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Comparison the Geochemical Background, Threshold and Anomaly with Pollution Indices in the Assessment of Soil Pollution: Al-Hawija, North of Iraq Case Study

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Abstract: ***The geochemical background, threshold and anomaly values are compared with pollution indices (Enrichment Factor, Contamination Factor, Geo-accumulation index and Pollution Load Index) in soil collected from Al-Hawija area. The main target is to clarify the differences between the real geochemical background values of heavy metals (Cd, Pb, Co, Cr, Ni, V, Cu, Zn, Mo, As, Th and U) and the results of pollution indices. The results showed that the Contamination Factor is often almost consistent with the geochemical background, the Enrichment Factor indicated a low to moderate contamination soil, Geo-accumulation index indicated unpolluted to moderately polluted soil and Pollution Load Index indicated perfection to deterioration soil. The real geochemical background showed a natural distribution of most heavy metals with anomaly of some other. These anomalies didn't attributed to the pollution, but rather reflect the source from which soil has been derived. Pollution indices depend almost entirely on the global reference averages, and don't take the soil origin into account. Consequently, they gave results differ than the geochemical background. The pollution assessment of the heavy metals using EF is more consistent with the geochemical background, but there is high variation when compared the geochemical background to the CF, I-geo and PLI indices.***

Keywords: Geochemical background, Threshold, Anomaly, pollution indices, Iraq.

1. Introduction

Evaluation of distribution and remediation of heavy metal pollution is the most concerned (Deng Hong-gui et al., 2012), because the metal pollution in soil causes a serious threat to the human health and agricultural products. In terms of the point of geochemist's view, heavy metals in sediments show anomalous concentrations which are derived from natural inputs and human activities (Barakat et al., 2012). Generally, soil pollution may be considered appreciable when concentrations of an element in soils were two-three times greater than the mean background levels (Logan and Miller, 1983). Often, the scientists who interested in protection of the environment use traditional parameters for the purpose of description pollution levels. These parameters are Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI) and Geo-Accumulation Index (I_{geo}).Geochemists often deals with geochemical anomaly; where it has been identified by setting threshold values, which mark the upper and lower limits of normal variation for a particular population of data (Hawkes, 1962). Values within the upper and lower threshold values represent background values and those above are anomalies. Geochemical anomaly can be done by many methods vary from simple to complex statistical calculations (Reimann et al., 2005).Consequently, soil samples of Al-Hawija area, north of Iraq were chosen as a case study to conduct this study. The study area is a part of Kirkuk governorate. It covers an area of about 630km² between latitudes (35°16′20"-35°32′33") and longitudes (43°45′50"-44°10′12") (Figure-1). This area is agricultural land bonded by the Lesser Zab River in the northwest, Btewa anticline to the east and northeast, Kirkuk-Beji motorway in the south and southeast, Al-Hawija Irrigation Project to the west and southwest. Some evidence of the study area have been obtained by the previous works indicated high concentrations of some metals. The surface soil is characterized by high content of some heavy metals, except of Co and V (Hassan, 2007), and therefore, based on geo-accumulation index, the area was expressed as an unpolluted to slight polluted. Al-Kazwini et al. (2007) stated that the sediment load provided a new material to the area. The geological formations in the study area are Fatha, Injana, Mukdadia and Bai Hassan formations exposed only in Btewa anticline, which represents the east and northeast border of the study area. Geological formations throughout the study area are covered by quaternary deposits that are consisting of river terraces, polygenetic deposits, slope deposits, residual gravels, flood plain and valley fill deposits(Sissakian, 1993).This study is an attempt to clarify the differences between geochemical anomalies andpollution indices that used in the pollution assessment.

