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Evaluation of Heavy Metals Contamination in Euphrates River and Some Springs and Wells in Haditha District, Western Iraq

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ABSTRACT

For the purpose of assessment pollution in surface, groundwater and some springs in Haditha town - Anbar province during dry season (July, 2022) in term of heavy metal to guarantee their suitability for agricultural and human consumption purposes, the elements Fe, Mn, Zn, Pb, Cd, Ni and Cu were analyzed in twenty-six samples. The average concentrations of these metals were (0.017, 0.154, 0.074, 0.002, 0.001, 0.102, 0.052) ppm in surface water, (0.047, 0.046, 0.014, 0.002, 0.0001, 0.318, 0.012) ppm in groundwater and (0.010, 0.0009, 0.058, 0.1, 0.026, 0.046, 0.002) ppm in springs respectively. Moreover, the concentrations of most elements indicated that they were within the acceptable limits of IQS (2009) and WHO (2017) standards, but the concentrations of (Mn, Ni) in most surface water and some wells, (Pb, Cd) in springs were exceeded the permissible limits. Some high level of the heavy metals could be attributed to the pollution of the water resources with discharge water enhanced with chemical fertilizers, industrial and domestic effluents. (HPI) and (MI) indices were applied to determine the water resources pollution in Haditha. The values of HPI in the water samples referred to unpolluted water except (R1, R2, S1, S2, S3, W2, W4 and W12 samples) were polluted. While the MI values show that all the samples unpolluted except (R1, R2, S1, S2, S3, W2, W3, W4, W5, W9 and W12 samples) were from strongly to seriously affected.

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تقييم التلوث بالعناصر الثقيلة في نهر الفرات وبعض الابار والينابيع في قضاء حديثة، غربي العراق

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الملخص

لغرض تقييم تلوث المياه السطحية و الجوفية وبعض الينابيع في مدينة حديثة _محافظة الانبار خلال موسم الجفاف (تموز 2022) بالعناصر الثقيلة لضمان ملائمتها لأغراض الاستهلاك البشري والزراعي تم تحليل كل من عناصر (الحديد والمنغنيز والزنك والرصاص والكادميوم والنيكل والنحاس) في (26) نموذج .أظهرت النتائج ان معدل تراكيز هذه العناصر (0.017 ، 0.154، 0.074، 0.002، 0.001، 0.102 0.052) في المياه السطحية و (0.047، 0.046، 0.014، 0.002، 0.0001، 0.318، 0.012) في المياه الجوفية و(0.010، 0.0009، 0.058، 0.1، 0.026، 0.046، 0.002) في الينابيع على التوالي. علاوة على ذلك اشارت تراكيز معظم العناصر انها واقعة ضمن الحدود المقبولة للمعايير العراقية ومنظمة الصحة العالمية (2017)، في حين ان تراكيز كل من المنغنيز والنيكل في معظم المياه السطحية وبعض الابار وكذلك تركيز عنصري الكادميوم والرصاص في الينابيع قد تجاوزت الحدود المسموح بها، ويعزى المستوى العالي لبعض العناصر الثقيلة الى تلوث الموارد المائية بمياه الصرف المدعمة بالاسمدة الكيمياوية بالإضافة الى النفايات السائلة المنزلية والصناعية. تم تطبيق مؤشر التلوث بالعناصر الثقيلة (HPI) والمؤشر المعدني (MI) لتحديد تلوث الموارد المائية في حديثة، إذ أشارت قيم مؤشر التلوث ان المياه غير ملوثة باستثناء العينات (R1, R2, S1, S2, S3, W2, W4, W12) في حين أظهرت قيم المؤشر المعدني ان جميع العينات غير ملوثة باستثناء العينات (R1, R2, S1, S2, S3, W2, W3, W4, W5, W9, W12) فقد كانت من متأثرة بشدة الى متأثرة بشكل خطير.

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Introduction

Water is considered a resource of great importance that absolutely indispensable and life is not possible on this planet without water (Al-Hadithy and Al-Mallah, 2023). One of important indicators of sustainable development are the quality and availability of water, based on the water that plays big role in economic development (Al-Ozeer and Al-Abadi, 2022). The heavy metals contamination of the water today is one of the serious environmental problems. In order to preserve living conditions water quality management, water pollution control, and environmental protection must all be prioritized (Al-Obaidi and Sarhat, 2022). The anthropogenic inputs from different sources into soils may be a source of heavy elements (Oleiwi and Al-Dabbas, 2022), like traffic emission, agricultural fertilizers, sewage sludge and atmospheric deposition. Using some indices to assessment of water for drinking and other purposes is very beneficial tool to solve the problems related to water quality (Al-Obaidi et al., 2023). The elements like iron, nickel, lead, cadmium, zinc, copper and manganese are heavy metals with more importance from a water pollution point of view. Some of these metals are essential heavy elements to growth and living organism's metabolism and has an important and effective role in the functioning of enzyme systems, but at higher concentrations become toxic such as (iron, copper and zinc), others like (lead and cadmium) have no known biological function, and may be toxic even when exposed at trace concentrations (Al-Hejuje, 2014). There are many studies related to the evaluation of heavy metals concentrations in the water include (Emad et al., 2015) studied assessment of heavy metals pollution in Euphrates River water, Amiriyah Fallujah, Iraq. (Saleh *et al*., 2021) studied evaluation of heavy metal content in water and removal of metals using native isolated bacterial strains.

The study area is situated in the northeastern of Al-Anbar governorate on the Euphrates River, the geographic coordinates of Hditha city are located between the longitudes 42° 14′ 30″ - 42° 31′ 00″ east and the latitudes 33° 59′ 00″ - 34° 15′ 30″ north with an area of 765 Km^2. Haditha city is located about 240 km North-West of Baghdad city (Fig. 1). The Euphrates River crosses through the center of the study area and splits it into two parts: Barwana and Haditha districts and bounded from the north by Haditha Dam. The Climatic information during the period (1990 - 2020) of Haditha station obtained from (IMO,2022), elements of climate were estimated as follows: the total yearly rainfall (121.5 mm), the evaporation (92855 mm), the monthly average temperature (21.8 °C), relative humidity (46.7 %) and wind speed (2.8 m/s). According on these informations, the climate in Haditha city is distinguished by an arid climate. The geological formations in the study area is represented stratigraphic sequence mentioned from oldest to the youngest as follows: Anah Formation, it consists of very solid limestone and corals with age (upper Oligocene); Euphrates Formation, it consists of dolostone, marl and fossiliferous limestone with age (Lower Miocene); Fatha Formation, it consists of cyclic deposits of gypsum, limestone, green marl, reddish brown claystone and silt with age (Middle Miocene) ; Quaternary deposits are consist gypsum, limestone, clay, sand and gravel with age (Pleistocene to Recent) (Fig. 2).

