Estimation of the Concentration of Some Heavy Metals in Groundwater in Rutba City

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Abstract. Toxic metal pollutants in groundwater should be identified to prevent future health risks. In this paper, the presence of heavy metals in groundwater in the western region of Iraq was investigated. The heavy metals concentrations, including Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\), Cr\(^{3+}\), Cd\(^{2+}\), As\(^{3+}\) and Hg\(^{2+}\) were explored in twenty selected aquifers near Rutba City and the results were presented as spatial distribution maps. Findings indicate that contamination with the investigated heavy metal ions possesses a serious threat to the study area’s groundwater quality when compared to WHO and IEPA guideline values. Thus, a new approach to remove or adsorb heavy metal ions can be developed for large-scale production and the safe use of these aquifers water. Results revealed that the highest concentrations in mg/L of 2.312 in w19, 1.098 in w2, 5.78 in w17, 0.292 in w9, 3.349 in w5, 0.32 in w13, 0.074 in w11 and 5.622 in w1 for Zn\(^{2+}\), Cr\(^{3+}\), As\(^{3+}\), Pb\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Cd\(^{2+}\) and Hg\(^{2+}\) were recorded, respectively.

1. Introduction
Surface water is becoming more polluted as a result of human activity and/or natural contaminants [1]; [2]. These pollutants may have an impact on groundwater [3]. Groundwater is one of the most important sources of water to meet the growing demand on fresh water. Many regions rely on groundwater as their main source of daily activities [4]; [5]. Earth’s geological layers of aquifers possess an impact on the physico-chemical properties of the groundwater [6] in addition to human activities near aquifers. Therefore, this necessitates regular evaluation of the characteristics of these water sources [7]. Groundwater is the main source of drinking, domestic and agricultural water in the study area (Rutba City).

Numerous studies on the water quality in Rutba have been performed. A study [8] was carried out for evaluating the water validity of ten wells in the Al-Dabaa/Rutba region, the western region of Iraq for drinking purposes. Water samples were collected quarterly from each well according to a model during the year 2012-2013. The results of the analysis showed that in spite of salinity and the values of its total content of salts, the degree of interaction, and the concentrations of magnesium and potassium negative ions and microelements are within the permissible limits for human use. The bacteriological study indicated that it is very clean and healthy water for not diagnosing colon bacteria in it. The results of the study indicated [9] that some of the groundwater wells in Rutba City have been drilled by the local...
community using traditional techniques without taking into account the hydrogeological factors and the necessary standards for well construction. Consequently, some of the wells have been found not to reach the required depth to reach reliable aquifers, so they produce water of lower quality than expected. Moreover, Gharbi and Byty studied the groundwater in Rutba City. 11 sites and wells were selected according to the sources of nutrition (the site of collecting wells from Dabaa wells and the site of collecting wells from the fifth station and the civil wells within the residential neighborhoods of Rutba City). The results were compared with the permissible limits for drinking purposes according to the specifications of (IEPA) and (WHO). The results of the study showed the validity of the groundwater of Rutba City and that it is within the permissible limits for drinking water purposes, except that of Al-Askari and West valley wells which is valid only for home use or garden watering [10]. Thus, this paper aims to display the concentrations of heavy metals, such as Zn$^{2+}$, Cr$^{3+}$, As$^{3+}$, Pb$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ in the groundwater of Rutba City and compare them to WHO and IEPA drinking water guideline values.

2. Materials and Methods

2.1. Study area

The study area was determined using two phases. The first phase included a study within longitude ($40^{\circ} 15' 28" - 40^{\circ} 18' 41"$) and latitude ($33^{\circ} 0' 48" – 33^{\circ} 03' 07"$) with a total area of (405) km$^2$ to show the hydrological situation of Rutba region. The second stage included the site study in the area defined by longitudes ($40^{\circ} 14' 19" - 40^{\circ} 34' 50"$) and latitudes ($32^{\circ} 58' 23" – 33^{\circ} 05' 12"$) whose area was estimated as occupying (13) km$^2$ (Fig. 1). A network of 20 civil wells was chosen within this area to investigate the concentration of certain heavy metals in the groundwater.