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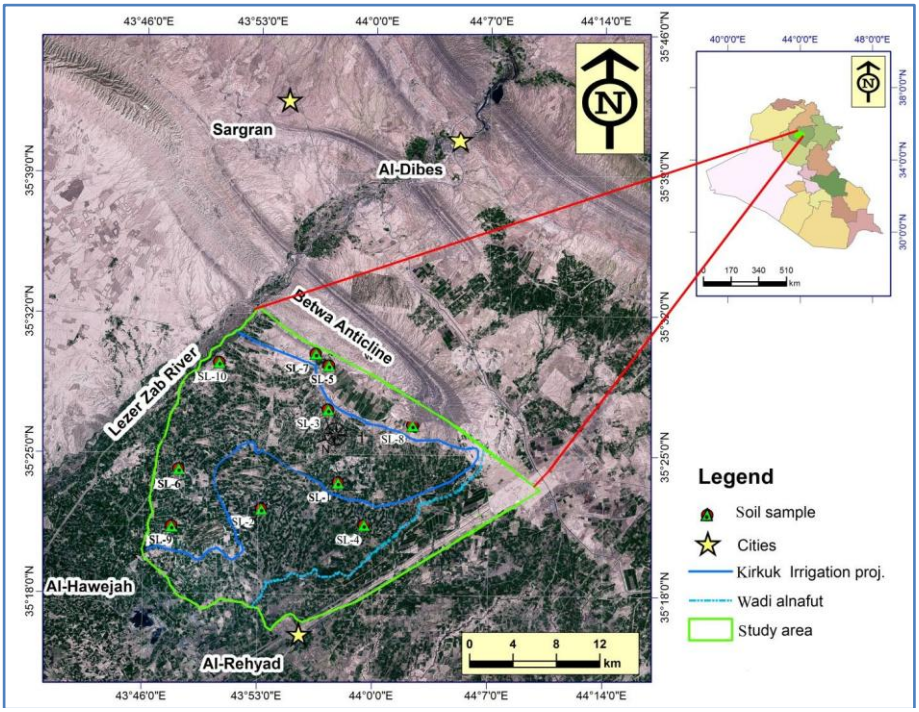


Figure 1: Location map of the study area and sampling sites

2. Materials and methods

A total of 10 soil samples were collected from depth of 10 cm. Samples were kept in 500ml size plastic containers. The coordinates of sampling sites are shown in Figure 1 and listed in Table 1.

Table 1: coordination of the sampling sites in the study area

Sample number	Longitude	Latitude
SL-1	43° 58' 16.4"	35° 23' 34.5"
SL-2	43° 53' 10.9"	35° 22' 15.3"
SL-3	43° 57' 12.1"	35° 27' 14.6"
SL-4	43° 59' 26.6"	35° 21' 29.5"
SL-5	43° 57' 13.7"	35° 29' 26.3"
SL-6	43° 48' 07.6"	35° 24' 13.2"
SL-7	43° 56' 25.2"	35° 30' 01"
SL-8	44° 02' 21.4"	35° 26' 29.8"
SL-9	43° 47' 43.2"	35° 21' 21.9"
SL-10	43° 50' 32.1"	35° 29' 33.4"

All samples were analyzed for Cd, Pb, Co, Cr, Ni, V, Cu, Zn, Mo, As, Th and U using ICP-MS in ALS Laboratory Group, Analytical Chemistry and Testing Services, Mineral Division-ALS Chemex at Sevilla, Spain.Background and threshold were computed according toHawkes and Webb (1962).The EF is defined as follows (Ergin et al., 1991):

$$EF = (M/Fe)_{sample} / (M/Fe)_{background}$$

Where:

$(M/Fe)_{sample}$: The ratio of metal and Fe concentrations of the sample.

$(M/Fe)_{background}$: The ratio of metal and Fe concentrations of the background.

The EF is the relative abundance of a chemical element in a soil compared to the bedrock (Hernandez et al, 2003). In this study, Fe was selected as a normalizing factor because it has a strong correlation with all heavy metals(Barakat et al., 2012).The CF wascalculated as follows:

$$CF = \frac{Metal\ content\ in\ the\ sediment}{Background\ level\ of\ metal}$$

Geo-accumulation index (I_{geo}) was employed to determine and define metal contamination in sediments by comparing current concentrations with background levels (Muller, 1981). I_{geo} is expressed by the following equation:

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

Where:

C_n: The measured concentration of the examined metal (n) in the sediment samples.

B_n: The geochemical background concentration of the metal (n).

1.5: The background matrix correction factor due to lithogenic effects.