The main goal of the current study is investigating the status of water quality and levels of contamination with heavy metal in Haditha district, west Al-Anbar province by using seven heavy metals were chosen for their importance in the estimation, also to apply heavy metals pollution index (HPI) and the metal index (MI) as an active tool to assess the water contamination with heavy elements. In order to help for interpretation, all data of geology, topography, industrial uses, drainage water system are observed. This integrated curriculum helps to provide an inclusive estimate of the water pollution in the study area.

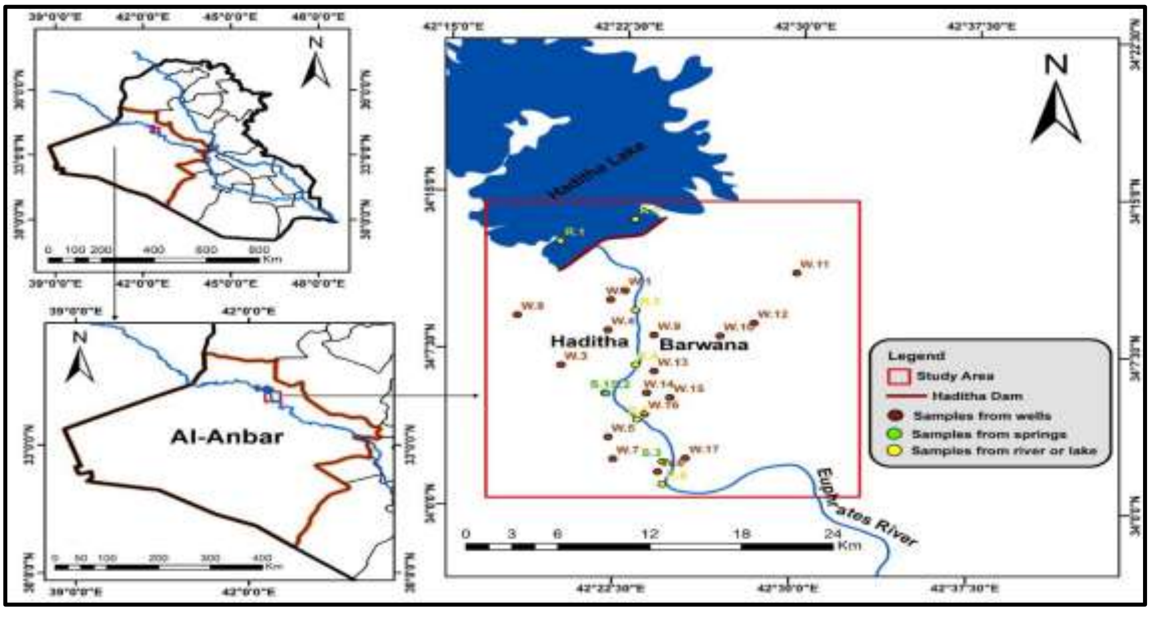

Fig. 1. Locations of the selected samples in the study area.

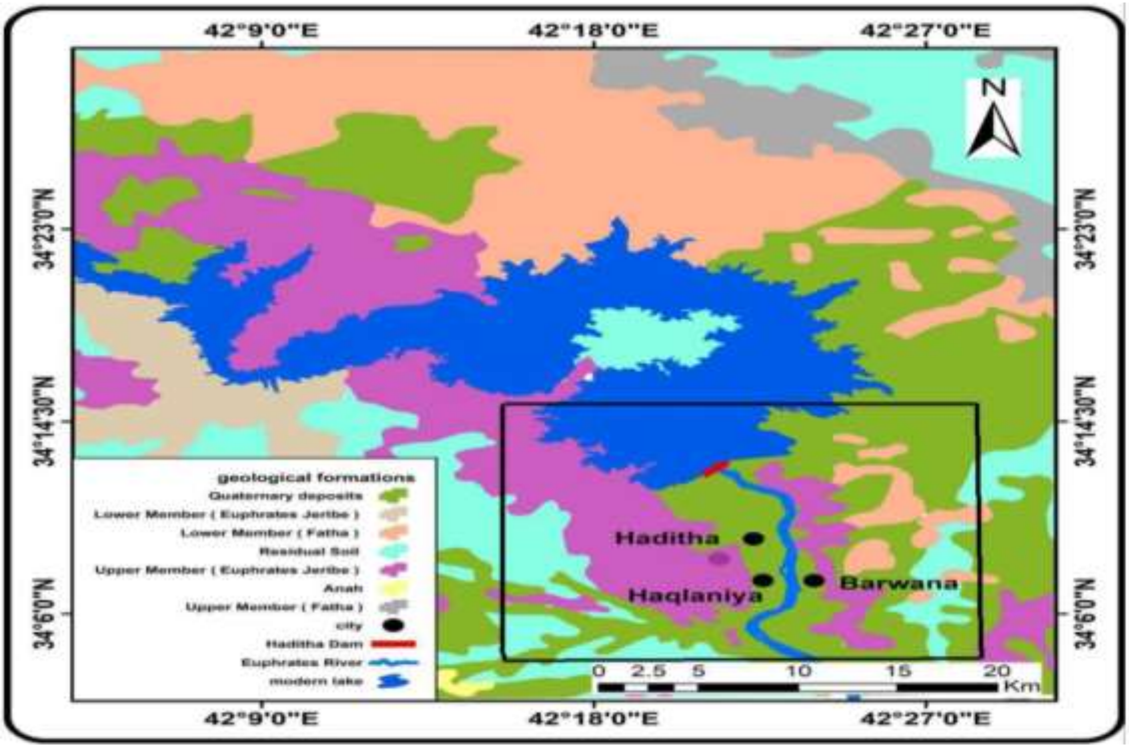

Fig. 2. Geological map of the study area (Al-Khalefawi, *et. al*, 2022)

Sampling and Laboratory work

The water sampling was performed during July 2022 in the dry season. The surface water samples (R) were collected from six different sites distributed equally at Euphrates River, while groundwater samples (W) collected from both sides of the river. Moreover, some of the springs samples (S) that flow into the Euphrates River were collected.

