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Heavy Metals Contamination in Agricultural Soils of Middle Basin of Sirwan (Diyala) River, East Iraq: Multivariate Analysis, Risk Assessment, Source Apportionment, and Spatial Distribution

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Abstract

This study conducted a comprehensive assessment of heavy metals in agricultural soils for the middle basin of Sirwan (Diyala) river, Iraq. Concentrations of sixteen heavy metals have been measured by inductively coupled plasma optical emission spectroscopy ICP-OES. The pollution index (PI) and ecological risk index (ERI), enrichment factor (EF) have been used to assess the pollution intensity in soil samples. Multivariate statistics of agglomerative hierarchical clustering (AHC) and principal component analysis (PCA) were also used to identify the sources of heavy metals. Considerable contamination of Cd, Hg, Li, Ni, and Pb have been observed. Sources of Cd, Hg, Ni, and Pb are most likely anthropogenic activities including vehicle exhaust and implementation of pesticides and fertilizers. The current study aims to enhance environmental monitoring and soil contamination prevention in Iraq.

1. Introduction

Since soil is a non-renewable source, soil contamination is greatly significant as it may extend to other sections of the environment such as sediment, air, surface water, and groundwater [1-3]. The increasing development of industrial and agricultural sectors leads to a rise of heavy metals levels in soil higher than the regular levels [4]. In the environment, heavy metals are considered extremely toxic and hazardous contaminants because of their non-biodegradable nature [5]. They tend to accumulate in biological systems causing serious consequences [6, 7]. The problem of soil contamination with heavy metals is the possibility to be transported to other parts by wind and runoff water causing an accumulation of these metals [8]. Heavy metals can find their way to the human food chain through enriched plants in agricultural areas. Furthermore, heavy metals accumulation in agricultural soil leads to a limit or even diminish crop productivity [9].

Many previous works have been made on rural soil contamination by heavy metals, especially for agricultural areas in different parts of the world. Many of these works found that soil contamination of heavy metal in such areas is mainly connected to anthropogenic activities [10-12]. However, for agricultural soils, most of the studies showed that heavy metals have levels lower than those of other urbanized soils [13].

To evaluate the contamination intensity of heavy metals in agricultural soils, various analyses have been followed. Even though it is difficult to distinguish which way is the most appropriate to evaluate such cases. But still implementing several indices such as pollution index, enrichment factor, and ecological risk index are widely used in agricultural soil contamination [14]. Furthermore, multivariate and geostatistical analysis are commonly performed [15]. Many of these methods are applied to explore and interpret how and from where different heavy metals had generated and then accumulated in agricultural soils.

Several studies were performed on the contamination of Iraqi rural and agricultural soils, but similar studies are almost not existing for the agricultural soil of the study area in this work and the majority were for other parts of Iraq. Even though the area of the middle basin of Sirwan (Diyala) river is mainly composed of agricultural areas, in which many important crops are planted.

This study aims to perform a comprehensive environmental evaluation on soil contamination by heavy metals in the agricultural area of the middle basin of Sirwan (Diyala) river. The studied area is currently one of considerably important crop production areas in East Iraq. The study assessed by implementing contamination evaluation indices with multivariate and geostatistical analysis, and to identify the origin of investigated heavy metals to be natural or anthropogenic sources. This work thus aids to better understand soil contamination condition and to protect human health in the study area.

2. Material and Methods

2.1. Description of the study area

The study area of middle basin Sirwan (Diyala) River (34° 55′ N, 45° 20′ E, 34° 80′ N, 45° 70′ E) is located in East Iraq (has a higher altitude of 200 m a.s.l.) covers an area about 1000 km^2. The population in the area has expanded in recent years due to both natural economic development and to the unusual ongoing political situation in Iraq. The annual rainfall of the area is 273 mm with no precipitation in the summer season [16]. The winds are mostly north-westerly and in summer season south-easterly winds considerably occur with a possibility of dust storms generation [17]. Geologically, the area is a semi-arid region, that is dominantly covered by soils belong to Quaternary deposits [18].

2.2. Soil sample collection and preparation

In this study, a total of ninety soil samples (at 0 to 20 cm depth) were collected from thirty different sites within five agricultural regions in the middle basin of the Sirwan (Diyala) River area during the two months of June and July in the year 2019 (a rainless season). Sampling sites are covering the most important agricultural points in the study area (see Figure 1).

All sampling locations (from ST1 to ST30) are away from roads with at least 200 m. At each site, three samples at different depths were collected (0, 10, and 20 cm) and then have been mixed into one composite sample for each sampling location. A wooden shovel was used to collect about 250 g for each sample. The samples were then packed in sealed plastic bags and transferred to the laboratory for analysis. At the instrumental research laboratory located at university of Garmian, the collected samples have been dried at room temperature and then sieved through a mesh of 2-mm. This to eliminate any large particle and impurities that probably were collected within soil samples. Then and there, sieved samples were put in sealed and clean plastic bags and ready for the analysis.

2.3. Sample analysis

All samples were analyzed to quantify heavy metals content by using inductively coupled plasma optical emission spectroscopy ICP-OES (Spectro across Germany). Heavy metals of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sr, V, and Zn were speciated in soil samples of the 30 sites that collected from the study area. A wet digestion procedure for soil samples was followed. Where all the samples were dried at 100 °C for 2 hours after that samples were cooled and acidified with 2% nitric acid (pH < 2). Samples were analyzed within 24 hours from collection time. Serial dilution of the 1000 mg/l was used to prepare the standard solutions. Distilled deionized water and glassware washing were always utilized for the dilutions.

