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Heavy Metals and Physico-Chemical Properties Inter-Relations in Agricultural Soils, Tanjaro Sub-District, Iraq

Hayder Mohammed Issa[1]* and Azad H. Alshatteri[2]
[1]*Department of Chemistry, College of Science, University of Garmian, Sulaimaniyah Province 46021, Kurdistan Region, Iraq*
[2]*Chemistry Department, College of Education, University of Garmian, Sulaimaniyah Province 46021, Kurdistan Region, Iraq*
Corresponding Author: Hayder Mohammed Issa, E-mail: hayder.mohammed@garmian.edu.krd

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ABSTRACT

In the current study, agricultural soil samples were collected from 30 different locations in Tanjaro sub-district, north of Iraq. Soil samples were analyzed for identifying the concentration of 16 heavy metals and 9 soil property parameters using inductively coupled plasma optical emission spectroscopy (ICP-OES) and other analyzing tools. Multivariate and geospatial statistics have been applied to investigate links between heavy metals and soil properties. Descriptive statistics showed considerable variation exists in concentrations of the investigated parameters among sampling locations. Multiple correspondence analysis (MCA) revealed that the highest relationships were for soil organic matter (SOM), particularly with Cd, Co, and Hg. Agglomerative hierarchical clustering (AHC) and factorial analysis (FA) classified soil property relationships with heavy metals into three distinctive categories of heavy metals: naturally existed; originated from anthropogenic sources; and with no significant relationships. Plotting spatial variation of investigated soil parameters using Kriging interpolation for extracted factor from FA showed that soil properties in northern parts of the study area are more impacted by heavy metals came from anthropogenic activities. This study gives further insight into relationship patterns of soil properties with heavy metals, leading to improve the sustainability of agricultural land.

1. Introduction

Investigations on spatial distribution or variability of soil properties are widely used in land use planning (Castrignanò et al., 2000). The obtained information on physical-chemical properties assists to establish reliable programs regarding ecological, environmental, agricultural, and natural sources management planning for any land (Budak, 2018). The significance and implication of such programs are shown in practicing land-use sustainability (Galford et al., 2013). However, traditional soil surveys are not able to provide the needed information on soil properties for specific purposes, as there is a wide variation across regions and areas in the same country (Lagacherie & McBratney, 2006). Obtaining detailed and precise data on agricultural soil properties is an important component in spatial distribution studies, and performs a key role in sustainable agricultural field management (Usowicz & Lipiec, 2017).

Heavy metals are one of the most widely existed groups of chemical properties of agricultural soils due to the excessive implementation of fertilizers and pesticides (Khalifa & Gad, 2018). The presence of heavy metals in agricultural soil poses a serious health risk issue, specifically when concentrations of such metals reach high levels. It is likely crops will uptake these heavy metals, moreover using such crops could pose a deleterious consequence of the health and life of consumers (Davies, 1992). In agricultural soils, heavy metals tend to establish significant relationships with soil physicochemical, and biological properties (KavitaVerma & Pandey, 2019).

This study aimed to evaluate and validate the spatial variation of the interrelationships between some significant physicochemical properties with heavy metals in agricultural soils of Tanjaro sub-district using geostatistical and multivariate analysis. This study will thus help to establish a sustainable development program for crop production in the study area and also in other parts of Iraq.

2. Literature Review

Recently, many studies were conducted various statistical analysis methods to explain the spatial variation of inter-relationships between physicochemical properties and heavy metals for agricultural soils (Uchimiya et al., 2011). However, geostatistics and multivariate statistics seem to be the most useful techniques in interpreting the spatial relationships in soil among physicochemical properties and exhibiting their inter-relationships with heavy metals as well. The geostatistical Kriging and Inverse distance weighted IDW interpolations have been commonly used to detect the spatial behavior of soil properties (Bhunia et al., 2018; Shit et al., 2016). Whilst, the multivariate statistics of agglomerative hierarchical clustering (AHC), canonical correlation analysis (CCorA), and correlation matrix (CM) are considerably applied to show spatial correlations of agricultural soil attributes (Sungur et al., 2014).

Despite that agricultural lands in Iraq are mostly located in Kurdistan region, north northeast of Iraq, including study area of Tanjaro sub-district in Sulaimaniyah province, studies on the spatial distribution of relationship of physicochemical properties with heavy metals in this part of Iraqi agricultural soils are almost not existing from a long time ago. This is partly caused by reasons of conflicts and unusual ongoing political situations in Iraq that lead to a lack of needed information in previous decades. Similar studies have been published for other parts of Iraq. The area of Tanjaro sub-district is mainly composed of intensively cultivated agricultural lands, in which many important crops are planted.

