whereas, all these elements are widely used in industry and agricultural activities [54, 55]. Positive correlation of OM with MgO, Cr, Co and Ni indicates that it is either due to the presence of organic debris or adsorption of organic matter on to the grain surface of mineral. Hence soil organic matter content played a fundamental role in the control of heavy metals sorption by soils. The general association of heavy metals with major elements and organic matter explains that they are being as a sink for these elements. No significant correlation between soil pH and heavy metal content is observed for analyzed soils Table-3. Negative correlations between some variables indicate that these variables are derived from different sources or they have different response to the affecting factors on their geochemical abundance.

Table 3- Pearson correlation matrix of the major oxides, heavy metals and physicochemical variables of the soil samples.

	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	SO_3	L O I	Na_2O	K_2O	P_2O_5	pH	OM	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
SiO_2	1																				
Fe_2O_3	0.65	1																			
Al_2O_3	0.33	0.21	1																		
TiO_2	0.52	0.56	0.76	1																	
CaO	-0.94	-0.83	-0.38	-0.57	1																
MgO	0.17	0.63	-0.48	-0.23	-0.36	1															
SO_3	-0.17	-0.16	-0.23	-0.15	0.21	0.01	1														
L O I	-0.94	-0.8	-0.35	-0.6	0.95	-0.33	0.09	1													
Na_2O	0.31	0.52	0.39	0.54	-0.39	0.14	-0.05	-0.52	1												
K_2O	0.73	0.27	0.61	0.53	-0.63	-0.28	-0.16	-0.68	0.44	1											
P_2O_5	0.34	0.51	-0.11	0.20	-0.40	0.38	-0.17	-0.41	0.23	0.16	1										
pH	-0.51	-0.66	-0.06	-0.35	0.58	-0.39	-0.09	0.55	-0.03	-0.17	-0.30	1									
OM	0.04	0.26	-0.18	-0.01	-0.14	0.38	-0.08	-0.05	-0.26	-0.31	0.5	-0.35	1								
Cr	0.2	0.53	-0.52	-0.32	-0.36	0.91	-0.03	-0.27	-0.12	-0.26	0.43	-0.52	0.48	1							
Mn	0.73	0.49	0.2	0.33	-0.7	0.15	-0.17	-0.65	0.00	0.52	0.37	-0.64	0.15	0.37	1						
Co	0.39	0.62	-0.36	-0.16	-0.52	0.83	-0.09	-0.43	-0.09	-0.07	0.46	-0.64	0.43	0.96	0.61	1					
Ni	0.2	0.54	-0.52	-0.33	-0.36	0.91	-0.05	-0.27	-0.14	-0.27	0.39	-0.53	0.48	0.99	0.36	0.95	1				
Cu	0.67	0.35	0.34	0.41	-0.61	-0.09	-0.17	-0.58	0.11	0.58	0.4	-0.38	0.01	0.06	0.87	0.32	0.04	1			
Zn	0.51	0.32	0.31	0.33	-0.51	-0.01	-0.17	-0.44	-0.01	0.46	0.4	-0.43	0.09	0.23	0.89	0.46	0.2	0.88	1		
Cd	0.07	0.1	0.21	0.25	-0.14	-0.09	-0.14	0.02	-0.37	-0.08	0.22	-0.31	0.31	0.13	0.51	0.27	0.11	0.53	0.69	1	
Pb	0.21	-0.01	0.36	0.2	-0.2	-0.24	0.11	-0.12	-0.17	0.29	0.22	-0.18	0.03	-0.05	0.52	0.13	-0.07	0.67	0.76	0.73	1

3.2.4.2 Cluster analysis

The results obtained by cluster analysis are presented by dendrogram, where the distance axis represents the degree of association between groups of variables, i.e. the lower the value on the axis, the more significant the association. Three main distinctive cluster groups and six individual case clusters are identified from clustering samples based on LULC classes Figure-5. Cluster one involve nine samples, one soil sample from each of virgin (Zs28), urban and built up land (Zs26), forest land (Zs1), bare soil (Zs21), and five samples from agricultural land Zs19, Zs22, Zs24, Zs25, and Zs27. Cluster two represent by five samples collected from different LULC classes include mixed barren land Zs20, urban and built up land Zs18, virgin soil Zs29, Zs7 and Zs12 from forest land. However, it is observed that clusters one and two, join together at a relatively higher level, possibly implying a common source. These two clusters highlight the significant controlling of geogenic origin on the geochemical characteristic of soil. Cluster three include four samples of agricultural land Zs13, Zs14 and Zs29, and one samples of urban and built up land Zs15 which reflect that the anthropogenic activates are the main factors controlling on the physiochemical characteristics of soil at these sites.