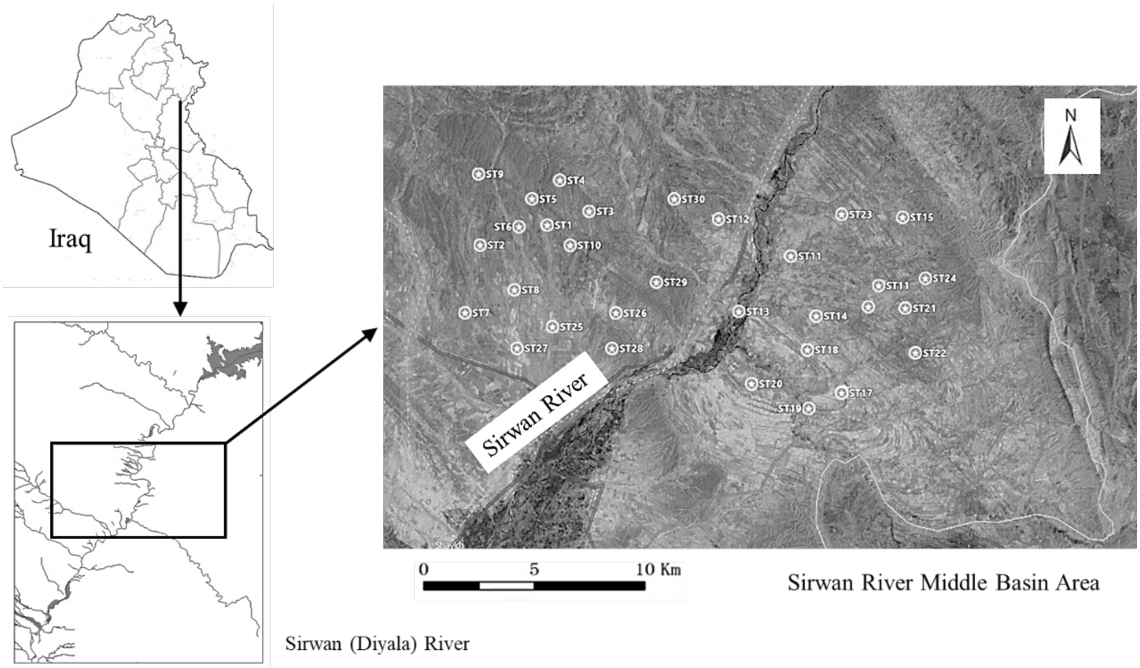

Figure 1: The study area identifying locations of soil sampling sites.

The instrument conditions for ICP-OES (Spectro Arcos) were: Spray chamber is Scott spray; Nebulizer: crossflow; RF power/W: 1400; pump speed: 30 RPM; Coolant flow (L/min): 14; Auxiliary flow (L/min): 0.9; nebulizer gas flow (L/min): 0.8; Preflush (s): 40; Measure time (s): 28; replicate measurement: 3; argon gas (purity ≥ 99.99); multi-elements stock solutions containing 1000 mg/L were obtained from Bernd Kraft (Bernd Kraft GmbH, Duisburg, Germany); standard solutions were diluted by several dilution into 0.1, 0.5, 2 ppm in 0.5% nitric acid as diluent.

2.4. Evaluation of analysis method

The performance method for elements measurement by ICP-OES has been evaluated according to limits of detection (LOD), the limit of quantification (LOQ), and linearity (linearity of the analyzed elements). The calibration curves for ICP-OES, are found reliant on the standard addition method. The LOD and LOQ have been assessed according to their relations with standard deviation. The ICP-OES reproducibility and accuracy of element measurements were determined by spiking and homogenizing three replicates of three samples collected randomly among sampling locations.

2.5. Multivariate statistical analysis

In this work, correlation matrix CM, Agglomerative hierarchical clustering AHC, and principal component analysis PCA have been applied. These methods are used to explore the implicit relations among the investigated heavy metals. For this purpose, CM was used to determine such relations and their strength or weakness. The AHC and PCA were implemented to verify and assess the soil dataset. AHC and PCA are widely implemented in health risk and environmental assessment. AHC classifies investigated parameters into several major classes that have distinctive influences on the observations.

PCA divides the data into independent factors called principal components. PCA shows the loading weight of affecting principle components on the final results, with presenting the loading weight of variables in each principal component. The multivariate statistics have been performed in this work using XLSTAT, version 2017 for Microsoft Excel 2013 software.

2.6. Contamination and risk assessment

2.6.1. Enrichment factor (EF)

Enrichment factor EF is a normalized impact factor that describes the severity of soil contamination by heavy metals or other pollutants. EF is calculated for each heavy metal in terms of a reference metal [19]. In this study, Fe was used as a reference metal. The EF was determined according to the following equation as proposed by Wang et al. [20].

$$\mathrm{EF} = \frac{[{}^{C_i}/_{C_{ref}}]_{sample}}{[{}^{C_i}/_{C_{ref}}]_{background}} \tag{1}$$

where C_i is the measured concentration (mg/kg) of each heavy metal in soil samples, C_{ref} is the concentration (mg/kg) of the reference metal. Sample and background subscripts refer to soil samples and soil's standards quality respectively.