3. Methodology

3.1 Description of the study area

The study area of Tanjaro sub-district (35° 15′ N, 45° 0′ E, 35° 35′ N, 45° 50′ E) is located in Sharazoor plain in northern Iraq, has a higher altitude of 1000 m a.s.l., and covers an area about 600 km2 of mostly arable lands. The average annual rainfall in the sub-district is ranging from 500 to 700 mm with slight precipitation in the summer season. The mean annual temperature is 20.7 °C. Winds in the area are mostly northwesterly and in summer season southeasterly winds considerably occur (Iraqi Meteorological Organization and Seismology, 2010). The physical feature of the study area is comprising of plain and hilly areas, surrounded by mountainous areas. The area is dominantly covered by soils belong to Quaternary alluvial deposits. Soils of Tanjaro sub-district are physically categorized into four main classes: shallow soil; stony soil; chestnut soil, and rough cracked soil (Buringh, 1960).

3.2 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) within agricultural areas in the Tanjaro sub-district in June and July 2019. The basis of choosing the sampling locations is to cover most of the agricultural areas in the Tanjaro sub-district (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 0C 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.

3.3 Laboratory analysis for soil samples

Analysis has been performed to quantify the content in each soil sample 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. Measurements were applied using inductively coupled plasma optical emission spectroscopy ICP-OES (Spectro across Germany). A procedure of wet digestion was followed for soil samples analysis. For heavy metals, soil samples were dried at 100 °C for 2 hours and then samples have been 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 extracted with

1 N ammonium acetate solution, neutral pH 7, and then measured by ICP-OES. In the analysis, always distilled deionized water and glassware washing were used for the dilutions.

Soil pH and soil electrical conductivity EC were measured using conductivity meter and pH meter in a soil-water suspension of 1:2 (w/v), after waiting for a half-hour for equilibrium (Behera & Shukla, 2015). Soil organic matter (SOM) content has been identified using the dry ashing method of the Walkley-Black method (Storer, 1984), while, total nitrogen was determined by the Kjeldahl method (Bremner & Mulvaney, 1983). Three replications were conducted for each sample.

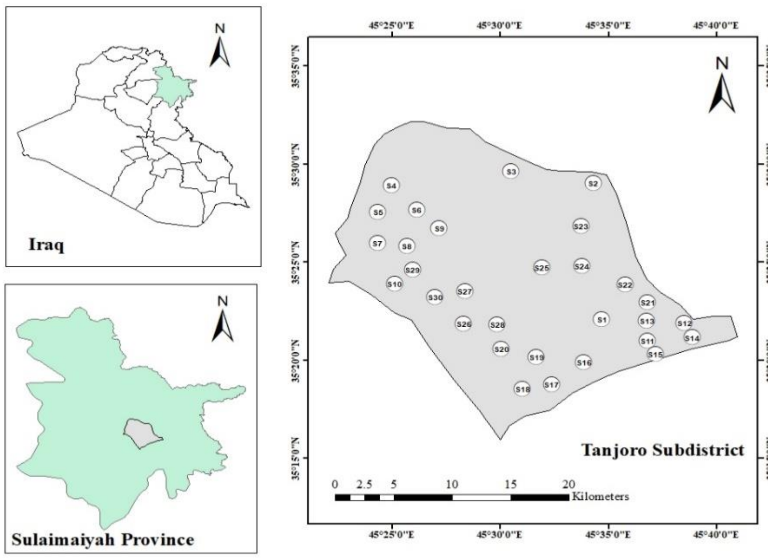

Figure 1. The study area with indicating sampling sites.

3.4 Statistical analysis and spatial distribution

In this work, different descriptive and inferential statistics were implemented for the collected soil samples such as ANOVA, correlation matrix CM, Agglomerative hierarchical clustering AHC, multiple correspondence analysis MCA, factorial analysis FA. Multivariate methods are widely used in environmental and health risk assessments. Correlation matrix CM is used to identify relationships among tested parameters. While, AHC, MCA, and FA are applied to reorder and categorize dataset. Categorizing investigated dataset into main categories helps to recognize individual and distinguishing impacts on the observations, by redistribution the dataset into several independent factors. FA method shows loading weights of factors on the dataset, and the loading weights of variables on each factor. The multivariate statistics were implemented in this study using the XLSTAT software, version 2017 for Excel 2013.

A geostatistical analysis tool of ArcGIS software (version 10.6.1) has been used to determine the sources and pollution intensities of the heavy metals. ArcGIS 10.6 (Kriging interpolation) was performed to determine the spatial distribution of soil properties in the study area.

4. Results and Discussion

4.1 Descriptive statistics of physicochemical soil properties and heavy metals

The descriptive statistics of the physicochemical parameters and heavy metal concentrations in soil samples from thirty locations in the study area is illustrated in Table 1. 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, SOM and EC in each soil samples.

