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Calculation of Pollution Indicators and Health Hazards of Heavy Elements in Surface Soils in Samarra City

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Abstract

The current study focuses on the assessment of pollution indicators and health risks of heavy elements in the surface soil of Samarra City. Twelve soil sample collected from different sites in Samarra City, analysis of soil sample to find the heavy metals concentrations which As, Br, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn, Zr, U, B, Cd, Hg, Th, Ce, La, Th, B, Ba .The results are compared with limit of world standard (12). The higher values which refer to pollution in heavy metal are Cr, Cu, Ni, Zn, Zr, Cd due to industry activity and Hg higher concentration because of Pharmaceutical Industries and Medical Waste . The high concentration in V, Br, Mo, Se, As because of agriculture activity. The enrichment factor calculated for the purpose of calculating saturation coefficient and treatment, analysis and conversion of the values of raw concentrations and the creation of the local background of Iraq. The most of the results are less than five ,but few value are greater than five indicating the anthropogenic input of these elements in soil in Samarra City which are Co, Mo, U in S2 because of agriculture activity and using fertilizer. Mo , Sn in S2 because of highly building activity. Cu, Mo, Zn in S5 Because industrial and motor oil spill. Uranium in S2, S4 and S11 because military activity. Contamination factor (CF) and the value of the pollutant load index are less than 4 that’s mean sites are polluted medium to high. After applying the health risk assessment model, the risk value for each non-carcinogenic heavy element is found to be less than 4 and for all three exposure methods (ingestion, skin contact and inhalation), in terms of carcinogenic components, the average daily dose (LADD)) And compared to slope coefficient (SF) collected from previous studies. Equations are applied to find less than 0.0001 which is indicative of the occurrence of cariogenic diseases that may affect people exposed to soil. The risk of soil or dust ingestion is more insecure in the area of activity in the effect of cobalt and manganese than on adults, and chromium has an effect on adults at a high level. HI value of inhalation that’s effect on adults and children revel the most hazardous heavy elements is Mn, Cr, Co for adults and children. HI value of dermal absorption the most hazard element Cr, Hg , Ce for adults and children which exposed to the soil. Swallow soil effect on children and adults. Especially chromium and mercury, which in turn affect the health exposed to the ingestion of polluted soil.

Keywords: pollution indicators, health hazard assessment, heavy elements, contaminated soil.

حساب مؤشرات التلوث والمخاطر الصحية للعناصر الثقيلة في التربة السطحية في مدينة سامراء

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الخلاصة

تركز الدراسة الحالية على تقييم مؤشرات التلوث والمخاطر الصحية للعناصر الثقيلة في التربة السطحية لمدينة سامراء. تم جمع اثنتا عشرة عينة من التربة من مواقع مختلفة في مدينة سامراء ، وتحليل عينة التربة للعثور على تركيزات المعادن الثقيلة وهي: As، Br، Co، Cr، Cu، Mn، Mo، Ni، Pb، Sn، V، Zn، Zr، U، B، Cd، Hg، Th، Ce، La، Th، B، Ba. تتم مقارنة النتائج مع الحد من المعايير العالمية (12). القيم العاليه التي تشير إلى التلوث في المعادن الثقيلة هي Cr و Cu و Ni و Zn و Zr و Cd بسبب النشاط الصناعي .اما التركيز العالي للزئبق يكون بسبب الصناعات الدوائية والنفايات الطبية . التراكيز العاليه للعناصر V, Br, Mo, Se, As تكون بسبب نشاط المناطق الزراعية.

