Geospatial and Multivariate Statistical Interpretations for Relationships between Physico-Chemical Properties and Heavy Metals in Some Agricultural Soils of Kalar and Quratoo Sub-Districts, East Iraq

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Abstract: In this study, ninety agricultural soil samples were collected from Kalar and Quratoo sub-districts east of Iraq. Where soil samples have been analyzed to quantify concentrations of nine soil physicochemical properties and sixteen heavy metals by using ICP-OES with other analyzing tools. Analysis results showed that significant variations exist in concentrations of the investigated parameters among sampling sites. Multivariate statistics have been conducted to identify relationships between heavy metals and soil properties. Multiple correspondence analysis MCA showed strong relationships for total nitrogen T.N. with Cu, Ni, and Hg. Agglomerative hierarchical clustering (AHC) and factorial analysis (FA) divided soil property relationships with heavy metals into three main categories in terms of heavy metals nature; naturally occurred, generated from anthropogenic sources, and of weak relationships. Spatial variation map showed that soil properties in middle parts of the study area are more impacted by heavy metals that came from anthropogenic sources. This study aids to improve the environmental protection and monitoring of agricultural lands in Iraq.

Keywords: Heavy Metals, Soil Contamination, Soils Properties, Multivariate Statistics, Spatial Distribution

1. Introduction

Studies on spatial variation and distribution of soil properties have a long tradition in land use planning (Castrignanò, Giugliarini, Risaliti, & Martinelli, 2000). There were growing demands for information on the physical-chemical properties of soil to assist in establishing consistent plans in environmental, and natural sources management for any land (Budak, 2018). The field of environmental management for land has gradually broadened in performing of such environmental plans of land-use sustainability (Galford, Soares-Filho, & Cerri, 2013). Most of the studies have indicated that traditional ways of soil survey are incompetent in presenting the necessary information of soil properties, due to differences among areas, even in the same country (Lagacherie & McBratney, 2006). Precise and accurate data on soil properties in agricultural and rural areas is always curial in spatial distribution of those properties, and therefore it is considered as a key factor in promoting agricultural land sustainability (Usowicz & Lipiec, 2017).

Excessive application of fertilizers and pesticides in agriculture led to the wide existence of heavy metals in agricultural soils (Khalifa & Gad, 2018; Savci, 2012). The main problem about existence of heavy metals in agricultural soils is that the life-threatening consequences of high concentrations of such metals on human health. This risk is mainly generated from crop uptake for heavy metals, putting consumer's life and health at serious risk (Davies, 1992). Heavy metals usually tend to create relationships with the physical, chemical, and biological properties of agricultural soils (Chen & Pu, 2007; KavitaVerma & Pandey, 2019). Various studies on soil property relationships with heavy metals have applied statistical analysis methods to explain the spatial variation of these relationships for agricultural soils (Uchimiya, Klasson, Wartelle, & Lima, 2011). Multivariate and geospatial statistics are mostly used for explaining the spatial relationships of physicochemical properties with heavy metals. The geostatistical Kriging and Inverse distance weighted IDW interpolations have been commonly used to detect the spatial behavior of soil properties and their relationships with heavy metals (Bhunia, Shit, & Maiti, 2018; Shit, Bhunia, & Maiti, 2016; Valladares, Camargo, Carvalho, & Silva, 2009). At the same time as correlation matrix CM, agglomerative hierarchical clustering AHC, canonical correlation analysis CCorA, and principal component analysis PCA are widely utilized to display spatial correlations of agricultural soil attributes and heavy metals (Gutiérrez et al., 2016; Sungur, Soylak, & Ozcan, 2014; Vega, Covelo, Andrade, & Marcet, 2004).

There is no previous research on the spatial distribution of heavy metals relationships with agricultural soil physicochemical properties in Iraq and, more specifically, for Kurdistan region, where the study area of Kalar and Quratoo sub-districts is located. Most probably the conflicts and unusual current political circumstances in Iraq led to this gap and lack of needed studies in the past decades. However, only a few studies have been made for heavy metals in soils of Iraq, but no previous study has investigated the spatial relationships of these heavy metals with soil properties. The study area of Kalar and Quratoo sub-districts primarily comprises of cultivated agricultural and arable lands, where many strategic crops are produced.

It is of interest to know the spatial variation for the relationship of heavy metals with soil properties in this important agricultural area. The current study aims to determine and assess the spatial variation of relationships between some significant physicochemical properties with heavy metals in agricultural soils of Kalar and Quratoo sub-districts using various reliable geostatistical and multivariate statistical techniques. The main contribution made by this work will be the wide applicability in land sustainability for crop production in the concerned study area.