The surface water samples were collected at depth of less than half meter and groundwater samples were collected after operating the well and running the water for several minutes in order to obtain perfect samples in new and preleased polyethylene bottles. The samples are kept in these bottles after being rinsed with the water of the same sample. Then a few drops of concentrated nitric acid (HNO_3) added to all the samples as a stabilizer for heavy metals in the water after the samplings process until the pH becomes (pH = 2) in order to prevent cations from reduces precipitation and adsorption at the walls of the container. Finally, keeping the samples in a refrigerator at a temperature of 4 degrees Celsius until the time of analysis. Laboratory work focused on heavy metals concentration analysis including Cadmium (Cd), lead (Pb), Iron (Fe), Manganese (Mn), Nickel (Ni), Copper (Cu) Zinc (Zn), in the General Commission laboratory for Ground water in Baghdad by using Atomic Absorption Spectrophotometer. Some heavy metal ions after the analysis were present less than detection level and therefore, they were store outside the scope of the present study.

Results and Discussion

Heavy metals

The heavy metals concentrations of water samples are compared with the WHO (2017) and IQS (2009) standards specifications are listed in (Table.1), these metals are Fe, Mn, Cd, Pb, Zn, Ni and Cu.

Table 1: The results of heavy metals concentrations (ppm) in surface, groundwater and springs.

Samples	Fe	Mn	Zn	Pb	Cd	Ni	Cu	HPI	MI
Surface water									
R 1	0.018	0.151	0.08	0.002	0.0028	0.197	0.084	83.728	5.586
R 2	0.019	0.15	0.072	0.002	0.0029	0.099	0.058	81.782	4.197
R 3	0.013	0.152	0.071	0.0022	0.0002	0.098	0.051	17.234	3.299
R 4	0.019	0.15	0.07	0.0023	0.0002	0.091	0.038	17.112	3.202
R 5	0.02	0.17	0.08	0.0033	0.0003	0.045	0.026	20.086	2.879
R 6	0.018	0.153	0.074	0.0025	0.0002	0.082	0.055	17.211	3.130
Springs water									
S 1	0.01	0.0009	0.03	0.1	0.02	0.04	0.002	699.586	17.291
S 2	0.01	0.0009	0.07	0.1	0.02	0.04	0.002	699.587	17.304
S 3	0.011	0.001	0.076	0.1	0.04	0.06	0.002	1181.7	24.263
Groundwater (Haditha)									
W1	0.013	0.07	0.02	0.002	BDL	0.2	0.033	14.719	3.823
W2	0.162	0.12	0.013	0.0021	BDL	1.4	0.048	69.410	21.978
W3	0.017	0.06	0.018	BDL	0.00013	0.33	0.001	19.052	5.420
W4	0.013	BDL	0.014	0.0018	0.0001	1.3	0.002	63.788	18.833
W5	0.01	0.13	0.011	BDL	BDL	0.2	0.004	11.678	4.196
W6	0.15	BDL	0.01	0.001	BDL	0.142	0.035	8.804	2.649
W7	0.16	0.012	0.016	BDL	0.00014	0.029	0.001	5.295	1.120
W8	0.04	0.14	0.01	0.0018	0.0002	BDL	0.001	11.838	1.783
Groundwater (Barwana)									
W9	0.04	BDL	0.02	0.0021	0.0002	0.271	0.002	21.433	4.289
W10	0.01	0.01	0.014	0.0019	0.0001	0.014	0.004	7.380	0.563
W11	0.02	0.014	0.015	BDL	BDL	0.156	0.039	7.248	2.459
W12	0.01	0.013	0.01	0.001	0.0001	0.714	0.003	36.432	10.501
W13	0.05	0.01	0.01	0.001	BDL	BDL	0.001	2.502	0.370
W14	0.02	0.013	0.02	0.01	0.0001	0.015	0.001	25.054	1.451
W15	0.013	0.01	0.012	0.0021	BDL	0.002	0.004	4.884	0.387
W16	0.07	BDL	0.01	0.0017	0.00012	0.002	0.002	6.825	0.476
W17	0.015	0.001	0.03	BDL	0.0002	0.003	0.032	5.005	0.195
WHO,2017	0.3	0.1	3.0	0.01	0.003	0.07	2.0		
IQS,2009	0.3	0.1	3.0	0.05	0.005	0.1	1.0		
BDL: Below Detection Level		Red : Greater than WHO and IQS					Yellow : Greater than WHO		

The concentrations of iron in the studied stations vary between (0.013-0.02) ppm in surface water samples with an average (0.0178) ppm; springs water samples, it ranged between (0.01 - 0.011) ppm with an average (0.010) ppm while in wells, it ranged between (0.01 - 0.162) ppm with an average (0.0478) ppm (Fig.3). All of these values considered within the permissible limit according to the World Health Organization (WHO,2017) and Iraqi Standard (IQS, 2009). Generally, the presence of industrial effluents causes water contamination of iron (Kumar et al., 2017).

