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Variation of the heavy metals concentration in some wells and springs water between Haditha dam and the site of Al-Baghdadi dam (west Iraq)

Kamal.B. A-Paruany[a] **Abdulhameed.A Al-Hadithy [b]**

[a] Environment and water Directorate, Ministry of Science and Technology, Baghdad, Iraq

[b]Department of Applied Geology, College of science University of Al-Anbar, Iraq

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ABSTRACT

The study area is located between latitude 33° 51.9 -34° 19 and latitudes 42° 15.83 to 42° 40.3 in the northwest part of the Governorate of Anbar. The research focuses upon the analysis of Heavy Metal variation between the dam of Haditha and the dam of Al Baghdadi in (8) wells and (4) springs. Nine heavy metals, including Zn^{2+}, Fe^{2+}, Cd^{2+}, Mn^{2+}, Pb^{2+}, $B^{2+}$and As^{2+}, were analyzed for the wells and springs samples in August 2019 and March 2020. Present study shows a spatial and temporal change in heavy metals, whereas all well samples did not exceed allowable limits suggested by WHO and IQS. A major source of High values of heavy metals in some water samples of springs may be due to the effects of Agriculture, Fertilizers, pesticides and fish lake. The results also show a variation in the depth and source of wells, reflected by different co-existing sources. In addition to some human activities, which raise the level of concentrations.

Keywords
Heavy metals, Haditha, springs, Wells and Human activity

1.NTRODUCTION

The term 'heavy metal' refers to any metallic chemical element that has a relatively high density , toxic and atomic number greater than 20 [1]. In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications.[2]. The importance of studying the heavy metals in the water lies in knowing the pollution of that water as a result of human and industrial activities and the drainage of healthy water, as it is harmful to the general health of humans and the environment. Heavy metals with low concentrations are an important factor for plant growth, but high concentrations are very harmful to human and animal health [3]. Both noting that the cumulative nature of these elements gives greater damage over time. Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations.[3,4]. The study area considered one of the most important areas adjacent to the Euphrates River due to using it for agricultural and fish breeding purposes, with the presence of government support in equipping spraying and drip stations. Many Hydro chemical and Hydrogeological, Environmental studies of groundwater and surface water have been conducted on the Haditha region [5, 6, 7. 8, 9, 10].

The study area is located in the western part of Iraq, The selected area are located in the left bank of the Euphrates River, between Haditha Dam and Al-Baghdadi Dam site, its lie between longitudes 42 ° 15.83 - 42 ° 40.3N and latitudes 33 ° 51.9 - 34 ° 19E. The studied area is about 320 km^2. The Euphrates River represents the most important natural phenomena in the region, while the Haditha Dam represents the most important construction phenomenon. Figure (1).The stratigraphic succession is composed of Anah (Oligocene), Euphrates Formation (Miocene), and Quaternary deposits *(Pleistocene-Holocene)*[11]. According to the meteorological data Haditha station for the period (2001–2019), generally characterized as being continental, dry and relatively hot in summer, cold and with little rain in winter,. The monthly Average of temperatures ($34.34^{0}C$), Evaporation (230.78mm), Rainfall (139.1mm).