The percentage of the coefficient of variation CV%, which was used to describe data variability, shows a moderate variation. On a CV% scale ranging between 10 and 100, the CV% obtained results for the heavy metals varied from 4.89 to 24.62% of Ni and Hg respectively. The CV% obtained results for the physicochemical parameters varied from 0.979 to 11.72 % of pH and Ca, respectively. Very low CV values for pH represents hydrogen concentration in soil, have also repeatedly reported in studies on agricultural soils (Hausherr Lüder et al., 2018; López-Granados et al., 2002). For the physicochemical parameters, Na, P, and total N showed moderately variable as well. K, Mg, and SOM were the least variable parameters. For heavy metals, medium CV% values, higher than 10%, were presented in Table 2 for As, Ba, Cd, Hg, and Sr, referring to a significant variability is existed for these tested parameters in the study area.

Skewness (Skew.) values display a nearly symmetrically distribution of soil parameters with minor positively or negatively skewed values. For soil physicochemical parameters, the highest positively skewed value was 0.707 for SOM, while the highest negatively skewed value was -1.679 for K. The highest positively skewed value was 1.2 for As, while highest negatively skewed value was -0.62 for Cu. The kurtosis (Kurt.) values in table 1 indicate a relatively normal distribution of the investigated parameters in soils of the study area, with a majority of soil sample values, which are closer to the mean.

Soils of the study area are rich in available P, it ranged from 152.8 to 191.5 mg/kg which is higher than the critical P concentration of 8.0 mg/kg in agricultural soils (Sillanpaa, 1990). The mean EC value of soils samples 0.565 mS/m, indicating that the nature of the soil is non-saline as it doesn't exceed the soil salinity threshold of 4 dS/m (Shrivastava & Kumar, 2015). The concentration of the exchangeable cation K in soils ranges from 3032 to 3443 mg/kg, showing that soils are enriched as that are higher than 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)	7923.25	12273.00	9841.70	9872.50	1153.68	0.468	0.031	11.72
K (mg/kg)	3032.00	3443.00	3325.86	3323.48	80.75	-1.679	4.971	2.43
Na (mg/kg)	154.30	198.75	181.23	180.67	9.16	-0.422	1.388	5.05
P (mg/kg)	152.80	191.50	175.19	175.30	9.75	-0.590	-0.002	5.56
Mg (mg/kg)	3164.00	3672.50	3406.08	3414.24	132.99	0.044	-0.932	3.90
N Total (%)	0.420	0.550	0.484	0.485	0.029	-0.068	0.095	5.94
pH (pH degree)	6.920	7.200	7.051	7.040	0.069	0.361	-0.152	0.979
SOM (%)	12.190	13.940	12.920	12.895	0.417	0.707	1.246	3.231
EC (mS/m)	0.479	0.678	0.565	0.561	0.050	0.407	-0.229	8.870
Heavy Metals								
Al (mg/kg)	6754.80	9875.00	8423.71	8382.50	826.34	-0.14	-0.72	9.81
As (mg/kg)	1.85	2.82	2.15	2.12	0.25	1.20	1.64	11.41
Ba (mg/kg)	104.85	182.00	139.13	140.05	20.61	0.43	-0.37	14.81
Cd (mg/kg)	0.80	1.15	0.95	0.94	0.09	0.62	0.00	9.67
Co (mg/kg)	3.70	4.80	4.25	4.27	0.31	0.08	-0.96	7.40
Cr (mg/kg)	16.20	21.30	18.95	18.85	1.28	-0.16	-0.77	6.77
Cu (mg/kg)	5.05	6.55	6.03	6.11	0.37	-0.62	0.07	6.14
Fe (mg/kg)	5764.35	6955.05	6335.69	6230.50	371.92	0.37	-1.06	5.87
Hg (mg/kg)	0.45	1.10	0.75	0.73	0.19	0.18	-0.94	24.62
Li (mg/kg)	40.89	51.80	46.15	46.18	2.94	0.11	-0.56	6.37
Mn (mg/kg)	139.10	183.60	160.95	159.81	13.18	0.30	-0.93	8.19
Ni (mg/kg)	29.40	36.80	33.88	33.84	1.66	-0.53	0.74	4.89
Pb (mg/kg)	11.32	13.75	12.49	12.51	0.70	0.07	-0.99	5.64
Sr (mg/kg)	74.30	130.40	102.66	102.90	17.83	-0.18	-1.34	17.37
V (mg/kg)	12.20	15.55	13.87	13.89	0.99	-0.12	-0.98	7.11
Zn (mg/kg)	32.20	40.45	36.33	36.36	2.58	-0.02	-1.22	7.11

4.2 Inter-relations among soil properties and with heavy metals

Analysis of variance (ANOVA), a one-way method as a function in Microsoft Excel 2013 software was implemented to validate the significant variance among sampling sites at 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 2713.05, and F critical value Fcrit was 1.532, which means a great variance does exist between tested groups. One-way ANOVA was employed for testing the spatial differences of soil sampling sites without replications.

