

Heavy Metals Contamination and Human Health Risk Assessment in Shallow Groundwater Wells in Qara-Hanjeer Sub-basin, NE Kirkuk -Iraq

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Abstract

Groundwater is one of the main sources for human consumption, and irrigation in arid and semi-arid rejoins in the world. Local peoples in the agricultural areas of Iraq generally consume shallow groundwater from farm wells. This study aims to evaluate health risk due to heavy metals contamination such as (Fe, Co, Zn, Ni, Mn, As, Cu, Cr, Mo and Pb) in groundwater from Qara-hanjeer sub-basin (NE Kirkuk-Iraq). The quantification of contamination index based on heavy metals; Cd, HPI and MI showed that anthropogenic activities have not modified the groundwater chemistry at least in a large scale. Health risk assessment model revealed that Hazard Quotient (HQ) values for both (HQ_{ing}), (HQ_{drm}) and HI for the heavy elements within water samples for dry and wet seasons were all significantly lower than (1) for the child and adults, suggesting no potential non-carcinogenic health risks via dermal exposure. However accessible concentrations of (Zn), (Mo) and (Pb) in some wells in the southern area of the study indicates that it is possible that over time and with increasing in concentrations of these elements in groundwater as a result of seepage of wastewater or sewage to the well, we have the environmental problems in the mentioned area.

Keywords: Health risk, Contamination, Groundwater, Heavy metals.

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تلوث المعادن الثقيلة وتقييم مخاطرتها على صحة الإنسان في آبار المياه الجوفية الضحلة في حوض قره هنجير الفرعي شمال شرق كركوك – العراق

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الملخص

تعتبر المياه الجوفية واحدة من اهم المصادر الرئيسية لشرب الانسان ولاغراض الري خاصة في المناطق الجافة وشبه الجافة من العالم. فالسكان المحليون في المناطق الزراعية من العراق يستهلكون كميات كبيرة من المياه الجوفية المستخرجة من الابار الضحلة المحفورة في حقولهم الزراعية.

يهدف البحث الحالي الى تقييم المخاطر الصحية بسبب تواجد المعادن الثقيلة التي تم رصدها في المياه الجوفية مثل (Fe, Co, Zn, Ni, Mn, As, Cu, Cr, Mo, and Pb)) في نماذج (6) محددة ومختارة ضمن حوض قرة-هنجير (شمال غرب كركوك-العراق). التقدير الكمي لحساب مؤشرات التلوث مثل (Cd, HPI an MI) تظهر بان الانشطة البشرية لم تؤثر على نطاق واسع على كيميائية المياه الجوفية في المنطقة وعلى الاقل في الوقت الحالي . وبينت قيم البشرية لم تؤثر على نطاق واسع على كيميائية المياه الجوفية في المنطقة وعلى الاقل في الوقت الحالي . وبينت قيم حصاب مؤشرات التلوث مثل (HQ) values for both (HQ_{ing}), (HQ_{drn}) البشرية لم تؤثر على نطاق واسع على كيميائية المياه الجوفية في المنطقة وعلى الاقل في الوقت الحالي . وبينت قيم حساب مخاطر التلوث ((HQ) values for both (HQ_{ing}), (HQ_{drn})) العناصر الثقيلة في عينات المياه الجوفية الموسمين الرطب والجاف بانها اقل من (1) للاطفال والبالغين مما يشير الى عدم وجود مخاطر صحية محتملة (مسرطنة او غير مسرطنة)سواء كان عن طريق التعرض للجلد او غيرها، مع ذلك فان الفحص الدوري للمياه ضروري نتيجة وجود زيادة في تراكيز بعض العناصر مثل (Zn, Mo, Pb) في بعض الابار الموجودة في جنوب منطقة الدراسة نتيجة ترشح مياه الفضلات والماحيان القل من (1) للاطفال والبالغين ما يشير الى عدم وجود مخاطر صحية محتملة (مسرطنة أو غير مسرطنة)سواء كان عن طريق التعرض للجلد او غيرها، مع ذلك فان الفحص الدوري للمياه ضروري نتيجة وجود زيادة في تراكيز بعض العناصر مثل (Zn, Mo, Pb) في بعض الابار الموجودة في جنوب منطقة الدراسة نتيجة ترشح المات الفصال الحاري اليها مما يشير الى مشاكل صحية في المنطقة. المادان الفصال الواحية ألمادن الفقيقة الدراسة نتيجة مرشح

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1. Introduction:

