Source Identification, Ecological Risk and Spatial Analysis of Heavy Metals Contamination in Agricultural Soils of Tanjaro Area, Kurdistan Region, Iraq

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Abstract

The current work accomplished a comprehensive evaluation of heavy metals pollution in soil of agricultural areas from Tanjaro sub-district, Sulaimaniyah province, Kurdistan Region, NE Iraq. Ninety soil samples were collected from thirty different locations. Concentrations of 16 heavy metals were measured by inductively coupled plasma optical emission spectrometry ICP-OES. The pollution index (PI), potential ecological risk index (Er), enrichment factor (EF), and ecological risk index (RI) were used to assess the pollution in soil samples. High levels of Li and Ni, and moderate Ba, Cd, Hg, and Pb according to the results of concentration analysis, pollution index (PI), and potential ecological risk (ERI). High levels of Cd and Hg according to the results of Er. Agglomerative hierarchical clustering (AHC) and principal component analysis (PCA) suggested that heavy metals were generated from different natural and anthropogenic sources like natural weathering, fertilizer application, and transportation. Origins of Hg, Cd, Ni, and Pb are probably from activities like overuse of pesticides and fertilizers, whereas Pb could be exhausted from vehicle exhausts as well. Furthermore, spatial distributions revealed nonpoint source pollution for the studied heavy metals. The obtained results help in the remediation techniques of contaminated soils such as dilution with decontaminated soil or extraction or separation of heavy metals.

Keywords: Heavy Metals Source, Ecological Risk Assessment, Soil Pollution, GIS, Kurdistan Region, Heavy Metals.

1. Introduction

Contamination by heavy metals in soils is greatly considered to be harmful. It is not limited to the lithosphere, but it may spread to other components of the earth system such as the atmosphere, hydrosphere, and biosphere (Haciyakupoglu et al., 2015). Fundamentally for agricultural soils, it is worthy of mention that anthropogenic activities, especially pesticides and fertilizers implementation and irrigation with wastewater, have a major action in increasing heavy metal levels in such soils (Doabi et al., 2018). It is not only the nonbiodegradability nature of heavy metals that make them highly poisonous and dangerous, but also their tendency to accumulate in biomass causing harmful consequences (Kim et al., 2015). Moreover, heavy metal accumulation in cultivated soils has a high possibility of passing into the food chain of humans, animals, and plants, as well as deterioration of land crop productivity (Hu et al., 2018).

It has been observed heavy metals contamination in farmed soils is mainly related to anthropogenic activities (da Silva et al., 2017). However, heavy metal levels in agricultural areas are, in general, lower than that of urbanized areas (Teng et al., 2014).

Even though it is complicated to assess correctly heavy metals contamination correctly, it can be observed various analytical statistics and pollution indices have been applied successfully in issues related to heavy metals pollution in

agricultural soils. Ecological risk index, pollution index, and many other pollution indices are widely considered to be reliable in related issues (Kowalska *et al.*, 2018). Multivariate methods and enrichment factors are usually used to find the origins of heavy metals for studied soil (Pan *et al.*, 2016).

Tanjaro sub-district is one of the main agricultural areas in the north of Iraq and it produces a variety of fruits and vegetables. Limited studies were conducted on the contamination in agricultural soil of Tanjaro sub-district among the studies that have been made to assess heavy metals pollution in rural and agricultural soil in Iraq. Studies on heavy metals in agricultural soils for the area are practically not existing.

The objective of the current study is to conduct a comprehensive environmental evaluation of heavy metals contamination in agricultural soils of Tanjaro sub-district, Sulaimaniyah province, Kurdistan region, Iraq. At present, the study area is a considerably important area for crop production in the north of Iraq. This study also identifies the sources of heavy metals using various assessment indices, and statistical analysis. Moreover, this study tries to explore heavy metals concentrations in the area and to determine its sources, natural or anthropogenic, to protect the life and health of people in this region.

2. Materials and Methods

2.1. The Study Area
The study area of Tanjaro sub-district of 600 km² (35° 15' N, 45° 0' E, 35° 35' N, 45° 50' E) is in northern part of Iraq, Arbat city is the center of the sub-district, and it is about 27 km southeast of Sulaimaniyah city. The climate of the area is similar to Sulaimaniyah city, the average annual rainfall in the sub-district is ranging mean annual precipitation is 703.7 mm, average annual air temperature is 19° C with slight precipitation in the summer season (Ahmad & Mustafa, 2008). The area is comprising of plains, hilly, and mountainous areas, the soil is mainly comprised of Quaternary alluvial sediments (Sürücü *et al.*, 2019).