The EF is categorized is into five main levels: minimal enrichment (EF < 1); minor enrichment (1 ≤ EF < 3); moderate enrichment (3 ≤ EF < 5); moderate to severe enrichment (5 ≤ EF < 10); severe enrichment (10 ≤ EF < 25); very severe enrichment (25 ≤ EF < 50); and extremely severe enrichment (EF ≥ 50) [21].

2.6.2. Pollution index (PI)

Pollution index PI is applied for the evaluation of the heavy metals contamination generated from different sources [22]. PI is a normalized factor calculated as a concentration ratio of heavy metal and a background metal. For PI, three classifications of heavy metal was suggested [23]: low pollution (PI ≤ 1.0); moderate pollution (1.0 < PI ≤ 3.0); and high pollution (PI > 3.0), by applying the following equation

$$\mathrm{PI} = \frac{C_i}{S_i} \tag{2}$$

C_i is as mentioned before, and S_i is the quality standard (background) concentration (mg/kg) of the same heavy metal in soil.

2.6.3. Ecological risk index (RI)

This index is first developed by Hakanson [24] to determine the ecological risk of heavy metals in the aquatic mediums. But it also has been successfully applied for agricultural soil contamination [25]. Ecological risk index RI combines the ecological risk of hazardous heavy metals with their environmental impact [26]. The RI is calculated as the following equations:

$$\mathrm{RI} = \sum_{1}^{n} Er^i \tag{3}$$

$$Er^i = Tr^i * C_f^i \tag{4}$$

$$\mathrm{C_f^i} = {}^{\mathrm{C^i_{o\text{-}i}}}/_{\mathrm{C^i_n}} \tag{5}$$

Where for i[th] heavy metal, C^i_f is the pollution factor, C^i_{o-i} is the concentration in the soil sample (mg/kg), C_n is the background concentration (mg/kg), Er^i is the potential ecological-risk, and Tr^i is the toxic response factor. The values toxic response factors Tr^i of the investigated heavy metals were adapted from Zheng-Qi et al. [27]. In this work, RI and Er^i were calculated by excluding Al, Ba, Li, and Fe, as their Tr^i values have not been found in the literature. RI is categorized into four classes: low risk (RI < 150); moderate risk (150 ≤ RI < 300); considerable risk (300 ≤ RI < 600); very high risk (RI ≥ 600). Similarly, the ecological risk Er is also classified into four levels: clean or light pollution (Er < 40); moderate pollution (40 ≤ Er < 80); significant pollution (80 ≤ Er < 160); extreme pollution (160 ≤ Er < 320) [28].

2.7. Geostatistical analysis

In this work, the geostatistical analysis tool ArcGIS software (version 10.6.1), IDW interpolation, has been used to configure the spatial distribution of heavy metals contamination in the study area.

3. Results and discussion

3.1. Heavy metals in soil samples

In this study 16 heavy metals of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sr, V, and Zn have been analyzed. The descriptive statics for total concentrations of the heavy metals in the study area including background values are illustrated in Table 1. Various background or threshold values for the heavy metals adapted from the literature as demonstrated in Table 1. From the obtained results, the maximum concentration for Al, As, Co, Cr, Cu, Mn, Pb, Sr, V, and Zn are below the limit of background values BV. In Table 1, Background values (BV) were adapted from literature [29], [30], [31], and [32]. Average shale values (ASV) was adapted from Kabata-Pendias [33]; Soil guideline values (SGV) was adapted from CCME [34].

Table1: Descriptive Statistics for Heavy Metal in Tested Agricultural Soil Samples (mg/ kg dry weight).

Parameter	Min	Max	Mean	Median	St. Dev.	Skew.	Kurt.	CV%	BV	ASV[e]	SGV[f]
Al	3674.00	5003.00	4216.56	4182.00	325.16	0.86	0.52	7.71	71000[c]	77440	--
As	1.05	2.10	1.48	1.35	0.31	0.96	-0.43	21.05	5[a]	2.0	12
Ba	48.32	72.43	58.07	57.54	5.51	0.61	0.76	9.48	62[b]	668	--
Cd	0.39	0.60	0.50	0.50	0.06	-0.10	-0.54	11.52	0.35[c]	0.102	1.4
Co	2.32	2.76	2.53	2.54	0.14	0.02	-1.38	5.71	8[c]	11.6	40
Cr	10.15	12.95	11.66	11.60	0.82	-0.08	-1.01	7.07	70[c]	35	64
Cu	3.12	3.57	3.33	3.32	0.14	0.21	-1.29	4.19	15[c]	14.3	63
Fe	3365.00	4287.15	3912.54	3928.75	235.11	-0.30	-0.26	6.01	4000[c]	30890	--
Hg	0.21	0.65	0.48	0.50	0.12	-0.48	-0.39	24.95	0.5[a]	0.056	6.6
Li	29.70	34.65	31.82	31.80	1.50	0.29	-1.00	4.71	11[b]	22	--
Mn	109.40	127.80	119.45	119.55	4.18	-0.11	0.09	3.50	455[b]	527	--
Ni	18.30	22.95	20.79	20.40	1.44	0.20	-1.23	6.93	5[c]	18.6	50
Pb	5.30	6.30	5.93	5.95	0.29	-0.61	-0.26	4.82	12[c]	17	70
Sr	109.30	126.10	117.07	116.60	4.95	0.30	-1.05	4.23	175[d]	316	--
V	8.00	9.75	8.83	8.87	0.51	0.09	-1.03	5.80	100[a]	53	130
Zn	18.32	29.50	22.51	22.81	3.19	0.40	-0.89	14.19	60[c]	52	200
pH*	7.25	7.86	7.46	7.40	0.16	1.28	0.73	2.19	--	--	--

BV Background Values; ASV Average Shale Values; SGV Soil Guideline Values; [a] adapted from [29]; [b] adapted from [30]; [c] adapted from [31]; [d] adapted from [32]; [e] adapted from [33]; [f] adapted from [34]; * unit is pH degree; CV% Coefficient of variation percentage; Skew. Skewness; Kurt. Kurtosis.