The PLI proposed by Tomlinson et al. (1980) represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample (Barakat et al., 2012). It was obtained by applying the equation below:

$$PLI = (CF_1 * CF_2 * CF_3 * CF_4 * \dots\dots\dots CF_n)^{1/n}$$

Where

PLI = Pollution Load Index.

CF = contamination factor.

n = number of metals.

The threshold values were estimated according to Hawkes and Webb (1962) by using the following equation:

$$Threshold = Mean \pm 2\ standard\ deviation$$

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The positive and negative output of the above equation refers to the upper and lower threshold values respectively, where background is a median of data.

3. Results

3.1 Geochemical Background, Threshold and Anomaly

The geochemical anomalies were identified based onthreshold limit values of the normal variations for the particular population of data.Values within the threshold limit values are referred to as background values and those above as anomalies (Reimann et al., 2005). Table 2 presents the result of the present study. The geochemical background of Pb (12.5), Co (16), Cr (385), Ni (111), V (87.5), Cu (25.5), Zn (65), As (7.5), Th (4.5) and U (1.5)are lower than of global reference values, except of Co, Cr, Cu and As. The vast majority of results represent background,but other some appearedhigher thanthe threshold. A slight geochemical anomalies of Pb, Zn, As and U in sample 2; Cr in sample 5; Co, Ni and V in sample 7; and As in samples 6 and 10 are detected(Figure 2).Soil of the study area has been derived from basic and ultrabasic rocks; so that, the background of some heavy metals being normally high. So, in this case, it isworth to consider the local anomalyas a geochemical background, attributed to the soil origin not to pollution.

Table 2: Results of pollution indices assessment for heavy metals compared to the geochemical background and threshold.

