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Geochemical Evaluation of Heavy Metals Pollution of Industrial Quarter Soils at Kirkuk City .Northern Iraq

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Abstract

The study is concerned with geochemical evaluation of heavy metals pollution in Kirkuk soil,northern Iraq.Samples were collected from twenty–eight locations of surface soils at Kirkuk industrial quarter.The results obtained from heavy metals determination in this study showed that the concentration of Pb ranged from 71 to 433 mg/kg,Ni concentration was from 49 to 285mg/kg,Zn ranged from 32to 186 mg/kg,Cd,Cr and Cu were in the range from 1.0 to 4.9 mg/kg,15 to 198 mg/kg and 24 to 182 mg/kg respectively.Variance coefficients revealed that one group of metals affected by anthropogenic pollution.Principal component analysis extracted two major components:PC1 with high loading of Cd,Pb,Ni, and Cr is suggested to be the result of industrial activities and PC2 with contribution of Zn and Cu due to use of soil constituent processes or anthropogenic influences.Assessment of environmental state of soil by means of geochemical load indices(GLI)calculated for each metal showed that concentration of heavy metals were great in elements Pb(2.1)and Cd(3.55) show moderately to high pollution at Kirkuk industrial quarter soil .

Introduction

Heavy metals are natural material (elements) of the earth's crust . Anthropogenic activities have radicalism altered the balance and the biogeochemical cycles of some heavy metals .Therefore,the concentration of heavy metals in soils has been an issue of great interest in the past years not only to farmers but also to environmentalist .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 and(Anazawa,et al.,2004).An evaluation of the environmental hazard due to soil pollution is of particular importance for agricultural areas,because heavy metals,which are chronic harmful to human health,remain in soils for a very long time(Moren,et al.,1994).The concentration of most elements such as Pb ,Ni ,Cd ,Se ,Zn ,Co ,V ,Zr ,Cr ,Mn ,Fc,…etc in soil shows a pattern related to geology,human activity and agricultural influences(Al-Jumaily,2007;Salmineh&Demetriades,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 accumulated in the food soft tissue and potential health risks as well as its detrimental effects on soil ecosystems(McLaughlin,et al.,1999).The city environment forms a mosaic of soils with different levels of physical surface transformations which makes the cause and affects analysis of soil pollution very hard.A lot of studies on the pollution of soils with heavy metals come down to the determination of their concentration in a few soil samples without considering the specificity of their random and systematic variations (Siepak ,et al. ,1996) .A good indicator of environmental pollution of soils by heavy metals is their geochemical load index.The present study,therefore,evaluates the geochemical determination of heavy metals in soil samples and identifies the possible origins of these metals in industrial soils of Kirkuk city.

Study Area

The city of Kirkuk lies in the north of Iraq,227 Km north of Baghdad.The climate is typically arid in nature.Kirkuk was found in2750 B.C,and during the first years of the 20^{th} century,the urban area was concentrated in the present city centre(app.15000 people and the city now has population of 1 million people approximately).Kirkuk city was built as agriculture,industries and now it is famous with oil fields.Kirkuk city is located within the Kirkuk block,which constitute part of the low folded zone of northern Iraq and it lies within the Hamrin Makhul sub zone and it is represented by a complex of reef, basinal units and the main limestone (Jassim&Goff,2006).Stratigraphically,the studied area covered by quaternary deposits,periodically flood and soil deposits(Buringh,1960).The soils of the area are formed of materials consisting mainly of mixture of gravel,boulders,sands,and clay(Jassim&Goff,2006).Therefore,the soil of Kirkuk city is alluvial,formed by periodic deposition and erosion during the different stage of river flooding and it is clayey silt sandy and gravel.