All other cluster of single cases belong to different LULC classes from different parts of the LZRB are indicating in a convincing way, high independency for each cluster. Theses independent clearly explain the complexity of the factor controlling the soil characteristic of the main basin and in particular the heterogeneity of parent materials of the LZRB soils, where it's derived from different exposed rocks and sediments from Paleozoic till recent. The individual cluster cases confirm different character as compared with the remaining samples. These cluster groups reveals that the natural conditions and parent rocks types still the main factors controlling the geochemical behavior of the basin while the anthropogenic effects can be noticed at specific locations.

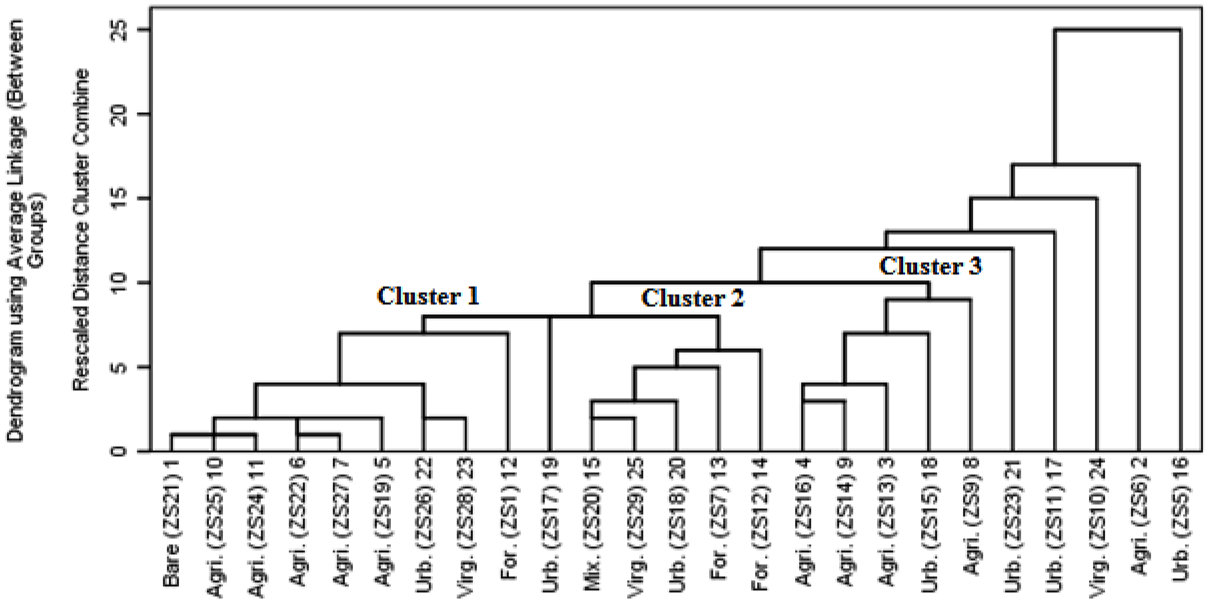


Figure 5- Hierarchical dendrogram for soil samples of LZRB using Q-mode cluster analysis

3.2.5 Assessment of soil contamination

3.2.5.1 Enrichment factor (Ef)

Enrichment ratios for eight metals are calculated using Eq. 2 [31, 32]. Values of Ef for different LULC soils is presented in Table-4. Ef values of most metals shown to be lower than minimal enrichment indicating of no or minimal pollution. Cr and Ni in five LULC classes, Co in the virgin soil and Mn in forest land are belong to moderate enrichment category therefore, Cr and Ni might pose risk to the surrounding environment Figure-6a. Sample Zs5 of urban and built up land is extremely enriched with Cr and Ni, significant enriched with Co and Mn, moderate enriched with Zn and Cd, and minimal enriched with Cu and Zn Table-4. Variation of Ef values for the different metals in the present soil samples may be due to the variation in the magnitude of each metal in the parent materials from which the soil is derived and/or the difference in the removal rate of each metal from the soil. All soil samples except Zs5 are located within minimal to moderate enrichment according to Ef categories Table-4.