S.No.	PLI	Para.	Elements (ppm)											
			Cd	Pb	Co	Cr	Ni	V	Cu	Zn	Mo	As	Th	U
SL-1	1.07	Conc.	BDL	15	15	470	111	85	26	71	BDL	11	5	1.3
		EF	---	1.14	0.89	1.15	0.95	0.92	0.96	1.03		1.39	0.97	0.82
		CF	---	1.20	0.94	1.22	1.00	0.97	1.02	1.09	---	1.47	1.02	0.87
		I_{geo}	---	0.24	0.19	0.24	0.20	0.19	0.20	0.22	---	0.29	0.20	0.17
SL-2	1.24	Conc	BDL	20	17	310	114	91	29	111	BDL	15	5.7	2
		EF	---	1.53	1.01	0.77	0.98	0.99	1.09	1.63		1.91	1.11	1.27
		CF	---	1.60	1.06	0.81	1.03	1.04	1.14	1.71	---	2.00	1.16	1.33
		I_{geo}	---	0.32	0.21	0.16	0.21	0.21	0.23	0.34	---	0.40	0.23	0.27
SL-3	0.91	Conc	BDL	12	16	500	106	85	23	58	BDL	3	5.1	1.5
		EF	---	1.01	1.05	1.36	1.00	1.02	0.95	0.94		0.42	1.09	1.05
		CF	---	0.96	1.00	1.30	0.95	0.97	0.90	0.89	---	0.40	1.04	1.00
		I_{geo}	---	0.19	0.20	0.26	0.19	0.19	0.18	0.18	---	0.08	0.21	0.20
SL-4	0.86	Conc	BDL	9	16	410	106	86	23	59	BDL	3	4.8	1.5
		EF	---	0.76	1.06	1.12	1.01	1.04	0.95	0.96		0.42	1.03	1.06
		CF	---	0.72	1.00	1.06	0.95	0.98	0.90	0.91	---	0.40	0.98	1.00
		I_{geo}	---	0.14	0.20	0.21	0.19	0.20	0.18	0.18	---	0.08	0.20	0.20
SL-5	1.05	Conc	BDL	15	15	600	123	89	26	66	BDL	7	4.5	1.4
		EF	---	1.19	0.93	1.54	1.10	1.01	1.01	1.01		0.92	0.91	0.92
		CF	---	1.20	0.94	1.56	1.11	1.02	1.02	1.02	---	0.93	0.92	0.93
		I_{geo}	---	0.24	0.19	0.31	0.22	0.20	0.20	0.20	---	0.19	0.18	0.19
SL-6	1.09	Conc	BDL	13	18	380	111	89	25	64	BDL	16	4.7	1.5
		EF	---	1.05	1.14	1.00	1.01	1.03	0.99	0.99		2.16	0.97	1.01
		CF	---	1.04	1.13	0.99	1.00	1.02	0.98	0.98	---	2.13	0.96	1.00
		I_{geo}	---	0.21	0.23	0.20	0.20	0.20	0.20	0.20	---	0.43	0.19	0.20
SL-7	1.08	Conc	BDL	9	20	350	132	102	30	72	BDL	8	5.8	1.7
		EF	---	0.70	1.21	0.88	1.15	1.13	1.14	1.08		1.04	1.15	1.10
		CF	---	0.72	1.25	0.91	1.19	1.17	1.18	1.11	---	1.07	1.18	1.13
		I_{geo}	---	0.14	0.25	0.18	0.24	0.23	0.24	0.22	---	0.21	0.24	0.23
SL-8	0.93	Conc	BDL	11	16	370	110	78	24	61	BDL	6	4.6	1.4
		EF	---	0.91	1.04	1.00	1.03	0.93	0.98	0.97		0.83	0.97	0.97
		CF	---	0.88	1.00	0.96	0.99	0.89	0.94	0.94	---	0.80	0.94	0.93
		I_{geo}	---	0.18	0.20	0.19	0.20	0.18	0.19	0.19	---	0.16	0.19	0.19
SL-9	0.89	Conc	BDL	14	15	390	110	81	24	56	BDL	3	4.7	1.6
		EF	---	1.17	0.98	1.05	1.03	0.96	0.98	0.90		0.42	1.00	1.11
		CF	---	1.12	0.94	1.01	0.99	0.93	0.94	0.86	---	0.40	0.96	1.07
		I_{geo}	---	0.22	0.19	0.20	0.20	0.19	0.19	0.17	---	0.08	0.19	0.21
SL-10	1.11	Conc	BDL	11	17	350	125	92	28	66	BDL	15	5.6	1.6
		EF	---	0.81	0.97	0.83	1.03	0.97	1.01	0.93		1.83	1.05	0.98
		CF	---	0.88	1.06	0.91	1.13	1.05	1.10	1.02	---	2.00	1.14	1.07
		I_{geo}	---	0.18	0.21	0.18	0.23	0.21	0.22	0.20	---	0.40	0.23	0.21
Min. of conc.			---	9	15	310	106	78	23	56	BDL	3	4.5	1.3
Max. of conc.			---	20	20	600	132	102	30	111	---	16	5.8	2
Mean of conc.			---	13	16	413	115	88	26	68	---	9	5	1.6
SD of conc.			---	3.3	1.6	87	9	6.6	2.5	16	---	5.2	0.5	0.2
*Global reference value			3.8	17	17	85	44	107	25	71	1.5	1.5	10.7	2.8
Background			---	12.5	16	385	111	87.5	25.5	65	---	7.5	4.9	1.5

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Upper threshold	---	19.6	19.2	559	125	102	30.5	97	---	13	5.9	1.9
Lower threshold	---	5.9	12.8	211	93	174	20	33	---	2	3.9	1.1

*Taylor and McLennan, 1995; BDL, below detection limit.