Material and Methodology

Twenty-eight samples of soil were collected from various locations in Kirkuk industrial quarter(Fig.1).These soil samples were obtained with a hand auger from surface soils(at depth 0-20 cm).In the laboratory,the soil samples after air drying at room temperature were sieved with nylon mesh.The sample fraction was grinded in agate mortar and pestle and passed through a 2 mm.sieve to remove large plant,root,and homogenized. For the analysis of heavy metals Lead(Pb),Nickle(Ni),Zinc(Zn),Cadmium (Cd),Chromium(Cr)and Copper(Cu),samples were analyzed by X-ray fluorescence(XRF-140 Micro analyzer)in Laboratory of Chemistry for technology in University of Brescia,Italy,using the following conditions: (tube(Mo), voltage(30 Kv),current(30 mA),time(60 sec.) and medium(air)) .For evaluation of soil contamination by heavy metals , a geochemical load index(GLI)was calculated(Birke&Rauch,1994).

$$GLI = \log_2 \frac{Ci}{B * 1.5}$$

Where:

Ci–concentration of an element in surface soil, mg/kg of soil dry weight,
B–natural background concentration of heavy metal–estimated for soil parent material (Connor&Shacklette,1975).The analytical results were treated statistically by summary statistics and factor analysis.

Results and discussion

The results of geochemical analysis are summarized in the Table1.Fig2 shows range in concentrations of the various elements in study area.The highest value for Ni,Cu,Zn and Cr were recorded at a location noted for mechanical garage while the maximum values for Pb and Cd were recorded at locations situated in and around metal workshops for painting of vehicles and waste dumps of scrap iron of the Kirkuk industrial quarter.Comparison with the local geochemical background(table 2).Shows that,Ni,Zn and Cu are significantly enriched in the surface soils.The enrichment of Cr in the same material is less significant.Variation Coefficient(VC),which is SD/mean,was used to reflect the degree of distribution of various metal elements contents and to indicate indirectly the activeness of selected element in examined environment. Variation Coefficient(VC)values indicate that all elements can be classified into one group(Pb,Ni,Zn,Cd,Cr and Cu) whose Variation Coefficient are higher than 0.4.Yongamine,et al.,2006,points out that the metals with Variation Coefficient lower than0.3 are dominated by a natural sources,while the elements having Variation Coefficient higher than0.3 are affected by anthropogenic sources,therefore,in the studied area one would expect that all heavy metals element dominated by anthropogenic sources especially a human activities. Factor analysis of the data set indicates that certain elements associations points to particular sources.This analysis applied to the auto scaled data matrix which shows differentiation in the heavy metals at the investigated site.The variables are correlated with three principal components in which81.428 % table3 of the total variance.The number of significant principal components is selected on the basis of the Kaiser Criterion with eigen value higher than one(Kaiser,1960). According to this criterion,only the first three principal components are retained because subsequent eigen values are all less than one.Hence reduced dimensionality of the descriptor space is three.The first component with48.298% of variance comprises Cd,Pb,Ni and Cr with high loadings.This association strongly suggest that these variables have similar sources.These metals may be derived mainly from industrial activities,as the level of anthropogenic input of these metals in Kirkuk industrial quarter,where industrial activity is minimal,are low.The geochemical meaning of PC1 also agrees with the correlation coefficient between these variables(table 4).The second component(PC2)contributes Zn and Cu at 19.863% total variance.These metals in the studied area may be derived from industrial influence.The heavy metals concentration in surface soil is a result of soil constituent processes and also industrial activities(Silverira,et al.,2003).The third component(PC3)alone explains 13.267% of variance of result.This factor can be suggested by its persistent level of anthropogenic influence in Kirkuk soil,where industrial activity is low.Table 5 shows classes of soil contamination with heavy metals that were prepared in the form of their geochemical loading index.The GLI was originally defined by Muller (1979)for quantitative measure of the metal pollution in environment (Ridgway&Shimmield,2002).Elevated GLI values identified for Pb and Cd in Kirkuk soil indicate that surface soils are contaminated to some extent, most probably as result of the anthropogenic activities such as metal workshops,garages and waste dumps.GLI values calculated for Pb(2.10)and Cd(3.55)showed higher values in the studied area,therefore as regards contamination,they were included in the third and fourth classes.The pollution levels of another metals such as Ni,Zn,Cr and Cu indicates that the Kirkuk environment is low polluted in this metals(class 1) (Muller, 1979).as result of industrial influences.

Conclusions

In this study,an attempt has been made to correlate the concentration of metals in the soil of Kirkuk industrial quarter to human effluents,associated with different urban activities that are mainly industrial.The calculated GLI values allocated for Cd and Pb indicate that the surface soil are moderately to high contaminated probably as result of anthropogenic activities.Finally, this study generally concludes that the geochemical evaluation can provide strong tool for monitoring the heavy metal sources in soil and for predicting the future soil contamination by anthropogenic activities.