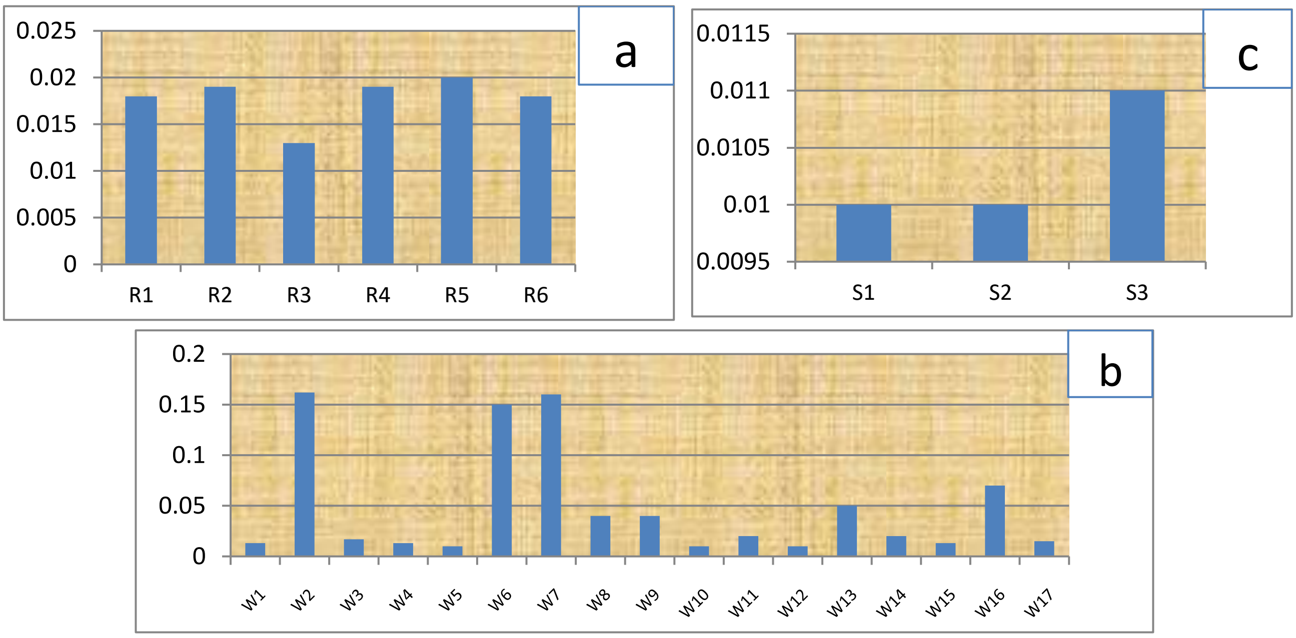

Fig. 3. Variation of iron concentration (ppm) for (a) surface, (b) groundwater and (c) springs water in the study area

The concentrations of manganese in the studied stations vary between (0.15 - 0.17) ppm in with an average (0.154) ppm; springs water samples, **it** ranged between (0.0009 - 0.001) ppm with an average (0.0009) ppm while in wells, **it** ranged between (0.001 - 0.14) ppm with an average (0.0463) ppm (Fig.4). All of these values considered within the permissible limit according to the World Health Organization (WHO,2017) and Iraqi Standard (IQS, 2009) except the surface water samples

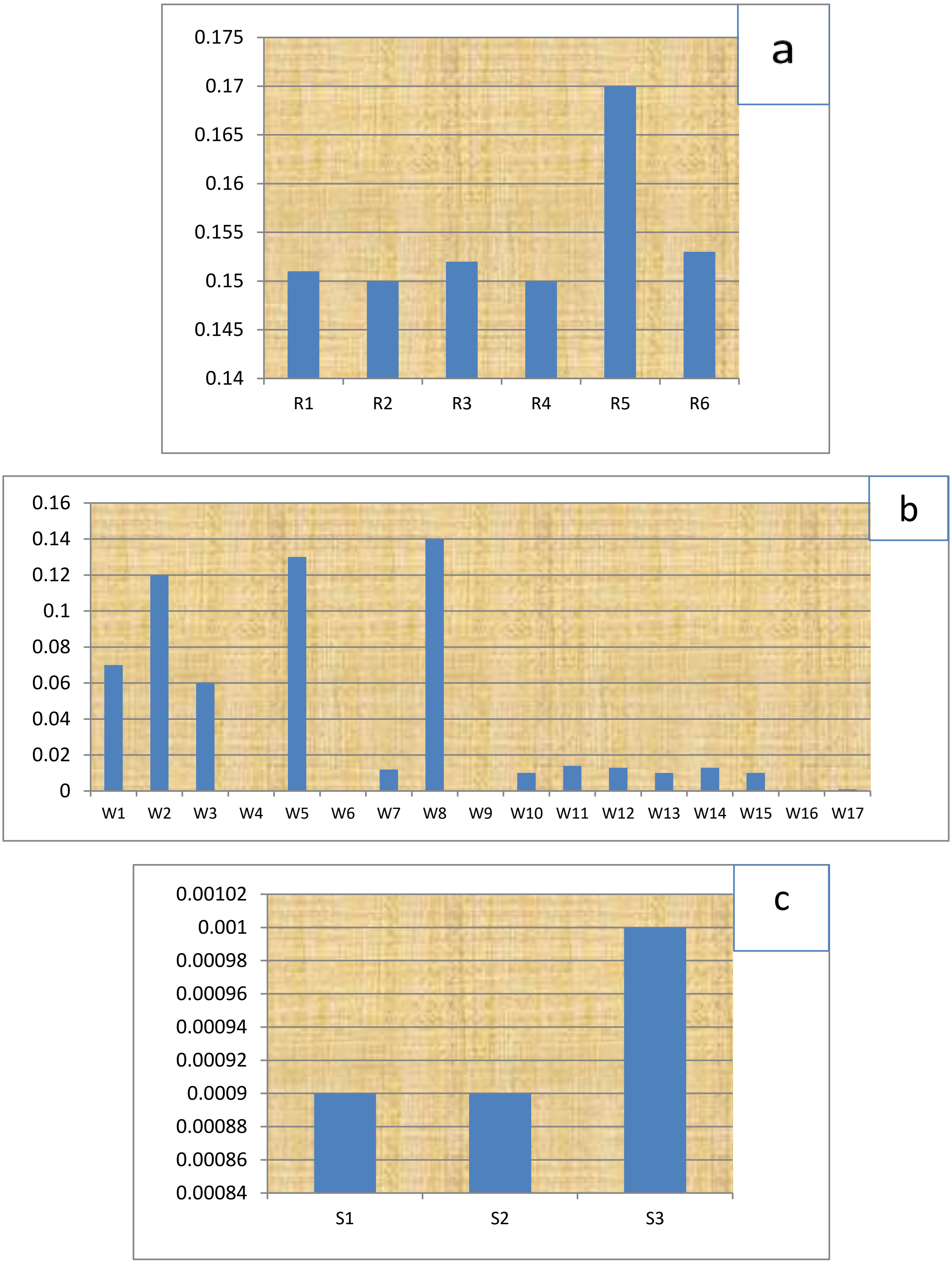

Fig. 4. Variation of manganese concentration (ppm) for (a) surface, (b) groundwater and (c) springs water in the study area

Zinc (Zn) is also considered an important and essential element in the human diet, but when the percentage of zinc increases can be harmful to health. The concentrations of zinc in the studied stations vary between (0.07 - 0.08) ppm in surface water samples with an average (0.074) ppm; springs water samples, it ranged between (0.03 - 0.076) ppm with an average (0.058) ppm while in wells, it ranged between (0.01 - 0.03) ppm with an average (0.0148) ppm (Fig.5). All of these values considered within the permissible limit according to the World Health Organization (WHO,2017) and Iraqi Standard (IQS, 2009).