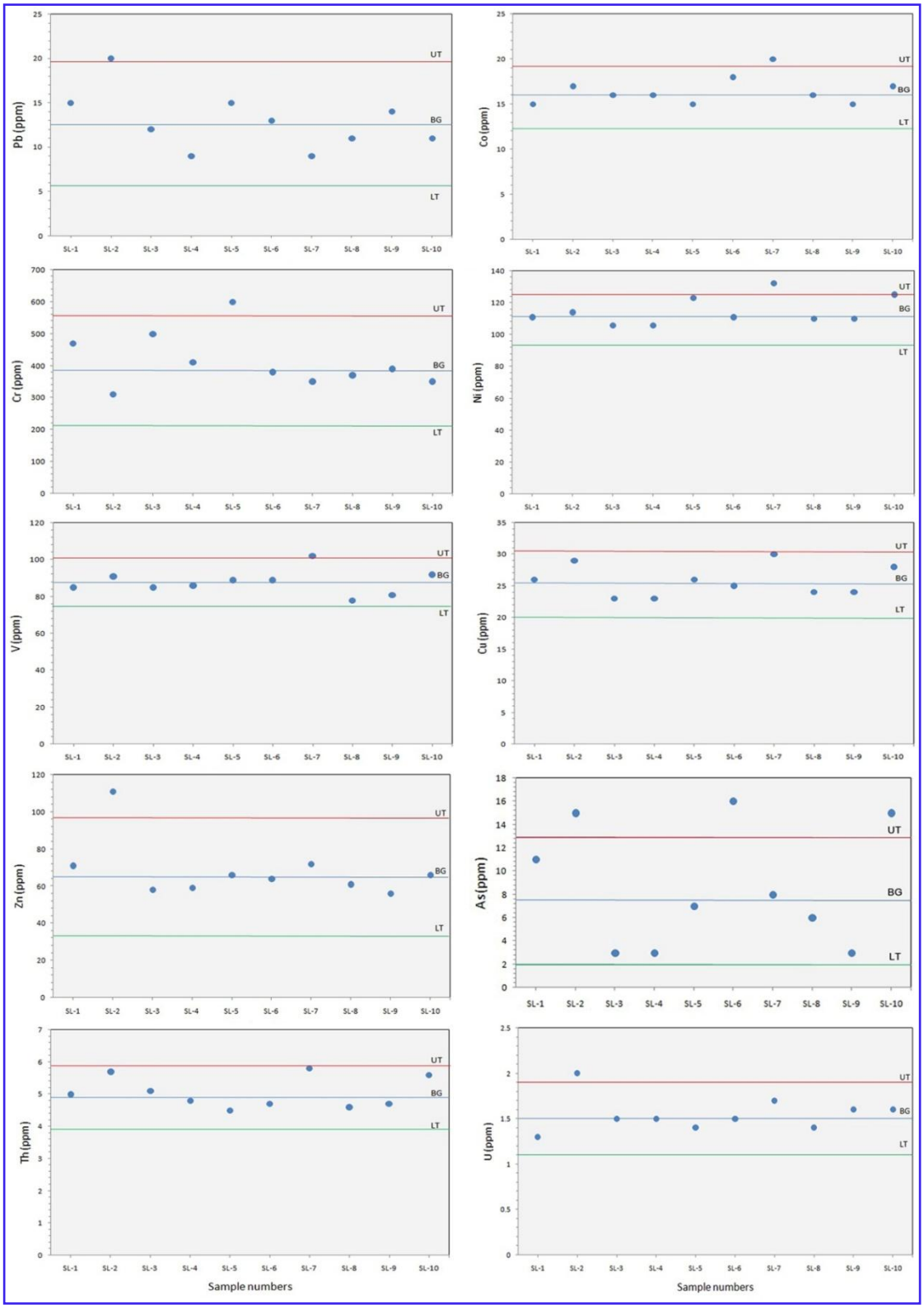


Figure 2: Geochemical background, lower and upper threshold (LT and UT) of the heavy metals in the study area.

3.2 Pollution parameters

The result of the present study in terms of EFare compared to the categories proposed by Mmolawa et al. (2011) (Table-3).The EF values for each samplesare less than 2.0, except for arsenic (As) in sample no.SL-6 is 2.16(Table-2). This confirms that the vast majority of samples corresponds to a deficiency to minimal categories, with exceptional of sample no. SL-6in which As is of moderate enriched (Table 3).Figure 2 displays an anomalous of Pb, Zn and U in SL-2,

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Co in Sl-7, Cr in Sl-5, Ni and V in Sl-7, As in SL-2, SL-6 and Sl-10. Consequently, it can be seen there is no matching between EF and geochemical anomaly.

Table 3: Enrichment factor (EF) categories (After Mmolawa et al., 2011)

EF	*Categories*
<2	Deficiency to minimal categories
2≤ to <5	Moderate enrichment
5≤ to <20	Significant enrichment
20≤ to <40	Very high enrichment
≥40	Extremely high enrichment

The computed CF values of the heavy metals seem to beclose toone, less ora little more(Table 2), it is therefore suitable to be described as of low to moderate pollution(Table 4).The global reference value of As is 1.5, in a sense, that the As in sample SL-2 has10-fold the reference value, itdeviatedfrom the normaldistribution as contained 15 ppm As (CF=2) (Table 2).Theassessment of the metals pollution using CF appears of more and it is not concordant with the real local geochemical background. Hence, CF index is considered as unsatisfied method.