يتم حساب معامل الاغناء لغرض حساب معامل الاشباع ومعالجة وتحويل قيم التركيزات الخام وايجاد الخلفية المحلية لتركيز العناصر في التربه المحليه. معظم النتائج أقل من خمسة ، بعض القيم أكبر من خمسة مما يشير إلى المدخلات البشرية لهذه العناصر في التربة في مدينة سامراء التي هي Co ، Mo في النموذج S2 بسبب نشاط الزراعة واستخدام الأسمدة. معامل اشباع عالي وجد في نموذج S2 لعنصري Mo ، Sn بسبب نشاط بناء عالية.Cu ، Mo, Zn في S5 بسبب تسرب النفط الصناعي وزيوت السيارات. ان اكثر عنصر متواجد في قيم معامل الاغناء هو اليورانيوم في النماذج S2 و S4 و S11 اليورانيوم متواجد بسبب النشاط العسكري. عامل التلوث وقيمة مؤشر الحمولة الملوثة أقل من 4 وهذا يعني ان التلوث متوسط الى مرتفع. بعد تطبيق موديل تقييم المخاطر الصحية ، وجد أن قيمة الخطر لكل عنصر ثقيل غير مسرطن أقل من 4 ولجميع طرق التعرض الثلاثة (ابتلاع ، ملامسة الجلد واستنشاق) ، وتم حساب متوسط الجرعة اليومية (LADD). مقارنة معامل الانحدار (SF) الذي تم جمعه من الدراسات السابقة. ان تطبيق المعادلات لإيجاد أقل من 0.0001 وهذا يدل على حدوث أمراض سرطانية قد تؤثر على الأشخاص المعرضين للتربة. إن خطر التربة أو ابتلاع الأتربة غير آمن بدرجة أكبر في مجال النشاط في تأثير الكوبالت والمنغنيز منه على البالغين ، والكروم له تأثير على البالغين على مستوى عال. قيمة الاستنشاق التي لها تأثير على البالغين والأطفال تكشف عن العناصر الثقيلة الأكثر خطورة هي Mn، Cr، Co للبالغين والأطفال. قيمة HI لامتصاص الجلد للعناصر الأكثر خطورة وهي Cr، Hg,Ce للبالغين والأطفال الذين تعرضوا للتربة. ان خطوره ابتلاع التربة للانسان (الأطفال والبالغين) وخاصة الكروم والزئبق تؤثر بدورها على الصحة لاستيعاب التربة الملوثة.

1. Introduction

More attention is paid to the deposition of heavy metals in soils due to human activity which have negative effects on human health [1], and their toxicity and persistence in the environment [2]. Soil contamination of heavy elements is mainly due to both natural processes such as mineralization and human activity related to industry, agriculture, waste oil, vehicle emissions and mining operations. Enrichment factor (EF) was used to evaluate element concentrations [3].

Enrichment factor is a powerful tool for distinguishing the sources of heavy metals whether natural or human activity. Other treatments such as the Index Load Pollution (PLI), which in turn depends on a enrichment factor[4]and Contamination factor (CF) heavy metals can move from the surface soil to the human body by entering soil minutes into the mouth, contact Soil with skin and soil inhalation[5].

Exposure of the skin to heavy elements that’s in soil occur through outdoor activities, especially for children. [6] Soil can easily be suspended in the air again by wind erosion or human foot movement dust that could pose a potential risk to human health by inhalation [7].

The objective of this study is to determine the source of soil surface pollution with some heavy elements in Samarra City by calculating the indicators of pollution, such as the enrichment factor, to children and adults living near these sites.

2. Study area

The study area is located in Samarra City. Focusing on the north part of the City between (34°11'22''- 34°12'50'' N) and (43°52'30''- 43°55'20'' E) the area at the left bank of Tigris River near the great Samarra Bridge (Figure-1).

Table 1-Location Of The Soil Samples Collected From Samarra City.

Soil samples	Site names	Coordinates		Land use
		N	E	
S1	Samarra Pharmaceutical Factory	34°13'143"	43°53'60"	Industrial
S 2	Al -Maemal	34°12'41.8"	43°52'27.90"	Residential
S 3	Al-Muetasim	34°11'84.53"	43°53'63.3"	Residential
S 4	Al-Hadi	34°11'20.83"	43°52'40.87"	Residential
S 5	Al -Sinaeih	34°10'07.42"	43°52'08.17"	Industrial
S 6	Al-Jabiriuh 2	34°11'73.14"	43° 53'94.71"	Residential
S 7	Al-Jabiriuh3 Landfill	34°10'80.08"	47°54'32.93"	
S 8	AL- Shuhada	34°11'92.87"	43°52'36.01"	Residential Agricultural
S 9	AL- Ziraeuh	34°13'39.11"	47°52'6.39"	Residential
S 10	A Park Well Al -Shiratih	34°12'08.1"	43°53'18.15"	Residential
S 11	Al-Afraz	34°12'80.88"	43°54'87.31"	Residential
S 12	Out of City Reference Point	34°12'0.01"	43°55'28.53"	Empty space