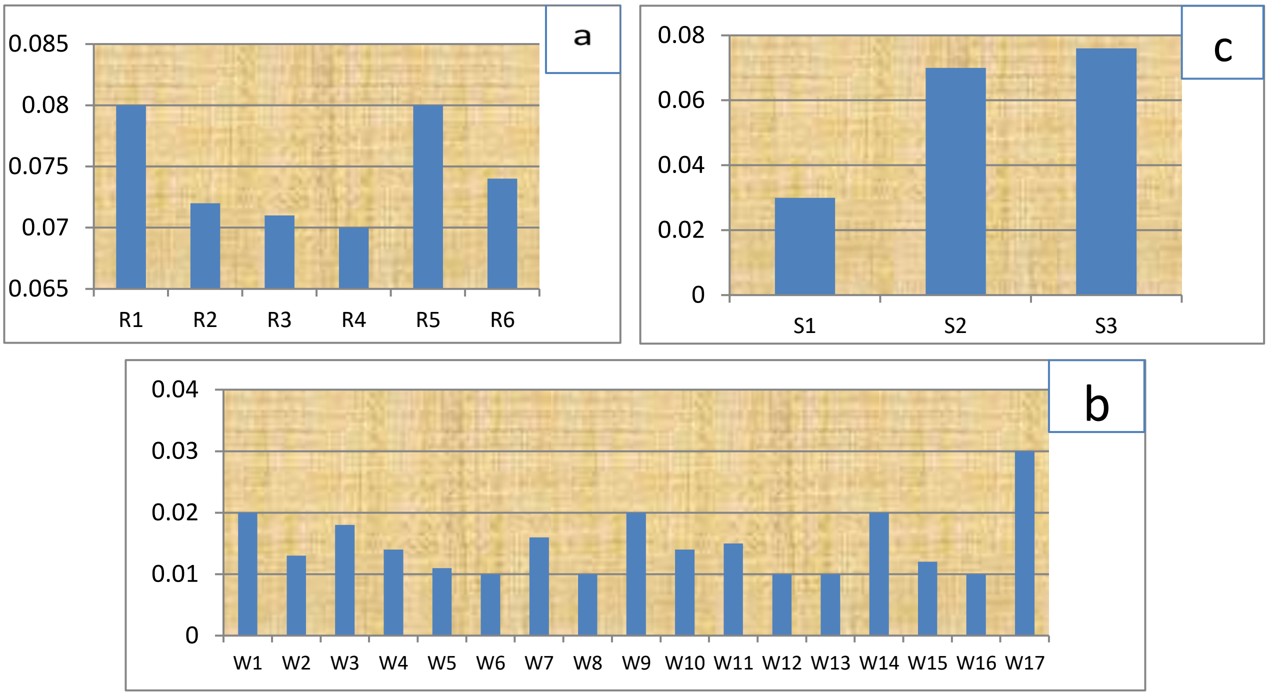

Fig. 5. Variation of zinc concentration (ppm) for (a) surface, (b) groundwater and (c) springs water in the study area

Lead (Pb) is a toxic metal, it lacks nutritional value to living creatures so it is considered non-essential element (Gautam et al., 2014; WHO, 2017). The concentration of lead in the studied stations vary between (0.002 - 0.0033) ppm in surface water samples with an average (0.002) ppm; springs water samples, it ranged between (0.1 - 0.1) ppm with an average (0.1) ppm while in wells, it ranged between (0.001 - 0.01) ppm with an average (0.002) ppm (Fig.6).

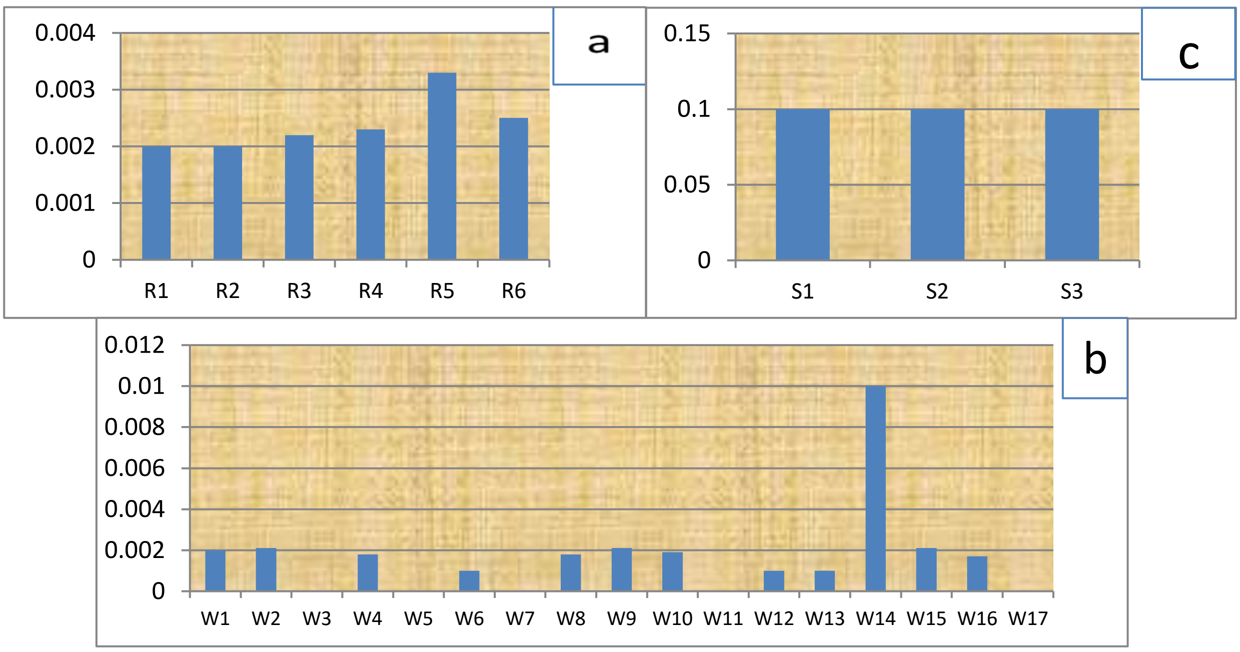

Fig. 6. Variation of lead concentration (ppm) for (a) surface, (b) groundwater and (c) springs water in the study area