Groundwater all over the world is becoming a natural resource of strategic importance due to its limited availability, quality deterioration, increasing demand and limited replenishment. Hence, increased usage of such water for personal and agricultural needs makes protection of groundwater resources to be seen as possible solutions to mitigating water scarcity in arid and semi-arid regions. A vast literature gathered over many years from all over the world, especially for arid areas of the Middle East, cite the inorganic, organic and biological content and contaminants in freshwaters focused primarily on urban and agricultural areas [1]. To highlight some of the geomedical issues related to heavy metals effects in groundwater on human health, investigation of their accumulation and concentrations in various environmental sampling media which can directly threaten wellbeing of exposed inhabitants via ingestion and dermal absorption routes. In agricultural areas, increased heavy metal accumulation induced by application of inorganic fertilizers (commercial fertilizers) contributes to excessive leaching of these metals such as cadmium (Cd), Lead (Pb) and zinc (Zn) into soil and ground- water bodies [2]. There is undoubtedly a lack of knowledge regarding potential soil and groundwater contamination in less populated areas and small rural cities in Iraq, especially in areas of agriculture where the inhabitants who lives in usually consumes water from wells. Investigations have outlined the environmental contamination of the intensively agricultural soils and groundwater in Qara-Hanjeer town in NE of Kirkuk Municipality – Iraq and typical rural villages around where mostly farmers have their homes are located in their farms, they almost consume groundwater is unaware of the risk of contamination of this water by some heavy metals. Specific object of this study is to characterize the potential health risks of heavy metals in groundwater on both adults and children and evaluate the most significant contaminant and exposure pathway with regard to human health, in this regard different indices were used to assess heavy metal pollution of water resources including; Cd (Contamination Degree), HPI (Heavy Metal Pollution Index) and MI (Metal index), to evaluate CDI(Chronic Daily Intake Indices), HQ (Hazard Quotient) and HI (Hazard Index) and the non-carcinogenic and carcinogenic potential health risks of human exposure to multiple environmental contaminants via soil and drinking water pathways.

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2. Materials and Methods:

2.1 The Study Area:

The Qara-Hanjeer sub-basin is located 25Km northeast of Kirkuk governorate (N-Iraq), between latitudes $(35^{\circ}16'00" - 35^{\circ}31'15")$ North, and longitude $(44^{\circ}20'20" - 44^{\circ}47'09")$ East Fig. 1. Covering an area of 337 km², with a population of 5000 inhabitant's lives in 47 villages belonging to Qara- Henjeer city. Agriculture is the main source of the local peoples, and the main agronomic crops of cultivated land are vegetables and fruits especially black Fig from where the local name (Qara –hanjeer) was derived. The climate of this region is mostly semi-arid with annual rainfall of (302) mm year⁻¹ and evapotranspiration of (2974) mm year⁻¹, with a mean maximum temperature of 43.9 °C during July and by a mean minimum temperature of 4.9 °C during January [3]. The main observed structure in the area is Qarahanjeer syncline (asymmetrical, double plunging, long and broad syncline extends for 65 Km in NW-SE direction), it is bounded by Chamchamal anticline and by Kirkuk anticline to the northeast and southwest respectively [4].

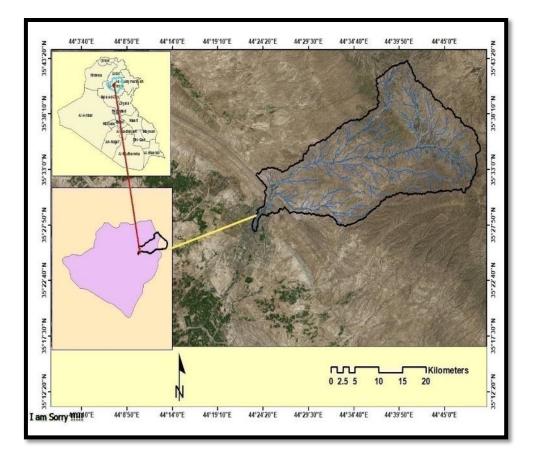


Fig. 1: The study area location.



2.2: Sampling and Analytical Methods:

A total of six water samples were collected from water wells in different villages distributed in the vicinity of the study area in two periods, the first was in October 2017 representing dry season and in April 2018 for the rainy season. For ground water sample collection, a (2L) Polyethylene sampling bottles were used, rinsed 3-4 times with the samples water which was to be collected, and acidified with diluted HNO₃. The PH, electrical conductivity (EC), and total dissolved solids (TDS) were measured in the field using portable multi-parameter analyzer model (TPS/90FL-T Field Lab Analyzer). The main cations and anions for all samples were analyzed according to the standard guidelines [5] in the laboratories of the General Company of Groundwater-Kirkuk, while for heavy metals analyses, six of these samples were selected and analyzed at the accredited ACME Analytical Laboratories of Vancouver- Canada by Inductively Coupled plasma spectrometry - mass spectrometry (ICP-MS).

3. Groundwater Quality:

All groundwater samples were analyzed for major ions and heavy metals, the results are tabulated in Tables 1, 2, and 3. The analysis results for all samples have normal contents of major ions which vary based on type of chemical content. The groundwater has average pH value of water (7.64) for dry season and (7.56) for wet season indicating low alkaline in nature. TDS value ranges between (215-559) mg 1^{-1} for dry season and (231-615) mg 1^{-1} for wet season, these values indicate the fresh nature of these groundwater, which is possibly attributed to the nature of the alluvial deposits in the area. Distribution of the groundwater samples in the Piper diagram Fig. 2, and 3 shows that these samples are characterized by the dominance CaHCO₃ type of Water, some samples fall in the field of mixed Ca-Mg-SO₄, and very few samples represent NaCl and mixed Ca-Na-HCO3 facies. The groundwater of the study area is used for irrigation and domestic purposes as most of the major ions have a low concentrations and they are within the permissible limits for drinking water standards [6].