3.2.5.2 Contamination factor (Cf)

Based on Cf values Table-4 and Figure-6b, samples of LZRB classified within low degree of contamination for all heavy metals in different LULC classes except for Cr and Ni in agriculture land, and Ni in urban and built up land, and virgin soil within moderate degree of contamination. Soil sample Zs5 classified within very high degree of contamination with respect to Cr and Ni, considerable degree of contamination with respect to Co, moderate degree of contamination with respect to Mn and low degree of contamination with respect to Cu, Zn, Cd and Pb. All soil samples except Zs5 are within low to moderate degree of contamination according to Cf categories Table-4.

3.2.5.3 Contamination degree (CD)

Considering the CD, all LULC classes showed a low degree of metal contamination except Zs5 site which indicates very high degree of contamination Table-4 and Figure-6c.

Table 4-Detail description result of soil pollution indices of different LULC classes, Ef: enrichment factor, Cf : contamination factor and CD: contamination degree.

Index	Sample ID.	ZS21	ZS6	ZS13	ZS16	ZS19	ZS22	ZS27	ZS9	ZS14	ZS25	ZS24	ZS1	ZS7
	LULC	Bar.*	Agriculture land										Forest	
EF	Cr	3.25	1.42	2.22	2.55	4.46	3.65	3.03	3.66	2.78	2.75	3.04	2.96	1.46
	Mn	1.69	2.26	1.49	2.08	1.41	2.07	1.75	2.03	2.64	1.67	1.79	2.06	2.14
	Co	2.05	1.76	1.56	1.96	2.23	1.97	2.11	1.93	2.16	2.05	1.79	1.99	1.46
	Ni	4.21	1.94	2.85	3.8	4.3	3.77	3.78	2.98	3.73	3.55	3.33	3.56	2.15
	Cu	1.24	1.02	0.87	1.08	1.17	1.07	1.09	1.5	1.54	1.22	1.12	1.09	1.16
	Zn	1.41	1.1	1.01	1.19	1.28	1.24	1.62	1.48	1.44	1.43	1.24	1.2	1.25
	Cd	2.22	1.26	1.98	2.41	2.38	2.15	2.19	1.46	1.77	2.63	2.16	2.1	1.16
	Pb	1.17	0.88	0.82	0.97	1.01	0.93	1.05	1.23	1.35	1.79	0.91	1	1.11
Cf	Cr	0.61	1.13	1.25	1.32	1.2	1.07	0.71	1.3	1.19	0.57	1.03	0.15	0.53
	Mn	0.32	1.79	0.83	1.08	0.38	0.61	0.41	0.72	1.13	0.35	0.61	0.11	0.78
	Co	0.39	1.4	0.87	1.02	0.6	0.58	0.5	0.69	0.93	0.43	0.6	0.1	0.53
	Ni	0.79	1.54	1.6	1.97	1.15	1.1	0.89	1.06	1.6	0.74	1.13	0.18	0.78
	Cu	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	Zn	0.27	0.87	0.56	0.62	0.34	0.36	0.38	0.53	0.62	0.3	0.42	0.06	0.46
	Cd	0.42	1	1.11	1.25	0.64	0.63	0.52	0.52	0.76	0.55	0.73	0.11	0.42
	Pb	0.22	0.7	0.46	0.5	0.27	0.27	0.25	0.44	0.58	0.37	0.31	0.05	0.41
CD		3.03	8.45	6.71	7.78	4.6	4.64	3.68	5.29	6.83	3.32	4.84	0.78	3.93