2. Materials and Methods

2.1 Description of the Study Area

The study area of Quratoo and Kalar sub-districts (34° 51' 32" N, 45° 10' 37" E, 34° 24' 54" N, 45° 45' 7" E) is located in eastern Iraq, has a higher altitude of 200 m a.s.l, and covers an area about 1000 km^2 of mostly arable lands. The population in the area has expanded in the last twenty years due to both economic growth and political situation in Iraq (Kurdistan Region Statistics/ Garmian Office, 2018). The annual rainfall of the area is 273 mm with no precipitation in the summer season (Garmian Region Agriculture Department, 2017). The winds are mostly northwesterly and in summer season southeasterly winds considerably occur with a possibility of dust storms generation (Iraqi Meteorological Organization and Seismology, 2010). The physical feature of the study area is comprising of plain and hilly areas. The area is dominantly covered by soils belong to Quaternary alluvial deposits. Soils of the study are physically categorized into four main classes: shallow soil; stony soil; chestnut soil, and rough cracked soil (Buringh, 1960). Geologically, the area is a semi-arid region, that is dominantly covered by soils belong to Quaternary deposits (Muhaimeed, Saloom, Saleim, & Alaane, 2014).

2.2 Soil Sample Collection and Preparation

In this work, a total of ninety samples were taken at different depths from the surface (0, 10, and 20 cm) from thirty sites (three samples for each site), 14 from Quratoo sub-district and 16 from Kalar sub-district, within agricultural areas in the study area in June and July 2019. The basis of choosing the sampling locations is to cover most of the agricultural areas in the Quratoo and Kalar sub-districts (Figure 1). All sampling sites (S1 to S30) are away from roads with at least 200 m. For each sampling site, the three collected samples at different depths, 250 g for each, were mixed into one composite sample. A wooden shovel has been used to take soil samples. The soil samples were then put in sealed plastic bags and taken to the laboratory for analysis.

At the laboratory of instrumental analytical chemistry (University of Garmian), the collected samples were preliminarily dried at a temperature of 60 ^{0}C for 2 hours to sieve them through a 2-mm mesh to remove any probable large particle and impurities that could be collected with the samples. After that, the sieved soil samples were packed in clean plastic bags and preparing them for chemical analysis.

2.3 Laboratory Analysis for Soil Samples

In each soil sample, concentrations for heavy metals of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sr, V, and Zn and for chemical exchangeable cations of Ca, K, Na, Mg, and total N, with available P. acidity pH, soil organic matter SOM and electrical conductivity EC have been quantified. Analysis has been performed using inductively coupled plasma optical emission spectroscopy ICP-OES (Spectro across Germany), according to a procedure of wet digestion for soil samples. Regarding heavy metals, soil samples were dried at 100 °C for 2 hours, and then samples were cooled and digested with concentrated nitric acid. All the samples have been analyzed within 24 hours from sampling time. A serial of dilution with 1000 mg/l was employed for standard solutions preparation. Standard solutions were diluted by several dilutions into 0, 0.1, 0.5, 2 ppm in 0.5% nitric acid as diluent. For exchangeable cations concentrations, Ca, K, Mg, Na, and P, samples were first extracted with 1 N ammonium acetate solution, neutral pH 7, and then measured by ICP-OES. In all analysis steps, distilled deionized water and glassware washing were used for the dilutions.

Soil pH and soil electrical conductivity EC were measured using pH meter and conductivity meter, respectively, in a soil-water suspension of 1:2 (*w*/*v*), after waiting for a half-hour to achieve equilibrium state (Behera & Shukla, 2015). organic matter (OM) content was determined using the dry ashing method of the Walkley-Black method (Storer, 1984). Total nitrogen has been identified using the Kjeldahl method (Bremner & Mulvaney, 1983). To confirm the validation of analysis results, three replications were performed for each sample.

