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

Soran N. Sadeq 1, Refan S. AbdulRahman2

1, 2 Department of Applied Geology, College of Science, Kirkuk University, Kirkuk, Iraq.

1soran_alsaraf@yahoo.com, 2Revan.shehab94@gmail.com

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_wg), (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.

DOI: http://doi.org/10.32894/kujss.2019.14.4.3
تلوث المعادن الثقيلة وتقييم مخاطرتها على صحة الإنسان في أبار المياه الجوفية الضحلة في حوض قره هنجير الفرعي شمال شرق كركوك – العراق

سهران نياد صادق، ريفان شياب عبجالرحسن

الملخص

تعتبر المياه الجوفية واحدة من أهم المصادر الرئيسية لشرب الإنسان ولاغراض الزراعة خاصة في المناطق الجافة وشبه الجافة من العالم. فالسكان المحليون في المناطق الزراعية من العراق يستهلكون كميات كبيرة من المياه الجوفية المستخرجة من الأبار الضحلة المحورة في حقولهم الزراعية.

يهدف البحث الحالي إلى تقييم المخاطر الصحية بسبب تواجد المعادن الثقيلة التي تم رصدتها في المياه الجوفية مثل معدن غرب كركوك– العراق، التقدير الكمي لحساس مؤشرات التلوث مثال (Cd, HPI an MI) وحماية البيئة لم تؤثر على نطاق واسع على كيميائية المياه الجوفية في المنطقة وعلى الأقل في الوقت الحالي. وبسبب قيم حساب مخاطر التلوث (HQ) للعناصر الثقيلة في عينات المياه الجوفية

والمؤسسات والجافات والرياح والبيئة قليلة من (1) للزالل والبالغين وما يشير إلى عدم وجود مخاطر صحية محتملة (سامة) أو غير سامة (سواء كان عن طريق التعرض الجيد أو غيرها، مع ذلك فإن الفحص الدوري للمياه ضروري نتيجة وجود

زيادة في تركيز بعض العناصر مثل (Zn, Mo, Pb) في بعض الأبار الموجودة في جنوب منطقة الدراسة نتيجة ترشح مياه الفضلات والمجاري إليها مما يشير إلى أنه مع مرور الزمن قد تكون هناك مشاكل صحية في المنطقة.

الكلمات الدالة: المخاطر الصحية، التلوث، مياه الجوفية، المعادن الثقيلة.

DOI: http://doi.org/10.32894/kujss.2019.14.4.3

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

28
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.
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°16'00" – 35°31'15") North, and longitude (44°20'20" – 44°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 Qara-hanjeer 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 HNO$_3$. 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 l$^{-1}$ for dry season and (231-615) mg l$^{-1}$ 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 CaHCO$_3$ type of Water, some samples fall in the field of mixed Ca-Mg-SO$_4$, 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].
Table 1: Concentration of heavy elements in the groundwater of the study area (for the dry season).

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

| Sample | As ppb | Co ppb | Cr ppb | Cu ppb | Fe ppb | Mn ppb | Ni ppb | Zn ppb | Mo ppb | Pb ppb |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| W1     | 0.5    | 0.14   | 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     |
Table 3: shows the mean and average value (Ph, EC, Water levels) of dry and wet Season

| Sample NO. | pH  | EC  μS/cm | TDS ppm | Water Level(m) | pH  | 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         |

Fig. 2: The piper diagram of water samples in study area (Dry 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: \( c_i \) can be obtained by the equation below:

\[
Cd = \sum_{i=0}^{n} c_i \\
\]

\[
c_i = \frac{CA}{CN} - 1
\]

Where: \( c_i \): Contamination factor for the \( i^{th} \) parameter
CA: Measured value for the \( i^{th} \) 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) Table 4.

Table 4: The value of (Cfi) and contamination degree (Cd) (for the dry season).

| Sample | As   | Co   | Cr   | Cu   | Fe   | Mn   | Ni   | Zn   | Mo   | Pb   | Cd=ΣCfi |
|--------|------|------|------|------|------|------|------|------|------|------|---------|
| 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 5: The value of (Cfi) and contamination degree (Cd) (for the wet season).

| Sample | As   | Co   | Cr   | Cu   | Fe   | Mn   | Ni   | Zn   | Mo   | Pb   | Cd=ΣCfi |
|--------|------|------|------|------|------|------|------|------|------|------|---------|
| 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| -8.26    |
| 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]:

\[ W_i = \frac{1}{s_i} \]  \hspace{1cm} (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).