	Sample ID.	ZS12	ZS20	ZS5	ZS11	ZS15	ZS17	ZS18	ZS23	ZS26	ZS28	ZS10	ZS29
Index	LULC	Forest	Mix.**	Urban and Built up land							Virgin soil		
EF	Cr	3.11	1.63	51.02	1.96	1.94	2.2	3.33	4.19	4.11	2.82	4.9	1.6
	Mn	3.39	1.58	5.32	1.09	1.67	1.08	1.95	1.75	2.23	2.21	2.23	1.78
	Co	3.02	1.35	17.77	1.42	1.59	1.68	2.05	2.16	2.35	2.1	3.77	1.64
	Ni	5.89	1.3	93.25	2.61	2.38	3.21	4.2	4.29	4.47	4.26	6.85	2.02
	Cu	2.37	0.85	1.6	0.93	1.09	1.16	1.15	1.19	1.21	1.28	2.43	1.01
	Zn	1.33	1.21	2.43	1.39	1.26	1.32	1.14	1.34	1.56	1.26	1.68	1.23
	Cd	0.86	0.67	2.8	2.53	1.48	3.44	1.05	1.72	1.92	1.22	1.43	0.7
	Pb	1.01	0.81	1.06	0.86	1.38	2.75	0.96	2.24	1.21	0.95	0.73	1.01
Cf	Cr	0.89	0.61	11.57	0.38	1.39	0.74	1.34	0.97	0.63	0.78	0.83	0.66
	Mn	0.97	0.59	1.21	0.21	1.2	0.37	0.79	0.4	0.34	0.61	0.38	0.74
	Co	0.87	0.51	4.03	0.27	1.14	0.57	0.83	0.5	0.36	0.58	0.64	0.68
	Ni	1.69	0.49	21.15	0.5	1.71	1.08	1.7	0.99	0.68	1.18	1.16	0.83
	Cu	0.04	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	Zn	0.38	0.46	0.55	0.27	0.91	0.45	0.46	0.31	0.24	0.35	0.28	0.51
	Cd	0.25	0.25	0.63	0.49	1.06	1.16	0.42	0.4	0.29	0.34	0.24	0.29
	Pb	0.29	0.3	0.24	0.17	0.99	0.92	0.39	0.52	0.19	0.26	0.12	0.42
CD		5.37	3.23	39.39	2.29	8.41	5.3	5.94	4.11	2.75	4.12	3.68	4.14