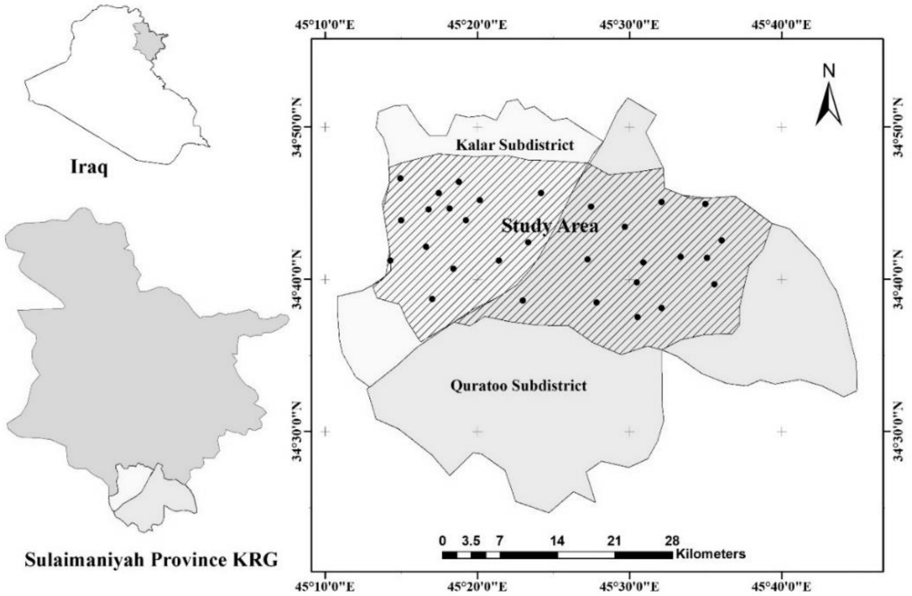

Figure 1: The study area showing sampling locations

2.4 Statistical Analysis and Spatial Distribution

In this paper, diverse descriptive and multivariate statistics were employed to interpret the soils dataset: Pearson correlation matrix CM, Agglomerative hierarchical clustering AHC, factorial analysis FA, and multiple correspondence analysis MCA. In similar cases of soil contamination assessment, multivariate statistics are broadly conducted. Pearson correlation matrix CM was commonly used to recognize relationships among tested soil property parameters. Whereas AHC, MCA, and FA are generally applied to classify the dataset into several main classes in order to distinguish individual impacts on the observations by created independent factors. FA exhibits loading weights of each extracted factors on the dataset, and also the loading weights of variables on each factor. The multivariate statistics were performed using the XLSTAT software, version 2017 for Excel 2013.

Furthermore, in the current study, geostatistics of ArcGIS software (version 10.6.1) was used to display the intensities of the heavy metals' relationships with soil properties. ArcGIS 10.6 (Kriging interpolation) was conducted to determine the spatial distribution of these relationships' variation in the study area.

3. Results and Discussion

3.1 Descriptive Statistics of Physicochemical Soil Properties and Heavy Metals

Table 1 presents the descriptive statistics of the physicochemical parameters and heavy metal concentrations samples from thirty different sites in the study area. 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, and 8 physicochemical parameters of Ca, K, Na, Mg, total N, pH, OM and EC in each soil samples were examined.

Descriptive statistics were calculated for all parameters used in the study using the percentage of the coefficient of variation CV%, which is performed to define data variability, demonstrates a moderate variation. For a CV% scale ranges between 10 and 100, in this work, CV% results for the heavy metals varied from 3.5 to 24.95 % of Mn and Hg respectively. CV% results for the physicochemical parameters varied from 2.19 to 15.05 % of pH and P, respectively. Results of low CV% values for pH indicates particularly hydrogen concentrations in soil samples, similar results have also previously reported in researches for agricultural soils (Hausherr Lüder, Qin, Richner, Stamp, & Noulas, 2018; López-Granados et al., 2002). Physicochemical parameters in soil samples, especially Na, P, and EC showed moderate variability, while Ca, K, Mg, OM, and total N showed low variability. For heavy metals, CV% values higher than 10% were reported for As, Ba, Cd, Hg, and Zn, indicating moderate variability for these heavy metals.

Results of skewness display a statistically nearly symmetrical distribution of soil parameters with minor positive or negative skews. For soil physicochemical parameters, the highest positively skewed parameter was the pH of value equals 1.28, while the highest negatively skewed parameters were OM of value equals -0.64. For heavy metals, the highest positively skewed metal was As (0.96), whereas the highest negatively skewed metal was Pb (-0.61). As shown in Table 1, kurtosis values for investigated parameters in soil samples reveal a moderately normal distribution for a majority of the concentration values.

The dataset presented in Table 1 also revealed that soil samples are relatively rich in available P, its concentration ranges from 55.43 to 94.7 mg/kg which is much higher than the required minimum P concentration of 8.0 mg/kg in agricultural soils (Sillanpaa, 1990). Similarly, for the exchangeable cation K, concentrations in soil samples are ranging from 1432.2 to 1739.8 mg/kg, indicate that soil samples are enriched with K as they exceed the critical limit for plant growth (Sillanpaa, 1990). High concentrations of Ca, K, and K were also observed in Table 1, indicating the nature of soil composition in the study area. The mean EC value 0.24 mS/m shows that the soil of the study area is non-saline, the soil salinity threshold is 4 dS/m (Shrivastava & Kumar, 2015). Similarly, for the exchangeable cation K, concentrations in soil samples are ranging from 1432.2 to 1739.8 mg/kg, indicate that soil samples are enriched with K as they exceed the critical limit for plant growth (Sillanpaa, 1990).