Results of Pearson CM analysis as presented in Table 2 show several significant relationships among soil parameters and heavy metals. Constantly, in such statistical analysis, a correlation coefficient closer to 1.0 indicates a strong relationship between the tested metals. As seen, at p-value less than 0.05, significant relationship coefficients > 0.2 are existing.

Among the soil properties, significant positive correlations can be observed in Table 2: Ca has a significant correlation with soil EC, Mg, total N (N.T.), and available P. On the other hand, Ca has a significant negative correlation with soil pH and OM. These negative correlations indicate that with the increase in pH the Ca concentration in soil decreased. K has only one positive significant correlation that is with Na. While, Na, Mg, and N.T. have also shown a positive significant correlation with P. A moderate negative pH correlation with EC were observed, it also reported by (Chamannejadian et al., 2011).

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

	Ca	K	Na	P	Mg	N.T.	pH	SOM	EC
Ca	1.00								
K	0.17	1.00							
Na	0.09	**0.29**	1.00						
P	**0.35**	0.16	**0.39**	1.00					
Mg	**0.28**	0.14	0.09	**0.22**	1.00				
N.T.	**0.27**	-0.07	-0.19	**0.25**	-0.13	1.00			
pH	**-0.22**	0.13	-0.08	0.09	-0.16	-0.15	1.00		
SOM	**-0.35**	-0.07	0.18	-0.06	0.04	-0.19	0.10	1.00	
EC	-0.17	0.05	0.11	0.04	0.05	-0.15	-0.13	0.05	1.00
Al	-0.01	**0.21**	-0.10	**0.20**	**-0.43**	0.16	0.07	-0.07	**0.33**
As	0.07	0.02	-0.09	-0.12	0.00	-0.02	-0.01	-0.18	0.02
Ba	-0.15	**0.26**	0.17	-0.08	0.06	-0.04	0.18	-0.01	-0.11
Cd	0.01	-0.10	**0.33**	0.07	0.02	0.12	-0.04	0.28	**0.27**
Co	0.19	**0.36**	**0.23**	-0.06	-0.08	0.15	-0.12	0.03	0.09
Cr	**0.36**	**0.35**	-0.07	0.06	-0.02	**0.45**	0.09	-0.03	-0.07
Cu	**-0.31**	**-0.33**	-0.12	0.03	0.07	0.11	0.17	0.10	**-0.26**
Fe	**0.40**	**0.22**	0.04	-0.03	**0.39**	-0.01	0.07	-0.03	**-0.22**
Hg	0.10	-0.11	**0.25**	-0.10	0.04	-0.12	-0.02	**-0.21**	-0.09
Li	**0.34**	0.17	0.14	0.15	0.17	-0.01	**-0.29**	-0.12	-0.02
Mn	-0.18	-0.09	-0.13	-0.09	0.06	0.04	0.18	0.03	0.07
Ni	-0.09	**-0.30**	**-0.36**	-0.09	**0.36**	-0.14	0.05	**-0.22**	-0.14
Pb	-0.12	-0.01	**0.40**	0.04	**-0.20**	0.15	0.13	**-0.24**	-0.01
Sr	0.10	-0.09	**0.29**	-0.06	0.02	0.09	-0.12	**0.30**	-0.10
V	**0.25**	0.18	-0.14	**0.25**	0.21	0.05	0.01	0.05	0.02
Zn	0.03	**-0.20**	-0.03	0.08	0.04	0.03	-0.11	-0.09	**-0.41**

* with a significance level alpha=0.05

CM of Interrelationships between soil property parameters with heavy metals, which illustrated in Table 2, reveals many significant correlations. SOM has a significant correlation with Sr, and significant negative correlations with Hg, Ni, and Pb. EC also showed some significant positive correlations with heavy metals of Al and Cd, and negative correlations with Cu, Fe, and Zn. Total N has a high positive correlation with Cr. Whilst, high positive correlations between Mg and Fe with Ni were observed. K showed positive significant correlations with heavy metals such as Ba, Co, Cr, and Fe. While K has negative significant correlations with Cu, Ni, and Zn. Na has a high positive correlation with Pb, while Ca high correlations were with Cr and Fe. P