As shown in Table 1, the descriptive statistics suggest that heavy metals in the study area are generally within acceptable ranges except for Ba, Cd, Hg, Li, and Ni. Even though the mean and median values for Ba in soil samples (58.07 and 57.54 mg/kg respectively) are higher than the BV limit of 60 mg/kg this would not propose a significant impact of on crops in the study area, Ba does not tend to accumulate in the human body, and thus this impact can be ignored [35]. Heavy metals Cd, Hg, Li, and Ni have a maximum concentration in soil samples of 0.6, 0.65, 34.65, 0.65, and 22.95 mg/kg respectively which are higher than the BV limits. The results reveal that heavy metals such as Cd, Hg, Li, and Ni have a more active contribution to the reduction of agricultural soil quality more than the remaining heavy metals in the study area.

The coefficient of variation percentage (CV %) shows a moderate variation of the data. On a CV% scale ranging from 10 to 100, the CV% of the heavy metals varies from 3.50 to 24.95%. The higher CV% values were for As and Hg (24.95 and 21.05 % respectively). These values refer to significant variability for the two metals in soil samples. The skewness values of the heavy metals display a nearly symmetrically distribution with minor positively or negatively skewed values. The highest positively skewed value was 0.98 for As. Considerably, the kurtoses values indicate a relatively normal distribution of the heavy metals concentration in the study area, with a majority of concentration are closer to the mean value.

3.2. Evaluation indices for heavy metals contamination

EF, PI, RI, and Er have been implemented in this work to evaluate contamination by heavy metals in the study area. Table 2 illustrates the descriptive statistics for EF, PI, and Er results. In Table 2, the EF ranges from minimal for Al (EF equals 0.06) to moderate enrichment for Cd, Hg, Li, and Ni (EF are 1.48, 1.0, 2.97, and 4.27 respectively). The mean values of EF for the remaining heavy metals are at minimal levels. These findings propose that the study area is considerably influenced by Cd, Hg, and Ni from anthropogenic sources, as their EF values are greater than 1. For the rest of the heavy metals, their EF values are less than 1, indicating they are generated from natural sources [21].

In Table 2, PI mean values for the heavy metals are ranging between 0.06 and 4.16. These results suggest that the study area is highly polluted by Ni, PI equals 4.16, and also it moderately polluted by Cd, Fe, Hg, and Li. Low pollution levels were noticed for the remaining.

Table 2: Values and contamination levels using EF, PI and Er indices of the heavy metals for agricultural soil samples in the study area

Metal	Enrichment Factor			Pollution Index			Ecological Risk Index		
	Mean	SD	Enrichment level	Mean	SD	Pollution level	Mean (Er)	SD	Contamination level
Al	0.06	0.01	Minimal	0.06	0.005	Low	-	-	
As	0.30	0.06	Minimal	0.30	0.062	Low	2.97	0.62	Low
Ba	0.96	0.10	Minimal	0.94	0.089	Low	-	-	
Cd	1.48	0.18	Minimal	1.44	0.166	Moderate	43.20	4.98	Moderate
Co	0.32	0.03	Minimal	0.32	0.018	Low	1.58	0.09	Low
Cr	0.17	0.01	Minimal	0.17	0.012	Low	0.33	0.02	Low
Cu	0.23	0.02	Minimal	0.22	0.009	Low	1.11	0.05	Low
Fe	-	-	-	1.0	0.059	Moderate	-	-	
Hg	1.00	0.28	Moderate	1.0	0.241	Moderate	38.64	9.64	Moderate*
Li	2.97	0.23	Moderate	2.89	0.136	Moderate	-	-	
Mn	0.27	0.02	Minimal	0.26	0.009	Low	0.53	0.02	Low
Ni	4.27	0.44	Moderate	4.16	0.288	High	20.79	1.44	Low
Pb	0.51	0.05	Minimal	0.49	0.024	Low	2.47	0.12	Low
Sr	0.69	0.05	Minimal	0.67	0.028	Low	-	-	
V	0.09	0.01	Minimal	0.09	0.005	Low	0.18	0.01	Low
Zn	0.38	0.05	Minimal	0.38	0.053	Low	0.75	0.11	Low

* this level considered moderate as its value is close to the lower limit of moderate level.

As stated in Table 2, the results of potential single ecological risk index Er were mostly at low levels, Er ranges between 0.18 and 20.70 for V and Ni respectively. The results of Er are indicating that a small risk can be generated due to the accumulation of certain heavy metals. Both Hg and Cd are presenting a potential moderate ecological risk because of their high Er mean values of 43.2 and 38.64 respectively. Even though, the actual mean value of the Hg single ecological risk index is 38.64, which is lower than 40 indicating that Hg is relatively considered at a low contamination level. But, because of Tr^i is high (equals 40). The study area was counted to be moderately polluted by Hg.

Finally, the calculated ecological risk index RI (sum of mean values of the single ecological risk indices for each sampling location) for the heavy metals in the study area is 112.54. RI value refers that the ecological risk status of the study area regarding the investigated heavy metals is low.