Table 1: Descriptive statistics of soil parameters

Parameter	Min	Max	Mean	Median	St. Dev.	Skew.	Kurt.	CV%
Soil Parameters								
Ca (mg/kg)	11328	15098	13092	12919	1148.1	0.25	-0.97	8.77
K (mg/kg)	1432.2	1739.8	1590.7	1567.2	88.9	0.19	-0.93	5.59
Mg (mg/kg)	2137.4	2834.1	2471.0	2445.5	178.1	0.36	0.12	7.21
Na (mg/kg)	142.50	217.35	172.89	169.95	22.96	0.45	-0.96	13.28
P (mg/kg)	55.43	94.70	73.65	72.30	11.09	0.38	-0.90	15.05
pH (pH degree)	7.25	7.86	7.46	7.40	0.16	1.28	0.73	2.19
OM (%)	5.32	6.60	6.06	6.10	0.35	-0.64	-0.25	5.81
EC (mS/m)	0.20	0.32	0.24	0.23	0.03	1.02	0.49	13.43
Total N (%)	0.27	0.32	0.30	0.30	0.01	-0.37	-0.56	4.44
Heavy Metals								
Al (mg/kg)	3674.00	5003.00	4216.56	4182.00	325.16	0.86	0.52	7.71
As (mg/kg)	1.05	2.10	1.48	1.35	0.31	0.96	-0.43	21.05
Ba (mg/kg)	48.32	72.43	58.07	57.54	5.51	0.61	0.76	9.48
Cd (mg/kg)	0.39	0.60	0.50	0.50	0.06	-0.10	-0.54	11.52
Co (mg/kg)	2.32	2.76	2.53	2.54	0.14	0.02	-1.38	5.71
Cr (mg/kg)	10.15	12.95	11.66	11.60	0.82	-0.08	-1.01	7.07
Cu (mg/kg)	3.12	3.57	3.33	3.32	0.14	0.21	-1.29	4.19
Fe (mg/kg)	3365.00	4287.15	3912.54	3928.75	235.11	-0.30	-0.26	6.01
Hg (mg/kg)	0.21	0.65	0.48	0.50	0.12	-0.48	-0.39	24.95
Li (mg/kg)	29.70	34.65	31.82	31.80	1.50	0.29	-1.00	4.71
Mn (mg/kg)	109.40	127.80	119.45	119.55	4.18	-0.11	0.09	3.50
Ni (mg/kg)	18.30	22.95	20.79	20.40	1.44	0.20	-1.23	6.93
Pb (mg/kg)	5.30	6.30	5.93	5.95	0.29	-0.61	-0.26	4.82

Sr (mg/kg)	109.30	126.10	117.07	116.60	4.95	0.30	-1.05	4.23
V (mg/kg)	8.00	9.75	8.83	8.87	0.51	0.09	-1.03	5.80
Zn (mg/kg)	18.32	29.50	22.51	22.81	3.19	0.40	-0.89	14.19

3.2 Relationships between Soil Properties and Heavy Metals

3.2.1 Statistical Analysis

Results obtained by Pearson's correlation matrix CM are shown in Table 2, significant relationships among soil parameters and heavy metals can be observed. Regularly, in CM analysis, a correlation coefficient that is closer to 1.0 is indicating a strong relationship between the assessed variables. At $P < 0.01$, several significant correlation coefficients > 0.3 are existing.

As seen in Table 2, among the soil properties parameters, some significant positive correlation coefficients are existing, (Na – available P), and (pH - OM). On the other hand, several negative correlation coefficients are existing: K with Mg, Na, and available P. Ca has a significant negative correlation with soil pH and OM. negative pH correlations with Ca, Mg, Na, EC, and total N were observed, similar correlations were also reported between pH and other soil parameters and micronutrients (Chamannejadian, Moezzi, Sayyad, Jahangiri, & Jafarnejadi, 2011; Lindsay, 2001).

Table 2 reveals also many significant positive correlation coefficients, $r > 0.3$ at $p < 0.01$, between heavy metals and soil properties: (K-Co); (K-Zn); (Na-Li); (Na-Pb); (available P-As); (available P-Fe); (available P-Sr); (pH-Zn); (EC-Al); (EC-Hg); (T.N.-Cd); (T.N.-Co); (T.N.-Hg); and (T.N.- Sr). Similarly, negative significant correlation coefficients $r < -0.3$ at $p < 0.01$, were observed between heavy metals and soil properties: (K-As); (Mg-Co); (available P-V); (pH-V); (OM-Cd); (OM-Cr); (OM-Cu); (EC-Sr); and (EC-Zn).

Significant correlations between (N with Cu and Cd) and (P with Fe) were also reported by (KavitaVerma & Pandey, 2019). Positive correlation coefficients, (P with Zn) and (P with Pb), and negative correlation coefficients, (pH with Pb) and (pH with Cu), were also reported by (Nan, Zhao, Li, Chen, & Sun, 2002). The negative correlation between Cu and pH suggests that an increase in Cu concentration in the soil causes a considerable decrease in pH of that soil, or high pH level in the soil leads to a decrease in Cu solubility in soil (Sürücü, Ahmed, Günal, & Budak, 2019). The negative correlations between OM and some heavy metals indicate that the presence of heavy metals is deteriorating OM of soils. Therefore, from the observed relationships of soil properties with heavy metals, it is clear that soil properties are susceptible to be altered in the presence of particular heavy metals (Adriano, 2001). Results of CM also suggest that the origin of some heavy metals is most probably is the natural composition soils or rocks of the area (Mileusnić et al., 2014), as those heavy metals have significant correlations with soil properties, with taking in account the contribution of anthropogenic activities in heavy metals occurrence in the study area. Although previous studies in the literature stated strong negative correlations between pH and various heavy metals in soils, this study suggests that only weak negative correlations are existing with specific heavy metals, no evidence could be detected in the CM may agree with those earlier findings.

