Heavy Metals Concentrations in Surface Soils of the Haweja Area South Western of Kirkuk, IRAQ

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Abstract

Twenty one samples of surface soils were collected in Haweja area of Kirkuk, Iraq. From the samples analysis the following heavy metal concentration (range) were obtained (in ppm): Mn(401-722), Cu(23-42), Zn(32-62), Co(30-43), V(28-60), Ni(110-189), Cr(270-360), Zr(110-212) and Fe (in wt %)(0.85-2.27).

The results indicate that, in comparison with Kirkuk soils, surface soils in Haweja area have elevated metal concentration as a whole, except those of Cobalt and Vanadium. R-mode factor analysis reveals three elements associations and two singular elements (Co, Zr), accounting for 86.92% of the total data variance. The three associations are: Zn-Cu; Mn-Fe and V-Cr. The geoaccumulation indices show that surface soils in Haweja area are unpolluted to slightly polluted.

Introduction

Soil, which comprised of detritus, in organic or organic particles, is relatively heterogeneous in terms of its physical ,chemical and biological characteristics (kotoky et al., 2003).Heavy metals are associated with various soil components in different ways, and these associations determine their mobility and availability (Ahumuda et al.,1999).

The role of trace elements in soil is increasingly becoming an issue of global concern at private and governmental levels, especially as soil constitute a crucial component of rural urban environment (USDA,2001),and can be considered as a very important ecological crossroad in the land escape (Thuy et al.,2000). All trace elements are toxic to living organisms at excessive concentration, but some are essential for normal healthy growth and reproduction by plants and animals at low, but critical concentration. Deficiencies in these essential elements or micronutrients can lead to disease and even death of the plant or animal.

The soil pollution of heavy metals has become a question of considerable public and scientific concern in the light of evidence of their extreme toxicity to human health and to biological systems (Anazawa et al., 2004) .The distribution and concentration of most elements in soil shows a pattern related to geology,human influences and agricultural activity

(Salmineh & demetriades,2006).The essential trace elements include Co, Cr, Cu, Mn, Ni, Zn, and Se while Ag, As, Cd, Hg, Pb and Sb have no known essential function but causes toxicity above certain tolerance level (Alloway,1995). The most important heavy metals with regards to potential hazards and the occurrence in contaminated soils are As, Cd, Cr, Hg, Pb and Zn (Alloway,1995). The concentration of these toxic elements in soils may be derived from various sources, including anthropogenic pollution, weathering of natural high background rocks, metal deposits(Asaah et al., 2006), and may be waste dumping ground containing elevated concentration of heavy metals can be a continuous source of metal spreading to the surrounding (Dudka&Adriano,1997),then it is accumulate in the food chain and may be become toxic to humans (Oqunyemis et al.,2003). The present study, therefore, examines the concentrations of heavy metals (Fe,Mn,Cu,Zn,Co,V,Ni,Cr and Zr) in the surface soils of the Haweja area and to identify their natural or anthropogenic sources by using principal component analysis and cluster analysis .

Description of study area

Haweja, located between latitude 38º 65⁻ and 39º 20⁻ N longitude 37º10⁻ and 41º 7⁻E , and it is located south western of Kirkuk (65 Km) far from Kirkuk (a city with appr. 200000 people) figure 1 . The study area is however, restricted to the agricultures activities that covers an area of 180 000 ha. In terms of geology, the Haweja is located within the Kirkuk block that is apart of the low folded zone of northern Iraq and it lies within the Hemrin – Makhul subzone(Jassim & Goff,2006).