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

\( M_i \): Measured value for the i\textsuperscript{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 i\textsuperscript{th} parameter,

\[ HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \]  \hspace{1cm} (5)

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

| Parameter | \( S_i = \) according to WHO(6) | \( W_i = 1/S_i \) |
|-----------|----------------|--------------------|
| As        | 10             | 0.1                |
| Co        | 50             | 0.02               |
| Cr        | 50             | 0.02               |
| Cu        | 2000           | 0.0005             |
| Fe        | 300            | 0.0033             |
| Mn        | 100            | 0.01               |
| Ni        | 70             | 0.0142             |
| Mo        | 6              | 0.166              |
| Pb        | 10             | 0.1                |
| Zn        | 300            | 0.1                |
| **Total** |                | \( \Sigma 0.43445 \) |

**Table 7** present that all samples in the study area for dry and wet seasons did not exceed 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.

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

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

**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) |

**Fig. 4:** Spatial variation of pollution in the study area based on (HPI) values of the heavy metals.
This index gives the state of water pollution based on its content of heavy metals [14].

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

(6)

\( C_i \): Measured value for the \( i^{th} \) parameter,

\( (\text{Mac})_i \): Standard value for \( i^{th} \) parameter, by ((Brraich & Jangu, 2015) [8], table (9)

Table 9: shows values \((\text{Mac})_i\) by (Brraich & Jangu, 2015).

| Element | \((\text{Mac})_i\) |
|---------|------------------|
| As      | 50               |
| Co      | 50               |
| Cr      | 50               |
| Cu      | 1000             |
| Fe      | 200              |
| Mn      | 50               |
| Ni      | 20               |
| Zn      | 5000             |
| Mo      | 60               |
| Pb      | 1.5              |

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      |
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).

\[
\text{CDI}_{\text{ing}} = \frac{\text{CW} \times \text{IR} \times \text{EF} \times \text{ED}}{(\text{BW} \times \text{AT})} \tag{7}
\]

\[
\text{CDI}_{\text{drm}} = \frac{\text{CW} \times \text{IR} \times \text{EF} \times \text{ED} \times \text{ET} \times \text{CF}_1 \times \text{CF}_2}{(\text{BW} \times \text{AT})} \tag{8}
\]

Where: \((\text{CDI}_{\text{ing}})\) and \((\text{CDI}_{\text{drm}})\) are the average daily dose (mg kg\(^{-1}\) day\(^{-1}\)) by ingestion, and dermal absorption respectively. \(\text{CW}\) is concentration of the estimated metal in water (mg l\(^{-1}\)) ; \(\text{IR}\) is the intake rate (L day\(^{-1}\)) ; \(\text{EF}\) is exposure frequency (days year\(^{-1}\)) ; \(\text{ED}\) is exposure duration (year) ; \(\text{BW} = \text{body weight (kg)}\); \(\text{AT} = \text{averaging time (days)}\), and \(\text{CF}_1\) is mass
conversion factor from μg 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 ingested from water (CDI ing)     | Mg.kg⁻¹.day                 | -     | -     |
| 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)                              | cm²                         | 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 × 365 |
| Average time (AT) – carcinogenic                                        | days                        | 70 × 365 |
| Dermal Permeability Coefficient (Kp)                                    | (1 x 10⁻⁴) for (As, Cu, Fe, Mn, Mo), Cr (2 x 10⁻³), Ni (2 x 10⁻⁴), Pb (1 x 10⁻⁴), Zn (6 x 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).
Metal elements were less than non-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 pathways in the study area for the dry season.