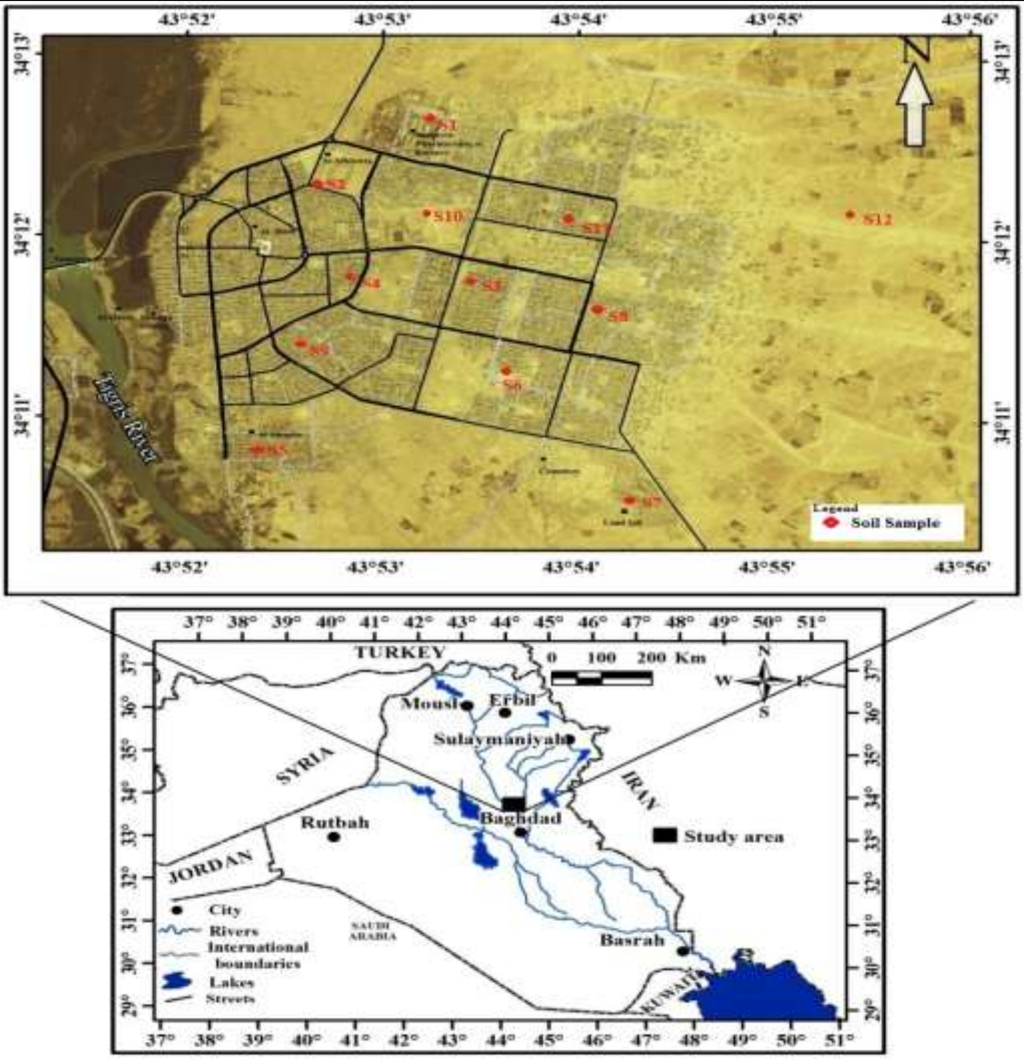

Figure1-Location Map of Urban Samarra City

3. Methodology

Twelve samples from Samarra City soil were collected during the field work two kilograms for each soil sample were collected in plastic bags, then dried at 40 °C after sampling for physical and chemical analyses. Latitudes, longitude for each sampling site of sediments are accurately determined by using the Global Positioning System (GPS).

Chemical analysis by X-Ray Fluorescence (XRF) device were conducted at University of Baghdad, College of Science, Department of geology, Iraq Germany Laboratory.

4.Trace elements

Concentrations of heavy metals, for twelve soil samples were measured using Bench XRF Spectrometer/SPECTRO XEPOS-2006 device at the Iraqi-German Laboratory at the University of Baghdad. Samples were sieved in a 2 mm sieve, then powdered to 0.063μm, and 5.0 g of each sample was used to determine the element concentrations. Soil are rich in heavy metals and its effect into the environment[8]. Thus, the soil could be a potential source of heavy metals that will be released into the overlying water via natural and anthropogenic processes [9], where they adversely effect on the drinking water quality and human health. Understanding the levels, distribution and sources of heavy metals in soil can aid environmental management and facilitate the supervision of water quality [10].