Stratigraphically, there are no any formation exposed in the area, it is covered by quaternary sediment, that consists of flood plain and soil deposits. The soils of area are derived the fluvial till deposits during pluvial and interpluval phase of Pleistocene (Buringh,1960).
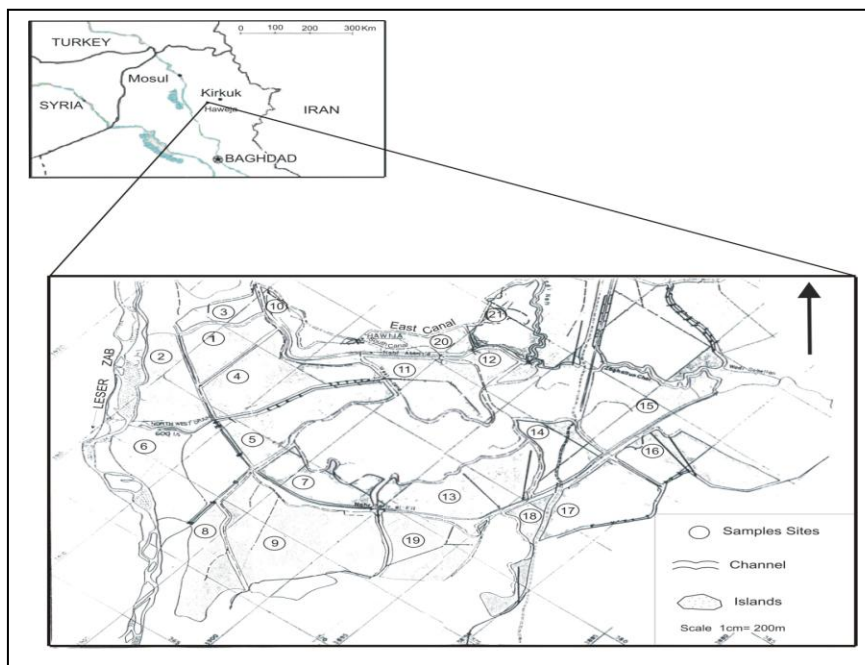
Fig.(1): Location Map of the study area (Modified: from Haweja Irrigation Office)

The course of Haweja canal passes through quaternary sediments and recent flood sediments covers the entire area (Al-Jumaily,2007). Soil of the study area is alluvial, formed by periodic depositions and erosion during various stage of river flooding, generally, it is clayey silty sandy and gravel.

Materials and Methodology

1- Sampling and analysis.

Twenty-one soil samples were collected randomly from different sites in studied area figure 1. The soil samples were obtained with a hand auger from top soil only (to maximum depth of 25 Cm),that is the A-horizon below the organic layer , also avoiding the surface contaminants. All the samples were passed through a 1 mm plastics sieve to remove large plant root and gravel sized materials, and then ground and homogenized with agate mortar and sieved through a 200 mesh sieve. Heavy metals were estimated depending the procedure of Sakata(1983) by atomic absorption spectrophotometer with a Perkin- Elmer model-2380 instrument using hallow cathode lamps light sources. Matrix matching , standard addition and background corrections were used to overcome interferences. After

every four determinations blanks and references standards (SO-1) with 95% confidence interval at ±2 standards deviation were also run to determine the precession and instrumental uncertainties. High purity certified/analar or its equivalent grade reagents were used through out the work. HNO_3 and HCl used in this study were purified through a sub-boiling distillation unit. Stock standard solutions of metal were prepared by dissolving ultra pure metal /compounds (99.99% pure).

2-Discriptive analysis and correlation coefficient.

Descriptive data analysis, including mean, standard deviation (SD), minimum and maximum concentrations, skewness, variation coefficient etc., was carried out. Together with SD ,variation coefficient (VC), which is SD/mean, was used to reflect the degree of discrete distribution of different metal element concentrations and to indicate indirectly the activeness of selected element in examined environment.Skewness was also utilized to reflect different distributions of the metals.   In addition, correlation coefficients were calculated to determine relation ship among different metals.

3- Multivariate analysis.

Principal component analysis (PCA) and cluster analysis (CA) are the most common multivariate statistical methods used in environmental studies (Miranda et al., 1996; Diaz etal., 2002) SPSS for windows, version 10.0 , was utilized for the multivariate statistical analysis, and for descriptive and correlation analysis. PCA is widely used to reduce data (Loska & wiechul, 2003) and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables. If large differences exist in the standard deviations of variables, PCA result will vary considerably depending on whether the covariance or correlation matrix is used (Farnham etal.,2003). The concentrations of the heavy metals evaluated in this study vary of magnitude. PCA was therefore applied to the correlation matrix for this study, and each variable is normalized to unit variance and therefore contributes equally. To make the results more easily interpretable, the PCA with VARIMAX normalized rotation was also applied, which maximize the variance of the factor loading across variables for each factor. Factor loading>0.71 are typically regarded as excellent to<0.32very poor (Garcia et al., 2004). In this study, all principal factors extracted from the variables were retained with eigen values >1.0, as suggested by the Kaiser criterion