2.2. Soil Samples
In the current study, 90 soil samples have been collected from three depths of 0, 10, and 20 cm for 30 locations within agricultural soils in Tanjaro sub-district for June to July 2019. The sampling sites (S1 to S30), are at least 200 m from the main roads as recommended by previous works (Liu *et al.*, 2015), represent the cultivated soils in Tanjaro area (see Figure 1). Each soil sample is a composite sample composed from the three depths samples. Then samples have been stored closed cup plastic containers and carried to the laboratory of instrumental analytical chemistry (University of Garmian) for analysis.

2.3. Chemical Analysis
Format chemical analysis was performed to quantify the content for the metals of Hg, Al, Cd, As, Ba, Co, Cu, Cr, Fe, Pb, Li, Mn, Ni, Sr, Zn and V in each sample using inductively coupled plasma optical emission spectroscopy ICP-OES. The ICP-OES (Spectro Across, made in Germany) instrumental conditions were consisting of conventional sample preparing procedure using different dilutions using 0.5% nitric acid (pH < 2). A procedure of wet digestion was followed for soil sample analysis (Amjadian *et al.*, 2016). In the analysis, always distilled deionized water and glassware washing were used for the dilutions.

2.4. Evaluation Methods
The performance of the heavy metals concentration analysis method by using ICP-OES was evaluated and confirmed according to the device limits of detection and quantification. The performance assessment was made by analyzing a known quality control standard after each 10 samples analysis (Al-Wabel *et al.*, 2017). The reproducibility of ICP-OES measurements has been verified by 3 repeats of samples taken from each sample location.

2.5. Statistics
Different descriptive and inferential statistics were implemented for analysis of the collected soil samples such as ANOVA, Pearson correlation (PC), principal component analysis (PCA), and cluster analysis (CA). A one-way ANOVA method was used to evaluate the significant variance between sample locations at 95 % level of confidence. Multivariate statistics are usually performed to discover the implied relationships among the heavy metals (Hou *et al.*, 2017). For this reason, PCA is a well-known method to define such relationships, whilst, PCA and CA are used in environmental and risk assessments. CA helps to categorize investigated heavy metals into main categories with individual and distinguishing impacts on the observations (Kaur *et al.*, 2018). PCA distributes the data on several independent factors named principal components. This method displays the loading weight of principle components on the dataset, and the

significance of variables on each principal component. The statistics of multivariate analysis were implemented using the XLSTAT add-in, 2014 for Excel 2016.
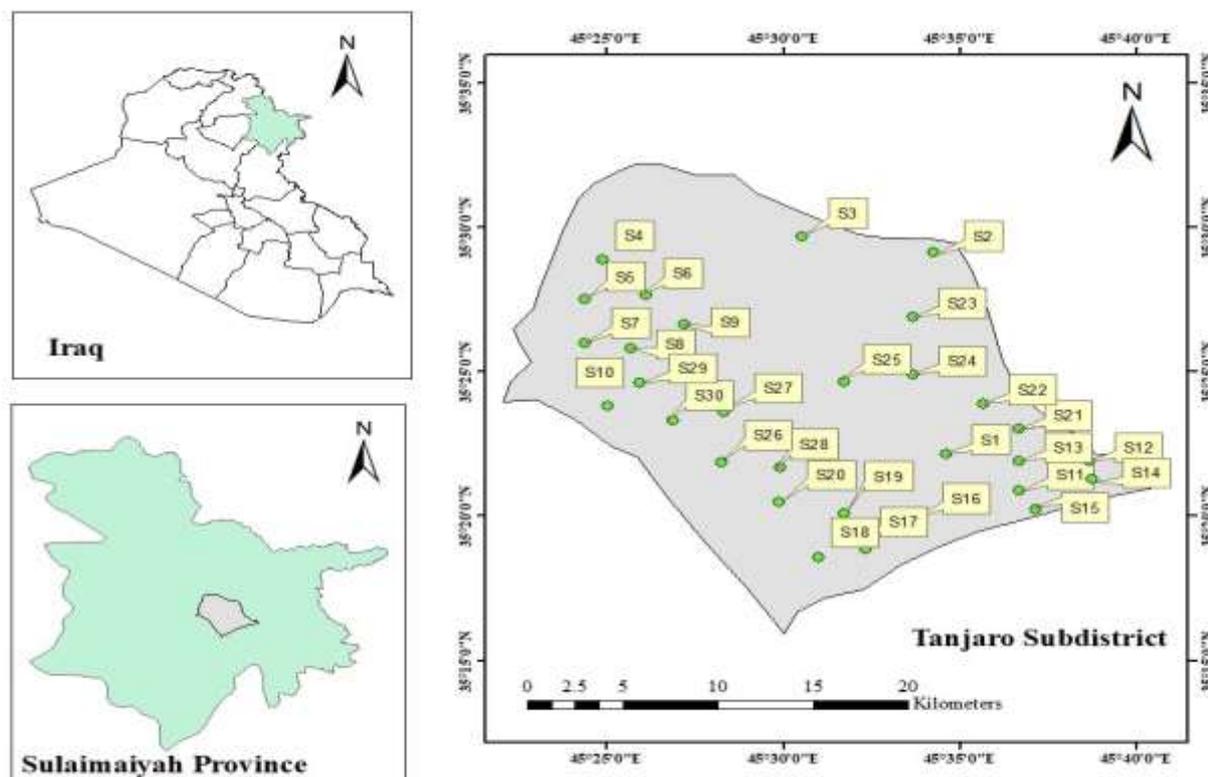
Figure 1. The Tanjaro Area Illustrating Soil Sample Sites.