![Fig1. Map of the location of study area.](image-url)
2.2. Rutba Zone Hydrology

2.3. The aquifers of the study area are located within the third major hydrogeological system (Hy-3) and the second main hydrogeological system (Hy-2) [11],[12].

2.3.1. Third Major Hydrogeological System. This system consists of aquifers in the limestone and sand layers dating back to the middle age. The water-bearing layers in the limestone formation of Malasa represent the saturated zone of the aquifer, while the transition zone consists of the limestone and dolomite layers of the Zour Hauran and Ubaid Al-Muntashfa formation in the northern and northeast part, extending to the sandy layers of the humid formation exposed in the western and southwestern part within the valley sections, which allows the penetration of water and its passage to the saturated range zone.

2.3.2. Second Main Hydrogeological System. This system consists of underground reservoirs in the sandy layers of the Permian-Carbonite period, represented by water-bearing layers in the Al-Kaara formation, which form the saturated range of the second aquifer (Al-Kaara Aquifer Reservoir).

2.4. Working Method and Modelling

2.5. In the current study, dual distilled water was used as a solvent. 1000 ppm standard solutions of related metal ions were placed into a solvent, comprising metal element standard solutions for the ions Ni$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Cr$^{3+}$, Cd$^{2+}$, As$^{3+}$ and Hg$^{2+}$ solutions.

2.6. Water samples were taken from 20 wells in Rutba City within longitudes (40° 14' 19'' - 40° 34' 50'') and latitudes (32° 58' 23'' – 33° 05' 12'') that were selected randomly and the coordinates were recorded using a hand-held GPS device (Table 1). Following the method for water sampling [13], samples of water from the aquifers were placed into 500 mL plastic bottles containing a few drops of 0.5% nitric acid. The samples then were brought for analysis in the laboratory of (Centre of the Desert Studies, University of Anbar). The analysis was performed using an atomic absorption spectrometer equipped with a GTA-110 graphite furnace; model AA-220 (Australia). A research map was drawn using a program (ARC GIS 10.4.1) to show the distribution of the studied elements within the borders of Rutba City.

Table 1. Well sites in the study area

| No Well | Geographical location | No Well | Geographical location |
|---------|-----------------------|---------|-----------------------|
|         | longitudes (E) | (N) latitudes |         | longitudes (E) | (N) latitudes |
| 1       | 40°16' 55.66'' | 33°01' 54.87'' | 11      | 40°17' 17.39'' | 33°01' 47.72'' |
| 2       | 40°16' 51.98'' | 33°01' 54.79'' | 12      | 40°17' 10.37'' | 33°01' 47.92'' |
| 3       | 40°16' 55.62'' | 33°01' 54.88'' | 13      | 40°17' 01.95'' | 33°00' 53.02'' |
| 4       | 40°17' 00.100'' | 33°01' 56.35'' | 14      | 40°17' 01.64'' | 33°01' 54.53'' |
| 5       | 40°17' 00.99'' | 33°01' 56.35'' | 15      | 40°17' 01.18'' | 33°01' 54.54'' |
| 6       | 40°16' 55.67'' | 33°01' 54.87'' | 16      | 40°17' 00.99'' | 33°01' 56.33'' |
| 7       | 40°16' 55.68'' | 33°01' 54.88'' | 17      | 40°06' 55.65'' | 33°00' 54.59'' |
| 8       | 40°17' 00.11'' | 33°01' 56.34'' | 18      | 40°17' 00.100'' | 33°01' 53.42'' |
| 9       | 40°17' 03.44'' | 33°01' 48.94'' | 19      | 40°17' 01.64'' | 33°01' 54.03'' |
| 10      | 40°17' 17.39'' | 33°01' 48.94'' | 20      | 40°16' 51.36'' | 33°01' 40.47'' |
3. Results and Discussion

Heavy metal ion concentrations in the groundwater samples taken from Rutba City were measured in this study. The heavy metal ions measured were Cd$^{2+}$, Cr$^{3+}$, Co$^{2+}$, As$^{3+}$, Hg$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$. The test results obtained were compared to the limits set by the Iraqi Environmental Protection Agency (IEPA) and the World Health Organization (WHO) for heavy metal ions concentration in drinking water in order to determine whether there are any ions in the study area with values that are higher than the acceptable limits (Table 2).