Table 2: Correlation matrix among soil physicochemical properties and interrelationships of soil physicochemical properties with heavy metals

Variables	Ca	K	Mg	Na	P	pH	OM	EC	T.N.
Ca	1.00								
K	0.17	1.00							
Mg	0.12	-0.32	1.00						
Na	-0.28	-0.33	-0.03	1.00					
P	0.14	-0.31	0.24	0.31	1.00				
pH	-0.08	0.22	-0.13	-0.20	0.16	1.00			
OM	0.03	0.04	-0.15	0.18	0.16	0.33	1.00		
EC	-0.10	-0.08	-0.21	-0.02	-0.26	-0.14	0.11	1.00	
T.N.	-0.10	0.00	-0.21	0.15	-0.10	-0.04	-0.23	0.07	1.00
Al	0.32	0.06	-0.27	-0.05	-0.21	-0.28	-0.21	0.31	0.08
As	-0.18	-0.30	0.11	0.10	0.35	0.05	-0.23	-0.11	-0.07
Ba	0.01	-0.06	0.20	0.01	0.17	0.18	0.14	-0.06	-0.01
Cd	0.04	0.06	0.10	0.16	0.19	0.00	-0.40	0.07	0.40
Co	-0.13	0.43	-0.33	-0.08	-0.26	-0.01	-0.12	0.08	0.38
Cr	0.11	0.29	-0.01	-0.25	-0.08	-0.10	-0.39	-0.25	-0.22
Cu	0.24	-0.02	0.03	0.11	0.12	-0.23	-0.30	-0.07	0.47
Fe	0.02	0.00	0.10	0.15	0.38	0.22	-0.20	-0.28	-0.10
Hg	-0.18	0.11	-0.08	-0.02	-0.07	-0.17	-0.07	0.35	0.31
Li	-0.08	-0.26	0.27	0.31	0.24	-0.08	0.05	-0.26	0.09
Mn	0.26	0.01	0.24	-0.05	0.23	-0.13	-0.13	0.11	0.12
Ni	0.21	0.12	0.04	-0.06	0.03	-0.04	0.00	-0.18	0.24
Pb	0.22	-0.28	0.17	0.33	0.13	-0.36	0.02	-0.07	-0.18
Sr	-0.06	0.19	-0.10	-0.01	0.43	0.24	0.21	-0.37	0.32
V	0.22	0.14	0.23	-0.27	-0.52	-0.21	-0.32	0.16	0.19

Zn	0.24	0.30	0.05	-0.17	0.28	0.47	-0.04	-0.35	-0.18

* at significance level alpha=0.01, significant correlations are in bold.

The CM showed certain significant relationships between certain soil properties and heavy metals, to investigate interrelationships between those parameters further statistical analysis has been performed using AHC. The AHC was submitted in this work based on Ward's method with Euclidean distance for measuring the dissimilarity. AHC classified the relation between soil properties and heavy metals into several main groups. The internal cluster homogeneity was established according to the similarity among concentrations of property parameters and heavy metals in soil.

3.2.2 Multivariate Statistical Analysis

Three main clusters have been recognized as shown in Figure 2. The dendrogram of AHC exhibits three distinctive correlations of soil properties with heavy metals: cluster 1, dominated by Mg, pH, OM, and P with certain heavy metals such as Cd, Cr, Fe, and Zn; cluster 2 relates Na with heavy metals for Pb and Li; cluster 3 involves soil properties of T.N., K, Ca with heavy metals of Cu, Ni, Co, Hg, V, and Al.

AHC analysis reveals complex interrelationships between soil properties and heavy metals in the study area that are divided into three classes. Heavy metals in clusters 3 have that have significant relationships with (Ca and Al), and at the same time have a significant relationship with Hg, well-known heavy metals of an anthropogenic origin. These interrelationships suggest that clusters 3 is representing a mixed source of heavy metals, natural and anthropogenic. Cluster 2 represents Pb, Li, and Na that have no significant relationships with the remaining soil properties and heavy metals. While cluster 1 involves heavy metals that have significant relationships with (Mg and Fe), therefore, cluster 1 suggest that the interrelationship between Fe and Mg with certain heavy metals might be originated as natural weathering of parent materials in the study area. Fe is permanently considered as free from anthropogenic effects and exists at abundant levels in the crust (Liu, Yang, Yun, Zhang, & Wang, 2015). Soils of the study area are belonging to the low rainfall region are containing more Mg or Ca carbonates in their profile (Azeez & Rahimi, 2017). In cluster 3, heavy metals such as Hg, Cu, Ni, Co, and V have a significant impact on soil properties of T.N., Ca, K, and EC, indicating an excessive application of pesticides and inorganic fertilizers that containing such heavy metals in Iraqi agricultural areas (Al-Tamimi & Ali, 2018).