				S	eason).					
Sample	As ppb	Co ppb	Cr ppb	Cu ppb	Fe ppb	Mn ppb	Ni ppb	Zn ppb	Mo ppb	Pb ppb
W1	0.5	0.11	2.6	1.7	152	2.49	0.8	27.3	1.4	0.5
W2	0.6	0.12	5	2	236	3.02	2.1	391.9	1.3	0.7
W3	0.9	0.31	8.3	2.8	190	3.69	1.5	13811	5.8	14.5
W4	0.6	0.02	8.7	1.4	109	1.08	0.8	27.2	1	0.4
W5	3.2	0.07	1.9	2.1	61	3.72	0.9	72.3	6.4	0.5
W6	0.6	0.09	9.9	1.8	114	2.86	1.1	67.6	1.2	1.1
Avg.	1.1	0.12	6.1	1.96	143.7	2.81	1.2	2399.6	2.9	2.9
WHO	10	50	50	2000	300	100	70	3000	6	10

Table 1: Concentration of heavy elements in the groundwater of the study area (for the dry

 Table 2: Concentrations of heavy elements in the groundwater of the study area (for the wet season).

Sampla	As	Co	Cr	Cu	Fe	Mn	Ni	Zn	Мо	Pb
Sample	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
W1	0.5	0.14	2.8	1.9	144	2.51	0.9	19.34	1.5	0.6
W2	0.6	0.12	5.7	2.1	228	3.08	2.2	401.43	1.5	0.9
W3	0.9	0.31	8.1	2.7	192	3.7	1.7	13954	5.7	14.6
W4	0.7	0.04	8.6	1.5	113	1.1	0.9	29.12	1.1	0.6
W5	3.2	0.08	2.1	2	72	3.78	1.1	77.2	6.3	0.6
W6	0.8	0.09	9.7	1.9	118	2.82	1.5	69.9	1.5	1
Avg.	1.11	0.13	6.16	2.016	144.5	2.83	1.38	2425.16	2.93	3.05
WHO	10	50	50	2000	300	100	70	3000	6	10

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		Dry	Season		Wet Season				
Sample NO.	рН	EC μS / cm	TDS ppm	Water Level(m)	рН	EC μS / cm	TDS ppm	Water Level(m)	
W1	7.05	674	404	96	7.12	698	489	78.5	
W2	7.42	620	372	102	7.34	381	229	89	
W3	7.78	755	528	56.5	7.45	779	545	55.5	
W4	7.58	538	323	10	7.73	574	329	9.5	
W5	8.3	789	559	40.5	7.98	879	615	29	
W6	7.73	359	215	93	7.76	361	231	91	
Average	7.64	622.5	400.1	66.3	7.56	524.5	406.3	58.75	

Table 3: shows the mean and average value (Ph, EC, Water levels) of dry and wet Season

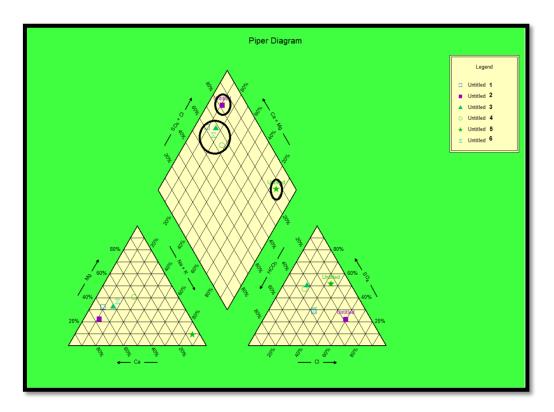


Fig. 2: The piper diagram of water samples in study area (Dry Season).

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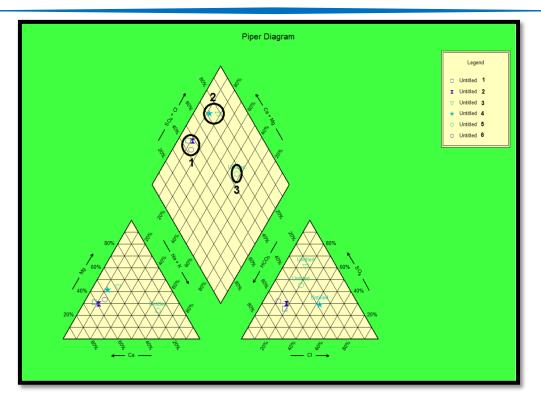


Fig. 3: The piper diagram of water samples in Study area (Wet Season).

Heavy metals analysis in the studied well shows that their concentrations, however they did not exceed the permissible limit of drinking water according to WHO. 2017, therefore one should avoid the use of polluted groundwater and must ensure that the water used is not polluted and subject to repeated testing and analyses [7].

3.1: Contamination Degree (Cd):

This index is used to determine the degree of contamination of groundwater samples with heavy metals [8]. This index shows the suitability of drinking water samples for domestic consumption. The degree of contamination is calculated by the following equation (1) [9].

Where: cf_i can be obtained by the equation below:

$$Cd = \sum_{i=0}^{n} cf_i \tag{1}$$

$$cf_i = \frac{CA}{CN} - 1 \tag{2}$$

Where: cf_i: Contamination factor for the ith parameter

CA: Measured value for the ith parameter,



CN: Standard allowed value for the ith parameter.