In the present study trace elements have been ordered in following sequence Sr>Cr>Zn >Zr>Ni> Cu >V >Pb>Mo>Co>Br>As> Cd >U>Hg>Se. The mean concentration values of trace elements in the soil of Samarra City have been compared with the natural occurrences of trace elements in world soil [11].

Chromium had mean concentration 179.65 ppm.

This mean value exceeded its natural occurrence limits in world soil [11], The maximum Cr concentration value 933.91 ppm has been detected at S_5, this high value due to the pollution industrial activity which is chromium dyeing .

Nickel (Ni) has mean concentration value of 92.3ppm, it considered greater than abundant limits in soil.

The mean concentration value of Zirconium (Zr) was 94.2 ppm, all detected values are within natural abundant limits of world soil [11].

Zinc (Zn) had a mean concentration value 99.6 ppm and with compare with mean and its higher than world soil[11].

Vanadium (V) exists in soil with mean concentration values of 43.5ppm. less than the natural occurrences of trace elements in world soil [11].

Copper (Cu) has been detected with mean concentration value of 43.713ppm. Cu was out of its natural abundance in world soil [11].

Bromide (Br) with mean value 5.2 ppm was much is very close to its natural abundance in world soil in all stations of sampling excluding S_1,S2,S6,S7,S9.

Lead (Pb) has a mean concentration of 17ppm which is very close to the world soil (17ppm) [11].

Molybdenum (Mo) and Selenium (Se) mean concentrations were exceeded limits of their abundance in world soil [11].

Arsenic (As) mean concentration value is less than natural abundance in world soil [11].

Cobalt (Co) mean concentrations value is very close to the natural abundance in world soil[11].

Uranium (U) has mean concentration value 1 ppm less than world soil (1.8 ppm) [11], exceeded its natural abundance at S_1, and S_9 (3.8 and 1.9 ppm respectively) those not exceeded according to [11].

Cadmium (Cd) concentrations are more than limits of natural abundance in world soil [12].

Mercury (Hg) has been detected with same concentration value <1 in all soil samples.

5. Enrichment Factor (EF)

Enrichment factor is powerful tool for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and the public [13].

$$EF = (C_x/C_{ref})_{Sample} / (B_x/B_{ref})_{Background} \quad (1)$$

Where:

Cx =	Content of the examined element in the examined environment
Cref =	Content of the examined element in the reference environment
Bx =	Content of the reference element in the examined environment
Bref =	Content of the reference element in the reference environment

The immobile element is often taken to be [14], Li, Sc, Zr [15]. The method that have been used in this study depended on standarad deviation (SD)method ,the ilterative 2SD technique (average +2SD) is mainly used to define background value because it approximates the original data set to normal distribution [16].this technique detailed by[17]. Based on the assumption that dataset beyond the average +2SD are iteratively omitted until all value lie within the range (normal distribution) .

In order to evaluate if the content of a chemical element in the soil from natural or anthropogenic sources, enrichment factor was calculated for all studied soil samples using zirconium (Zr) as a reference element. The enrichment factor is the relative abundance of a chemical element in a soil sample compared to the bedrock.

Zirconium is generally considered as mainly originated from natural lithogenic sources (rock weathering of mineral zircon) and has no significant anthropogenic source. It has widely been used in geochemical studies of mineral weathering as a 'conservative' lithogenic element, against which relative enrichments has been compared [15]. Total elemental concentrations (ppm) in the world soil according are considered to calculate EF. EF < 2 shows deficiency to low enrichment and can be considered in the range of natural variability. $2 < EF < 5$ shows low enrichment (i.e. some enrichment caused by anthropogenic input). $5 < EF < 20$ is a clear indication of human activity (significant enrichment caused by anthropogenic inputs). EF 20 to 40 is very high enrichment and EF > 40 is extremely high enrichment.

The result of EF calculations for Samarra city sample ,all value low enrichment and can be considered in range of natural variability except the value that colored in red consider anthropogenic input in cause of chemical in industrial activity.