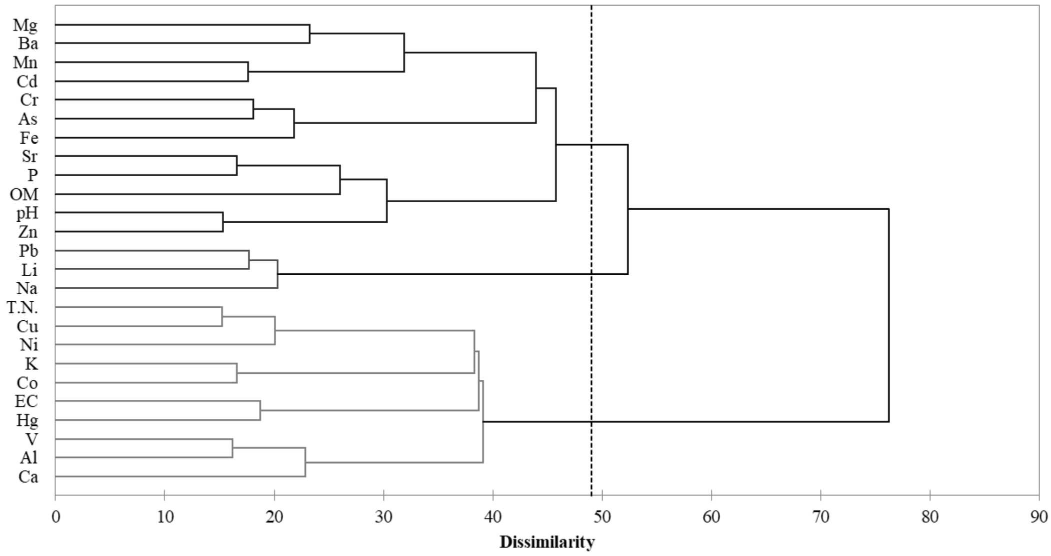

Figure 2: Dendrogram for inter-relationships between soil physicochemical properties with heavy metals in the study area

MCA was submitted for further investigation of the interrelationships between soil property parameters and heavy metals in the study area. MCA was application was based on normalized values of correlations established between two groups. MCA in this research aids to distinguish interrelationships among soil property parameters in their group, and also with each heavy metal in the second group. MCA results show, for 73.82% of the total variance of relationships dataset in soil, correlations can be represented by four main factors: factors F1, F2, F3, and F4 are accounting for 26.40%, 18.62%, 16.40%, and 12.40 % of the total variance of interrelationships between soil parameters and heavy metals, respectively. MCA analysis is illustrated in Figure 3, where 73.82% of total variance was displayed as symmetric plots.

Figure 3, for 73.82% of the total variance, shows that soil properties are significantly impacted by the investigated heavy metals. T.N. is strongly correlated with Cu, Ni, and Hg in soils of the study area. Similarly, it observed that pH is highly correlated with Zn, and also Ca is highly correlated with Al. Likewise, P is strongly correlated with Fe and V. At all times, Cu is negatively correlated with P. Mostly, Na has a high correlation with Pb, indicating its agreement with AHC results. OM is highly correlated to Cd and Cr in a later stage, similar findings are expected for OM, as OM bounds with heavy metals in soil (Zeng et al., 2011).

Figure 3 (a) displays 45.02% of the total variance in relationships, Ca, EC, and pH was strongly correlated with Zn, and Al. On the other hand, Co, Cr, and Cd are negatively correlated to pH, suggesting that the existence of such heavy metals leading to a decrease in pH.

In Figure 3 (b), representing 28.80% of total relationships, it can be seen that OM is highly related to Cd, indicating that always there are certain heavy metals in soils that are linked with OM (Jones & Jacobsen, 2009). It is worth pointing out that there is no inconsistency between results of AHC and MCA, MCA links each soil property to heavy metals regardless of their source, whereas AHC categorizes relationships between soil properties and heavy metals with considering their sources.

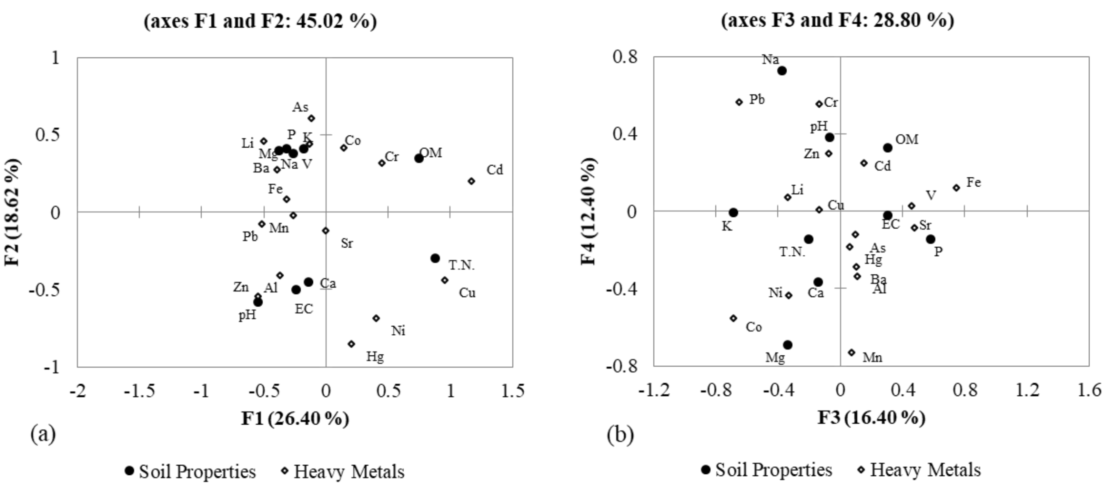

Figure 3: Symmetric plots based on MCA, (a) for factors F1 and F2 and represents 45.02% of total variance between soil properties and heavy metals, (b) for factors F3 and F4 and represents 28.80% of total variance between soil properties and heavy metals.