In relation to this, Plum et al (2010) argue that a high amount of Zn$^{2+}$ metal in water causes a variety of health issues [14]. For all of the assessed wells, Zn$^{2+}$ concentrations ranged between 0.023 and 2.3 ppm (Fig. 2a). This shows that these aquifers contained Zn$^{2+}$ ions within the permitted limit value in relation to the allowable limit values of the WHO and IEPA (3.0 ppm). Although the majority of the water wells examined have no Cr$^{3+}$ ion concentration, some of them (2, 5, 6, 8, 12, 14, and 18) do have Cr$^{3+}$ ion concentrations that exceed WHO and IEPA acceptable levels (Fig 2b). In well 2, a high value of 1.098 ppm has been reported. Except for wells 2, 5, and 19, which had As$^{3+}$ ion concentrations ranging from 0.323 to 5.78 ppm, the majority of the wells were free of As$^{3+}$ ions (Fig 2c). Smith and Steinmaus (2009) confirmed health problems associated with high Cr$^{3+}$ and As$^{3+}$ levels [15]. All of the aquifer well samples contained Pb$^{2+}$ ion concentrations ranging from 0.017 to 0.292 ppm (Fig 2d), which is higher than the WHO and IEPA acceptable limits of 0.01 ppm. However, only five of the wells (6, 11, 14, 18, and 19) did not contain any Pb$^{2+}$ ions. Fig. 2e shows that the concentrations of Ni$^{2+}$ ions in all collected samples ranged between 0.582 and 3.249 ppm, with a higher value in well 5 (3.249 ppm) and well 16 (3.141 ppm). When compared to the WHO and IEPA permitted limit value (0.02 ppm), all groundwater samples exhibited greater levels of Ni$^{2+}$. Brera and Nicolini (2005) discussed the health concerns raised by high Ni$^{2+}$ levels in drinking water. [16]. In terms of the presence of Co$^{2+}$ ion concentration in the water samples, wells 6 and 8 were free of Co$^{2+}$, while wells 1, 9, 10, 18, and 19 contained Co$^{2+}$ ions within the WHO and IEPA standard limits (Fig. 2f). Other wells contain more Co$^{2+}$ ions than the stated limit of WHO and IEPA (0.05 ppm), ranging from 0.055 to 0.103 ppm, with the exception of well 13 which has a higher value of Co$^{2+}$ (0.32 ppm). A study on the health impacts of high Co$^{2+}$ ion concentration in drinking water was discussed by [17]. The concentrations of Cd$^{2+}$ ions show fluctuation between the studied wells whereby some of them were free of Cd$^{2+}$ ions but the others contain a high value which exceeds the stated limit of WOH. Moreover, the values in wells 1, 3, 6, 9, 10, 13, and 15 ranged from 0.006 to 0.04 ppm, which is higher than the IEPA’s stated limit (Fig 2g). Bernard (2008) addressed the health consequences of the high concentration of Cd$^{2+}$ ions in drinking water [18]. In most of the tested wells, substantial concentrations of Hg$^{2+}$ ions were found in the range of 0.121 to 5.622 ppm (Fig. 1h). All values exceeded the WHO and IEPA standards except for wells 2, 7, 10, 12, 15, and 18, which were free of Hg$^{2+}$ ions. Stolzenburg et al (1986) investigated the seriousness of the hazard of mercury in water on human health [19].
Table 2. Concentration of active ingredients in wells in Rutba area