EF values greater than five (Table 2), indicating the anthropogenic input of these elements in soil in Samarra City. Elements that's effected by human activity are cobalt S2, zinc and copper high values in S5 because of high industrial activity in this area , uranium and molybdenum is highly enrichment in S2 and S10 , tin highly inrichment in S3 because of highly building activity, uranium in S4 and S11 because drilling and military activity.

Table 2-Results Of Enrichment Factor Of Soil Samples.

Elements	EFs_1	EFs_2	EFs_3	EFs_4	EFs_5	EF_{s6}	EFs_7	EFs_8	EF_{s9}	EF_{S10}	EF_{S11}	EF_{S12}	Local Geochemical Background *	Mean
As	0.7461	1.5832	2.0453	0.1362	1.4430	0.3468	2.311	0.7605	0.953	0.8769	0.8807	1.1282	1	0.9172
Br	1.0001	2.3247	0.1579	1.0971	0.6408	2.7057	2.426	0.6299	1.034	0.0512	0.5872	1.7584	4	1.0171
Co	1.0972	8.7310	1.8252	0.0590	0.9396	0.9702	0.558	0.3588	3.482	1.3605	1.7269	0.7915	2	1.0337
Cr	0.5320	2.1121	1.8730	0.7928	3.0214	0.8055	1.342	0.6365	0.743	0.7601	0.8381	1.8114	100	0.8218
Cu	0.6796	1.3090	1.3406	0.8451	5.8001	1.2134	3.281	0.5722	0.555	2.200	0.5445	1.8461	40	1.2612
Mn	1.0693	1.3580	1.9541	1.2404	2.2059	0.7826	1.543	0.9925	1.166	1.1922	1.1368	1.0112	170	1.1792
Mo	0.5222	12.481	16.239	0.4628	4.8140	0.9444	1.327	0.6076	0.790	9.0603	0.2523	0.9174	5	0.9304
Ni	1.2262	1.7341	1.5421	2.4479	0.5113	0.9045	1.723	1.0941	1.504	1.5179	1.4056	2.0291	60	1.5108
Pb	0.4650	0.5852	2.2476	0.7754	1.7669	1.1963	2.877	0.4073	0.535	0.3162	0.3908	0.5323	6	0.5604
Sn	0.5294	2.1203	8.653	1.384	0.8834	0.9062	1.357	0.8487	0.704	0.6081	0.6107	0.4436	0.01	0.8661
V	0.9122	1.9105	1.7481	2.6602	1.6025	1.0085	0.682	0.9750	1.214	0.8950	1.0085	3.6626	40	1.1114
Zn	2.8178	2.5001	2.051	1.877	8.1106	2.5483	4.755	0.7119	0.905	0.3398	0.7246	1.8605	70	1.9642
Zr	1	1	1	1	1	1	1	1	1	1	1	1	30	1
U	0.6650	10.654	2.3528	9.9096	1.1098	1.4799	1.704	1.5993	0.885	0.6111	5.2938	2.5076	0	1.6521
B	0.2909	1.5510	0.9571	1.0705	0.5968	1.0911	1.320	1.4556	1.075	1.1046	0.8187	0.7763	1	1.0727
Cd	0.4117	1.6491	2.1851	1.0764	0.6871	1.0573	2.111	0.6601	0.548	0.4729	0. 4	0.8625	2	0.7748
Hg	0.782	1.64	2.91	1.07	0.68	0.704	1.0	0.66	0.5	0.472	0.47]	1.725	1	0.74
Th	0.741	0.51	1.71	0.58	0.26	0.827	0.6	0.87	0.8	1.054	0.91	0.607	0	0.78
Ce	0.592	2.37	2.09	1.55	0.98	3.451	1.5	0.95	0.7	0.885	0.68	1.242	1	1.11
La	0.411	1.64	2.18	1.07	0.68	1.057	2.1	0.66	0.5	0.472	0.47	0.862	1	0.77
Ba	0.777	1.87	0.04	1.14	0.11	0.950	1.3	1.27	0.0	0.014	0.86	0.03	3	0.82

*Local geochemical background calculated for Samarra City according to(17).

6. Contamination factor (CF)

Contamination factor would be a ratio between the measurements with the officially permitted levels. Enrichment factor would be a ratio of the measurements and levels of metals occurring in the water of non-contaminated areas. Based on Cf value, all sample are classified as low contamination degree in all different site [18].