Factorial analysis FA has also been applied in this work to further categorize relationships of soil properties with heavy metals. From AHC results, there are three distinct types of soil properties relationships with heavy metals: soil properties linked strongly to heavy metals of natural origin, represented by cluster 1; soil properties highly correlated with heavy metals of heavy metals came from anthropogenic sources; limited relationships between soil properties with heavy metals.

Greatly, the first category was dominated by Fe, representing the natural composition of soils in the study area, the second group is highly dominated by Hg, indicating the impact of anthropogenic activities on soil properties. FA was conducted by using Varimax rotation with Kaiser Normalization, whereas a significant enhancement in percentages of factors loading and eigenvalue was achieved after rotation. After rotation, factors with high eigenvalues are taken into account, where nine factors were extracted, representing 66.28 % of the total variance of the dataset as shown in Table 3.

Table 3: Correlations between variables and factors after Varimax rotation, by using FA*

	D1	D2	D3	D4	D5	D6	D7	D8	D9
Ca	-0.09	0.15	0.15	0.00	0.72	-0.04	-0.01	-0.14	0.05
K	-0.08	0.71	0.12	-0.11	0.06	0.11	0.13	-0.04	-0.21
Mg	0.03	-0.14	-0.01	0.10	0.11	-0.10	0.00	-0.05	0.97
Na	0.18	-0.64	0.04	-0.12	-0.12	0.06	0.13	-0.06	-0.10
P	0.78	-0.33	0.14	-0.09	0.27	-0.12	0.13	0.00	0.11
pH	0.37	0.37	0.01	-0.24	-0.17	-0.19	-0.05	-0.17	-0.05
OM	0.17	-0.02	-0.09	-0.95	0.01	-0.06	-0.23	0.02	-0.07
EC	-0.34	-0.11	-0.29	-0.07	0.03	-0.10	0.11	0.40	-0.21
T.N.	-0.18	-0.10	0.49	0.10	-0.27	-0.04	0.51	0.13	-0.16
Al	-0.52	-0.07	0.06	0.11	0.36	-0.03	-0.01	0.10	-0.31
As	0.51	-0.17	-0.07	0.38	-0.09	0.28	-0.03	-0.03	0.10
Ba	0.06	0.01	0.14	-0.09	0.03	-0.79	-0.01	-0.08	0.13
Cd	0.13	-0.05	0.00	0.23	0.01	-0.15	0.69	0.02	0.02
Co	-0.22	0.28	0.11	-0.10	-0.16	0.46	0.61	-0.11	-0.22
Cr	0.18	0.40	-0.24	0.44	0.20	0.50	0.03	-0.08	0.00
Cu	-0.09	-0.18	0.70	0.18	0.19	0.01	0.21	0.10	-0.02
Fe	0.51	0.06	-0.19	0.27	-0.04	-0.14	0.13	-0.37	0.02
Hg	-0.07	0.04	0.22	0.03	-0.11	0.06	0.08	0.92	-0.01
Li	0.17	-0.38	0.36	-0.06	-0.15	0.45	-0.20	0.00	0.24
Mn	0.07	0.04	-0.08	0.01	0.44	0.08	0.55	0.25	0.23
Ni	-0.07	0.09	0.71	-0.04	0.16	-0.06	-0.14	0.01	0.03
Pb	-0.10	-0.50	0.11	-0.03	0.43	0.49	-0.18	-0.05	0.14
Sr	0.35	0.19	0.58	-0.21	-0.15	-0.14	0.13	0.10	-0.04
V	-0.64	0.15	0.09	0.21	0.16	-0.01	0.03	-0.03	0.18
Zn	0.52	0.39	0.28	0.13	0.21	0.03	-0.17	-0.31	0.05

*correlations ≥ 0.4 were considered significant and presented in bold.

Table 3 for FA results shows a great agreement with the results of AHC, proposing that certain soil properties are directly bonded to heavy metals of natural origins, on the other hand, the remaining soil properties are significantly linked to heavy metals of anthropogenic origins. FA results show that strong correlations within rotated factor D1 for Fe and confirms particularly that this factor represents relationships between physicochemical soil properties with heavy metals that exist naturally as abundant minerals of earth's crust. D1 is explaining mainly variation of Fe in soil samples, therefore D1 is, at the same time, representing the highest values of that heavy metal. The rotated factor D8 represents relationships between soil properties with well-known heavy metals generated from anthropogenic sources of Hg.