*Bar.; Bare soil, **Mix.; Mixed barren land

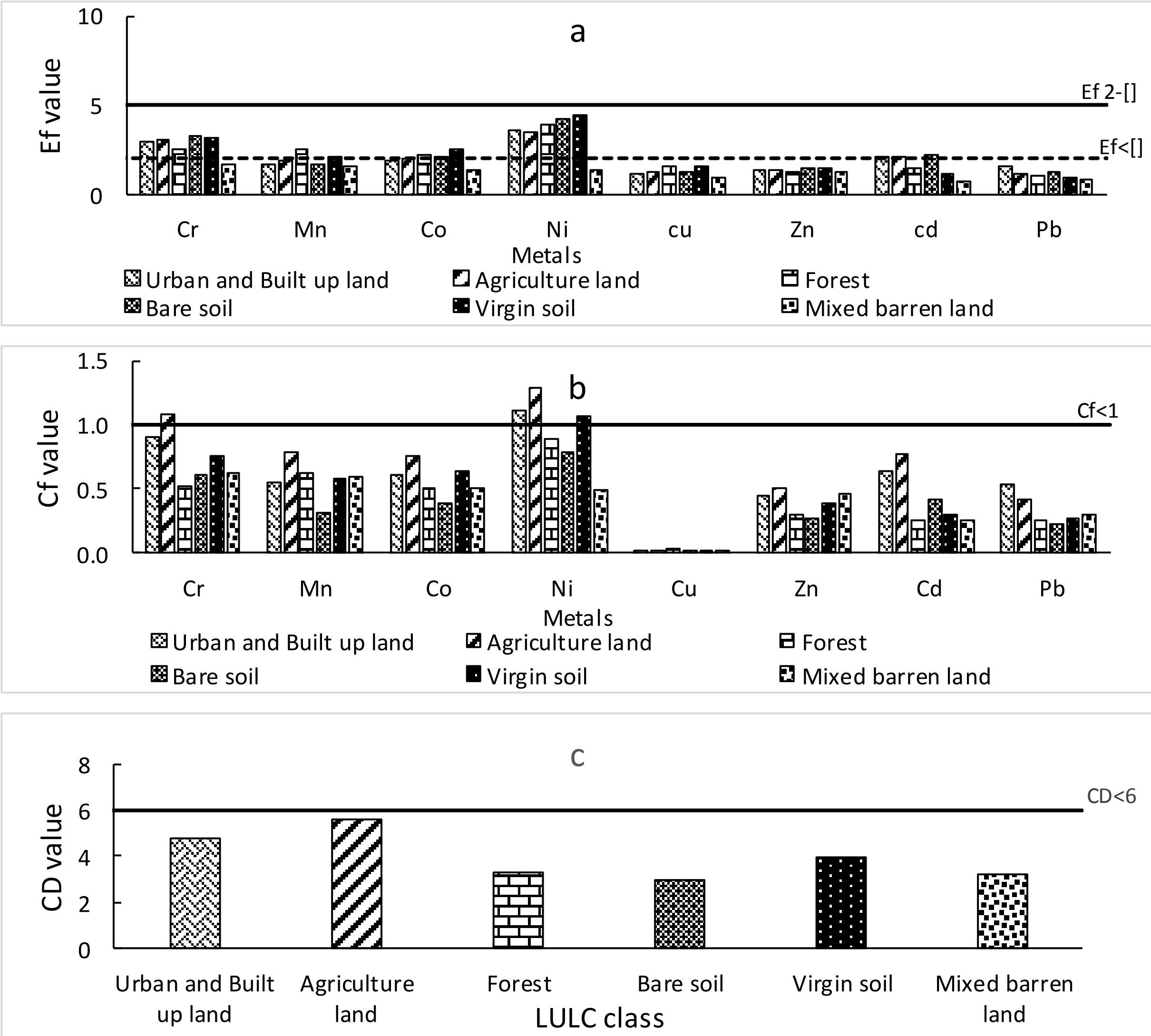


Figure 6- a, b and c: Heavy metals enrichment factors of Ef value, Cf value and CD value, respectively of different LULC classes in LZRB.

Conclusion

Heavy metals concentrations for different LULC classes of the LZRB were established in this study. The variations in heavy metals contents throughout the LZRB may be influenced by the intensities of various land use activities, soil types and chemistry and environmental conditions. The soils of the LZRB are moderately alkaline and characterized by low organic content. Comparing heavy metal in soil from different LULC classes were evidently affected by the human impact whereas, the higher accumulation of Mn, Cr, Ni, Zn, Cu, Co, and Cd is found in agriculture land and Pb is found in urban and built up land. The high content of most heavy metals in soils of the northeastern and southeastern parts of LZRB can be attributed to the occurrence of mafic or ultramafic rocks and lithologies rich in Fe and Mn metals. However, it is evident that the concentration of all studied heavy metals, show a wide range of variation between the minimum and maximum contents which reflect the heterogeneity in the lithostratigraphy and variations in the LULC of the main basin. The results indicate that the regional geology is a key factor to determine soil geochemical baselines for soil pollution assessment. Heavy metals distribution in different LULC, indications possible human influences superimposed on natural soil background concentrations. Phosphate fertilizers and pesticides containing heavy metals are also important sources of heavy metals in soils.

The results obtained by correlation show that the positive correlation of MgO with Cr, Ni and Co suggest that are derived from direct weathering of ultramafic and mafic rocks and from the recycling of sedimentary rocks enriched in ultramafic debris which are predominance in the upper part of the main basin. Positive correlations of major oxides suggest that they are associated with different types of accessory minerals that concentrate these elements and can be attribute mainly to the fine fraction of feldspar and clay minerals. Positive correlation of P_2O_5 with OM, Cr, Co, Ni, Cu and Zn which are geochemically quite different can be interpreted by the anthropogenic pollution. Whereas, all these elements are widely used in industry and agricultural activities. In addition, the presence of phosphorus is an indicator of applying phosphate fertilizers. Strong correlating of all heavy metals except Cr with Mn and some heavy metals as Cr, Mn, Co and Ni with Fe_2O_3 probably refers that they are adsorbed on Fe and Mn oxide/hydroxide.