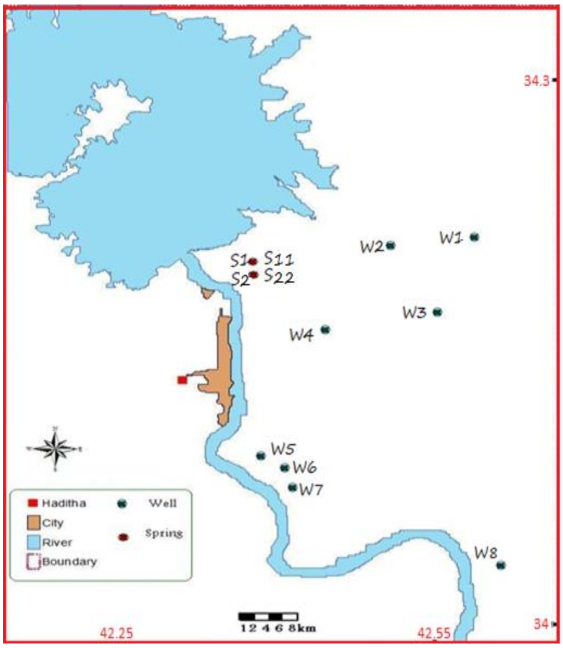

Figure 1. location map of studied area

2.METHODOLOGY

2.1 Sampling and analysis

Two seasonal samplings were carried out in the area between Haditha reservoir and site of Al-Baghdadi Dam in March, August 2019-2020. Water samples were collected from all the twelfth sites (eight wells and four springs) to analyze for heavy metals. Water samples were collected in polyethylene bottles (washed with detergent then with double-distilled water followed by 2 ml nitric acid, then double-distilled water again and finally with sampled water). Water samples were acidified with 10% HNO_3, brought to the laboratory and kept refrigerated until needed for analysis. These 2.2 Field measurements (pH, EC, T) were done in suite.

3.RESULTS AND DISCUSSION

3.1.

RESULTS

The results of the quality analysis of heavy metals in the study area are tabulated in Table 1A,1B and 2A,2B.

analyses were conducted at the Laboratory of water research in Ministry of Science and Technology. The samples were analyzed using standard procedures [12], using Atomic Absorption.

Table 1A. The con. of heavy metals in August.

Sample	T	Ec µs/cm	pH	ASppm	Bppm
W1	23	5300	7.2	0.0001	0.03
W2	22	8000	6.9	0.0002	0.034
W3	23	5000	7	0.0001	0.014
W4	23	2000	7.7	0.0005	0.03
W5	22.5	9200	8	0.0003	0.09
W6	24	4200	7.78	0.0019	0.31
W7	23	4390	7.2	0.0019	0.034
W8	24	2500	7.2	0.002	0.089
S1	21	6790	7.3	0.007	0.02
S2	22	5450	7.4	0.005	0.019
S11	21	6800	7.1	0.007	0.067
S22	23	5700	7	0.0043	0.023

Table 1B. The con. of heavy metals in August.

Sample	Feppm	Pbppm	Cdppm	Mnppm	Znppm
W1	0.008	0.041	0.003	BDL	BDL
W2	BDL	0.025	0.001	0.07	BDL
W3	BDL	0.01	0.001	BDL	0.008
W4	0.015	0.0051	BDL	0.009	BDL
W5	0.014	BDL	BDL	0.005	0.08
W6	BDL	BDL	0.004	0.02	0.033
W7	0.019	0.045	0.005	0.032	0.036
W8	0.015	0.06	0.004	0.049	0.02
S1	0.4	0.003	0.003	0.16	0.099
S2	0.29	0.0021	0.0019	0.159	0.089
S11	0.5	0.007	0.09	0.19	0.15
S22	0.34	0.0021	0.012	0.167	0.145

Table 2B. The conc. of heavy metals in March

Sample	Feppm	Pbppm	Cdppm	Mnppm	Znppm
W1	0.018	0.052	0.004	BDL	0.089
W2	0.021	0.029	0.002	0.09	0.001
W3	0.024	0.022	0.002	0.011	0.009
W4	0.019	0.008	0.0015	0.0092	0.002
W5	0.021	0.0099	0.006	0.006	0.011
W6	0.021	0.001	0.007	0.03	0.043
W7	0.039	0.085	0.005	0.044	0.038
W8	0.027	0.089	0.006	0.008	0.03
S1	0.43	0.021	0.0023	0.019	0.02
S2	0.39	0.0029	0.0023	0.178	0.01
S11	0.52	0.0098	0.029	0.21	0.13
S22	0.46	0.0024	0.0192	0.197	0.165

Table 2A. The conc. of heavy metals in March.

Sample	T	Ec	pH	ASppm	Bppm
W1	22	4970	7.1	0.00013	0.052
W2	21	6810	6.7	0.00012	0.051
W3	22	4980	7	0.00013	0.057
W4	22	1989	7.5	0.0008	0.053
W5	21	8900	7.9	0.0005	0.094
W6	23	3819	7.54	0.0024	0.39
W7	22	4312	7.18	0.0021	0.099
W8	23	2370	7.2	0.0023	0.099
S1	24	6360	7.3	0.009	0.024
S2	26	6000	7.3	0.009	0.023
S11	25	6589	7.1	0.027	0.077
S22	25.5	5900	6.9	0.0057	0.033