3.3. Heavy metals in soil samples

Analysis of variance (ANOVA), a one-way method a function in Microsoft Excel 2013 software, was implemented to validate the significance of variance among sampling sites at a 95 % confidence level. The obtained results exhibited that all tested heavy metals were significantly different at p-value < 0.05. The p-value was 0.00, F value was 5675, and F critical value F_{crit} was 1.688, which means a great variance does exist between tested groups. ANOVA of one-way was employed for testing the spatial differences of soil sampling sites without replications.

The CM was performed to find potential relationships among the heavy metals in soil samples. Constantly, in such statistical analysis, a correlation coefficient closer to 1.0 indicates a strong relationship between the tested metals. A correlation coefficient of 1.0 is only reached for a parameter that is related to itself. Table 3 illustrates the CM among the sixteen heavy metals. As noticed, no significant relationship coefficients appear with values greater than 0.5 at a level of significance of 0.05 and with a p-value less than 0.05. Nonetheless, there might be some merit in CM, few moderate correlations were observed, for example, moderate positive relations (Fe with Mn), (Al with V), (As with Cr), (Cu with Ni) and (Pb with Li). Simultaneously, a moderate negative correlation for Ba with Cr was observed. Anyway, CM leads to identify that several pairs of heavy metals have common natural sources, the geological structure of soil and rocks of the study area, as there is no significant correlation between Hg and these heavy metals.

The correlation between heavy metals has also been investigated using AHC. The AHC was performed in this work based on Ward's method as an agglomeration method with Euclidean distance for measuring the dissimilarity. AHC is usually implemented in such studies to identify sources of heavy metals and also to relate them as several main groups. The internal cluster homogeneity is determined according to the similarity among heavy metals in soil samples.

Three main clusters have been established as presented in the dendrogram presented in Figure 2. The dendrogram of AHC shows that several significant dual heavy metals correlations exist in cluster 1 including Pb with Li; V with Al; Ni with Cu, and at later stages with Sr, Hg, and Ba. While the second cluster relates heavy metals for Mn, Cd, and Co. Finally, the third cluster shows a relationship of the rest of the heavy metals in the study area, Cr with As and Zn with Fe, as one group.

Regarding AHC analysis, the first cluster suggests mixed sources of heavy metals involving natural sources for Al, Ba, Cu, Pb, Sr, and V and anthropogenic sources for Hg, Li, and Ni (their EF are greater than 1). For cluster two, the correlation of the heavy metals (Mn, Cd, and Co) indicates that they have been generated from a common origin of natural sources (EF is less than 1 as illustrated in Table 2) for Mn and Co [36], and from anthropogenic activities for Cd (EF are greater than 1). For the heavy metals that are grouped in cluster 3, significant correlations between As, Cr, and Zn with Fe arise suggesting that these heavy metals are predominantly originated from natural weathering of parent materials or the crust of in the study area [37].

The PCA has been performed in this study to identify the variance of agricultural soil samples in terms of heavy metals concentrations and originating sources. The calculated eigenvalues in such analysis are usually referred to as the significance of established PCA factors, where the PCA factors of higher eigenvalues are considered the most significant factors. Factor loading in PCA analysis shows that six-factor were considered in the calculation representing about 71% of heavy metals variance in the obtained results.

As shown in Table 4, by employing the PCA, the results were reduced to six main factors representing about 71.1% of heavy metals concentration variance. Factors are ranging in significance from F1 (16.2% in variability) is the strongest to F6 relatively moderate (7.3% in variability). The remaining factors are counted less important in terms of absolute loading values as illustrated in Table 4 of the factors pattern. The first and second factors are involving 29.84 % of the total variance in heavy metals concentration. In this work, no Varimax rotation has been applied in the PCA as there is no considerable improvement in the variance percentage that was noticed after the rotation.

Table 3: Pearson linear correlation coefficient matrix* for the 16 heavy metals in agricultural soil samples.

	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Hg	Li	Mn	Ni	Pb	Sr	V	Zn
Al	**1.00**															
As	-0.36	**1.00**														
Ba	-0.08	-0.20	**1.00**													
Cd	-0.07	0.11	0.07	**1.00**												
Co	0.08	-0.09	-0.38	0.26	**1.00**											
Cr	0.02	0.38	-0.46	0.01	0.21	**1.00**										
Cu	0.14	0.08	0.15	0.17	0.19	-0.16	**1.00**									
Fe	-0.26	0.33	0.12	0.20	-0.10	0.23	-0.23	**1.00**								
Hg	0.09	-0.07	-0.10	0.05	0.00	-0.11	0.25	-0.37	**1.00**							
Li	-0.12	0.26	-0.38	-0.17	-0.05	-0.11	0.17	-0.05	0.11	**1.00**						
Mn	0.03	0.00	-0.01	0.39	0.22	0.21	0.13	0.01	0.21	-0.14	**1.00**					
Ni	0.16	-0.21	0.13	-0.06	-0.05	-0.15	0.46	-0.23	0.11	0.23	-0.04	**1.00**				
Pb	0.13	0.21	-0.29	-0.21	-0.06	0.02	0.26	-0.27	-0.06	0.39	0.17	0.08	**1.00**			
Sr	-0.14	0.02	0.24	0.03	0.13	-0.16	0.29	0.02	0.23	0.11	0.00	0.40	-0.29	**1.00**		
V	0.44	-0.18	0.04	-0.08	0.15	0.05	0.13	-0.21	0.04	-0.15	0.07	0.08	0.14	-0.16	**1.00**	
Zn	-0.32	0.33	0.12	-0.03	-0.09	0.28	0.13	0.38	-0.26	0.05	-0.01	0.34	0.03	0.17	-0.17	**1.00**