| No | Well | Zn<sup>2+</sup> | Cr<sup>3+</sup> | As<sup>3+</sup> | Pb<sup>2+</sup> | Ni<sup>2+</sup> | Co<sup>2+</sup> | Cd<sup>2+</sup> | Hg<sup>2+</sup> |
|----|------|----------------|----------------|-------------|--------------|----------|------------|----------|-------------|
| 1  |      | 0.049         | 0              | 0           | 0.063        | 0.637    | 0.038      | 0.013    | 5.622       |
| 2  |      | 0.112         | 1.098          | 0.323       | 0.178        | 1.447    | 0.059      | 0.071    | 0           |
| 3  |      | 0.067         | 0              | 0           | 0.079        | 0.582    | 0.087      | 0.04     | 0.32        |
| 4  |      | 0.087         | 0              | 0           | 0.046        | 2.614    | 0.21       | 0        | 1.606       |
| 5  |      | 0.037         | 0.231          | 2.273       | 0.017        | 3.249    | 0.175      | 0        | 0.243       |
| 6  |      | 0.032         | 0.439          | 0           | 0            | 1.11     | 0          | 0.006    | 1.188       |
| 7  |      | 0.497         | 0.046          | 0           | 0.106        | 2.242    | 0.059      | 0.066    | 0           |
| 8  |      | 2.244         | 0.203          | 0           | 0.221        | 2.943    | 0          | 0.032    | 0.835       |
| 9  |      | 0             | 0              | 0           | 0.292        | 2        | 0.033      | 0.013    | 2.038       |
| 10 |      | 0.396         | 0              | 0           | 0.075        | 0.963    | 0.046      | 0.009    | 0           |
| 11 |      | 2.284         | 0              | 0           | 0            | 2.997    | 0.055      | 0.074    | 0.895       |
| 12 |      | 0.169         | 0.991          | 0           | 0.068        | 1.616    | 0.122      | 0        | 0           |
| 13 |      | 0.523         | 0              | 0           | 0.06         | 1.149    | 0.32       | 0.007    | 0.121       |
| 14 |      | 0.079         | 0.487          | 0           | 0            | 1.274    | 0.096      | 0.014    | 0.532       |
| 15 |      | 0.154         | 0              | 0           | 0.23         | 2.969    | 0.094      | 0.011    | 0           |
| 16 |      | 1.245         | 0              | 0           | 0.167        | 3.141    | 0.085      | 0        | 0.953       |
| 17 |      | 0.023         | 5.78           | 0           | 1.79         | 0.107    | 0          | 0.238    | 0           |
| 18 |      | 0.301         | 0.147          | 0           | 0            | 0.721    | 0.019      | 0.041    | 0           |
| 19 |      | 2.312         | 0.619          | 0.12        | 2.932        | 0.038    | 0          | 1.73     | 0           |
| 20 |      | 1.226         | 0              | 0.141       | 2.293        | 0.097    | 0          | 3.025    | 0           |
| WHO|      | 3.00          | 0.05           | N/A         | 0.05         | 0.02     | 0.05       | 0.03     | 0.01        |
| IEPA|     | 3.00          | 0.05           | 0.01        | 0.02         | N/A      | 0.003      | 0.001    |             |
Fig 2 (a, b, c, d). Map of the Heavy metals distribution for wells in the study area.
Fig 2 (e, f, g, h). Map of the Heavy metals distribution for wells in the study area.
There is no industrial activity in the study area which results in heavy metal pollution of the groundwater. As a result, this contamination could be the outcome of the aquifer systems. In the majority of aquifer environments, groundwater is exposed to various geological formations and dissolved molten elements have a propensity to mix with the groundwater [20,6]. On the other hand, wastewater produced by domestic use in the study area can often contribute to an increase in the concentration of heavy metals in the groundwater.

Results suggested that the groundwater for the wells under investigation could not be used directly. Prior to use, this water must be treated using a variety of methods including ion exchange and activated carbon [21]and[22,23].

4. Conclusion and Recommendations
Groundwater in Rutba City wells were drilled by people using traditional techniques without regard to government regulations and proper building standards. Accordingly, many of the breached wells have groundwater as a result of heavy water reservoirs for residential areas draining into those wells, causing a high concentration of heavy elements and producing poor quality water. This is an issue of great importance because groundwater is the main source of drinking water. Hence, efficient use and protection of water resources and prediction of change in groundwater environments are important as groundwater is the only water source.

The study recommends the use of scientific methods in the drilling of wells according to government regulations, and that drilling should be to far depths. Moreover, the study recommends the use of the lining process to avoid mixing the groundwater with heavy tank water or any water leakage to maintain public health, as well as conducting periodic water checks by government agencies. These checks are required to instruct not to use wells with negative results due to their invalidity.

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