(Kaiser, 1960). The PC loading were plotted and the plot was inspected for similarities observed as clusters in the PC loading plot. Cluster analysis (CA) was performed to further classify elements of different sources on the basis of the similarities of their chemical properties. Hierarchical cluster analysis, used in this study, assisted in identifying relatively homogenous group of variables, using an algorithm that starts with each variable in a separate cluster and combines clusters until only one is left. Adendrogram was constructed to assess the cohesiveness of the clusters formed, in which correlations among elements can readily be seen.The PCA is complementary to the CA.

Results and discussion

1- Heavy metal concentration.

Description statistics of heavy metal concentration of surface soils in studied area, as well as background values of Kirkuk soils. (Ismail , 2004)which are considered to be the reference values are represented in table 1. The mean concentrations of Fe,Mn,Cu,Zn,Co,V,Ni,Cr and Zr are 1.572%, 562.4,31.7,51.33,36.29,42.143,152.3,310.5 and 146.8 ppm, respectively. Each heavy metal shows wide range of values, except Co and V compared with background values of Kirkuk soil, the heavy metal mean concentration of surface soils in Haweja are much higher, except Co and V, which renders them distinct from the other elements. Mn mean concentration in this study is nearly 7 times higher than the reference value, the mean concentration of lowest elements, V, is lower than the reference value. In contrast, Fe mean concentration is approximately the same as its reference values. The suggested that Fe may has mainly a natural source, while the other elements may came mainly from human activity such as addition of fertilizers to the soil from the farmers in study area. Skewness values indicate that all elements approach a normal distribution and can also be confirmed by the fact that the median concentrations of these metals are much approximately than their concentration. It seems that, based on their variation coefficients (VCs), the examined element can be classified into one group Fe, Mn, Cu, Zn, Co, V, Ni, Cr, and Zr whose VCs are lower than 0.3. (Yongamine etal.,2006) refers that the metals hose VCs are lower than 0.4 are dominated by a natural sources, while the elements have VCs higher than 1.0 are affected by anthropogenic sources, therefore, in Haweja surface soils, would expect those all elements dominated by a natural source to have low VCs. this is especially the case for surface soils,

of they have undergone erosion and transport of quaternary sediments before deposition.

Table1. Heavy metal concentration of Haweja area (ppm,except Fe in %)

Element	Range	mean	Median	SD	-VC	Skewness	Reference*
Fe	0.85-2.27	1.572	1.55	0.346	0.220	0.088	1.23
Mn	401-722	562.4	570	69.63	0.124	0.009	75
Cu	23-42	35.7	36	5.95	0.167	0.041	_
Zn	32-62	51.33	51	8.22	0.160	0.629	_
Co	30-43	36.29	37	4.113	0.113	0.135	62
V	28-60	34.143	34	9.0570	0.265	0.467	191
Ni	110-189	152.3	148	22.54	0.148	0.080	46
Cr	270-360	310.5	315	25.59	0.098	0.080	100
Zr	110-212	146.8	138	32.56	0.222	0.991	_

‑ not limited

-VC-SD/mean

Ismail ,2004 *

2-Correlation coefficient analysis

Pearson's correlation coefficient of heavy metal elements in Haweja surface soils are summarized in table 2. In this study, the geochemical data was used in calculating the correlation coefficient using the SPSS (statistical program for the social science) computer software package (SPSS inc., version 10.). From table 2, Mn is significantly positive correlated with Fe, which may suggest a common origin. Fe is a major constituent of soil and sediments as a structural element of clay and organic matter (Miko et al., 2003), it has a strong positive correlation with many minor elements (such as Mn) in soils, in which it is considered a natural element content in soils, While Cu and Zn form another group based on their positive correlation. Cr is also positively correlated to V and Ni, indicating that from a natural source, and though both of them may originate mainly from soils. Hydrated oxides of Fe and Mn seem to play a major role in the non-specific absorption of these metals (Assah et al., 2006), therefore, in study area the hydrate oxide and clay minerals, as well as organic matter in the form of humus, give the soils sorptive properties.