2.6. Evaluation Parameters

2.6.1. Factor of Heavy Metals Enrichment

Factor of heavy metals enrichment (EF) is a factor defines soil contamination mostly happened by heavy metals and could be implemented to explore the level of anthropogenic impact in the contamination. EF is considered for each heavy metal as a function of a background heavy metal (Baltas *et al.*, 2020). In the current study, Fe has been chosen as a reference for heavy metal. The following EF equation was used.

$$EF = \frac{[\frac{C_i}{C_{ref}}]_{sample}}{[\frac{C_i}{C_{ref}}]_{background}} \qquad (1)$$

C_i refers to a measured level of concentration in (mg kg^{-1}) in each sample, C_{ref} is the reference metal concentration (see Table 1) of the same heavy metal (mg kg^{-1}). The subscripts signifying the soil sample and reference values respectively.

EF can be classified into 7 main levels: starts with clean enrichment situation of EF less than 1; slight situation of EF between 1 and 3; moderate situation of EF between 3 and 5; moderate to acute situation of EF between 5 and 10; acute situation of EF between 10 and 25; very critical situation of EF between 25 and 50; extremely acute situation of EF greater than 50 (Esmaeilzadeh *et al.*, 2019). The EF value greater than 1 means anthropogenic sources, while EF less than 1 indicates a natural source for heavy metals (Luo *et al.*, 2015).

Table 1. Illustrative Statistical Analysis of Metal Concentrations (mg/kg - on Dry Weight).

Parameter	Minimum	Maximum	Mean	Standard Deviation	BV	ASV[e]	SGV[f]
Mercury	0.21	0.65	0.48	0.12	0.5 [a]	0.056	6.6
Aluminum	3674.0	5003.0	4216.56	325.16	71000[c]	77440	--
Cadmium	0.39	0.60	0.50	0.06	0.35[c]	0.102	1.4

Arsenic	1.05	2.10	1.48	0.31	5[a]	2.0	12
Barium	48.32	72.43	58.07	5.51	62[b]	668	--
Cobalt	2.32	2.76	2.53	0.14	8[c]	11.6	40
Copper	3.12	3.57	3.33	0.14	15[c]	14.3	63
Chromium	10.15	12.95	11.66	0.82	70[c]	35	64
Iron	3365.0	4287.15	3912.54	235.11	4000[c]	30890	--
Lead	5.30	6.30	5.93	0.29	12[c]	17	70
Lithium	29.7	34.65	31.82	1.50	11[b]	22	--
Manganese	109.4	127.80	119.45	4.18	455[b]	527	--
Nickel	18.30	22.95	20.79	1.44	5[c]	18.6	50
Strontium	109.3	126.10	117.07	4.95	175[d]	316	--
Zinc	18.32	29.50	22.51	3.19	60[c]	52	200
Vanadium	8.00	9.75	8.83	0.51	100[a]	53	130
pH*	7.25	7.86	7.46	0.16	--	--	--

BV Background Values; ASV Average Shale Values; SGV Soil Guideline Values; [a] adapted from (Tóth *et al.,* 2016); [b] adapted from (Reimann *et al.*, 2018); [c] adapted from (UNEP, 2013); [d] adapted from (Kabata-Pendias, 2010); [e] adapted from (Wedepohl, 1995); [f] adapted from (Canadian Council of Ministers of the Environment (CCME), 2007); * unit is pH degree.

2.6.2. Index of Pollution

Index of pollution, IP, is employed to evaluate heavy metals contamination in soil that is generated from various sources (Simon *et al.*, 2013). IP is a factor of concentration ratios of the concerned metal and a reference metal. IP has 3 groupings (Sun *et al.*, 2010): a low level of pollution of IP equals or less than 1; mild level of pollution of IP between a and 3; and finally a severe condition of pollution of IP greater than 3.

$$PI = \frac{C_i}{S_i} \qquad (2)$$

C_i is metal concentration (mg kg-1) in each sample, and S_i is the reference metal concentration (mg kg^{-1}) of metal (See Table 1).