CF= (Cm) Sample /(Cm) Background (2)

7. Pollution load index (PLI)

The pollution load index result in soil in most of studied sample indicate that sample are polluted medium to high

PLI= (CF1*CF2*CF3*…..*CFn) 1/n (3)

PLI is pollution load index, n is the number of pollutant assesses (3). PI is the single factor pollution index of each metal.

PLI = 0 (background concentration); 0 < PLI ≤ 1 (Unpolluted); 1 < PLI ≤ 2 (Moderately to unpolluted); 2 < PI ≤ 3 (Moderately polluted); 3 < PI ≤ 4 (Moderately to highly polluted); 4 < PI ≤ 5 (Highly polluted); PI > 3 (Very highly polluted) [19].

8. Health risk assessment model

For the purpose of evaluating the health hazard, equations are applied after we hypothesized that the residents (children and adults)of Samarra exposed directly to the soil, as there are three methods of exposure are [20].

1- Ingestion
2- skin (dermal) absorption .
3 - Inhalation particle of soil located in the air .

Where each type of exposure was calculated the chronic daily intake , (CDI) table3 show the variables that's used in applying equation ,as it shown in the following equation [21], [22].

$$CDIing = Csoil * \frac{IngR*EF*ED}{BW*AT} * CF \quad ....(4)$$

$$CDIdrm = Csoil * \frac{SA*SAF*DA*EF*ED}{BW*AT} * CF \quad ....(5)$$

$$CDIinh = Csoil * \frac{InhR*EF*ED}{PEF*BW*AT\ ...} \quad .... (6)$$

$$HQ = \frac{CDI_{pathway}}{RfD} \quad ....(7)$$

$$HI = \sum HQ = HQing + HQdrm + HQinh \quad .... (8)$$

The carcinogenic and non-carcinogenic side effects of each element were calculated and the hazard index (HI) ,the HI value higher than this means that there is a possibility of non-carcinogenic diseases .

$$LADD = \frac{C*EF}{AT} * \frac{CRchild*EDchild}{BWchild} + \frac{CRadult*EDadult}{BWchild} \quad ...... (9)$$

$$R = LADD * SF \quad .... (10)$$

In terms of carcinogenic components, lifetime Average Daily Dose (LADD), was calculated and compared with the Slope Factor (SF) coefficient collected from previous studies. The equations were applied to find that less than 0.0001 It is indicative of the occurrence of cancerous diseases that may affect those exposed to the soil [23].

Table 3-Variables That's Used In Health Risk Assessment Equations.

Variable	Adults	children	Variables
AT_c (day)	127 *Age		Average time of carcinogenicity
AT_{nc} (day)	127 * ED		Average time of non-carcinogenic carcinogenicity
BW (kg)	51	17	Body weight
C_{soil} (mg/kg)			Element concentration in soil
DA (unitless)	1.111		Skin absorption factor

CDI_{ing} (mg/kg/day)			Daily intake of chronic
CDI_{drm} (mg/kg/day)			Daily intake of chronic Skin dermis
CDI_{inh} (mg/kg/day)			Daily intake of chronic Inhalation
ED (year)	11	2	Exposure period
EF (day/year)	171		Repeat exposure
IngR(mg/day)	111	211	Rate of soil ingestion
InhR (m^3/day)	21	5.2	Inhalation rate
PEF (m^3/kg)	$1.36 * 10^9$		Average emission rate
SA (cm^2)	7511	2811	Area of exposed skin
SAF (mg/cm^2)	1.15	1.2	Skin adhesion factor
RfD_{ing} (mg/kg/day)	Zn=0.3, Cu=0.049, Pb=0.0014, Co=0.0003, Cr=0.003, Ni=0.02, Mn=0.024		Chronic oral reference dose
RfD_{drm} (mg/kg/day)	Zn=0.06, Cu=0.008, Pb=0.00042, Co=0.00006, Cr=0.000075, Ni=0.00008, Mn=0.000096		Chronic dermal reference dose
RfD_{inh} (mg/kg/day)	Zn=0.3,Cu=0.042, Pb=0.035, Co=0.0000057, Cr=0.000028, Ni=0.02, Mn=0.000014		Reference dose by chronic inhalation

The risk assessment on health was illustrated by graph that compares adults and children. Values above 1 mean that there is a health problem in the health of the child and adults as shown in Figure-2. [24]