* with a significance level alpha = 0.05

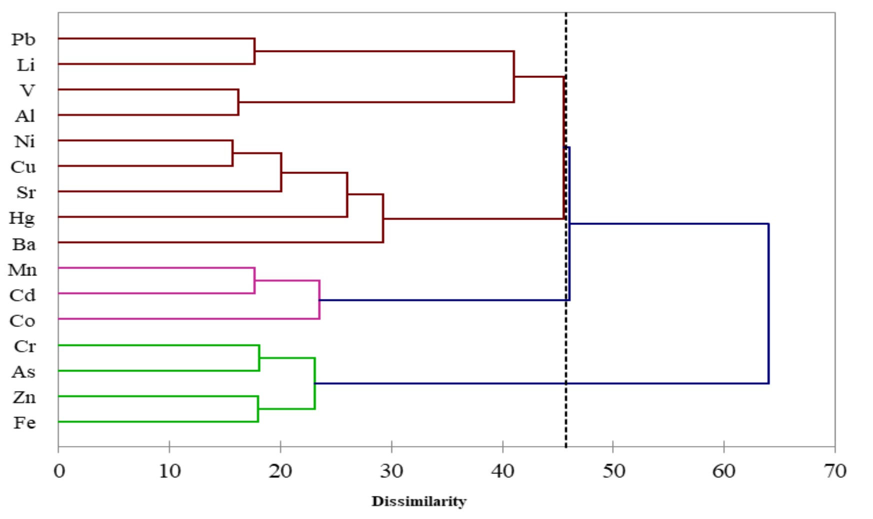

Figure 2: Dendrogram for 16 heavy metals investigated for the study area.

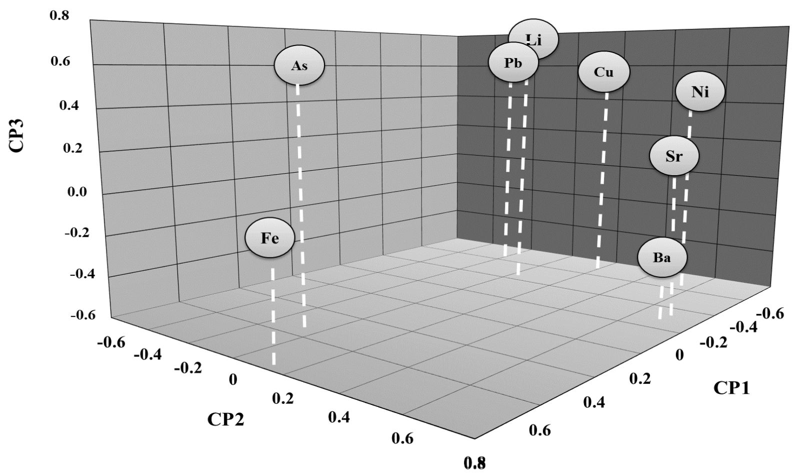

Figure 3: 3D plot of some of the significant loading for components PC1, PC2, and PC3.

As illustrated in Table 4, Al, As, Ba, Cd, Co, Cu, Fe, Hg, Li, Mn, Ni, Pb, and Sr are the most significant heavy metals contributing to results variation from their positive and negative loading on five principal components PC1, PC2, PC3, PC4, and PC5. Each heavy metal of a substantial correlation coefficient value within the principal components is regarded as a significant parameter contributing to the variation in the results. It was noticed in Table 4, no individual important loading has been recognized concerning the principal component PC6.

As seen in Table 4, the first principal component PC1, which accounts for 16.17% of dataset variance, exhibits a notable loading on As and Fe (0.597 and 0.744 respectively) with negative loading on Al with a value of -0.597. While the second principal component PC2, which represents 13.67 % of dataset variance, has considerable loadings on Ba, Ni, and Sr with loading values of 0.696, 0.513, and 0.663 respectively. Whilst, the third principal component PC3, which has 13.19 % of variability, shows considerable loadings on Cu, Li, and Pb with values of 0.532, 0.684, and 0.569 respectively. The graphical representation for the first three principal components PC1, PC2, and PC3, they represent 43% of dataset variation, with important loading of heavy metals is illustrated in Figure 3 as a three-dimensional 3D plot. In Figure 3, distinctive groups that have been generated from the considerable loading for most of the tested heavy metals: As with Fe; Ba with Sr and Ni; Li with Pb and Cu have been observed.

The principal component PC4, which explains 11.65% of the total variance, has a considerable loading on Cd, Co, and Mn with values of 0.735, 0.586, and 0.657 respectively. The principal component PC5 was also showed a significant loading on Hg and V. PC6 did not show any important loading on a particular heavy metal. In Figure 4, radar-filled charts present Cd, Co, Hg, Mn, and V with significant loading by the remaining principal components that are not illustrated in Figure 3, particularly PC4 and PC5. Figure 4 shows that PC4 is considerably correlated with Cd, Co, and Mn. Whereas PC5 has a significant loading on Hg and V.

The results obtained by AHC and PCA are greatly consistent, both methods showed different categories have been established regarding the origins of the heavy metals. The results exhibit that the investigated heavy metals in the soil of the study area have different sources. As regards the origin of examined heavy metals, PCA results reveal three distinctive principal components that have been established for soil samples in the study area. A natural component of PC1 dominated by the heavy metals Al, As and Fe, the component is considerably controlled by parent materials.