2.6.3. Index of Ecological Risk

Index of ecological risk RI index was originally established by Hakanson (1980) in order to identify the ecological risk of metals in water modes. Then the index was effectively used for agricultural soil contamination in rural areas (Keshavarzi & Kumar, 2019). This index can associate the potential risk of metals and ecological effects (Trujillo-González *et al.*, 2016), RI equation is as follows

$$RI = \sum_{1}^{n} Er^i \qquad (3)$$

$$Er^i = Tr^i * C_f^i \qquad (4)$$

$$C_f^i = \frac{C_{o-i}^i}{C_n^i} \qquad (5)$$

C_f^i is pollution parameter, C_{o-i}^i is metal concentration in the sample (mg kg^{-1}), C_n is reference concentration (mg kg^{-1}), Er^i is the potential index of ecological risk, finally and Tr^i is the toxicity response factor adapted from Zheng-Qi *et al.* (2008). Both RI and Er^i have acquired with eliminating Ba, Al, Fe, and Li since the values of Tr^i are not established in the literature. Ecological risk index is classified into 4 groups: slight risk of RI less than 150; mild risk of RI between 150 and 300; significant risk of RI between 300 and 600; Ultimate considerable risk of RI greater than 600. Likewise, the potential Er was categorized into 4 ranges that are based on Er^i values: less than 40 (clean or light pollution); 40 - 80 (moderate pollution); 80 - 160 (significant pollution); 160 - 320 (extreme pollution).

2.7. Spatio-statistical Analysis

The spatio-statistical analysis is mainly applied using geospatial tools of ArcGIS (version 10.7) was used to determine the sources and pollution intensities of the metals. Like previous works (Ogunkunle & Fatoba, 2014), ArcGIS (IDW interpolation) has been performed to identify the geo-distribution of heavy metals concentration.

3. Results

3.1. Concentrations of Heavy Metal

The illustrative statistical analysis of metal concentrations in concerned samples is presented in Table 1, in which, concentrations of Hg, Al, Cd, As, Ba, Co, Cu, Cr, Fe, Pb, Li, Mn, Ni, Sr, Zn and V were identified. Different

reference values have been employed as illustrated in Table 1 to evaluate the measured concentrations. For example, the maximum concentrations for some heavy metals like Co, Cu, Pb, and V are below the limit of reference values. While, the mean, and maximum values of Cd and Ni exceed the maximum allowable limit of BV, meaning that majority of the sampling sites are polluted by these two metals. For example, the Cd concentration distribution shows the mean and maximum values in soil samples (0.60 and 0.50 mg kg^{-1} respectively) are greater than the reference BV of 0.35 mg kg^{-1}.

3.2. Contamination Assessment

Table 2 shows the contamination levels for studied evaluation factors RI, EF, Er and IP, Er in the studied samples. The EF ranges from no enrichment with the minimum value of aluminum (EF = 0.08) to medium enrichment of nickel Ni (EF is 4.29). The EF mean values for the rest are at minimum. From Table 2, IP values show high pollution rages regarding Ni and Li and moderately polluted regarding investigated metals Pb, Ba, Cd, and Hg. According to IP, minimal ranges were observed for the rest. IP mean values of the tested metals at the thirty sites are ranging from 0.12 to 6.78 of Al and Ni respectively. In general, IP values demonstrate that the soil can be considered reasonably contaminated.

According to EF and PI, the study area is polluted by several heavy metals more than the remaining tested metals. Up to a point, a convergence between the results of EF and Er can be observed (See Table 2). Nevertheless, the outcomes of the potential Er are generally acceptable, mean values range from 0.28 to 81.19 of V and Cd respectively. Er values are demonstrating a high accumulation of the heavy metals of Cd and Hg. Hg displays a different behavior for lower Er mean values of 60.37, which is under 80, referring that Hg is measured at a moderate range. Whilst, the Tr^i value is high-level of 40, the region is ranked to be highly polluted by Hg. As a final point, RI index is 192.36 for the studied soils. This results for such area indicates that the ecological risk condition is moderately polluted.

Table 2. Contamination Levels by Heavy Metals Using Er, EF, and IP Indices.