Lead content (pb^{2+})

The main source of lead is a feldspar rocks and mica minerals. and concentration of lead in water ranges between 0.001-0.01 [13]. The concentrations of lead in wells ranged between (0.0051-0.06ppm) with a mean of (0.031ppm) in August and between

Iron content (Fe^{2+})

Iron is found widely in the earth's crust and is found in Shale rocks and Alluvial deposits, as well as in the minerals Amphibolite and Magnetite. Fe concentration in natural waters ranges from less than 0.5 ppm [14]. Iron concentrations of wells in the study area ranged between (0.008-0.019ppm) with mean of (0.014ppm) in August and between (0.018-0.039ppm) with a mean of (0.023pp) in March. while the lead concentrations in Bishina springs, Zwachi springs, in August and March, were (0.29-0.5ppm), (0.39-0.52 ppm) with mean of (0.386ppm) and (0.4516ppm) respectively. The maximum allowable limit for Iron as per WHO guidelines is 0.3 mg/L. Iron concentration levels in all studied samples except in Bishina and Zwachi springs are less than WHO permissible limit .

Zinc content (Zn^{2+})

Available in concentrations close to copper and nickel and affected by pH. Zinc concentrations in wells ranged between (0.008-0.08ppm) with mean of (0.030ppm) in August and between

(0.001-0.089ppm) with mean of (0.0369ppm) in March. while the lead concentrations in the Bishina spring , and Zwachi springs, in two periods August and March 2019-2020, were (0.0021-0.007ppm), (0.0024-0.021ppm), with mean of (0.0030ppm) and (0.009ppm) respectively. The permissible limit (WHO) of lead is 0.003 mg/L. In our study area all sampling zone were Manganese concentrations more than (WHO) permissible limit except in Bishina and Zwachi springs.

(0.001-0.089ppm) with mean of (0.027ppm) in March. while the lead concentrations in Bishina spring, Zwachi spring, in August, were (0.089-0.15 ppm), (0.01-0.165ppm), with mean of (0.120ppm) and (0.081ppm) respectively. The permissible limit (WHO) of Zinc is 0. 3 mg/L. In this study all sampling zone were zinc concentrations less then (WHO) permissible limit.

Cadmium content (Cd^{2+})

It is present in the natural form of hydroxides and carbonates, its concentration in fresh water ranges between 0.0001-0.003 ppm [14]. Cadmium causes water pollution through fertilizing fertilizers in addition to pollutants in the air [15]. Cadmium concentrations in wells ranged between (0.001-0.005ppm) with mean of (0.003ppm) in August and between (0.0015-0.006ppm) with mean of (0.003ppm) in March. while the lead concentrations Bishina spring, Zwachi spring, in August and March, were between (0.0019-0.09ppm), (0.0023-0.029ppm), with mean of (0.026ppm) and (0.013ppm) respectively. The permissible limit (WHO) of Cadmium is 0.003 mg/L. In current study, all sampling zone were Cadmium concentrations with (WHO) permissible limit except in Bishina spring.

Manganese content (Mn^{2+})

The presence of manganese is mainly due to the dissolution of soil and sediments. It is present in concentrations of 0.02ppm, which is similar to iron in its presence in clay minerals [15]. Manganese concentrations in wells ranged between (0.005-0.07ppm) with mean of (0.03ppm) in August and between (0.006-0.09ppm) with mean of (0.028ppm) in March. while the Manganese concentrations in Bishina, Zwachi spring, in August and March, were between (0.159-0.19ppm), (0.019-0.21ppm), with mean of (0.17ppm) and (0.151ppm) respectively. the permissible limit (WHO) of manganese is 0.05 mg/L. In our study area all sampling zone were Manganese concentrations less then (WHO) permissible limit except in Bishina and Zwachi springs.

Boron content (B^{2+})

Boron is an essential element for plant growth, but the range between the element's need for growth and its toxicity is very narrow. The boron concentrations in wells ranged between (0.014-0.31ppm) with mean of (0.034ppm) in August and between (0.051-0.39ppm) with mean of (0.11ppm) in March. while the concentration of Boron in Bishina and Zwachi spring between (0.019-0.067ppm), (0.023-0.077ppm) with mean of (0.032ppm) (0.0398ppm) respectively. The maximum allowable limit for Boron as per WHO guidelines is 0.5 mg/L. Boron concentration levels in all studied samples are less than WHO permissible limit .