In this study, all the heavy metals measured and researched by plasma are used and compared with other index. Although concentrations of heavy metals are low in groundwater and below the permissible limit (WHO, 2017), which do not pose a threat, but it is necessary to calculate water quality indicators, to determine the water quality according to the pollution index. The values are classified into three groups, which include low contamination (Cd<1), moderate contamination (1<Cd<3) and high contamination (Cd>3). In this study ten heavy metals were measured and the result was (Zn > Fe > Cr > Pb > Mo > Mn > Cu > Ni > As > Co) which shows that the groundwater of the study area is not polluted for dry and wet seasons as the results are less than (1) Tables (4,5) .

Sample	As	Со	Cr	Cu	Fe	Mn	Ni	Zn	Mo	Pb	Cd=∑Cfi
W1	-0.95	-0.99	-0.94	-0.99	-0.49	-0.97	-0.98	-0.99	-0.76	-0.95	-9.059
W2	-0.94	-0.99	-0.9	-0.99	-0.21	-0.96	-0.97	-0.86	-0.78	-0.93	-8.572
W3	-0.91	-0.99	-0.83	-0.99	-0.36	-0.96	-0.97	3.60	-0.03	0.45	-2.024
W4	-0.94	-0.99	-0.82	-0.99	-0.63	-0.98	-0.98	-0.99	-0.83	-0.96	-9.163
W5	-0.68	-0.99	-0.96	-0.99	-0.79	-0.96	-0.98	-0.97	0.06	-0.95	-8.245
W6	-0.94	-0.99	-0.80	-0.99	-0.62	-0.97	-0.98	-0.97	-0.8	-0.89	-8.982

Table 4: The value of (C_{fi}) and contamination degree (Cd) (for the dry season).

Table 5: The value of (C_{fi}) and contamination degree (Cd) (for the wet season).

Sample	As	Со	Cr	Cu	Fe	Mn	Ni	Zn	Мо	pb	Cd=∑Cfi
W1	-0.95	-0.99	-0.94	-0.99	-0.52	-0.97	-0.98	-0.99	-0.75	-0.94	-9.055
W2	-0.94	-0.99	-0.88	-0.99	-0.24	-0.96	-0.96	-0.86	-0.75	-0.91	-8.526
W3	-0.91	-0.99	-0.83	-0.99	-0.36	-0.96	-0.97	3.65	-0.05	0.46	-1.97
W4	-0.93	-0.99	-0.82	-0.99	-0.62	-0.98	-0.98	-0.99	-0.81	-0.94	-9.102
W5	-0.68	-0.99	-0.95	-0.99	-0.76	-0.96	-0.98	-0.97	0.05	-0.94	-8.206
W6	-0.92	-0.99	-0.80	-0.99	-0.60	-0.97	-0.97	-0.97	-0.75	-0.90	-8.906

3.2: Heavy Metal Pollution Index (HPI):

The coefficient of (HPI) measures the distribution of heavy elements in water, evaluates the content and the degree of groundwater contamination by these elements, and explains the



difference in concentrations of elements and their impact on water quality and the critical value is 100 [10]. This parameter is calculated according to the following equations [11]:

$$W_i = \frac{1}{s_i} \tag{3}$$

W_i: The relative weight of element i coefficients, ranged between (0-1), Table 6.

 s_i : The maximum allowable value of elements (i) in (ppb), based on (WHO 2017) .

$$Q_i = \sum_{i=1}^n \left(\frac{M_i - I_i}{S_i - I_i} \right) * 100$$
(4)

 M_i : Measured value for the i^{th} parameter,

 $I_i\!\!:\!$ Ideal value for ith parameter and is equal to zero for the studied elements [12] .

Q_i: Sub index calculated for the ith parameter,

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}$$
(5)

Table 6: Standard values S_i and W_i used in the calculation (HPI).

Parameter	S _i = according to	$Wi = 1/S_i$
	WHO(6)	
As	10	0.1
Со	50	0.02
Cr	50	0.02
Cu	2000	0.0005
Fe	300	0.0033
Mn	100	0.01
Ni	70	0.0142
Мо	6	0.166
Pb	10	0.1
Zn	300	0.1
Total		∑ 0.43445

Table 7 present that all samples in the study area for dry and wet seasons did not exceeds the critical values of (HPI) values, and the samples (according to a classification by [13]



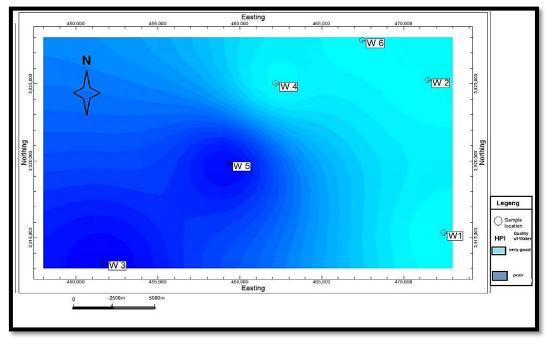
Table 8, they are classified as good quality of water except for sample (W3) which shows poor quality water, as shown in Fig. 4.