Parameter	EF			IP			Er		
	Average value	St. Dev.	Condition	Average value	St. Dev.	Condition	Average value	St. Dev.	Condition
Aluminum	0.08	0.01	No enrichment	0.12	0.01	Minor	-		
Arsenic	0.27	0.03	No enrichment	0.43	0.05	Minor	4.31	0.49	Minor
Barium	1.42	0.22	Minor	2.24	0.33	Considerable	-		
Cadmium	1.72	0.20	Minor	2.71	0.26	Considerable	81.19	7.85	Maximal
Cobalt	0.34	0.03	No enrichment	0.53	0.04	Minor	2.66	0.20	Minor
Chromium	0.17	0.01	No enrichment	0.27	0.02	Minor	0.54	0.04	Minor
Copper	0.25	0.02	No enrichment	0.40	0.02	Minor	2.01	0.12	Minor
Iron	-	-	-	1.58	0.09	Considerable	-		
Mercury	1.00	0.24	Minor	1.51	0.37	Considerable	60.37	14.86	Considerable *
Lithium	2.66	0.22	Minor	4.20	0.27	Maximal	-		
Manganese	0.22	0.02	No enrichment	0.35	0.03	Minor	0.71	0.06	Minor
Nickel	4.29	0.31	Considerable	6.78	0.33	Maximal	33.88	1.66	Minor
Lead	0.66	0.05	No enrichment	1.04	0.06	Considerable	5.20	0.29	Minor
Strontium	0.37	0.06	No enrichment	0.59	0.10	Minor	-		
Vanadium	0.09	0.01	No enrichment	0.14	0.01	Minor	0.28	0.02	Minor
Zinc	0.38	0.04	No enrichment	0.61	0.04	Minor	1.21	0.09	Minor

* is measured as considerable as it is closer to the minimum limit of the considerable level and has a high Tr value.

3.3. Multivariate Statistical Analysis

The outcomes interprets the heavy metals are meaningfully varying with p value less than 0.05. The p value is zero while the F-value is 3754.56, and F$_{critical}$ is 1.689, meaning that a spatial significant divergence exists among the soil sets. One-way analysis of variance (ANOVA) was the method that used to reach this result.

Correlation analysis was achieved in this work as presented in Table 3 to define the relationships among the heavy metals in the area. Therefore Table 3 shows the correlation matrix between the considered heavy metals.

The correlations at p value less than 0.05 for the heavy metals, it is worth mentioning, as indicated in Table 3 positive and negative considerable relationships, higher than 0.3, are existing. The highest positive significant correlations between Ba with Co and Pb were observed. Negative considerable correlation Al with Cu, As with Cu, Ba with V, Ni with Sr, Co with Zn, and V with Zn were noticed as examples.

To gain further insight into the relationships among the remaining heavy metals, CA has been accomplished. CA (with Ward method and Euclidean measuring for similarity) is applied to search for sources of heavy metals and also to reorder the dataset into several main groups.

In Figure 2 significant correlations were observed between Pb and Ba, and Co and Cr, they were related to form a cluster. Cu and Ni showed a significant correlation between them, they were connected at later stages with Cd, Hg, and Mn. A third cluster was established for As, Li, and Zu as they lack significant relationships with the remaining heavy metals in soil samples.
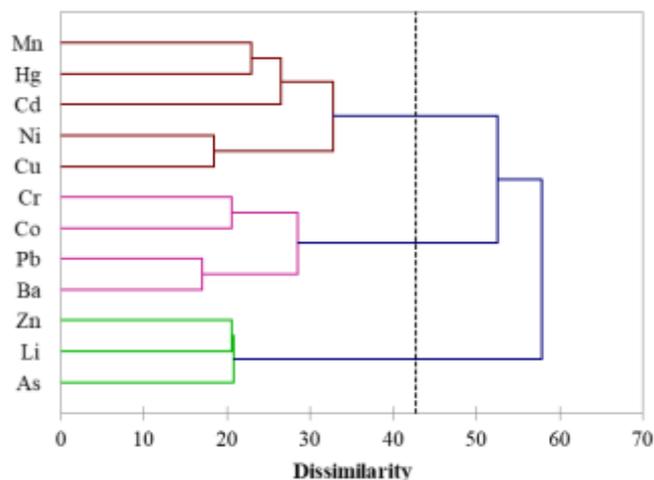
Figure 2. Significant Dissimilarity Relations Among Metals Obtained by CA.

Table 3. Correlation Coefficients Between Tested Metals in Tanjaro Soils.