Cadmium (Cd) this metal is one of the most dangerous elements in the environment, classify as toxic heavy metal and it is considered a disease-causing agent such as cardiovascular and cancer diseases because it accumulates over time, especially in the kidney (Priti et al., 2016). The concentrations of cadmium in the studied locations vary between (0.0002 - 0.0029) ppm in surface water samples with an average (0.001) ppm; springs water samples, it ranged between (0.02 - 0.04) ppm with an average (0.0266) ppm while in wells, it ranged between (0.0001 - 0.0002) ppm with an average (0.00013) ppm (Fig.7).

This indicates that cadmium and lead concentrations increase in springs more than surface and groundwater, the reason may be due to the occurrence of many anthropogenic activities near or around springs such as: human waste, agriculture, sewage, construction works and garbage. In particular is due to vehicle exhausts emitted into the air, which are increasing with traffic congestions what causes the increase in emitted pollutants by the engine of car and thus the increase of these pollutants in the air, including lead metal.

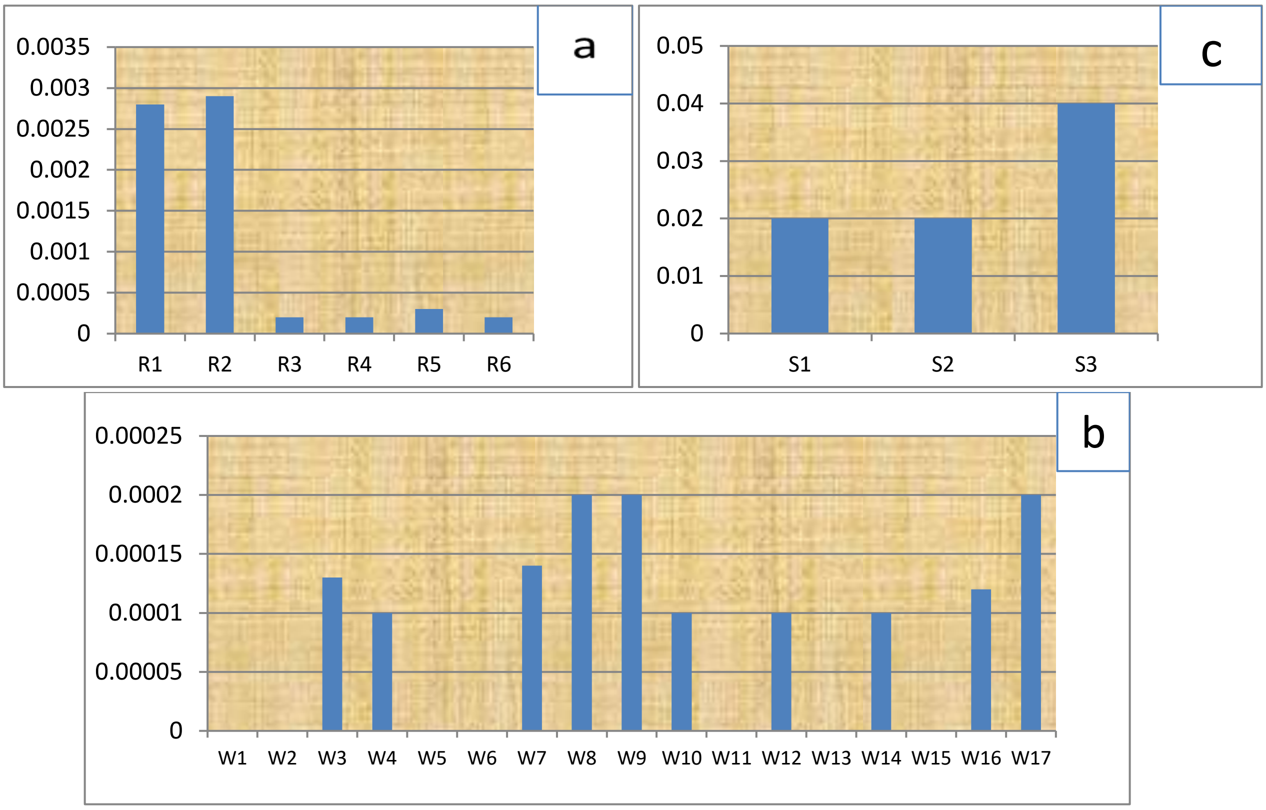

Fig. 7. Variation of Cadmium concentration (ppm) for (a) surface, (b) groundwater and (c) springs water in the study area

The concentrations of Nickel in the studied stations vary between (0.045 - 0.197) ppm in surface water samples with an average (0.102) ppm; springs water samples, it ranged between (0.04 - 0.06) ppm with an average (0.0466) ppm while in wells, it ranged between (0.002 - 1.4) ppm with an average (0.318) ppm (Fig. 8). This indicates that Nickel concentrations increase in groundwater more than springs and surface water, the reason is due to irrigation and fertilization operations at agricultural lands, which aid on to the concentration increase of Ni metal. Also, Ni leached from soil during of infiltration process of water to ground water.