Table 4: Percentage of variance for PCA factors (significant factor loading ≥ 0.50 level are stated in bold).

Component	Initial eigenvalues			Extraction sums of squared loading		
	Eigenvalue	Variability (%)	Cumulative %	Eigenvalue	Variability (%)	Cumulative %
F1	2.588	16.174	16.174	2.588	16.174	16.174
F2	2.187	13.667	29.841	2.187	13.667	29.841
F3	2.110	13.188	43.029	2.110	13.188	43.029
F4	1.864	11.650	54.679	1.864	11.650	54.679
F5	1.393	8.705	63.384	1.393	8.705	63.384
F6	1.168	7.303	70.686	1.168	7.303	70.686
F7	0.910	5.690	76.377			
F8	0.775	4.847	81.224			
F9	0.697	4.356	85.580			
F10	0.600	3.750	89.330			
F11	0.515	3.216	92.546			
F12	0.390	2.437	94.983			
F13	0.270	1.687	96.669			
F14	0.216	1.351	98.020			
F15	0.180	1.123	99.143			
F16	0.137	0.857	100.000			
Heavy metal	**Component matrix (loading values for heavy metals)**					
Component matrix	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**
Al	**-0.597**	-0.322	-0.136	0.022	0.367	-0.096
As	**0.597**	-0.078	**0.507**	0.019	-0.052	0.194
Ba	-0.075	**0.696**	-0.447	0.027	0.252	0.331
Cd	0.114	0.066	-0.038	**0.735**	-0.131	0.280
Co	-0.137	-0.307	0.172	**0.586**	-0.061	-0.414
Cr	0.437	-0.489	0.245	0.286	0.273	-0.274
Cu	-0.443	0.321	**0.532**	0.271	0.167	0.172
Fe	**0.744**	0.154	-0.103	0.150	0.188	0.006
Hg	-0.470	0.053	0.181	0.208	**-0.512**	0.052
Li	-0.027	-0.007	**0.684**	-0.393	-0.292	-0.015
Mn	-0.073	-0.182	0.141	**0.657**	0.020	0.388
Ni	-0.418	**0.513**	0.427	-0.029	0.327	-0.195
Pb	-0.186	-0.376	**0.569**	-0.316	0.190	0.415
Sr	-0.116	**0.663**	0.233	0.251	-0.183	-0.342
V	0.519	-0.464	-0.306	-0.103	**0.5189**	-0.007
Zn	0.489	0.481	0.392	0.400	0.4892	-0.085

PC2 and PC3 are components of heavy metals generated in the soil from mixed sources: Ni in PC2 and Li with Ni in PC3 are likely to be from anthropogenic sources, however, Ba, Sr in PC2 and Cu and Pb in PC3 could most likely be generated from natural sources and with a considerable anthropogenic input. Cu, Ni, and Pb could most likely be generated from fertilizers and pesticide applications as well as, with vehicle exhaust as a major source of Pb [37]. PC4 and PC5 are anthropogenic components. PC4 combines Cd, Co, and Mn as per their origin, the significant loading on Cd (EF is greater than 1) suggest an anthropogenic source of these heavy metals. In the same way, PC5 is controlled by Cd and V is leading to propose these heavy metals have the same source which is most probably to be anthropogenic. Suggesting that sources of Cd and Hg are most likely anthropogenic such as transportation [38] and fertilizer implementation [39].

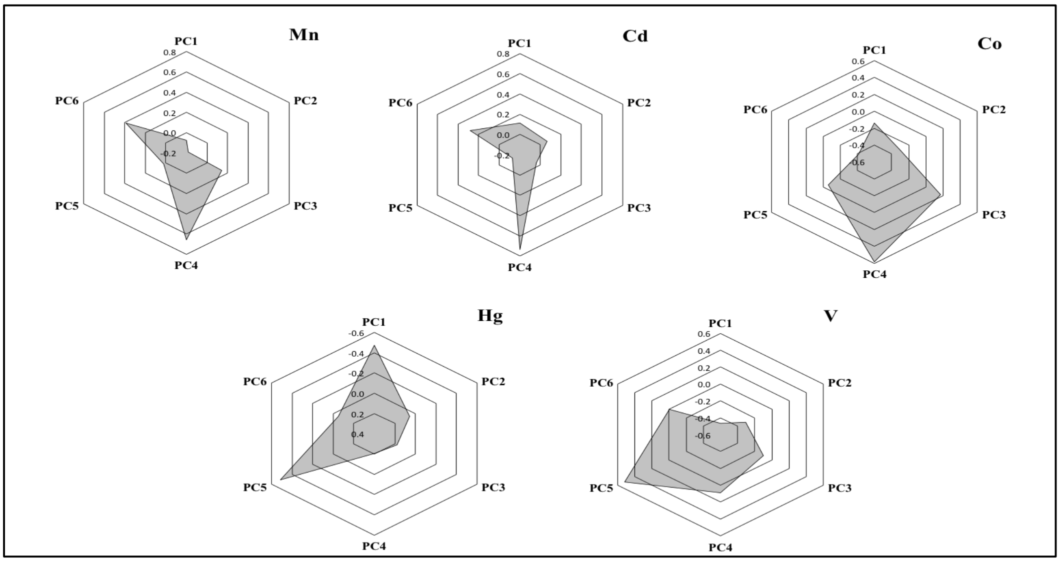

Figure 4: Radar filled charts of some heavy metals (Mn, Cd, Co, Hg, and V) that significant loading for the last three main components PC3, PC4, and PC6.