Arsenic content (As^{2+})

Arsenic concentrations in the study area ranged between (0.0001 - 0.002ppm) with mean of (0.0008ppm) in August and between (0.00012-0.0024ppm) with mean of (0.00106ppm) in March. while arsenic concentrations in Bishina, Zwachi spring in August and March of were between (0.0034-0.007ppm), (0.005-0.027ppm) with mean of (0.005ppm) (0.026ppm) respectively. the permissible limit (WHO) of Arsenic is 0.01 mg/L. In our study area all sampling zone were Arsenic concentrations less then (WHO) permissible limit ..

For EC values in the wells stations, ranged between (2000-9200 s / cm) in August, while the values ranged between (1989-8900 μs / cm) in March, while the conductivity values in the Bishina and Zwachi springs were characterized by a high In August and March (5400-6800 μs / cm) and (5900-6589 μs / cm). Wells of the study area recorded varying pH values between 6.9-8 in August. the values ranged between 6.9-7.9 in March. Whereas the pH values in the springs water were between 7-7.4 in August and 6.9-7.3 in March. The pH values showed that well and springs water tends between light alkaline to light acidity and in both periods. For the temperatures, the range of water temperature in well water in August and March, (22-24^{0}C) and (21-23^{0}C) respectively, while the range of water temperature were (21-23^{0}C) in August and (24-26^{0}C) in March.

3.2.DISSCUSION

From the results above, it can see that the variation in heavy metal concentration of wells water and springs water is mainly from interaction from natural and human activities, , but it fluctuates with time, due to the change in the salts values and the accompanying ions (12). it was noticed that there was a variation in these concentrations. Based on the wells, heavy metals were classified into two groups. The first group represented by wells W1, W2, W3, and W4. The concentrations in this wells are not affected by any factors and fall within the permissible limits for their use for drinking purposes according to [16], WHO, 2008; IQR 2009 [17].

The second group represents wells W5, W6, W7, W8 which are not more than 500 meters from the Euphrates river. The results indicate that a clear variation in the concentrations of heavy metals, and this variation is reflected in the concentrations of elements during the two seasons. One of the most important reasons that contribute to Raising the concentrations of these elements in these wells are mixing processes with Euphrates river, in addition to human and household activities . the use of the irrigation system with sprinklers and drips may lead to the accumulation of these elements on the leaves and fruits, causing a decline in the quality of production [18]). Therefore, the stations of the first group recorded less concentrations compared to the second group. The variation of the elemental concentrations of well and springs water for both periods are represented in Figures (2,3).

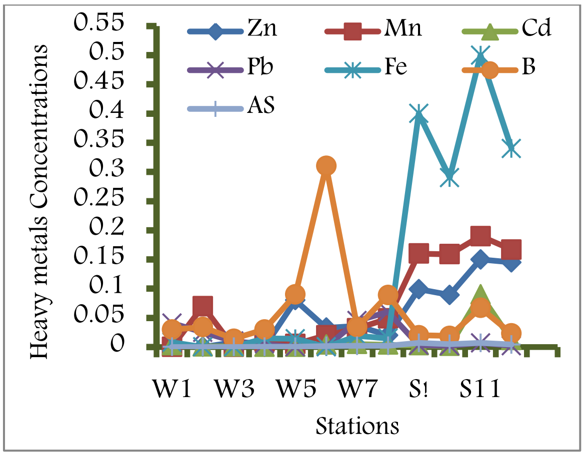

Figure 2. Variation in heavy metals, August.

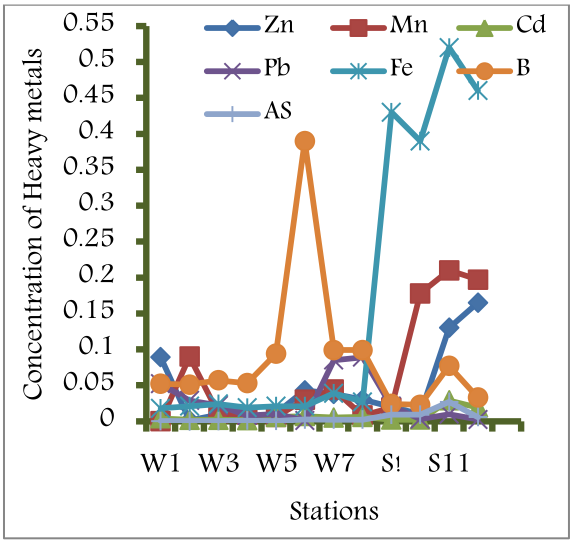

Figure 2. Variation in heavy metals, March.