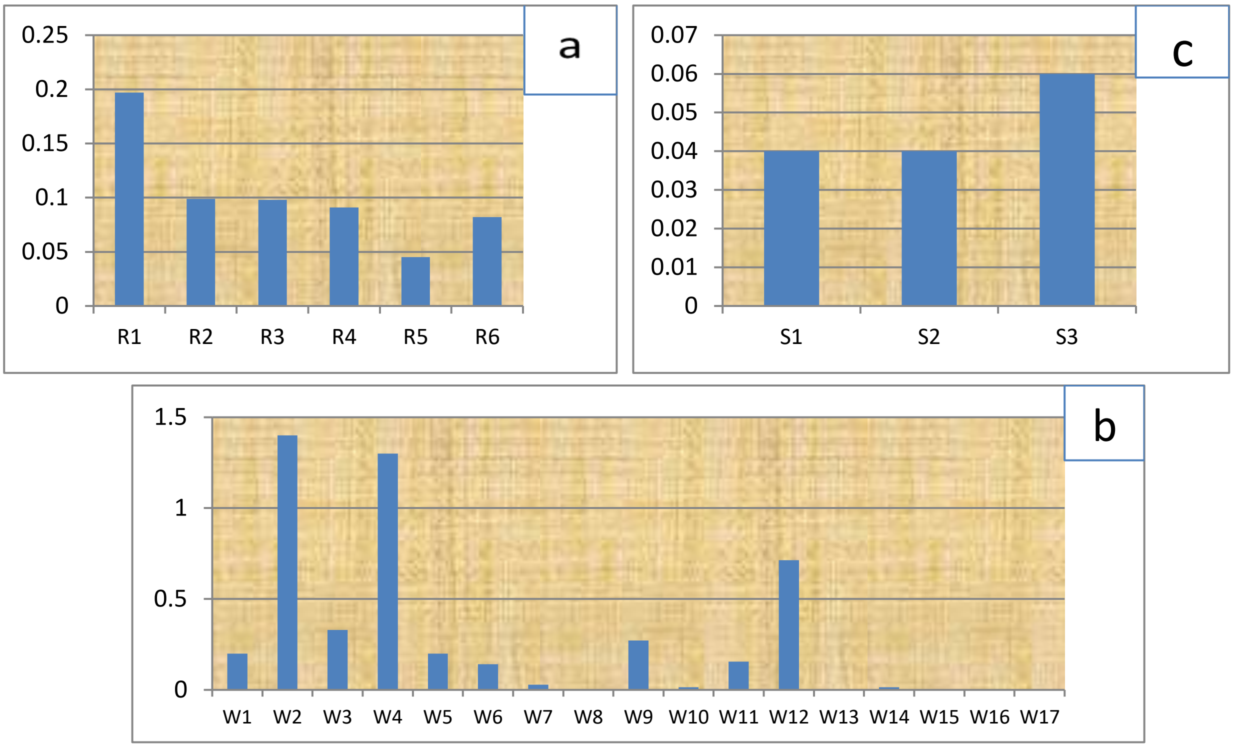

Fig. 8. Variation of Nickel concentration (ppm) for (a) surface, (b) groundwater and (c) springs water in the study area

The concentrations of copper in the studied stations vary between (0.026 - 0.084) ppm in surface water samples with an average (0.052) ppm; springs water samples, it ranged between (0.002 - 0.002) ppm with an average (0.002) ppm while in wells, it ranged between (0.001 - 0.048) ppm with an average (0.0125) ppm (Fig. 9). All of these values considered within the permissible limit according to the World Health Organization (WHO, 2017) and Iraqi Standard (IQS, 2009).

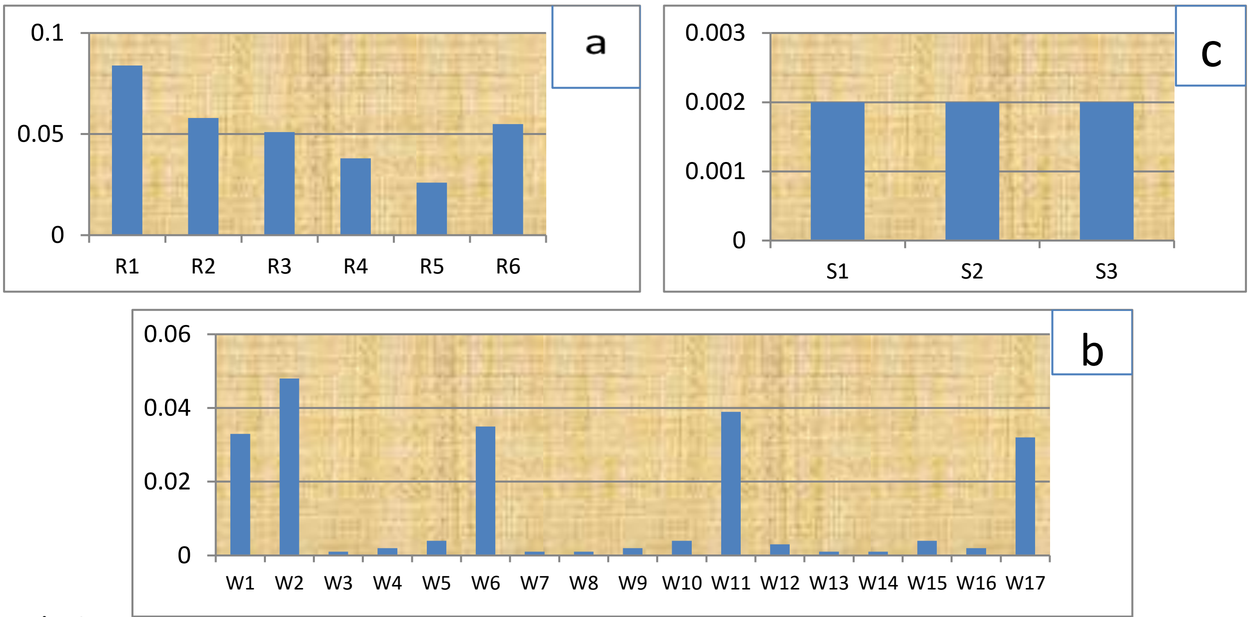

Fig. 9.
Variation of copper concentration (ppm) for (a) surface, (b) groundwater and (c) springs water in the study area

All elements were within the acceptable limits except the element (Mn) in surface water, (Pb and Cd) in springs water and (Mn and Ni) in some well's samples were greater than the permitted limits. This disparity was found among stations may be owing to agricultural activities and weathering of clay minerals in the Quaternary deposits which cover the area, in addition to exist industrial area.