| Metal | Avg. | Age   | Ingestion | Dermal | HI=∑HQ |
|-------|------|-------|-----------|--------|--------|
|       |      |       | CDI<sub>ing</sub> | RfD<sub>ing</sub> | HQ<sub>ing</sub> | CDI<sub>derm</sub> | RfD<sub>derm</sub> | HQ<sub>derm</sub> |
| As    | 1.066| Adult | 2.92×10<sup>-7</sup> | 0.0003 | 0.097 | 1.5×10<sup>-7</sup> | 0.0003 | 5.0×10<sup>-4</sup> | 0.09 |
|       |      | Child | 6.81×10<sup>-8</sup> | 0.0003 | 0.227 | 4.5×10<sup>-7</sup> | 0.0003 | 1.5×10<sup>-4</sup> | 0.22 |
| Co    | 0.12 | Adult | 3.28×10<sup>-8</sup> | 0.0003 | 0.01 | 1.7×10<sup>-8</sup> | 0.0003 | 5.7×10<sup>-4</sup> | 0.01 |
|       |      | Child | 7.6×10<sup>-8</sup> | 0.0003 | 0.025 | 5×10<sup>-8</sup> | 0.0003 | 1.6×10<sup>-4</sup> | 0.02 |
| Cr    | 6.066| Adult | 1.66×10<sup>-7</sup> | 0.003 | 0.055 | 1.7×10<sup>-8</sup> | 0.000075 | 2.3×10<sup>-4</sup> | 0.07 |
|       |      | Child | 3.8×10<sup>-7</sup> | 0.003 | 0.129 | 5.1×10<sup>-6</sup> | 0.000075 | 6.8×10<sup>-2</sup> | 0.19 |
| Cu    | 1.966| Adult | 5.38×10<sup>-8</sup> | 0.04 | 0.001 | 2.8×10<sup>-7</sup> | 0.04 | 7.03×10<sup>-8</sup> | 0.001 |
|       |      | Child | 1.25×10<sup>-9</sup> | 0.04 | 0.003 | 8.2×10<sup>-7</sup> | 0.04 | 2.07×10<sup>-8</sup> | 0.003 |
| Fe    | 143.66| Adult | 3.93×10<sup>-1</sup> | 0.3 | 0.013 | 2×10<sup>-5</sup> | 0.14 | 1.4×10<sup>-4</sup> | 0.01 |
|       |      | Child | 9.18×10<sup>-2</sup> | 0.3 | 0.03 | 6×10<sup>-5</sup> | 0.14 | 4.3×10<sup>-4</sup> | 0.03 |
| Mn    | 2.81 | Adult | 7.69×10<sup>-8</sup> | 0.14 | 0.001 | 4×10<sup>-7</sup> | 0.00183 | 2.2×10<sup>-4</sup> | 0.0007 |
|       |      | Child | 1.79×10<sup>-8</sup> | 0.14 | 0.001 | 1.1×10<sup>-8</sup> | 0.00183 | 6.4×10<sup>-4</sup> | 0.001 |
| Ni    | 1.2 | Adult | 3.28×10<sup>-8</sup> | 0.02 | 0.001 | 3.4×10<sup>-8</sup> | 0.0008 | 4.2×10<sup>-5</sup> | 0.001 |
|       |      | Child | 7.67×10<sup>-9</sup> | 0.02 | 0.003 | 1×10<sup>-7</sup> | 0.0008 | 1.2×10<sup>-4</sup> | 0.003 |
### Metals

| Metals | Avg. | Age | Ingestion | Dermal | HI=∑HQ |
|--------|------|-----|-----------|--------|--------|
|        |      |     | CDI<sub>ing</sub> | RfD<sub>ing</sub> | HQ<sub>ing</sub> | CDI<sub>derm</sub> | RfD<sub>derm</sub> | HQ<sub>derm</sub> |      |
| Mo     | 2.85 | Adult | 7.8×10<sup>-5</sup> | 0.005 | 0.015 | 4.07×10<sup>-7</sup> | 0.0019 | 2.1×10<sup>-4</sup> | 0.015 |
|        |      | Child | 1.82×10<sup>-4</sup> | 0.005 | 0.036 | 1.2×10<sup>-6</sup> | 0.0019 | 6.3×10<sup>-4</sup> | 0.037 |
| pb     | 2.95 | Adult | 8.08×10<sup>-9</sup> | 0.0035 | 0.023 | 4.21×10<sup>-8</sup> | 0.0035 | 1.2×10<sup>-5</sup> | 0.023 |
|        |      | Child | 1.88×10<sup>-7</sup> | 0.0035 | 0.053 | 1.24×10<sup>-7</sup> | 0.0035 | 3.5×10<sup>-5</sup> | 0.053 |
| Zn     | 2399.5 | Adult | 6.57×10<sup>-4</sup> | 0.3 | 0.219 | 2×10<sup>-4</sup> | 0.3 | 6.8×10<sup>-4</sup> | 0.21 |
|        |      | Child | 0.153 | 0.3 | 0.511 | 6×10<sup>-4</sup> | 0.3 | 2.02×10<sup>-3</sup> | 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
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_{lng}), (HQ_{drrm}), 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).
[3] I.M.O.S. Iraqi Meteorological Organization and Seismology, "Technical report", Baghdad, Iraq (2017).

[4] V. Ditmar, J. Afonasiev, B. Briousov, 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).
[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,Turky", 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).