Table 2.Pearson ˌs correlation matrix for the heavy metal concentrations

	Fe	Mn	Cu	Zn	Co	V	Ni	Cr	Zr
Fe	1.00								
Mn	0.52*	1.00							
Cu	- 0.25	-0.34	1.00						
Zn	-0.10	-0.05	0.46*	1.00					
Co	-0.26	0.22	-0.20	- 0.16	1.00				
V	-0.10	0.20	-0.32	0.02	0.25	1.00			
Ni	-0.31	0.19	0.43*	-0.34	0.03	0.07	1.00		
Cr	0.25	0.25	-0.10	-0.31	-0.13	0.43*	0.53	1.00	
Zr	-0.2	0.01	0.22	0.19	-0.03	0.20	0.32	-0.09	1.00

*significant at level(95 %).

3-Multivariate analysis

   The data of nine variables (metals) considered in this study were subjected to R-mode analysis using of five factor model, which accounted for 86.923% of the total data variance. The resulting varimax is summarized in table3, and 3-D plot of the PCA loading is presented in figure2. The computations were performed by means of the SPSS computer software package. Only variables with loading >0.4 were considered as significant. The factors extracted from table3 and 3-D plot of the PCA loading in figure2 are as follows:

Table3: rotated component matrix for data of Haweja surface soils.

| Elements	Factor1	Factor2	Factor3	Factor4	Factor5	communality
Fe	-0.183	0.812	-0.008	-0.390	0.114	0.843
Mn	-0.003	0.885	0.150	0.285	0.004	0.889
Cu	0.721	-0.370	0.375	-0.202	0.006	0.842
Zn	0.830	0.009	-0.105	-0.102	0.206	0.762
Co	-0.127	0.001	0.006	0.935	0.001	0.896
V	0.161	0.002	0.883	0.276	0.114	0.895
Ni	-0.688	0.246	0.188	-0.143	0.544	0.885
Cr	-0.455	0.202	0.742	-0.282	-0.001	0.879
Zr	0.139	-0.009	0.005	0.003	0.984	0.932
Eigen values	2.511	1.661	1.375	1.195	1.082	
Percentage of variance	27.899	18.453	15.276	13.278	12.017	
Cumulative percent	27.899	46.352	61.628	74.909	86.923	

Component Plot in Rotated Space
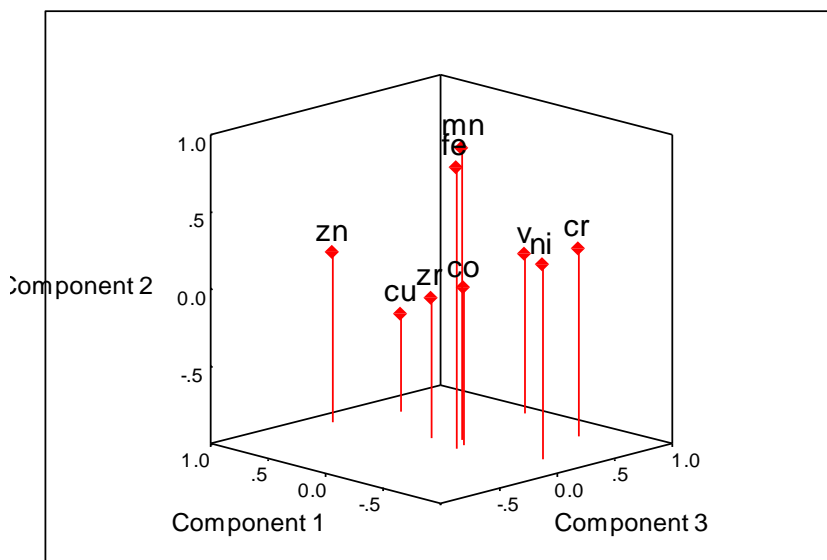
Fig.2. PCA loading 3-D plot (PC1 vs.PC2 vs.PC3) for nine heavy metals.