Table 4: Contamination factor (CF) and categories (after Hakanson, 1980)

Contamination factor	**Category**
CF<1	Low contamination
1≤CF<3	Moderate contamination
3≤CF<6	Considerable contamination
CF>6	Very high contamination

The I_{geo}index that has been designed by Muller (1969)andconsidered by many researchers, e.g. Huu et al. (2010) was applied. The values of this index (≤0 to >5) include seven classes (0-6) vary from unpolluted to extremely polluted(Table 5). The highest class (6) reflects a 100-fold enrichment and (0) reflects the background concentration (Awadh, 2013). The results of this index arecharacterized by low values, where all are close to the zero referring to an unpolluted to moderately pollution category, with a clear tendency towards unpolluted category. This index seems to be more consistent with the real geochemical background than the rest of other indices.

Table 5: Classification of sediment grade based on I_{geo} index (after Muller, 1969).

I_{geo} value	**Class**	**Category**
≤ 0	0	Unpolluted
>0 - 1	1	From unpolluted to moderately polluted
>1 - 2	2	Moderately polluted
>2 - 3	3	From moderately to strongly polluted
>3 - 4	4	strongly polluted
>4 - 5	5	From strongly to extremely polluted
>5	6	extremely polluted

The PLI proposed Tomlinson et al. (1980) with three categories reflects a soil diversity between perfection for samples SL-3, SL-4, SL-8 and SL-9 and deteriorated category for samples SL-L, SL-2, SL-5, SL-6, SL-7 and SL-10(Table 6).

Table 6: Categories of the sediment quality according to PLI (after Tomlinson et al., 1980)

Pollution Load Index	*Categories*
PLI < 1	Perfection
PLI = 1	Only baseline levels of pollutants are presented
PLI > 1	Deterioration

The EF, CF, PLI and I_{geo} parameters as well as background and threshold of the soil samples of the study area were computed for heavy metals (Cd, Pb, Co, Cr, Ni, V, Cu, Zn, Mo, As, Th and U)and compared with the upper continental crust given by Taylor and McLennan (1985 and 1995) as a global reference values (Table-2).

4. Discussion

Most of the samples were within the local natural background with a slight rise in some elements in some samples. Cr, Ni, Cu and As are higher than the reference values, whereas Pb, Co, V, Zn, Th and U are lower than of the reference values (Figure 3a). This is attributed to the soil origin as a clear contribution of igneous rocks from adjacent high lands. Organic matter and clay minerals have had a significant impact in absorbed elements and increasing concentrations. The high range (3-16 ppm) and average (9 ppm) of As which was considered as 6-fold the reference value may be accumulated by adsorbing on the clay mineral surfaces and organic matter. Arsenic combines C and H as organic arsenic (ATSDR, 2005).1.5 ppm arsenic in the igneous rocks was suggested by Onishi (1969)and Taylor and McLennan (1995). The Foothill Zone in Kirkuk Embayment is characterized by long anticlines and very broad synclines exposing Mio-Pliocene molasse along their limbs. The inner parts of the synclines contain Quaternary deposits consisting mainly of a mixture gravel and clay (Jassim and Goff, 2006).Quartz (22-29%) and calcite (18-27%) are the predominant constituents followed by plagioclase (4-9%), gypsum (4-8%) and dolomite (1-3.5%)(Alkilabi, 2013). Chlorite in the study area is a predominant clay mineral (19-23%) followed by illite (12-15%) and palygorskite (3-6%) (Alkilabi, 2013).Chromium and Ni exists as an insoluble fraction in the soil top horizon as a reflection of the clay content (Oliver et al., 2002). They are more abundant in basic (250–300 ppm), ultrabasic igneous rocks (2300 ppm) and shales (100 ppm) than in granites and sandstones (10–35 ppm) (Reimann and De Caritat, 1998). In the study area, Cr content ranges from 310 to 600 ppm with an average of 413 ppm. It is higher than the reference value by 4.86 times. CrO_4^{2-} at acidic and neutral pH can be adsorbed on Fe and Al oxide surfaces (Davis and Leckie, 1980; Zachara et al., 1987; Ainsworth et al., 1989) and can also be adsorbed in form Cr^{6+} by ground water alluvium due to iron oxides and hydroxides coating the alluvial particles (Stollenwerk and Grove, 1985).Nickel is strongly enriched in ultramafic and mafic rocks relative to felsic igneous rocks. Mielke (1979) reports Ni in igneous rocks as: ultramafic 2000 ppm; basaltic 130 ppm; granitic 4.5-15 ppm, and a crustal abundance of 99 ppm. Nickel content in the study area ranges 106-132 ppm with an average of 115 ppm, it is a 2.6-fold of the reference values (44 ppm).The high values of Cr and Ni in the studied area