	Mercury	Aluminium	Cadmium	Arsenic	Barium	Cobalt	Copper	Chromium	Iron	Lead	Lithium	Manganese	Nickel	Strontium	Zinc	Vanadium
Mercury	1															
Aluminium	-0.11	1														
Cadmium	0.10	0.07	1													
Arsenic	-0.28	-0.03	-0.13	1												
Barium	-0.04	-0.04	0.04	0.01	1											
Cobalt	0.03	0.18	0.24	-0.09	0.41	1										
Copper	0.11	-0.40	0.07	-0.43	-0.08	-0.15	1									
Chromium	-0.21	0.17	-0.19	-0.10	0.10	0.29	-0.34	1								
Iron	0.10	-0.25	-0.08	0.10	0.01	0.13	0.00	0.17	1							
Lead	0.29	-0.02	0.18	-0.11	0.41	0.15	0.04	0.08	0.13	1						
Lithium	0.29	0.14	0.05	0.29	-0.08	-0.09	-0.49	-0.03	0.03	-0.09	1					
Manganese	0.21	0.01	0.14	-0.44	0.01	-0.03	0.31	0.17	0.20	0.21	-0.19	1				
Nickel	-0.01	-0.22	-0.11	0.28	-0.03	-0.27	0.36	-0.46	0.09	-0.19	0.07	0.14	1			
Strontium	-0.14	-0.30	-0.05	-0.15	0.16	0.34	0.11	0.31	0.26	0.20	-0.32	0.00	-0.40	1		
Zinc	-0.01	-0.40	-0.22	0.28	0.03	-0.43	-0.12	-0.13	0.00	0.09	0.29	-0.27	0.19	-0.29	1	
Vanadium	-0.12	0.17	-0.11	-0.11	-0.42	-0.01	0.21	-0.0	0.24	-0.47	0.03	-0.12	-0.03	0.14	-0.47	1

* Correlations at significance level 0.05

PCA was applied to figure out the variance of trace metals levels and identify their origins. High scores of eigenvalues are set to be weightier. Varimax rotation with Kaiser Normalization were employed to improve the heavy metals loading and eigenvalue of the sixth factor was achieved after the rotation. Results show that six factor might be the more significant in representing of 80.1% of the results for tested metals difference.

By performing PCA, the dataset was reduced to six main components representing 80.1% of heavy metals concentrations variance. Table 4 shows that six rotated way with eigenvalues more than one that have been extracted. PC1 represents 20.60% of dataset variance, exhibits strong positive loading on Li and strong negative loading on Cu, with a moderate positive loading on As. PC2, which explains 18.00% of dataset variance, is significantly correlated with Cd and Cr, with moderate loading on Hg. This factor agrees with EF results of Cd and Hg, they are 1.72 and 1.00 respectively. PC3, accounting for 13.11% of dataset variance, has strong positive loading on Mn and Hg, with significant negative loading on As. PC4, that refers to 10.92% of dataset variance, exhibits strong loadings to Ba with Pb. PC5, which represents 10.07% of dataset variance, exhibits strong impact of Co with a significant Zn negative with moderate impact of Cd. PC6 accounts for 7.39% of dataset variability, is dominated by Ni.

Table 4. Total Variance for PCA Factors.

Comp.	Initial eigenvalues			Extracted sums for squared loading			Rotation sums of squared loadings		
	Eigenvalue	Variability (%)	Cumulative %	Eigenvalue	Variability (%)	Cumulative %	Eigenvalue	Variability (%)	Cumulative %
F1	2.47	20.60	20.60	2.47	20.60	20.60	1.75	14.61	14.61
F2	2.16	18.00	38.60	2.16	18.00	38.60	1.38	11.46	26.07
F3	1.57	13.11	51.71	1.57	13.11	51.71	1.78	14.90	40.97
F4	1.31	10.92	62.63	1.31	10.92	62.63	1.58	13.20	54.17
F5	1.21	10.07	72.70	1.21	10.07	72.70	1.68	13.98	68.14
F6	0.89	7.39	80.09	0.89	7.39	80.09	1.44	11.95	80.09
F7	0.78	6.47	86.56						
F8	0.55	4.60	91.16						
F9	0.40	3.33	94.50						
F10	0.28	2.31	96.81						
F11	0.22	1.86	98.67						
F12	0.16	1.33	100.00						