Factor1: Zn and Cu – this factor accounts for 27.899% of the total data variance. These metals are may be derived mainly from human activities, as the levels of fertilizer input of these metals in Haweja surface soils. The heavy metals concentration in top soil is a result of soil-forming processes, as well as agricultural and human activities (Silverira et al., 2003).

Factor2: Mn and Fe. This factor accounts for 18.453% of the total data variance (table3). These elements are derived mainly from natural sources and may be come from soil constituent. Which indicate the strong association to the geochemical matrix between the two elements in soil.(Chatterje et al.,2006) refers that Fe and Mn have close distribution pattern in sediment, and associated with different factors such as erosion, differences in hydrodynamics periodic dredging activities etc.

Factor3: V and Cr. This factor accounts for 15.276 of the total data variance (table3). These metals are derived mainly from natural sources.
Factor4: Co. this factor has only one element Co, and accounts for 13.278% of the total data variance Derived mainly from natural source.

Factor5: Zr. This single-element factor accounts for 12.017% of the total data variance, and reflects the distribution of this metal in the quaternary deposits, especially as their natural source input to environment of Haweja area from erosion & transportation of the quaternary sediments.

Cluster analysis:

A CA was applied to the standardized bulk concentration data war's method, with Euclidian distance as the criterion for forming clusters of elements. in general, this form of CA is regarded as very efficient, although it tends to create small clusters. Figure3 displays four clusters: (1) Cu-Co-V-Zn-Fe;(2)Ni-Zr;(3)Cr;(4)Mn. It is observed,

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        Linkage          Distance

    0         5        10       15       20       25
    +---------+---------+---------+---------+---------+

Cu      ┐
CO      ┤
V       ┤
Zn      ┤
Fe      ┘
Ni      ┐
Zr      ┘
Cr
Mn
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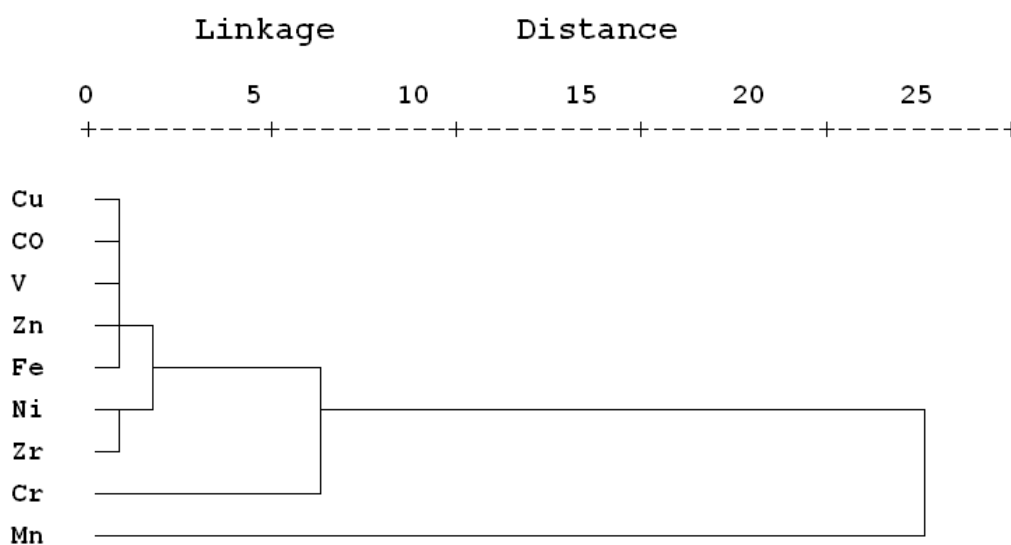
Fig.3. Hierarchical dendogram for nine elements obtained by War 's hierarchical Clustering method.

However, that cluster 1,2and 3 join together at relatively higher level implying perhaps a common source, while the long distance of the Mn in cluster 4 reveal that this cluster can be indicated perhaps a natural source and may be form the soil source.

The first group elements consist of Cu-Co-V-Zn-Fe. All these elements show low mean concentrations, with comparison of the reference elements. Hydrated oxides of Fe and clay mineral give the soil sportive properties (Li et al., 2001; Asaah etal; 2006) hydrated oxides of Fe seem to play a major role in the non-specific adsorption and precipitation of this element. This explains why most of the metals are concentrated in cluster1.