only showed a significant positive correlation with Al and V. Significant negative correlations between Pb and SOM were also reported by (Nan et al., 2002; Vega et al., 2004), and by (KavitaVerma & Pandey, 2019) for correlations between SOM and Ni with Pb, they investigated a part of SOM as microbial biomass. These findings indicate that the presence of Pb and Ni is deteriorating OM of soils. CM interrelationships with heavy metals reveal that soil properties are susceptible to be altered in the existence of various heavy metals (Adriano, 2001). CM results also suggest that the origin of heavy metals is most probably is the geological structure of soil and rocks of the area (Mileusnić et al., 2014), as there are significant correlations were observed for the chemical properties of the soil without ignoring the impact of anthropogenic activities in the area would contribute to their occurrence. Although many studies in the literature pointed out a significant correlation between pH and heavy metals in soils, this study suggests that no evidence could be observed in the obtained CM agrees with those studies.
The inter-relations between soil properties and heavy metals have also been investigated using AHC. The AHC was conducted in this work based on Ward's method as an agglomeration method with Euclidean distance for measuring the dissimilarity. AHC was used to relate soil properties with heavy metals as several main groups. The internal cluster homogeneity is determined according to the similarity among property parameters and heavy metals in soil samples.

Three clusters were established as presented in the dendrogram presented in Figure 2. The dendrogram of AHC results shows that several significant correlations of soil properties with heavy metals exist in cluster 1: including Mg and Ca with Fe and V. While the cluster 2 relates only heavy metals for As, Cd, and Zn. Finally, the cluster 3 exhibits a significant relationship between soil properties of total N, EC, K, Na, pH, and OM with heavy metals of Co, Al, Cd, Sr, Cr, Ba, and Pb.

AHC analysis reveals that heavy metals in the study area are divided into three categories. The first cluster suggests some of the heavy metals involving Mn, Hg, Ni, Cu, Fe, and V have significant relationships with Ca and Mg. the second cluster represents a group of heavy metals of As, Zn, and Li that no relationships with soil properties. While, the third cluster involves heavy metals of Al, Cr, Co, Ba, Pb, Sr, and Cd that have relationships with more soil properties such as SOM, EC, pH, K, Na, total N, and P. Therefore, cluster 1 suggest that the interrelationship between Ca and Mg with certain heavy metals is arising from the natural composition of soils in the study area. Fe is free from anthropogenic impact and naturally appears at abundant levels of the crust (Liu et al., 2015). Furthermore, soils in the region of low rainfall are containing more Ca and Mg carbonates in their profile (Azeez & Rahimi, 2017). Cluster 2 suggests that Li, Zn, and as have not affected soil properties in the study area as no significant correlation of them was noticed with soil physicochemical properties in the study area. For cluster 3, this may indicate the significant heavy metals, Cd, Sr, Pb, Ba, Co, Cr, and Al, those have significantly impacted soil properties of SOM, EC, pH, K, Na, total N, and P suggesting that these heavy metals are predominantly originated from the application of organic fertilizers (manures), pesticides and inorganic fertilizers in Iraqi agricultural areas (Al-Tamimi & Ali, 2018).

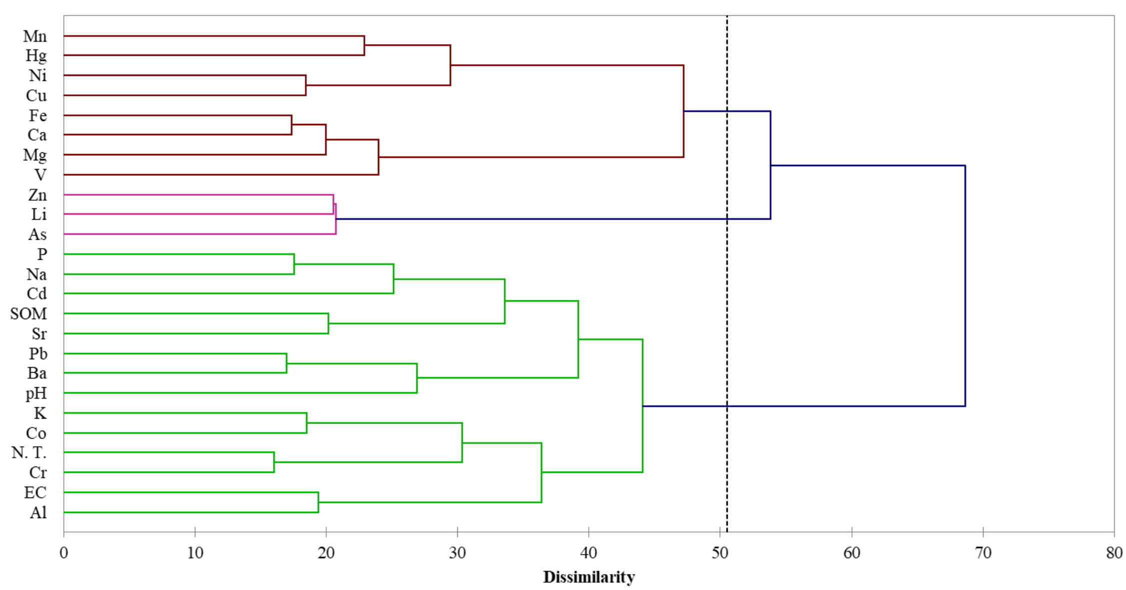

Figure 2. Dendrogram for inter-relations between soil physicochemical properties with heavy metals in the study area