For both periods, the concentration of heavy metals in Bishina and Zwachi spring in march recorded higher than those in August due to the dissolution processes, on the other hand, the concentrations of heavy elements in Bishina spring water recorded higher than those in Zwachi spring water. Comparing the stream stations and source stations of Bishina and Zwchi springs, specifically before the estuary in the Euphrates River, we find that the concentrations increased, this due to use of these springs for washing and drainage purposes.

On the other hand, when comparing the heavy metals of the study area with Hajlan springs and some selected wells on the right side of the Euphrates [8]. We find that the concentrations of heavy metals in the current study have recorded higher values than on the right side of the Euphrates River, due to natural causes (the presence of the Fatha formation) and human activities, and as shown in Table (3 and 4) .

Table 3. Wells and springs in the study area

Wells and springs in the study area				Heavy metals
Spring's water		Well water		
March	August	March	August	
0.138	0.170	0.138	0.032	Mn^{+2}
0.014	0.033	0.032	0.003	Cd^{+2}
0.0099	0.0039	0.004	0.031	Pb^{+2}
0.451	0.386	0.038	0.014	Fe^{+2}

Table 4. Wells and springs /right bank

Hajlan springs and wells/right bank				Heavy metals
Hajaln spring		Well water		
March	August	March	August	
0.102	0.105	0.110	0.121	Mn^{+2}
0.00024	0.0019	0.0002	0.00016	Cd^{+2}
0.0031	0.0024	0.002	0.0012	Pb^{+2}
0.115	0.11	0.11	0.1	Fe^{+2}

To assess the suitability of water for agriculture purposes, the springs and wells water in the study area are compared with the German Development Foundation [19] ,proposed to cultivate plants depending on the degree of their sensitivity to boron, Table (5).

According to German Development Foundation classification, all water samples are within the percentage very sensitive to plant uses. Therefore, it can be suggested to cultivate most of the plants because the boron concentrations in the water samples are low. Bauder, 2007 classified the water depending on the conductivity values [20], Table (6).

Table 5. Use the plants depend on of Boron. purpose [20]

EC	classes of water
250	Excellent
250-750	good
750-2000	permissible
2000-3000	Doubtful
>3000	Unsuitable

Table 6. Use the water for Agriculture

Conc.	uses
0.5-0.75	Very sensitive to boron, such as lemon
0.75-1	sensitive to boron such as wheat
1-2	Moderate (potato, carrot ,pepper)
2-4	Medium (barley cauliflower)
4-6	Possibility , tomato
6-8	High ability

According to electrical conductivity values of wells and springs water in the study area, these wells and springs are unsuitable for agricultural and irrigation uses except W4, all conductivity values have exceeded 3000µs / cm (unsuitable).

4. CONCLUSIONS

1- There is a clear spatial and temporal variation in heavy metals concentrations of water wells and Springs water, this variation was reflected as a result of several factors, natural and industrial in addition to the excessive use of fertilizers and pesticides, to increase these concentrations, and here we need periodic monitoring.

2. Agriculture, Fertilizers, pesticides and fish lake as a major sources of heavy metals in the study area .

3. The high concentrations of heavy metals in the stream stations of the springs are the result of human activities and mixing.

4. Depending on the amount of dissolved salts, it was found that the water in the study area is not suitable for irrigation except for well W4, while many plants can be suggested depending on the boron concentration.

5. RECOMMENDATIONS

1. Do not discharge the waste near the springs, in order to keep the change in chemistry of those springs.

2. Conducting detailed hydrogeological studies of the springs waters as well as an assessment of the ages and origin.

3. Study the concentrations of heavy elements in the soil and plants to assess the linking factor between those variables.

4. Enhancing springs monitoring by administering of Haditha dam.

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