3.2.3 Geospatial Analysis

The spatial distribution of soil properties relationships and heavy metals in the study area was displayed by showing scores of the factor D8 over the study area using Kriging interpolation, ArcGIS 10.6 software, as seen in Figure 4. It was confirmed by FA results that D8 explains specifically relationships of soil properties with heavy metals originated from anthropogenic activities, therefore higher values of interpolated data for D8 would display the spatial relationships of soil properties that are mainly with heavy metals accumulated due to anthropogenic activities, and therefore, soils with lower values of D8 interpolated data are representing relationships of soil properties with abundant heavy metals of earth's crust composition.

From Figure 4 it can be observed that in some of the middle regions of the study area soil physicochemical properties are greatly impacted by heavy metals that mostly originated from anthropogenic activities. These findings are supported by the fact that these parts are close to the main road passing through the area. Most probably, these parts are highly affected by most probably by atmospheric deposition of heavy metals from vehicle exhausts, and excessive fertilizers and pesticides applications as well, these findings agree with results reported by (Sürücü, Mohammad, Günal, & Budak, 2018).

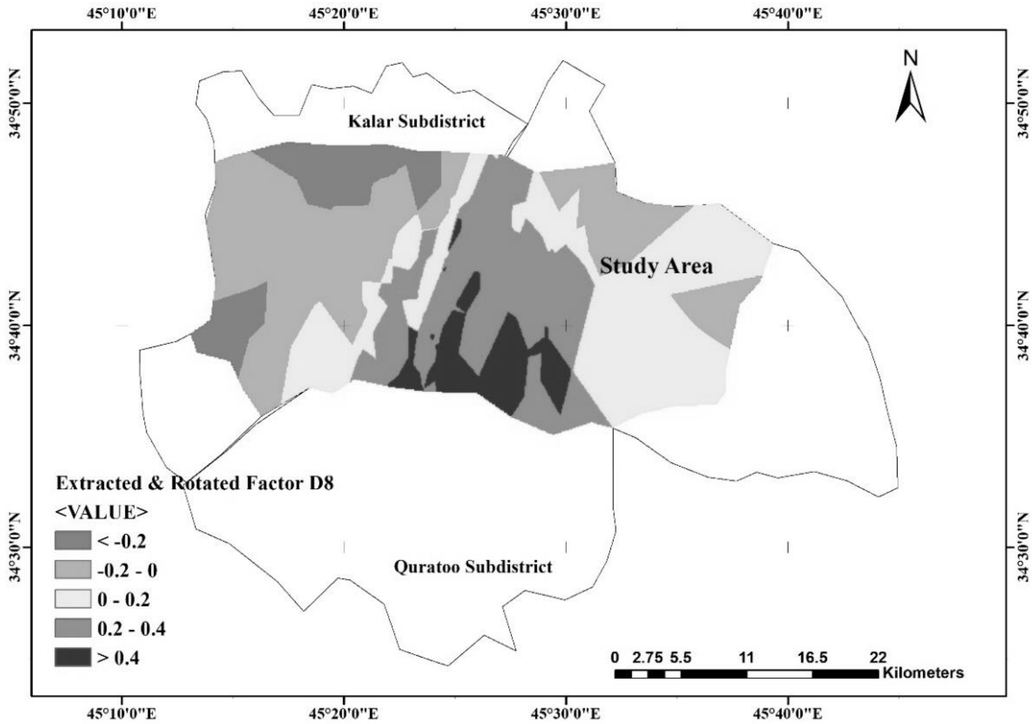

Figure 4: Graph for scores of the rotated factor D8 calculated by FA for soil samples of the study area, obtained by Kriging interpolation, in ArcGIS software.

4. Conclusions

In the present work, multivariate and geospatial statistics were performed on the obtained dataset of soil samples collected from the study area to realize and to establish a reliable prediction for relationships between soil physicochemical properties and heavy metals. In the study area, inter-relationships between soil physicochemical properties with important heavy metals have been discovered using multivariate statistical methods such as CM (Pearson), MCA, AHC with Ward's, and Euclidean methods, FA with Varimax rotation and Kaiser Normalization. Investigated soil samples showed varying correlations with heavy metals. AHC was able to reorder these correlations into three distinctive types in terms of heavy metals sources. However, MCA showed strong relationships were occurring between T.N. and Cu, Ni, and Hg. Also, pH was highly correlated with Zn. Ca was highly correlated with Al. In agreement with AHC results, the extracted factor after rotation D8 was representing heavy metals that originated from anthropogenic sources, the factor is mainly predominated by Hg. Kriging interpolation was performed to display the spatial distribution of soil properties relationships with heavy metals. The spatial distribution map showed that soil properties in the middle parts of the study area are more impacted by the heavy metals generated from anthropogenic activities, most probably from vehicle exhausts. This work assists to evaluate the types of relationships between heavy metals and some physicochemical soil properties in the study area, by which more improvements of environmental programs of land sustainability can be achieved.

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