The inter-relations between soil property parameters and heavy metals are further investigated using MCA, depending on the correlation between these two groups and after normalizing their values. MCA helps to distinguish correlations among soil property parameters in the same group and with each heavy metal as well. Based on MCA analysis, 81.19 % of the total variance of the relationship between the two groups dataset in soil samples are represented by four factors: factors F1, F2, F3, and F4 are accounting for 28.89 %, 22.67%, 16.65%, and 13.65 % of the total variance in links between soil properties and heavy metals, respectively. In soil samples, results of MCA analysis are shown in Figure 3, where 81.86 % of total variance of the inter-relationships between the physicochemical soil properties and heavy metals are presented in symmetric plots.

From Figure 3, for 81.19% of total variance, it can be seen that NT is strongly correlated with Cr, and Zn has a lesser impact on soil properties in soils of the study area. Similarly, it observed that Na is highly correlated with Hg and Pb. Zn is mostly negatively correlated with pH, similar findings were reported by (Zeng et al., 2011). Figure 3 (a), in which 51.56 % of the total relationships were displayed, reveals that SOM is highly impacted by certain Hg, Pb, As, Cd, Sr, while Ca, K, and pH were strongly correlated with Ba, Mn, Co, Li, and Cu. On the other hand, Mg, P, and EC have lesser correlations to heavy metals. Furthermore, Zn is negatively correlated with SOM, also Cu is negatively correlated to pH, suggesting that the existence of Zn or Cu is significantly causing a decrease in SOM or pH respectively, a similar observation was reported by (Sürücü et al., 2019).

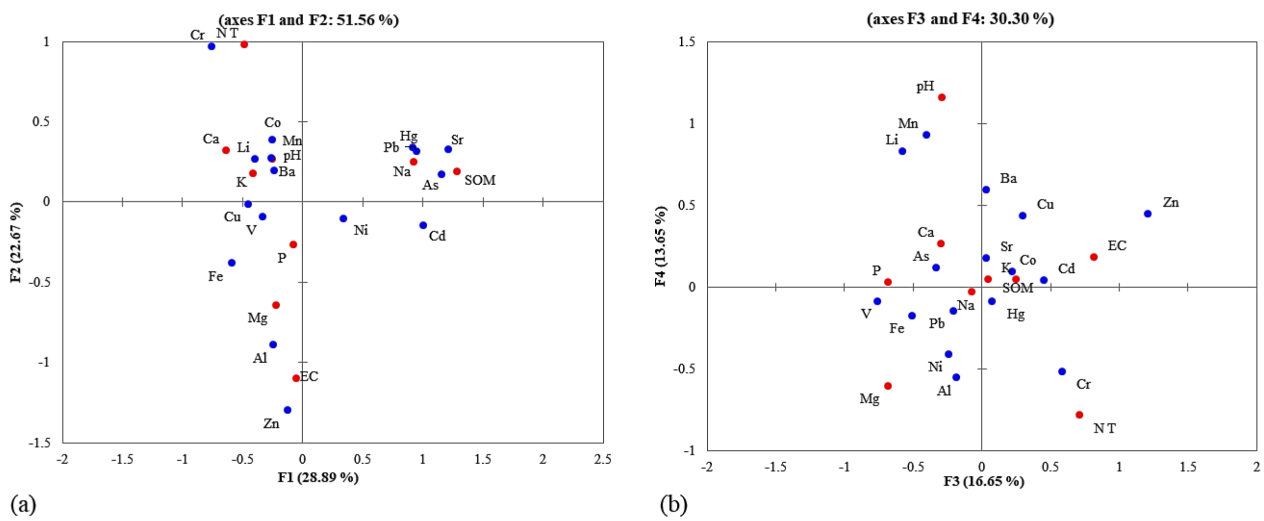

Figure 3. Symmetric plots based on MCA, (a) for factors F1 and F2 and represents 51.56% of total variance between soil properties and heavy metals, (b) for factors F3 and F4 and represents 30.30% of total variance between soil properties and heavy metals.