3.4. Spatial distribution of the heavy metals

The spatial distribution of certain significant heavy metals (As, Cd. Cr, Hg, Ni, and Pb) are presented in Figure 5. The spatial distributions of As agree with PCA and EF results, verifying that the origin of As predominantly comes from natural weathering of parent materials from crust composition of the study area since a nonpoint pollution distribution was noticed.

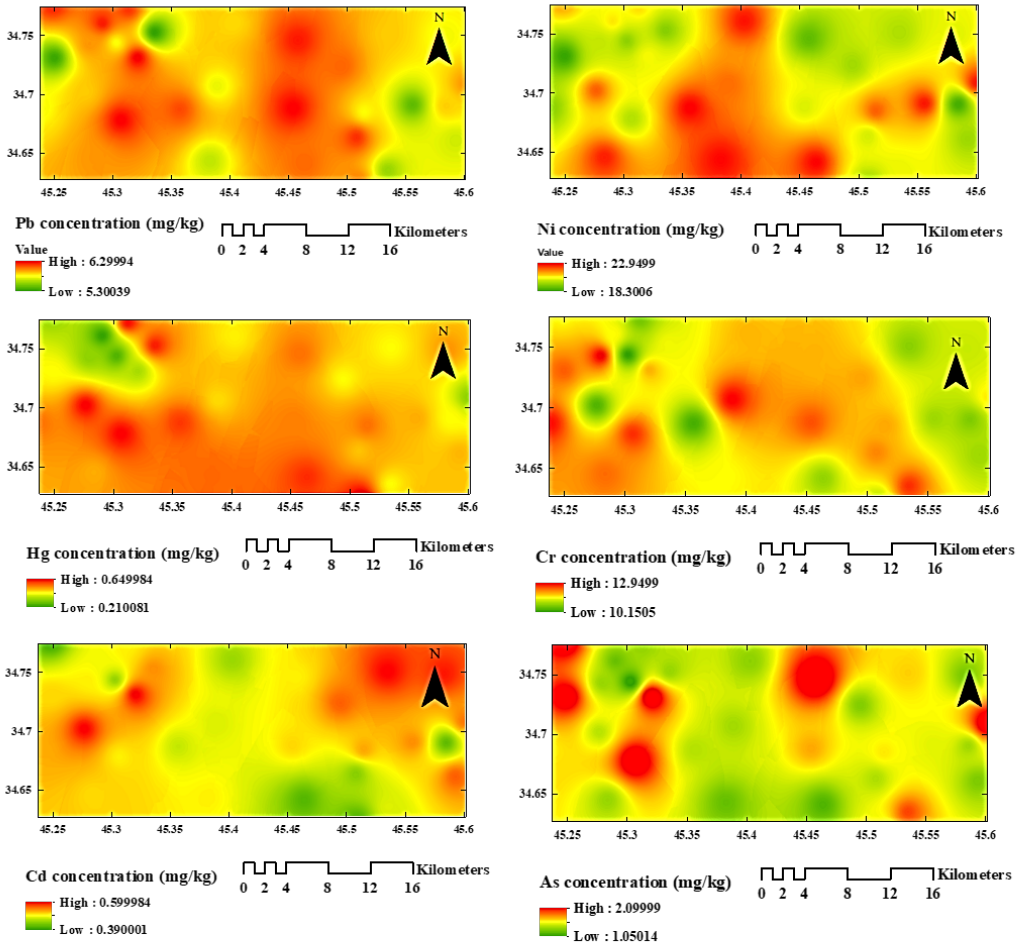

Figure 5: Spatial distribution maps of concentrations for heavy metals As, Cd, Cr, Hg, Ni and P in the study area soil.

In Figure 5, high concentrations of Hg, Ni, and Pb are presented in most parts of the study area. This condition of Hg reveals an excessive implementation of fertilizers and pesticides by agricultural activities or wastewater discharges [40]. Moreover, Pb high concentration in some sites suggests that vehicle exhausts might be causing this increase [41], as the main road in Iraq is passing through the study area. Cd and Cr show a similar manner of spatial distribution with moderate concentrations in the study area.

Conclusion

In this work, a comprehensive investigation of the contamination of heavy metals was done for the agricultural soil of the middle basin Sirwan (Diyala) river, East Iraq. The study involved an evaluation of potential ecological risk and source apportionment. Pollution indices have been implemented and as well as multivariate statistical methods such as PCA, CM, and AHC. Concentration results and PI showed that moderate contamination levels of Cd, Hg, Li, and Ni have occurred. Whilst, RI classified Cd and Hg to be at a moderate ecological risk level. AHC, EF, and PCA revealed three distinct sources that could be considered for the investigated heavy metals: anthropogenic; lithogenic; and the source comes from a mixed contribution of anthropogenic and lithogenic factors. The most anthropogenic contribution in the heavy metals in the study area appears in Hg and Cd, Ni and Pb in the lower level. The assessment interpreted that origin of As and the remaining tested heavy metals in the area is most likely to be a natural source. The spatial distribution of the heavy metals presented nonpoint pollution in the soil of the study area. The results of assessments and analysis described in this study support the use of multivariate methods and risk indices as a decisive way for reliable contamination evaluation of agricultural soils in the rest of Iraq.

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