Parameter	Loading values						Rotated loading values					
	PC1	PC2	PC3	PC4	PC5	PC6	PC1	PC2	PC3	PC4	PC5	PC6
Arsenic	0.72	-0.26	0.04	0.31	0.21	0.19	0.43	-0.05	-0.65	0.05	-0.12	0.36
Barium	-0.28	-0.36	0.33	0.68	-0.08	0.14	-0.03	-0.10	-0.12	0.86	0.19	0.11
Cadmium	-0.36	0.00	0.34	-0.07	0.62	-0.17	0.05	0.64	0.10	0.10	0.46	-0.12
Cobalt	-0.50	-0.55	0.03	0.19	0.39	0.17	0.08	-0.02	-0.09	0.38	0.76	-0.16
Chromium	-0.26	-0.63	-0.33	-0.16	-0.43	0.25	0.12	-0.78	0.09	0.10	0.24	-0.38
Copper	-0.38	0.79	-0.10	0.22	-0.01	-0.12	-0.73	0.30	0.34	-0.05	-0.09	0.29
Mercury	-0.23	0.21	0.69	-0.42	-0.07	0.04	0.33	0.39	0.67	0.11	-0.12	-0.09
Lithium	0.49	-0.26	0.53	-0.43	0.10	0.28	0.90	0.11	0.05	-0.09	-0.13	0.07
Manganese	-0.58	0.34	0.05	-0.15	-0.28	0.52	-0.18	-0.24	0.79	0.06	0.20	0.25
Nickel	0.35	0.63	0.10	0.35	0.14	0.51	-0.04	0.12	0.02	-0.06	-0.17	0.94
Lead	-0.41	-0.15	0.59	0.31	-0.34	-0.18	-0.03	0.12	0.29	0.78	-0.14	-0.23
Zinc	0.61	0.07	0.34	0.17	-0.45	-0.23	0.22	0.01	-0.20	0.20	-0.80	0.07

3.4. Spatial Exploration

Figure 3 illustrates the spatial spreading of some important heavy metals of barium, cadmium, mercury, cobalt, lithium, nickel and lead within Tanjaro sub-district. The distribution of investigated metals agrees with statistical and environmental contamination assessments, indicating that these heavy metals originated from natural and anthropogenic sources. In Figure 3 shows high concentrations of nickel in most of the studied soils.

4. Discussion

The results presented in Table 1 reveal potential significant impacts of Al, Ba, Cd, Fe, Ni, and Pb could exist in crops in the study area. Since Ba chemistry is relatively similar to Ca, Ba does not tend to accumulate in living creatures (Adriano, 2001), therefore they could be overlooked. Naturally, Al and Fe appear at abundant levels of the crust, they are free from anthropogenic impact, and thus their high concentrations would be barely considerable. Whilst, high levels of Pb, Ni, Cd, and Hg high concentrations in the studied area reveal more influence of these metals in the reduction of agricultural soil quality with higher potential pollution risk.

From these findings shown in Table 2, it is evident the studied soils are considerably polluted by Ba, Cd, Hg, Li, and Ni, as their mean EF value is equal or/and greater than 1. Origins of Hg, Ni, and Cd were probably industrial actions, however, EF of a value lower than 1 suggests natural sources for the remaining. From Table 2, in general, IP values demonstrate that a moderate pollution. According to EF and IP, the pollution is mainly caused by certain metals. Er levels are suggesting that an ecological risk can be generated due to the accumulation of Hg and Cd, as significant levels are counted to these metals.

CM results of positive correlations propose the origin of tested metals like V or Sr is most probably is the natural composition of studied soils, by means of no important correlations were observed for Hg or any well-known heavy metal from anthropogenic sources, and no anthropogenic activity in the area would contribute to their occurrence.
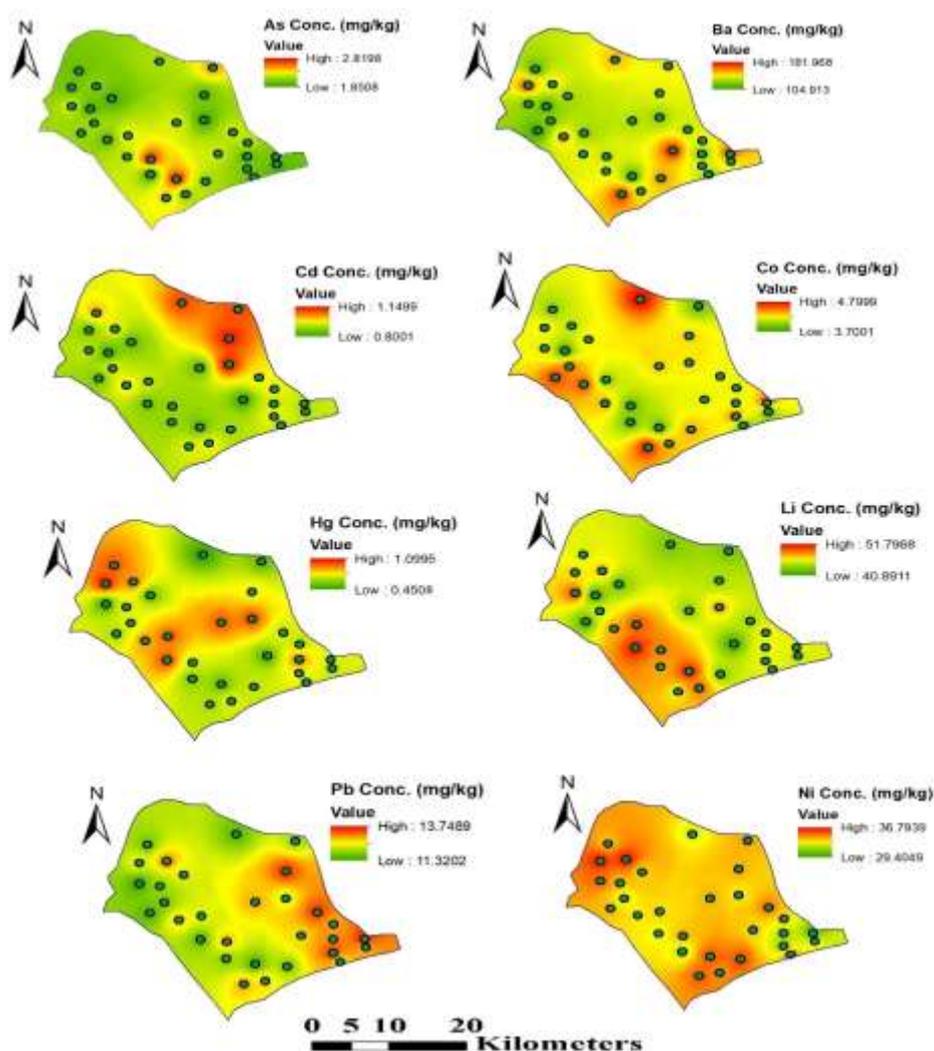
Figure 3. Distribution of Certain Heavy Metals Concentrations in Tanjaro Sub-District.