In Figure 3 (b), which represents 30.30% of total relationships, SOM is highly related to Cd, Co, and Hg. In the same figure, it can be seen that pH, Mg, and NT were less impacted by heavy metals than the remaining soil properties. These results indicate, as expected, that many heavy metals in soils are connected with organic matter (Jones & Jacobsen, 2009). It is worthy to mention that there is no contradiction between results of AHC and MCA, as the MCA associated each soil property to heavy metals regardless of the origin of those heavy metals, whereas AHC has classified relationships between soil physicochemical properties concerning sources of studied heavy metals.

In this work, FA has been applied to categorize relationships of physicochemical properties in soils of study region according to heavy metals. AHC established three different types of such relationships: soil property parameters linked strongly to heavy metals originated from natural weathering of parent materials; heavy metals have limited relationships with soil properties; lastly, soil property parameters are highly related to heavy metals came from anthropogenic activities.

Mostly, the first group is dominated by Fe and Ca or Mg, representing the natural composition of crust in the study area. FA was performed using Varimax rotation with Kaiser Normalization, as a considerable improvement in factors loading percentage and eigenvalue were accomplished after the rotation. After rotation, factors of higher eigenvalues are considered the most significant factors, ten factors were extracted, representing 68.11% of the total variance of the dataset as shown in Table 3.

Table 3. Correlations between variables and factors after Varimax rotation, made by FA*.

	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10
Ca	0.06	0.27	-0.18	**0.45**	0.21	0.26	**0.57**	-0.09	0.10	-0.22
K	0.05	0.41	0.21	0.16	0.31	-0.07	-0.12	-0.22	0.40	-0.01
Mg	-0.13	0.02	-0.11	**0.87**	0.16	-0.07	-0.10	0.15	-0.04	0.04
Na	**0.43**	0.08	0.37	0.12	**0.54**	0.32	-0.27	0.32	0.00	-0.16
P	-0.03	0.01	-0.08	0.06	**0.92**	-0.05	0.23	0.08	-0.02	-0.01
pH	-0.10	-0.08	0.20	-0.13	0.16	-0.15	-0.24	-0.35	0.10	0.31
SOM	0.40	-0.08	-0.11	0.01	0.02	-0.32	-0.37	0.24	-0.05	0.13
EC	-0.06	0.19	-0.08	-0.16	0.00	-0.11	-0.16	**0.51**	0.24	0.08
N.T.	0.04	-0.07	0.03	-0.11	0.12	-0.10	**0.86**	0.02	-0.01	0.06
Al	-0.21	0.34	-0.09	**-0.58**	0.18	-0.07	0.16	0.12	0.43	0.10
As	-0.27	0.21	0.06	0.07	-0.14	-0.20	-0.01	-0.08	-0.12	**-0.55**
Ba	0.02	0.03	**0.77**	0.08	-0.01	-0.12	-0.08	-0.05	0.11	-0.03
Cd	0.06	-0.07	0.14	-0.03	0.12	0.09	0.01	**0.59**	0.08	0.09
Co	0.26	0.10	**0.42**	0.09	-0.08	0.02	0.22	0.17	**0.54**	-0.10
Cr	0.36	**0.42**	0.12	0.08	0.00	-0.27	**0.55**	-0.28	0.11	0.36
Cu	-0.04	**-0.84**	-0.07	0.08	0.09	0.04	-0.01	-0.08	0.01	0.31
Fe	0.09	0.04	0.05	**0.61**	-0.02	0.13	0.09	-0.26	0.13	0.08
Hg	-0.05	-0.02	0.07	0.06	-0.04	**0.92**	-0.08	0.05	-0.03	0.20
Li	-0.22	**0.42**	-0.14	0.15	0.14	0.33	0.06	0.13	-0.16	-0.27
Mn	-0.10	-0.10	0.09	0.12	-0.13	0.09	0.04	0.09	0.05	**0.85**
Ni	**-0.74**	-0.31	-0.04	0.36	-0.17	-0.08	-0.08	-0.02	-0.13	-0.07
Pb	0.12	-0.06	**0.71**	-0.12	0.10	0.32	0.13	0.03	-0.08	0.17
Sr	**0.77**	-0.19	0.13	0.24	-0.13	-0.11	0.14	-0.02	0.16	-0.06
V	0.07	-0.12	**-0.72**	0.21	0.26	-0.03	0.02	-0.19	**0.54**	-0.08
Zn	-0.15	0.07	0.13	0.06	0.08	0.03	0.05	-0.25	**-0.86**	-0.29

*correlations $\geq$ 0.4 were considered significant and presented in bold.