Indicators of heavy metal contamination

Heavy metal pollution index (HPI)

The pollution index of heavy metal was first suggested by Mohan *et al.*, (1996), HPI is utilized as an indicator to explain the effect of heavy elements individually or in combination on the overall quality of water. For the purpose of computing the HPI models (Mohan et al.,1996), three basic steps have been made: (1) calculation of weight (wi) for each select element (i^{th}), (2) classification quality (Qi) for each heavy element, and (3) classification of sub-indicators in general (Singh and Kamal, 2017). The values of HPI index were classify into three categories as listed in table. 2, and the allowed value of the indicator was designation at 100 (Zeid et al., 2017). The weighing value was between zero and one, reflecting the relative importance of individual quality considerations, the following equation is used (Sarhat and Al-Obaidi, 2023):

$$\mathbf{Wi = K/Si = 1/Si} \quad \ldots\ldots\ldots\ldots (1)$$

Where k: is the proportionality constant (k=1).

Si: the standard value of the parameter.

The sub index of the i^{th} parameter (Qi) is calculated from the following equation:

$$\mathbf{Qi = \sum_{i=1}^{n} (Mi\text{-}Ii)/(Si\text{-}Ii) * 100} \quad \ldots\ldots\ldots\ldots (2)$$

Where Mi: the monitored value of heavy metal of parameter.

Ii: the ideal value of the parameter (Ii=0).

$$\mathbf{HPI = \sum_{i=1}^{n} WiQi / \sum_{i=1}^{n} Wi} \quad \ldots\ldots\ldots\ldots (3)$$

Where n: the parameters number considered.

Wi: the unit weightage of the parameter.

Qi: the sub index of the parameter and calculated by equation (2).

Table 2: Classification of HPI values depending on (Tiwari et al., 2015).

Status	HPI values	HPI in study area
Low	<15	W1. W5. W6. W7. W8. W10.W11. W13.W15. W16.W17
Moderate	15 – 30	R3. R4. R5. R6. W3. W9. W14
High	>30	R1. R2. S1. S2. S3. W2. W4. W12

After completing the application of equations (1, 2, 3), the results of heavy metal pollution index (HPI) were extracted for the study area samples as shown in (Table 1). According on (Tiwari et al.,2015) classification shown in Table 2, the water samples of the Euphrates River were classified within the category of medium pollution, except for samples R1 and R2, it was within the category of high pollution, and the samples of springs water were also classified within the category of high pollution. As for the samples of the wells, it was classified within the category of low pollution, except for samples (W3, W9, W14) were medium pollution and samples (W2, W4, W12) were high pollution.

The range and average of HPI in Euphrates River were 17.11 to 83.72 and 39.52, respectively. while the range and average of HPI in springs were 699.58 to 1181.7 and 892.43 respectively. as well as the range and average of HPI in groundwater were 2.50 to 69.41 and 20.69 respectively. These results of heavy metal pollution index illustrate that all the water samples were less than the critical value (100) of the pollution index, and pollution with respect to heavy metals is not critically except the samples (R1, R2, S1, S2, S3, W2, W4, W12) were critically polluted. Generally, the HPI values on different sites in the study area were slightly high, and the reason is due to the high values of the Pb, Cd, Mn and Ni elements on these same sites. However, it is expected that these values of heavy metal may increase in the future when effective and necessary measures are not taken to minimize the heavy metal load getting into water resources in the region.

Metal Index (MI)

The metal index is utilized to evaluate the metal pollution of the water resources for different purposes in the area, where Metal Index (MI) indicates the composite influences of each metal on the overall quality of water (Tamasi and Cini, 2004; Akobundu, 2012). The equation (4) is suggested to calculate (MI) value (Sarhat and Al-Obaidi, 2023):

$$MI = \sum Ci / (MAC)I \qquad \text{…………. (4)}$$

Where

Ci: is the concentration of a monitored metal.

MAC: is maximum allowable concentration of the same metal.

MI (metal index): is classify into five categories depending on its values as listed in (Table 3).

Table 3: Classification of MI values depending on (Akobundu, 2012).

Class	Characteristics	MI values	MI in study area
1	Very pure	<0.3	W17
2	pure	0.3-1	W10.W13. W15.W16
3	Slightly affected	1-2	W7. W8. W14
4	Moderately affected	2-4	R3. R4. R5. R6. W1. W6. W11
5	Strongly affected	4-6	R1. R2. W3. W5. W9
6	Seriously affected	>6	S1. S2. S3. W2. W4. W12

After completing the application of equation 4, the results of metal index (MI) were extracted for the study area samples as shown in (Table 1). According on (Akobundu, 2012) classification shown in table 3, the water samples of the Euphrates River were classified within the category of moderately affected, except for model R1 and R2, it was within the category of strongly affected, and the samples of springs water were also classified within the category of seriously affected. As for the samples of the wells, it was classified from very pure to the sample (W17), pure (W10, W13, W15, W16), slightly affected (W7, W8, W14), moderately affected (W1 W6 W11), strongly affected (W3, W5, W9) to seriously affected (W2, W4, W12).

Conclusion

A study of heavy metals in different types of water in Haditha District, western Iraq, showed an increase in concentrations (Mn and Ni) of most surface water and some well samples as well as concentrations (Pb and Cd) of spring water samples. These concentrations exceed the permissible limits of the World Health Organization (WHO, 2017) and Iraqi Standard (IQS, 2009). The influence of heavy metal pollution on water was assessed in the current study using two pollution indicators: the metal index (MI) and the heavy metal pollution index (HPI). With the exception of the samples (R1, R2, S1, S2, S3, W2, and W12) that were severely contaminated, the HPI results make it evident that none of the water samples are severely polluted with heavy metals. Consequently, all of the samples fall into one of the following categories according to the results of the MI index: very pure (W17), pure (W10 W13 W15 W16), slightly affected (W7 W8 W14), moderately affected (R3 R4 R5 R6 W1 W6 W11), strongly affected (R1 R2 W3 W5 W9), and seriously affected (S1 S2 S3 W2 W4 W12). These findings indicate that metal pollution for various uses poses a concern to some samples in the current area (MI > 1). In general, the main cause of pollution in the spring water of the study area with cadmium and lead was from human and agricultural activities and car exhausts. The reason for the contamination of most surface and groundwater with nickel and manganese were due to a lithological factor and human activities.

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