The second group elements consist of Ni-Zr. The two element show high mean concentration, compared with the reference element, and though both of them may be indicated that from a natural source.

The third group of elements consists of Cr. This element show high mean concentration, compared with the reference, and may be derived from natural source, Cr is significantly correlated with V, in PCA, though separated with other element in CA, which may suggests this element may be derived from natural source. The fourth group of elements consists of Mn only. It is obviously separated from the other elements in CA, and the long distance between Mn and other elements may suggest a mainly non-anthropogenic source. According to Al-Jumaily(2007), Mn may be derived from weathering of sediments and may be human activity, therefore, in study area, the skewness shows that the Mn concentration approach normal distribution, which further supports the conclusion that it has mainly natural source from weathering of quaternary deposits.

Geoaccumulation index (Igeo):

The Geoaccumulation index(Igeo)was used in determining metal pollution in soils (Muller,1979; Singh, 2001). The formula used for the calculation of Igeo is $\log_2 Cn/1.5*Bn$, where Cn is the measured content of element "n", and Bn the element content in"average shale"(Turkian &Wedepohle ,1961).

The geo accumulation index consists of seven grades (0-6) ranging from unpolluted to very high polluted. These seven descriptive classes are as follows: <o= practically uncontaminated; 0-1 = uncontaminated to slightly contaminated; 1-2 = moderately contaminated; 2-3 =moderately to highly contaminated; 3-4= highly contaminated, 4-5= highly to very highly and >5= very highly strongly contaminated. (Muller, 1979). In present study, the surface soils of the Haweja area can be described as uncontaminated to slightly contaminated since all the samples collected showed unpolluted to slightly pollute in all locations. The geo accumulation index values (Igeo) showed very low values in all the metals Fe (0.11), Cu (0.078), Zn (0.037) Co (0.181), V (0.027), Ni (0.070), Cr (0.061) and Zr (0.30) indicating surface soils in Haweja area are uncontaminated to slightly contaminated (Muller, 1979) as a result of anthropogenic (human) activities.

Conclusion

In this study, based on the comparison of heavy metal concentrations of surface soil and reference values of Kirkuk soils, the examined elements were classified into one group according to natural source. Then, PCA and CA analysis, coupled with correlation analysis, were used to gain additional insight into the origins of different elements were there by identified. Mn and Fe are attributed to hydrated oxides in soils. Vanadium,

Chromium, Zinc, Copper, and Cobalt originate mainly from natural source from weathering of recent sediments. Based on the geo accumulation index values, the surface soils in Haweja area can be classified as unpolluted to slightly polluted.

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تركيز العناصر الثقيلة في الترب السطحية لمنطقة الحويجة–جنوب غرب كركوك/العراق

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الخلاصة

تم جمع إحدى وعشرين نموذجا من الترب السطحي لمنطقة الحويجة في كركوك، وجد أن هـــذه العينـــات تحتوي على تراكيز مختلفة من العناصر الثقيلة التالية مقاسه بالجزء من المليـــون. $Cu(23-$ $Mn(401-722)$, إضافة إلـــى $42), Zn(32-62), Co(30-43), V(28-60), Ni(110-189), Cr(270-360), Zr(110-212)$ الحديد التي كانت نسبته الوزنية($0.85-2.27\%$). وقد أظهرت النتائج في ارتفاعا ملحوظا في قيم معظم العناصر الثقيلة ما عدا عنصري الكوبالت والفناديوم مقارنة بتربة كركوك. اظهر التحليل ألعاملي بصـــيغة R-mode أن هناك ثلاثة أنماط وتجمعات إلى جانب وجود عنصرين هما (Co,Zr) منفردين، مسئولين عـــن 86.92% مـــن الاختلاف في النتائج. وهذه الأنماط هي: V-Cr; Mn-Fe; Cu-Zn أما التحليل ألموقعي ألتجمعي فقد أشار إلى أن الترب السطحية في منطقة الحويجة يعتبرمن الأماكن الخالية من التلوث–إلى ملوثة قليلا.