Acnowledgment

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Table 1: Total concentration of heavy metals of soil samples collected from the study area (mg/kg).

Element	Mean	Median	Mode	Minimum	Maximum	S.D*	# VC
Pb	232.79	219.45	71.4	71.4	433.4	108.48	0.47
Ni	161.93	171.8	199.9	48.8	285.3	70.84	0.44
Zn	114.33	128.8	41.6	32.4	185.6	55.80	0.49
Cd	3.03	3.15	4.3	1.00	4.9	1.35	0.44
Cr	127.56	151.5	14.7	14.7	198.10	67.72	0.53
Cu	103.1	104.0	95.4	24.6	182.1	55.23	0.54

* Standard Deviation
#Variation Coefficient

Table 2: Mean values of the contents of elements in soil from the city of Kirkuk, Haweja and Adhaim regions, Iraq

Element (mg/kg)	Present study (N[&]=28)	Haweja* (N=21)	Adhaim# (N=7)
Pb	233	–	–
Ni	162	152	133
Zn	114	51	69
Cd	3	–	–
Cr	128	310	37
Cu	103	36	51

[&] N= number of samples
*Al-Jumaily, 2007
[#]Ali, 1996

Table 3: Principal component factor analysis of the correlation matrix. Rotated factor loading and communalities. (Varimax rotation)

variables	Factor 1	Factor 2	Factor 3	communality
Pb	0.895	0.007	-0.002	0.806
Ni	0.883	-0.203	0.007	0.827
Zn	0.003	0.798	0.589	0.985
Cd	0.927	-0.004	0.138	0.879
Cr	0.617	-0.116	-0.005	0.397
Cu	0.277	0.702	-0.649	0.990
Variance	48.298	19.863	13.267	
Cumm.%Var.	48.298	68.161	81.428	

Table 4: Correlation coefficient of heavy metals in the soils of the study area.Values less than or equal to 0.3 are not significant at 95% level(n=28).

	Pb	Ni	Zn	Cd	Cr	Cu
Pb	1.00	0.679	0.059	0.820	0.425	0.269
Ni		1.00	-0.079	0.832	0.446	0.088
Zn			1.00	0.053	0.020	0.189
Cd				1.00	0.399	0.150
Cr					1.00	0.100
CU						1.00

Table 5: Discription of geochemical loading index in study area.

GLI	Class of GLI	Level loading ##	Element	GLI in present study
< 0	0	Depleted to non- polluted	Pb	2.10
0-1	1	non-polluted to slightly polluted	Ni	1.10
1-2	2	slightly polluted to moderately polluted	Zn	0.18
2-3	3	Moderately	Cd	3.55
3-4	4	Moderately to high polluted	Cr	0.42
4-5	5	high polluted	Cu	0.51