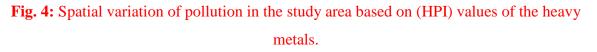
Dry S	eason	Wet Season				
Sample	HPI	Sample	HPI			
W1	11.712	W1	12.823			
W2	12.064	W2	14.308			
W3	73.414	W3	73.763			
W4	9.014	W4	11.150			
W5	49.570	W5	49.391			
W6	11.975	W6	15.035			

Table 7: (HPI) Values for water samples of the study area for dry and wet seasons.

Table 8: (HPI) Classification of water pollution levels by (Majhi and Keshari, 2016) [13].

HPI	QUALITY OF WATER
0-25	Very good
26-50	Good
51-75	Poor
Above 75	Very poor (unsuitable for drinking)







This index gives the state of water pollution based on its content of heavy metals [14].

(6)

$$MI = \sum_{i=1}^{n} \frac{C_i}{(Mac)_i}$$

C_i: Measured value for the ith parameter,

(Mac)_i: Standard value for ith parameter, by ((Brraich & Jangu,2015) [8],table(9)

Element	(Mac)i
As	50
Со	50
Cr	50
Cu	1000
Fe	200
Mn	50
Ni	20
Zn	5000
Мо	60
Pb	1.5

Table 9: shows values (Mac)i by (Brraich & Jangu,2015).

MI water quality classification according to [15] as presented in table (10) shows that the samples are slightly to moderately affected by pollution based on their content of heavy metals indicating anthropogenic activities to be source of pollution within the area table (11), and they are on the threshold of danger of drinking (MI = 1), except the sample (W3) which shows a serious pollution by heavy metal and it is non-potable for drinking purposes (MI> 1).

Table 10: (MI) Water quality classify according to (Siegel, 2002)[15].

MI	Characteristic
< 0.3	Very pure
0.3-1.0	Pure
1.0-2.0	Slightly affected
2.0-4.0	Moderately affected
4.0-6.0	Strongly affected
> 6.0	Seriously affected



Table 11: Results of (MI) values for the study area for dry and wet seasons.

Dr	y Season	Wet Season				
Sample	MI	Sample	MI			
W1	1.289	W1	1.317			
W2	2.039	W2	2.147			
W3	13.865	W3	13.956			
W4	1.091	W4	1.239			
W5	1.037	W5	1.109			
W6	1.672	W6	1.637			

4. Health Risk Assessment Model:

Humans exposed to heavy metals through different pathways, such as by inhalation by mouth and nose or by most common methods through direct ingestion and skin absorption by skin exposure to heavy metals. The risk assessment method is used to assess the actual or potential adverse effects of pollutants on humans, animals and plants living in an area and focus on causes of these pollutants [1]. To evaluate the health hazard of the heavy elements in the groundwater of the study area, the following indices has been calculated:

4.1: Chronic Daily Intake Indices (CDI):

The chronic daily dose of heavy elements in water is estimated by the two tracks, namely, ingestion [16] and skin contact [17]. The health risks of non-carcinogenic and carcinogenic effects were evaluated using mathematical expressions achieved from the USEPA Risk Assessment Guidance for Superfund methodology. The dose received through the individual pathway considered was determined using Equations (7) and (8) from the US Environmental Protection Agency [18]. See Table (12).

$$CDI_{ing} = \frac{CW \times IR \times F \times * D \times f1}{(BW \times AT)}$$
(7)

$$CDI_{drm} = \frac{CW \times A \times KP \times EF \times D \times ET \times cf_1 \times cf_2}{(BW \times AT)}$$
(8)

Where: (CDI_{ing}) and (CDI_{drm}) are the average daily dose (mg kg⁻¹ day⁻¹) by ingestion, and dermal absorption respectively. CW is concentration of the estimated metal in water (mg l⁻¹); IR is the intake rate (L day⁻¹); EF is exposure frequency (days year⁻¹); ED is exposure duration (year); BW = body weight (kg); AT is averaging time (days), and CF₁ is mass



conversion factor from μ g to mg (0.001); CF₂ is unit conversion factor (L/1,000 cm³) (0.001); SA is drinking water exposed skin area(cm2), Kp is dermal permeability coefficient (cm hr⁻¹), ET is exposure time during bathing and shower (min day⁻¹), EF is exposure frequency (days year⁻¹).

Table 12: shows the variables used in the assessment of the health risk in the water of the study area for both children and adults according to (USEPA, 2012; Caylak, 2012) [18][19].

Symbol	Unit	Adult	Child
Concentration of element (C _{Water})	ppb	-	-
average daily intake of heavy metals	Mg.kg ⁻¹ .day	-	-
ingested from water (CDI _{ing})			
exposure dose via dermal contact (CDI _{dermal})	Mg. kg ⁻¹ .day	-	-
Ingestion Rate (IR _{ing})	Day ⁻¹	2	1
Body weight (BW)	kg	70	15
Conversion Factor (CF)	cm ⁻³	10-3	10-3
Skin area available for soil contact (SA)	cm ²	18000	6600
Exposure Time (ET)	h.day ⁻¹	0.58	1
Exposure frequency (EF)	Days.year ⁻¹	350	350
Exposure duration (ED)	years	30	6
Average time (AT) - Non carcinogenic	days	ED	0× 365
Average time (AT) – carcinogenic		70	× 365
Dermal Permeability Coefficient (K _p)	$(1 \text{ x} 10^{-3})$ for (A	s, Cu, Fe,	Mn,Mo),
	Cr (2×10^{-3}) , N	i (2×10^{-4}) ,	
	Pb (1×10^{-4}) , Zi	n (6×10 ⁻⁴)	

4.2: Hazard Quotient (HQ) and Hazard Index (HI) Indices:

Health Risk Index (HI) is used to assess the probability of non-carcinogenic effects of heavy metals. HI represents the total risk of the two cycles (HQ) [19]. If both (HQ) and (HI) are exceeded, they indicate that there are carcinogenic effects of the elements from the two main pathways (ingestion and skin contact), which may have adverse effects on human health [20]. The HQ (ingestion and dermal contact) and HI for non-carcinogenic risk of some trace metals in drinking water can be calculated using Equations. (9), (10), and (11).