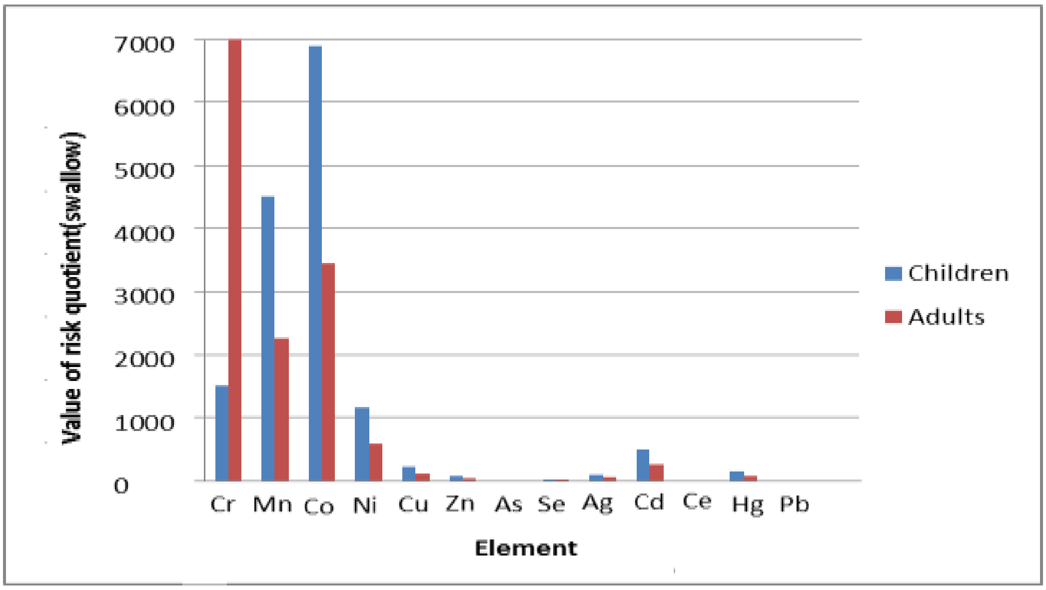

Figure 2-Value of Risk Quotient HQing (Swallow) Of Element

In the other side the dermal absorption of heavy metal is accepted of all element less than one ,except the Cr and Hg as its shown in Figure-3 adult are effected in nickel and chrome.

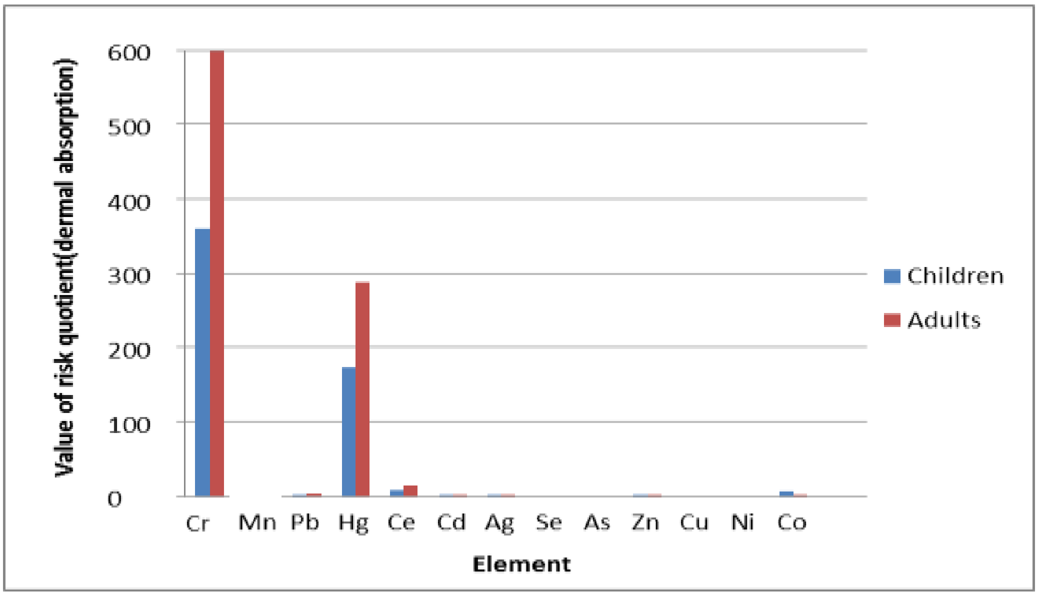

Figure 3-Value Of Risk Quotient HQ drm (dermal absorption) Of Element.