FA results agree with AHC, suggesting that there is soil properties are linked to heavy metals of natural origins, while other soil properties are highly correlated to heavy metals arises from anthropogenic activities. Based on FA results, the strong correlations with rotated factor D4 for Fe, Ca, and Mg confirms adequately this factor represents relationships between physicochemical parameters in soils and heavy metals that originated naturally in soils of the study area. As the rotated factor D4 mainly explains the variation of Fe, Mg, and Ca in soil samples, therefore D4 is also representing the highest values of these parameters. The remaining rotated factor are representing the relationships between soil properties with well-known heavy metals generated from anthropogenic sources: factor D3 for Pb; factor D8 for Cd; and D6 for Hg.

To display the spatial distribution for inter-relationships patterns between physicochemical properties and heavy metals in the study area the rotated factor D4 was plotted using Kriging interpolation, ArcGIS 10.6 software, as seen in Figure 4. It was confirmed in FA results that D4 represents the relationship with natural heavy metals, therefore higher values of interpolated data for D4 display the spatial correlation of soil properties with abundant heavy metals of earth's crust composition, and subsequently, soils with lower values of D4 interpolated data are pointing to soil properties of high correlations with heavy metals from anthropogenic sources. Figure 4 shows that soil physicochemical properties in northern parts of the study area are highly impacted by heavy metals that mostly originated from anthropogenic activities. These findings are supported by the fact that northern parts are adjacent to Sulaimaniyah city, the capital of the province, and the fourth city in Iraq regarding population and industrial activities. These parts are highly affected by wastewater discharge, traffic, and solid waste disposal generated from the city, this agrees with results reported by (Khorshid & Thiele-Bruhn, 2016).

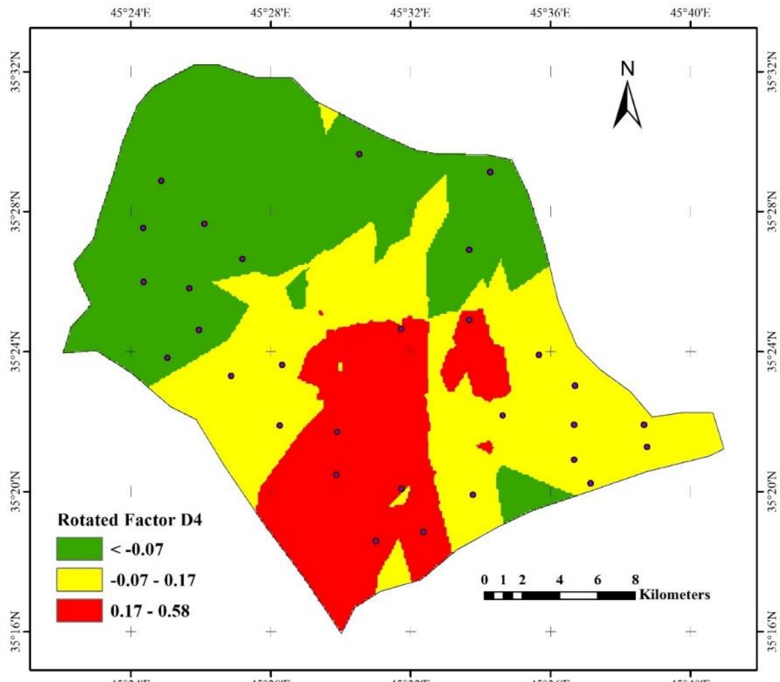

Figure 4. Graph for scores of the rotated factor D4 calculated by FA for soil samples of the study area, obtained by Kriging interpolation, in ArcGIS software.

5. Conclusion

In the present study, the applied multivariate and spatial geostatistics assist to reach a reasonable prediction for the relationships between soil physicochemical properties and heavy metals in the study area of Tanjaro sub-district, Iraq. Correlations and relationships between soil physicochemical properties with a group of significant heavy metals in the study area have been investigated using different multivariate statistics of CM (Pearson), MCA, AHC (Ward's with Euclidean methods), FA (Varimax rotation with Kaiser Normalization). Soil properties showed different correlations with each other and with heavy metals. AHC classified relationships between soil properties and heavy metals into three distinctive types in terms of heavy metals sources. While, MCA showed strong relationships between SOM and Cd, Co, and Hg. pH, Mg, and NT were less related to heavy metals in soil samples. In agreement with AHC results, the extracted factor after rotation D4 was representing heavy metals that originated from natural sources, the factor is highly predominated by Mg and Fe. Kriging interpolation was conducted to show the spatial variation of soil properties with heavy metals. The spatial distribution map exhibits that soil properties in northern parts of the study area are more impacted by the heavy metals generated from anthropogenic activities. Thus, this work will aid a better evaluation of relationships between heavy metals and soil properties and therefore it allows more enhancements of the existing tools of land sustainable development.

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