The Ef values for most metals are lower than minimal enrichment indicating of no or minimal pollution. Among heavy metals only Cr and Ni in five LULC class, Co in virgin soil and Mn in forest land lay within moderate enrichment categories. Soils of LZRB classified within low degree of contamination based on Cf categories, for all heavy metals in different LULC classes, except of Cr and Ni in agricultural land and also Ni in virgin soil and in urban and built up land which lie within moderate degree of contamination. Considering the CD, soils from all LULC classes showed a low degree of metal contamination except Zs5 site which indicate very high degree of contamination.

Acknowledgements

The authors wish to acknowledge the Ministry of Higher Education and Scientific Research of Iraq (MoHESR) for their funding assistance during the Ph.D. research program. We are grateful to the laboratory staff of the TU Bergakademie Freiberg and Geological Survey of Iraq who assisted immensely in the analytical work. The authors are grateful to Ph.D. Hussein A. Jassas, and B.S. Rand M. Al-Saati for their valuable comments.

References

1. Skordas, K. and Kelepertsis, A.**2005**. Soil contamination by toxic metals in the cultivated region of Agia, Thessaly, Greece. Identification of sources of contamination. *Environmental Geology*, Springer, 48, pp:615–624.
2. Shacklette, H. T. and Boerngen, J. G. **1984**. Element concentrations in soils and other surficial materials of the conterminous United States. U.S. Geological survey professional paper No. 1270 (USGPO).
3. Brown, C. J. and Thomas, M. A. **2014**. Major and trace element geochemistry and background concentrations for soils in Connecticut. *Northeastern Geoscience*. 32, pp:1–37.
4. Smith D.B, Cannon W.F, Woodruff L.G, Solano F., Kilburn J.E., Fey D.L. **2013**. Geochemical and mineralogical data for soils of the conterminous United States. US Geological Survey Data Series 801, p:19.
5. He Z-W, Kong B, Weng Z-Yand Shi Z-M. **2015**. The spatial relationship between human activities and C, N, P, S in soil based on landscape geochemical interpretation. *Environmental geochemistry and health*, pp:1-18.
6. He, Z. L., Yang, X. E. and Stoffella, P. J. **2005**. Trace elements in agroecosystems and impacts on the environment. *Journal of Trace Elements in Medicine and Biology*, 19(2), pp:125-140.
7. Kabata-Pendias, A. **2010**. Trace elements in soils and plants. (CRC press).
8. Raji, B. A., Jimba, W. B. and Alagbe, S. A. **2015**. The distribution and geochemical assessment of trace elements from the semi-arid to sub-humid savanna of Nigeria. *Environmental Earth Sciences* 73(7), pp:3555–3564.
9. Plant, J., Smith, D., Smith, B. and Williams, L. **2001**. Environmental geochemistry at the global scale. *Applied Geochemistry*, 16, pp:1291–1308.
10. Al Manmi, D. A. **2008**. Water resources management in Rania area, Sulaimaniyah NE-Iraq. Unpubl. Ph.D. Thesis, University Baghdad, p:225.
11. Ali, A. R. **2012**. Major and trace elements distribution in stream sediments of the lesser zab river at northeatern Iraq:implications to weathering and transportation. *Iraqi Bulletin of Geology and Mining* 8, pp:25–44.
12. Rasul, A. K. **2013**. Hydrochemistry and geochemistry of recent sediments of Lesser Zab River and Dokan reservoir, Kurdistan Region – NE Iraq Unpubl. Ph.D. Thesis, Salahaddin University – Erbil, p:146.
13. Al-Saady, Y. I., Merkel, B., Al-Tawash, B. and Al-Suhail, Q. **2015**. Land use and land cover (LULC) mapping and change detection in the Little Zab River Basin (LZRB), Kurdistan Region, NE Iraq and NW Iran. *FOG - Freiberg Online Geoscience*, 43, pp:1–32.