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 $HQ_{ing} = \frac{CDI_{ing}}{Rf_{ing}}$

$$HQ_{drm} = \frac{CDI_{drm}}{Rf_{drm}}$$
(10)

$$HI = HQ_{ing} + HQ_{drm}$$

(11)

(9)

Where: (HQ_{ing}) is the risk product of the ingestion pathway (HQ_{dermal}), the risk factor of the skin contact pathway; (RfD_{ing}) is the oral reference dose measured in (μ g.kg⁻¹.day⁻¹); (RfD_{drm}) is the skin reference dose measured in (μ g.kg⁻¹.day⁻¹) [20]. Values of HQ_{ing} and HQ_{drm} for the water samples for both seasons are summarized in Tables 13, 14.The results for groundwater within study area reveals that the values of (HQ_{ing}) and (HQ_{drm}) of the heavy elements (As, Co, Cr, Cu, Fe, Mn, Ni, Zn, Mo, Pb) within water samples for dry and wet seasons were all significantly lower than (1) for the child and adults, suggesting no potential non-carcinogenic health risks via dermal exposure. Also; the HI values for children for all elements were less than (1) suggesting no health hazards via ingestion and dermal exposure.

Table 13: Values of Chronic Daily Intake (CDI) and Hazard quotient (HQ) and Hazard Index

(HI) of the main	groundwater	nathways	in the	study area	for the dry season
(III) Of the main	groundwater	painways	In the	study area	101 the try season

Metal	Avg.	Age	Ingestion			Dermal			HI=∑HQ	
S	Avg.	Age	CDI _{ing}	RfD _{ing}	HQing	CDI _{derm}	RfD _{derm}	HQ _{derm}	m−∠ng	
As	1.066	Adult	2.92×10 ⁻⁵	0.0003	0.097	1.5×10 ⁻⁷	0.0003	5.08×10 ⁻⁴	0.09	
115	1.000	Child	6.81×10 ⁻⁵	0.0003	0.227	4.5×10 ⁻⁷	0.0003	1.5×10 ⁻³	0.22	
Со	0.12	Adult	3.28×10 ⁻⁶	0.0003	0.01	1.7×10 ⁻⁸	0.0003	5.7×10 ⁵	0.01	
CO	0.12	Child	7.6×10 ⁻⁶	0.0003	0.025	5×10 ⁻⁸	0.0003	1.6×10 ⁻⁴	0.02	
Cr	6.066	6.066	Adult	1.66×10 ⁻⁴	0.003	0.055	1.7×10 ⁻⁶	0.000075	2.3×10 ⁻²	0.07
0.00	0.000	Child	3.8×10 ⁻⁴	0.003	0.129	5.1×10 ⁻⁶	0.000075	6.8×10 ⁻²	0.19	
Cu	Cu 1.966	Adult	5.38×10 ⁻⁵	0.04	0.001	2.8×10 ⁻⁷	0.04	7.03×10 ⁻⁶	0.001	
Cu 1.9	1.900	Child	1.25×10 ⁻⁶	0.04	0.003	8.2×10 ⁻⁷	0.04	2.07×10 ⁻⁵	0.003	
Fo	Fe 143.66	Adult	3.93×10 ⁻³	0.3	0.013	2×10 ⁻⁵	0.14	1.4×10 ⁻⁴	0.01	
re		Child	9.18×10 ⁻³	0.3	0.03	6×10 ⁻⁵	0.14	4.3×10 ⁻⁴	0.03	
Mn	Mn 2.81	Adult	7.69×10 ⁻⁵	0.14	0.001	4×10 ⁻⁷	0.00183	2.2×10 ⁻⁴	0.0007	
IVIII		Child	1.79×10 ⁻⁴	0.14	0.001	1.1×10 ⁻⁶	0.00183	6.4×10 ⁻⁴	0.001	
Ni	1.2	Adult	3.28×10 ⁻⁵	0.02	0.001	3.4×10 ⁻⁸	0.0008	4.2×10 ⁻⁵	0.001	
111	1.2	Child	7.67×10 ⁻⁵	0.02	0.003	1×10 ⁻⁷	0.0008	1.2×10 ⁻⁴	0.003	