Muller, 1979

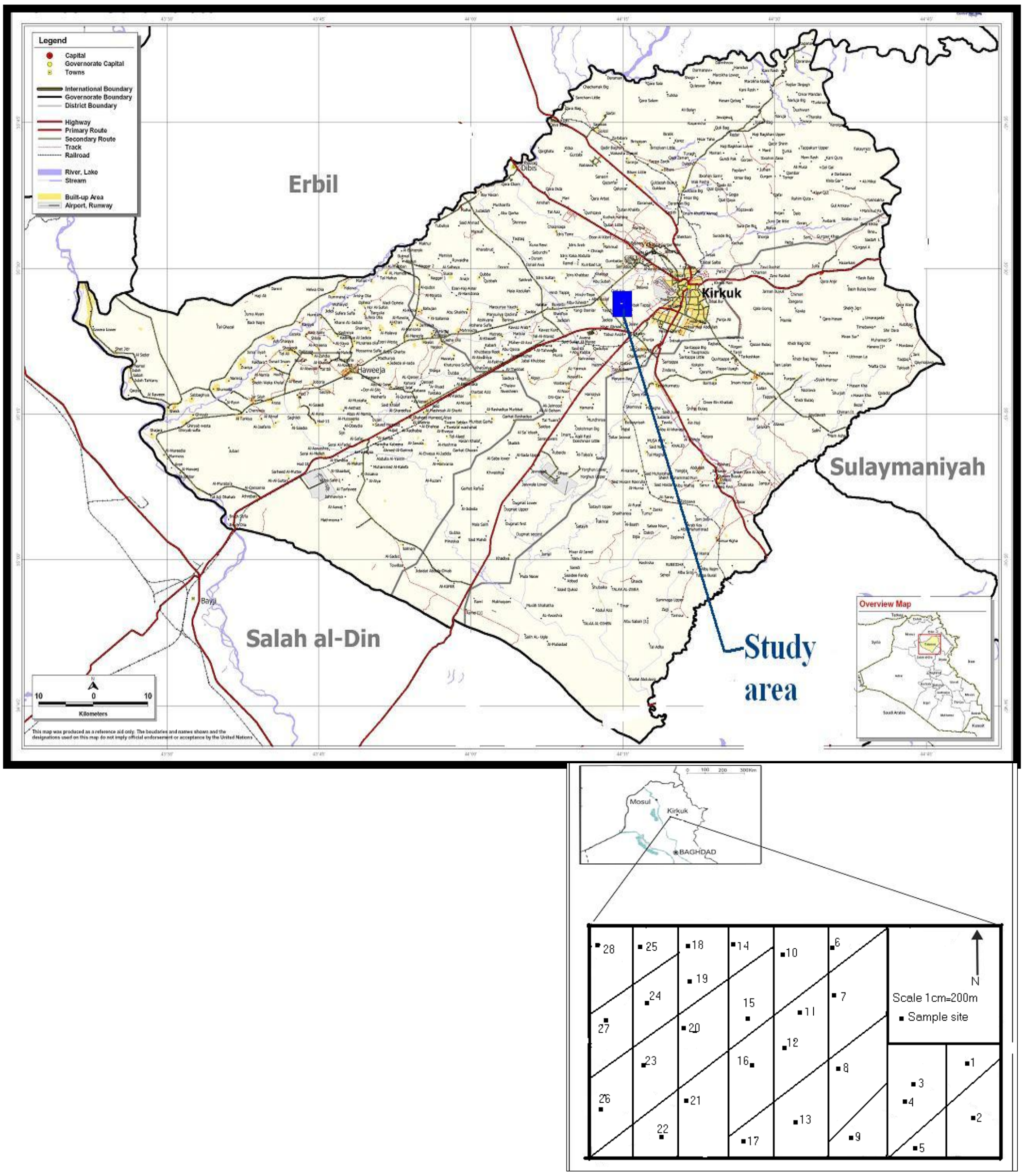

Fig.1: Map showing the study area and samples location

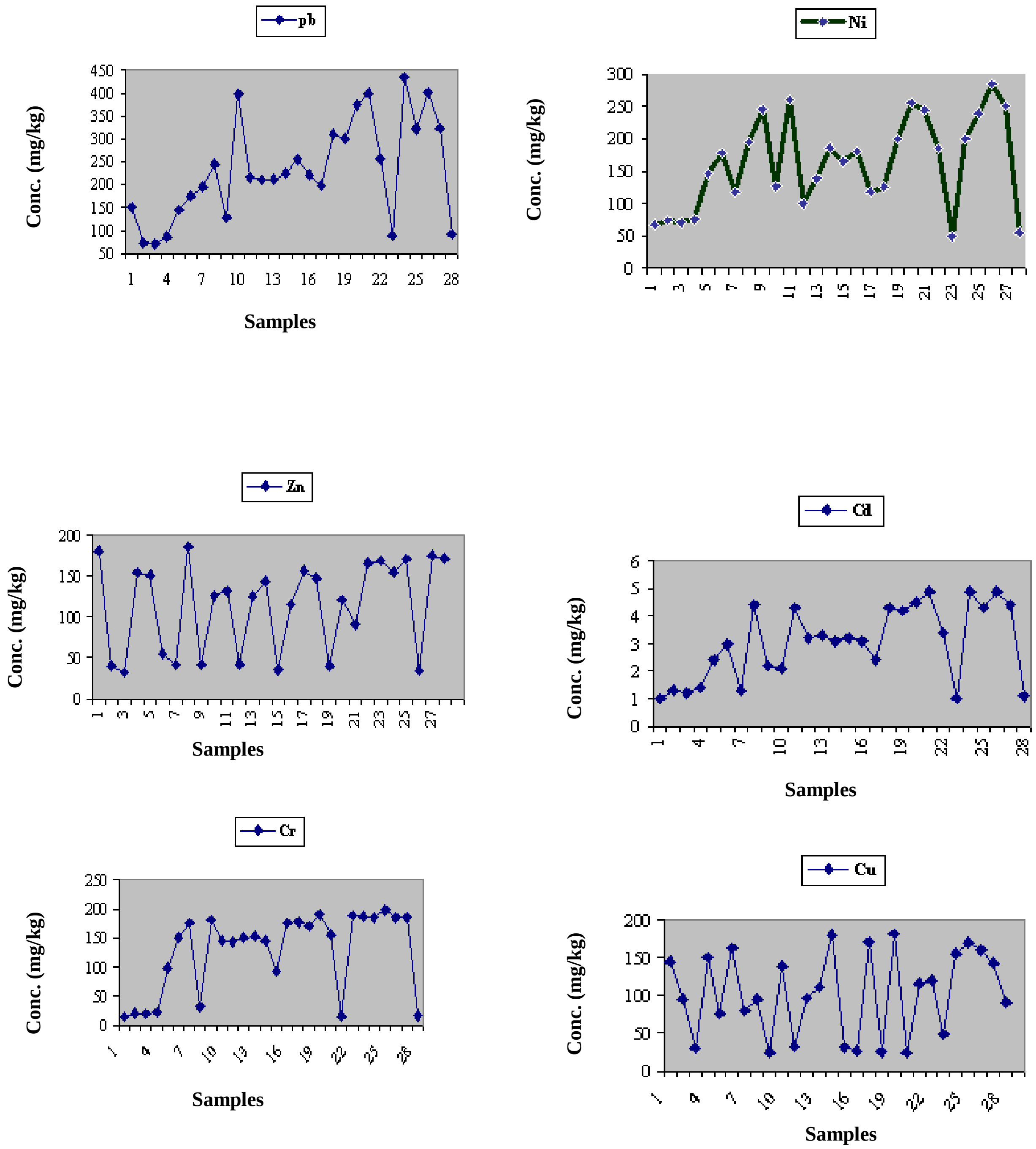

Fig 2.Distribution of heavy metals in study area.

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التقيم الجيوكيميائي لتلوث تربة الحي الصناعي في مدينة كركوك بالعناصر الثقيلة

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الخلاصة

تعرض الدراسة الحالية التقيم الجيوكيميائي لتلوث تربة الحي الصناعي في مدينة كركوك بالعناصر الثقيلة.فقد تم جمع ٢٧ نموذجا من هذه الترب وكانت مديات تراكيز العناصر المدروسة ومقدرة بوحدة (mg/kg)والمتمثلة بعناصر الرصاص والنيكل والزنك والكادميوم والكروم والنحاس هي(71.4-433.4،48.8-285.3،32.4-185.6،1.00-4.9،14.7-198.1،24.6-182.1)على التوالي بين تحليل التباين هذه العناصر الثقيلة تقع جميعها ضمن مجموعة واحدة والتي تعكس تأثير التلوث البشري المنشأ.كما اظهر التحليل العاملي بان هذه العناصر تتوزع على مركبتين اساسيتين الاولى وتكون ذات تحميل عالي لعناصر الكادميوم والرصاص والنيكل والثانية تكون محملة عليها عناصر الزنك والنحاس وهذا التحميل قد يعكس تأثير الفعاليات البشرية المنشأ من ناحية او بفعل العمليات المؤثرة على مكونات التربة من ناحية اخرى.ولقد تم تقدير الحالة البيئية ومدى تلوث التربة وذلك بأستخدام معامل التحميل الجيوكيميائي واظهرت منطقة الدراسة تلوثها بالعناصر الثقيلة وخصوصا عنصري الرصاص و الكادميوم وكانت درجة التلوث من متوسطة الى عالية التلوث في تربة الحي الصناعي في كركوك.