14. Azizi, H. and Moinevaziri, H. **2009**. Review of the tectonic setting of Cretaceous to Quaternary volcanism in northwestern Iran. *Journal of Geodynamics*, 47, pp:167–179.
15. Jassim, S. Z. and Goff, J. C. **2012**. *Geology of Iraq*. Geological Society of London, 2006, p:341.
16. Fouad, S. F. **2012**. Tectonic Map of Iraq scales 1: 1000 000, Third Edition, GEOSURV, Baghdad, Iraq.
17. Ghorbani, M. **2013**. The Economic Geology of Iran, Springer Science and Business Media, pp:45–64.
18. Sissakian, V. K. **1992**. The geology of Kirkuk Quadrangle sheet NI-38-2 (GM 9) SCALE 1:250 000. Int. report, Geosurv-Iraq.
19. Mohajjel, M. and Fergusson, C. L. **2014**. Jurassic to Cenozoic tectonics of the Zagros Orogen in northwestern Iran. *International Geology Review*, 56, pp:263–287.
20. Nezhad, E. **1973**. Geological Quadrangle map of Iran No:B4 (Mahabad), Scale1:250000. Ministry of economy, Int. report, Geological survey of Iran.
21. Ma'ala, K. A. **2007**. The geology of Sulaimaniyah Quadrangle sheet NI-38-3, GEOSURV, Baghdad, Iraq. Int. Rep. No. 3095. Geosurv-Iraq.
22. Kottek, M., Grieser, J., Beck, C., Rudolf, B. and Rubel, F. **2006**. World map of the Köppen-Geiger climate classification updated. Meteorologische Zeitschrift, 15, pp:259–263.
23. Matschullat, J., Ottenstein, R. and Reimann, C., **2000**. Geochemical background–can we calculate it? *Environmental Geology* 39, pp:990–1000.
24. Gałuszka, A. **2006**. Methods of determining geochemical background in environmental studies. Problems of landscape ecology. Polish association of landscape ecology. Warsaw (in Polish with English Summ. 16, pp:507–519.
25. Dissanayake, C. B., Tobschall, H. J., Palme, H., Rast, U. and Spettel, B. **1983**. The abundance of some major and trace elements in highly polluted sediments from the Rhine river near Mainz, West Germany. *Science of the total environment* 29, pp:243–260.
26. Zgłobicki, W., Lata, L., Plak, A. and Reszka, M. **2011**. Geochemical and statistical approach to evaluate background concentrations of Cd, Cu, Pb and Zn (case study: Eastern Poland). Environ. *Environmental Earth Sciences* 62, pp:347–355.
27. Hernández-Crespo, C. and Martín, M., **2015**. Determination of background levels and pollution assessment for seven metals (Cd, Cu, Ni, Pb, Zn, Fe, Mn) in sediments of a Mediterranean coastal lagoon. *Catena* 133, pp:206–214.
28. Tukey, J.W. **1977**. *Exploratory data analysis*, First Edition., Pearson, p:688.
29. de Lima Rodrigues, A. S., Malafaia, G., Costa, A. T. and Nalini-Jr, H. A. **2014**. Background values for chemical elements in sediments of the Gualaxo Do Norte River Basin, MG, BRAZIL. *Revista de Ciências Ambientais*, 7(2), pp:15-32.
30. Li, S. and Zhang, Q. **2010**. Spatial characterization of dissolved trace elements and heavy metals in the upper Han River (China) using multivariate statistical techniques. *Journal of Hazardous Materials*,176, pp:579–588.
31. Islam, S., Ahmed, K. and Masunaga, S. **2015**. Potential ecological risk of hazardous elements in different land-use urban soils of Bangladesh. *Science of the Total Environment*, 512, pp:94–102.
32. Dantu, S. **2009**. Heavy metals concentration in soils of southeastern part of Ranga Reddy district, Andhra Pradesh, India. *Environmental monitoring and assessment*, 149, pp:213–222.
33. Massas, I., Ehaliotis, C., Gerontidis, S. and Sarris, E.**2009**. Elevated heavy metal concentrations in top soils of an Aegean island town (Greece): total and available forms, origin and distribution. *Environmental Monitoring and Assessment*, 151, pp:105–116.
34. Rashed, M. N. **2010**. Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. *Journal of Hazardous Materials*, 178, pp:739–746.
35. Sutherland, R. A.**2000**. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, 39, pp:611–627.
36. Dimitrijević, M. D., Nujkić, M. M., Alagić, S. Č., Milić, S. M. and Tošić, S. B. **2016**. Heavy metal contamination of topsoil and parts of peach-tree growing at different distances from a smelting complex. *International Journal of Environmental Science and Technology*, 13, pp:615–630.
37. Varol, M. **2011**. Assessment of heavy metal contamination in sediments of the Tigris River

(Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous Materials*, 195, pp:355–364.

38. Turekian, K. K. and Wedepohl, K. H. **1961**. Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin*, 72, pp:175–192.

39. Hakanson, L. **1980**. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, 14, pp:975–1001.

40. Luo, W., Lu, Y., Giesy, J. P., Wang, T., Shi, Y., Wang, G. and Xing, Y. **2007**. Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China. *Environmental Geochemistry and Health*, 29, pp:459–471.

41. Younos, T. M. **1987**. *Land Application of Wastewater Sludge.* New Yourk: American Society of Civil Engineers, p:95.

42. Mackenzie, F. T. **2005** Sediments, diagenesis, and sedimentary rocks: *Treatise on Geochemistry*. Elsevier, 7, p:446.

43. Wedepohl, K. H. **1995**. The composition of the continental crust. *Geochimica et cosmochimica Acta*, 59, pp:1217–1232.

44. Nadaska, G., Lesny, J. and Michalik, I. **2010**. Environmental aspect of manganese chemistry. *Hungarian Journal of Sciences*, ENV-100702-A 1–16.

45. Howe, P. D., Malcolm, H. M. and Dobson, S. **2004**. Manganese and its compounds: environmental aspects. WHO, Geneva, Concise international chemical assessment document (CICAD) 63.

46. Smith, I. C. and Carson, B. L. **1977**. *Trace metals in the environment*. Ann Arbor Science Publishers, 1, p:394.

47. Ferrante, M., Conti, G. O., Rasic-Milutinovic, Z. and Jovanovic, D.**2013**. *Health Effects of Metals and Related Substances in Drinking Water*. IWA Publishing, p:126.

48. McGrath, S. P. and Smith, S.**1998**. Chromium and nickel. *Heavy metals in soils*, 7, pp:152–178.

49. Sissakian, V. K. **1998**. The geology of Erbil and Mahabad Quadrangle sheet NJ-38-14 and NJ-38-15 (GM 5 and 6) scale 1:250 000, Geosurv-Iraq, Int. report.

50. Alloway, B. J. **1995**. *Heavy metals in soils*, 2nd. Ed. Blackie Acad. Prof. New York. p:368.

51. Nicholson, F. A., Smith, S. R., Alloway, B. J., Carlton-Smith, C. and Chambers, B. J. **2003**. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Science of the Total Environment*, 311, pp:205–219.

52. Mukai, H., Tanaka, A., Fujii, T. and Nakao, M. **1994**. Lead isotope ratios of airborne particulate matter as tracers of long-range transport of air pollutants around Japan, *Journal of Geophysical Research: Atmospheres*, 99(D2), pp: 3717-3726.

53. Mohiuddin, K. M., Zakir, H. M., Otomo, K., Sharmin, S. and Shikazono, N. **2010**. Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. Int. *International Journal of Environmental Science & Technology*, 7, pp:17–28.

54. Hale, M. and Plant, J. A. **1994**. *Drainage Geochemistry*. European Materials Research Society Symposia Proceedings. Elsevier. P:766.

55. Dinelli, E., Cortecci, G., Lucchini, F. and Zantedeschi, E. **2005**. Sources of major and trace elements in the stream sediments of the Arno River catchment (northern Tuscany, Italy). *Geochemical Journal*, 39, pp:531–545.