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are attributed to the basic and ultrabasic origin of soil. Generally, heavy metal contents have a natural distribution and do not attributed to pollution, with attention to the pesticides that may add such these metals to the soil. Logan and Miller (1983) stated that the soil pollution may be considered appreciable when concentrations of an element in soils were two-three times greater than the mean background levels. Pollution indices (EF, CF, I-geo and PLI) display a uniform feature (Figure 3b). EF and CFindicesare close to 1.0 with reflection high concentration of Cr, Ni and As, but I-geo seems much less than 1.0 and PLI is 1.02 close to unity.

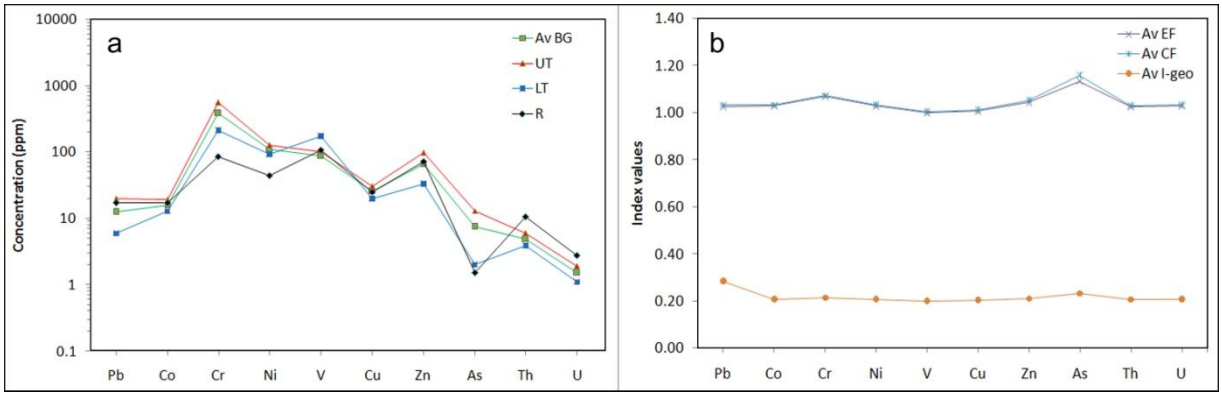


Figure 3: Distribution patterns of geochemical factors (a), and pollution factors (b).

5. Conclusions

It is very clear an unreality are there when applying the pollution indices for the soil assessment. The reason is dueto the assumption of any high value is as additional value originated by pollution. Certainly, it is not true. Thus, the invitation to take the soil origin in consideration before assessing pollution is recommended; and the geochemical background, threshold and anomaly should be adopted. Some other findings are drown here:

1) Cd and Mo are characterized by low concentrations of below the detection limit of the analytical method.
2) The assessment of the geochemical background and anomaly of heavy metals using pollution indices (EF, CF, I-geo and PLI) is unsatisfied. It is not concordant with the real local geochemical background, due to excluding the soil origin.
3) EF is more consistent with the geochemical background, but there is high variation when compared the geochemical background to the CF, I-geo and PLI indices.
4) Geochemical background of Cr, Ni, Cu and As are higher than of the global reference values, whereas of Pb, Co, V, Cu, Zn, Th and U are lower than those reference.

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