The ihalalation Not harmful to the health of children or adult that exposed to dust and particle except the manganese the HQ is more than one (2.5-3) and its effect on children more than adult (23) .

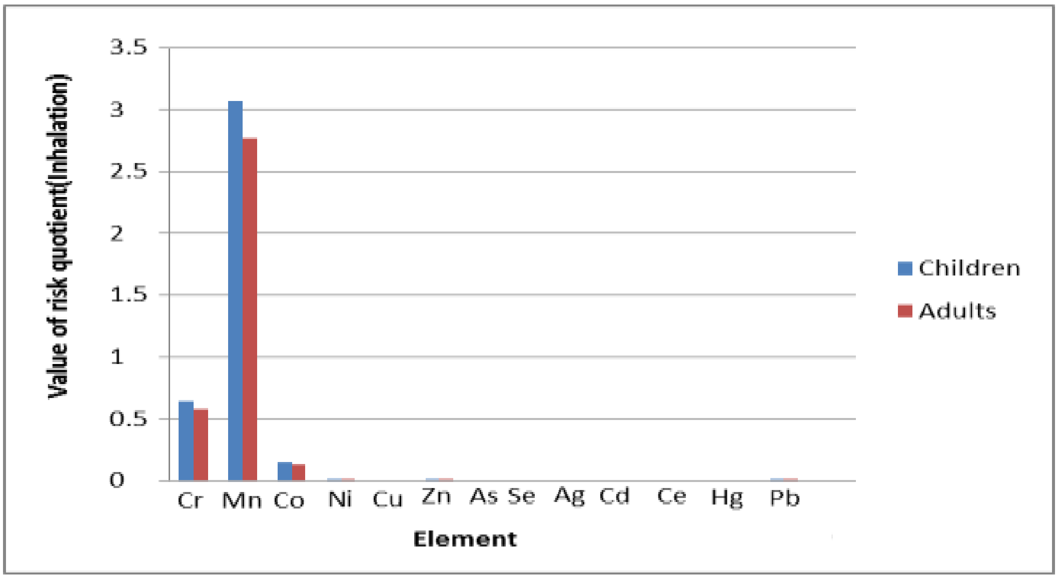

Figure 4-Value of Risk Quotient HQ inh (inhalation) Of Element.

9. Conclusions and discussion

1. Analysis of soil sample to find the heavy metals concentrations which are As, Br, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn, Zr, U, B, Cd, Hg, Th, Ce, La, Th, B, Ba . the results is compared with limit of world standard (12). The higher value which refer to pollution in heavy metal are Cr, Cu, Ni, Zn, Zr, Cd due to Industrial activity and Hg higher concentration because of Pharmaceutical Industries and Medical Waste . The high concentration in V, Br, Mo, Se, As because of agriculture activity.
2. The enrichment factor are calculated for the purpose of calculating saturation coefficient and treatment, analysis and conversion of the values of raw concentrations and the creation of the local background of Iraq. The most of the results are less than five ,but few value are greater than five indicating the anthropogenic input of these elements in soil in Samarra City which are Co, Mo, U in S2 because of agriculture activity and using fertilizer. Mo ,Sn in S2 because of highly building activity. Cu, Mo, Zn in S5 Because industrial and motor oil spill. Uranium in S2,S4 and S11 because military activity.

3. Contamination factor is and the value of the pollutant load index was less than 4 that's mean sample are polluted medium to high.
4. The effect of swallowing soil on humans can make it clear from the highest pollution to the least polluted for adult Co>Mn>Cr>Ni>Cd>Cu>Hg>Ag>Zn>As>Se>Ce>Pb. for children Cr>Co>Mn> Ni>Cd>Cu>Hg>Ag>Zn>As>Se>Ce>Pb.
5. Hazard of dermal exposure of the soil from the highest to the lowest dangerous to health is describe as for adults Cu>Hg>Ce>Pb>Ce>Zn>Mo>Se>As>Cu>Ni , for children Cr>Hg>Ce>Co>As>Zn>As>Se>Mo>Pb>Cu
6. The risk of inhalation of soil can be determined from the top to the least dangerous to the health of adults and children as follows adults Mn>Cr>Co>Mn>Zn>As>Se>Ag>Cd>Ce>Hg>Pb.
7. Children Mn>Cr>Co>Mn>Zn>As>Se>Ag>Cd>Ce>Hg>Pb.

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