Significant correlations of Ba with Co and Pb suggest that they have originated most likely because of intensive using of pesticides or fertilizers in the area.

According to AHC analysis, the origin of examined metals in agricultural soil is categorized into three classes. The last cluster of As, Li, and Zn is probably the one that was originated from natural origins in the studied soils. EF values are less than 1 for As and Zn indicating that the area is not contaminated by them.

From PCA analysis, PC1is suggesting that heavy metals Li, Cu, and As have originated from natural sources. EF values of Cu and As in the studied soils are under 1, indicating no enrichment in the soil, and subsequently, their sources are likely to be natural. Although EF values of Li are higher than 1, the source of Li is wholly natural, weathering of parent materials as no known anthropogenic activity originates Li in the area. PC2 is highly correlated to Cd and Cr, with moderate loading on Hg. Based on EF results, the level of Hg and Cd are 1.00 and 1.72 respectively, PC2 suggests anthropogenic sources of these metals, whereas the level of EF for Cr is 0.17, indicating no enrichment levels of soil samples. Compared to Cr background value, Cr concentrations in soil samples are much lower, indicating that Cr concentrations were affected by anthropogenic activities. PC3 of strong loading on Mn and Hg, with significant negative loading on As, signifying origin of these metals comes from mixed sources of natural and anthropogenic. The anthropogenic activities that release As and Hg in agricultural soils are mainly fertilizer and pesticide applications. Mn concentrations in soils, which are mainly controlled by natural sources (Gong *et al.*, 2010), seem to be associated with natural sources (the composition of rocks and soil) in the study area. PC4 is suggesting inputs of Ba and Pb, from anthropogenic activities such as the implementation of fertilizers. Another anthropogenic origin of Pb is atmospheric

deposition from exhausts of vehicles. PC5 suggests mixed lithogenic and anthropogenic sources of Co, Zn, and Cd, similar factor loading was reported by (Huang *et al.*, 2015) for these heavy metals. The component PC6 of Ni is an anthropogenic one with an EF value equals 4.29, indicating a moderate enrichment of soil samples. Excessive Fertilizer applications are usually causing high Ni levels in agricultural soils (Cai *et al.*, 2015). Figure 3 displays an extreme application of manures and pesticides impact in the study area (Zhong *et al.*, 2016).

5. Conclusion

Considerable contamination concentrations of both Ni and Li, and moderate pollution levels for Ba, Cd, Hg, and Pb have been indicated by the results of concentration analysis and PI. ERI results considered Cd, Hg, and Ni at moderate to high ecological risk levels, respectively. CA, PCA and EF show that there are 3 separate origins of examined heavy metals; natural, anthropogenic and mixed contributions. Most anthropogenic contributions were for Hg, Cd, Pb, and Ni. The distribution map showed generally that non-point pollution sources in soils. The valuations and investigation established in the current work will enhance the implication of statistical multivariate and ecological risk analysis as a reliable method for the assessment of heavy metals contamination in agricultural soils for the remaining parts of Kurdistan Region.

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