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		Adult	7.8×10 ⁻⁵	0.005	0.015	4.07×10 ⁻⁷	0.0019	2.1×10 ⁻⁴	0.015
Mo 2.	2.85								
		Child	1.82×10^{-4}	0.005	0.036	1.2×10^{-6}	0.0019	6.3×10 ⁻⁴	0.037
		Adult	8.08×10 ⁻⁵	0.0035	0.023	4.21×10 ⁻⁸	0.0035	1.2×10 ⁻⁵	0.023
pb 2.95					7		5		
		Child	1.88×10^{-4}	0.0035	0.053	1.24×10 ⁻⁷	0.0035	3.5×10 ⁻⁵	0.053
Zn 2	2399.5	Adult	6.57×10 ⁻²	0.3	0.219	2×10 ⁻⁴	0.3	6.8×10 ⁻⁴	0.21
		Child	0.153	0.3	0.511	6×10 ⁻⁴	0.3	2.02×10 ⁻³	0.51
		Ciniu	0.155	0.5	0.311	0~10	0.5	2.02×10	0.51

Table 14: Values of Chronic Daily Intake (CDI) and Hazard quotient (HQ) and Hazard Index(HI) of the main groundwater pathways in the study area for the wet season

Metals	Avg.	Age	Ingestion			Dermal			HI=∑HQ
			CDI _{ing}	RfD _{ing}	HQ _{ing}	CDI _{derm}	RfD _{derm}	HQ _{derm}	m-∠nq
As	1.116	Adult	3.05×10 ⁻⁵	0.0003	0.097	1.59×10 ⁻⁷	0.0003	5.32×10 ⁻⁴	0.102
115	1.110	Child	7.13×10 ⁻⁵	0.0003	0.227	4.71×10 ⁻⁷	0.0003	1.5×10 ⁻³	0.239
Со	0.13	Adult	3.5×10 ⁻⁶	0.0003	0.01	1.85×10 ⁻⁸	0.0003	6.1×10 ⁵	0.011
00	0.12	Child	8.3×10 ⁻⁶	0.0003	0.025	5.4×10 ⁻⁸	0.0003	1.8×10 ⁻⁴	0.027
Cr	6.166	Adult	1.6×10 ⁻⁴	0.003	0.055	1.76×10 ⁻⁶	0.000075	2.3×10 ⁻²	0.079
Cr	0.100	Child	3.9×10 ⁻⁴	0.003	0.129	5.2×10 ⁻⁶	0.000075	6.93×10 ⁻²	0.200
Cu	2.016	Adult	5.52×10 ⁻⁵	0.04	0.001	2.88×10 ⁻⁷	0.04	7.2×10 ⁻⁶	0.001
Cu	2.010	Child	1.28×10 ⁻⁶	0.04	0.003	8.5×10 ⁻⁷	0.04	2.12×10 ⁻⁵	0.003
Fe	144.5	Adult	3.95×10 ⁻³	0.3	0.013	2×10 ⁻⁵	0.14	1.48×10 ⁻⁴	0.013
10	111.5	Child	9.23×10 ⁻³	0.3	0.03	6×10 ⁻⁵	0.14	4.35×10 ⁻⁴	0.031
Mn	2.831	Adult	7.75×10 ⁻⁵	0.14	0.001	4×10 ⁻⁷	0.00183	2.21×10 ⁻⁴	0.0007
	2.001	Child	1.81×10 ⁻⁴	0.14	0.001	1.19×10 ⁻⁶	0.00183	6.53×10 ⁻⁴	0.0019
Ni	1.383	Adult	3.79×10 ⁻⁵	0.02	0.001	3.9×10 ⁻⁸	0.0008	4.9×10 ⁻⁵	0.0019
111	1.505	Child	8.84×10 ⁻⁵	0.02	0.003	1.1×10 ⁻⁷	0.0008	1.4×10 ⁻⁴	0.004
Mn	2.933	Adult	8.08×10 ⁻⁵	0.005	0.016	4.18×10 ⁻⁷	0.0019	2.21×10 ⁻⁴	0.016
1411	2.755	Child	1.87×10^{-4}	0.005	0.037	1.23×10 ⁻⁶	0.0019	6.51×10 ⁻⁴	0.038
pb	3.05	Adult	8.35×10 ⁻⁵	0.0035	0.023	4.36×10 ⁻⁸	0.0035	1.2×10 ⁻⁵	0.023
իս		Child	1.94×10 ⁻⁴	0.0035	0.055	1.28×10 ⁻⁷	0.005	3.67×10 ⁻⁵	0.055
Zn	2425.1	Adult	6.64×10 ⁻²	0.3	0.219	2×10 ⁻⁴	0.3	6.94×10 ⁴	0.222
LII		Child	0.155	0.3	0.511	6.1×10 ⁻⁴	0.3	2.04×10 ⁻³	0.518

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5. Conclusion:

In order to assess the impact of heavy metals on groundwater resources of Qara-hanjeer sub basin. The chemical quality and the sources of the heavy metals (As, Co, Cr, Cu, Fe, Mn, Ni, Zn, Mo and Pb) in (6) shallow water wells have been investigated in this work. Estimated pollution indexes based on reference back groundwater coupled to Contamination Degree, Heavy Metal Pollution Index (HPI) and Metal index calculations revealed that anthropogenic activities have not modified the water chemistry at least in a large scale. A risk assessment model adopted by the USEPA demonstrated that although, the concentrations of few contaminants do not exceed drinking water standard for the current time yet the consumption of groundwater containing appreciable amounts of heavy metals may exacerbate the health status of local people. The non-carcinogenic effects of heavy metals for groundwater within study area reveals that the calculated values of (HQ_{ing}), (HQ_{drm}), and HI for the heavy elements As, Co, Cr, Cu, Fe, Mn, Ni, Zn, Mo, Pb within water samples for dry and wet seasons were all significantly lower than (1) for the child and adults, suggesting no potential non-carcinogenic health risks via dermal exposure. However accessible concentrations of (Zn) in well No.3, (Mo) in well No. 5 and (Pb) in well No.(W3) samples showed that their effects are not of particular concern but may act as a trigger for future health effects on children and adults specially with continuous adding of these element through anthropogenic activities specially from seepage of wastewater or sewage from the Banja Ali residential complexes nearby this well.

References:

- [1] E. Kelepertzis, "Investigating the sources and potential health risks of environmental contaminants in the soils and drinking waters from the rural clusters in Thiva area", Department of Geology and Geoenvironment, University of Athens, Greece, 258 (2014).
- [2] R. K. Rattan, S. P. Datta, P.K. Chhonkar, K. Suribabu & A.K. Singh, "long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops, and groundwater- a case study". Agriculture Ecosystem and Environment, 109, 310 (2005).

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- [3] I.M.O.S. Iraqi Meteorological Organization and Seismology, "*Technical report*", Baghdad, Iraq (2017).
- [4] V. Ditmar, J. Afonasiev, B. Brioussov, and S. Shaban, "Geological Conditions and Hydrocarbon prospects of the republic of Iraq", Vol.1, northern and central parts. Manuscript report, INOC Lib., Baghdad, Iraq (1971).
- [5] APHA (American Public Health Association); "Standard methods for examination of water and waste water", 20th Ed., Washington DC, USA (2003).
- [6] WHO (World Health Organization). "Guidelines for Drinking-water Quality. 4th Edition, incorporating the first addendum. Brazil", World Health Organization, 518p (2017).
- [7] N.S. Soran and M. Hoshmend., "Impact of Leachate on Soil and Groundwater Quality in Vicinity of Landfill Sites of Kirkuk City (Kirkuk-Iraq)", International Journal of Current Research and Academic Review.4 (8), 1 (2016).
- [8] S. Onkar, Brraich and Sulochana. Jangu., "Evaluation of Water Quality Pollution Indices for Heavy Metal Contamination Monitoring in the Water of Harike Wetland (Ramsor sit)", Indian International Journal of Scientific and Research Publications, 5(2), (2015).
- [9] H.M.Mona, R.G. Lashkaripour., .D. Pooria, "Assessing the Effect of Heavy Metal Concentrations. (Fe, Pb, Zn, Ni, Cd, As, Cu,Cr) on the Quality of Adjacent Groundwater Resources of Khorasan Steel Complex". International Journal of Plant, Animal and Environmental Sciences, 511 (2014).
- [10] B. Prasad, K.K. Mondal, "The impact of filling an abandoned opencast mine with fly ash on ground water quality": A case study. Mine Water Environment, 27(1), 40 (2008).
- [11] S. V.Mohan, P. Nithila and S. J. Reddy, "*Estimation of heavy metal in drinking water and development of heavy metal pollution index*", J. Environ. Sci. Health A., 31(2), 283 (1996).

Web Site: www.uokirkuk.edu.iq/kujss E-mail: kujss@uokirkuk.edu.iq, kujss.journal@gmail.com



- [12] O.T. Dede, "Application of the heavy metal pollution Index for surface waters": A Case study for Camlidere, Hacettepe J. Biol. & Chem., 44(4), 323 (2016).
- [13] M. Allian, and K.B. Subhari, "Application of HPI (Heavy Metal Pollution Index) and Correlation Coefficient For The Assessment Of Ground Water Quality Near Ash Ponds Of Thermal Power Plants", (2016).
- [14] G. Tamasi, , & R. Cini, ," Heavy metals in drinking waters from Mount Amiata (Tuscany, Italy) Possible risks from arsenic for public health in the province of Siena, Elsevier, Science of The Total Environment", 327(1), 41 (2004).
- [15] F. R. Siegel, "Environmental geochemistry of potentially toxic metals. Springer, Berlin". (2002).
- [16] S. Chowdhury, and P. Champagne, "Risk from exposure to trihalomethanes during shower Probabilistic assessment add control", Science of The Total Environment. Elsevier pub., 407(5), 1570 (2009).
- [17] USA.EPA; "Ieubk Model Mass Fraction of Soil in Indoor Dust (MSD) Variable, Office of Solid Waste and Emergency Response, Washington, DC", 7 (1998).
- [18] USEPA (*US Environmental Protection Agency*). Ground water and drinking water. http://www.water.epa.gov/drink/index.cfm. Accessed 01/15/2011 (2012).
- [19] C.,Emrah. "Health risk assessment for Trace metals, polycyclic aromatic hydrocarbons and trihalomethanes in drinking water pf cankiri,Turkry", E-journal of Chemistry, 9(4),1976 (2012).
- [20] U.S. Environmental Protection Agency (U.S.EPA); "Risk Assessment Guidance for Superfund", Volume I, Washington, D.C, 3 (2004).