Statistical analysis of groundwater quality parameters in selected sites at Kirkuk governorate/ Iraq

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Abstract. This study aims to clarify the distribution of groundwater qualitative characteristics in Daqouq district within Kirkuk governorate, the study included 14 wells that were selected in the area located in the southern part of Kirkuk province, and which included different activities such as agricultural, industrial and residential to the north in the Daqouq district. Water samples were collected from the wells once every two months from December 2016 to April 2017. The physical tests were performed such as electrical conductivity, total dissolved solids and chemical tests that included pH, cations such as calcium and magnesium, anions such as sulphates, nitrates and chlorides and concentrations of trace elements such as lead, cadmium and zinc were measured using standard methods. The three-dimension contour maps were drawn to illustrate the distribution of the above properties in the study area. The wells showed that the highest rate of electrical conductivity was 1600 μS/cm in W4 and the highest concentration of calcium in W5 was 260 mg/L and the highest rate of lead was 2.2 μg/L in W13, and they showed that the difference in the quality of water was according to land use, agricultural, residential or industrial, in the properties of electrical conductivity, total dissolved solids, nitrates, chlorides, and trace elements.

Keywords: Groundwater; Three Dimension Contour Maps; Trace elements; Water quality

1. Introduction

The high rate of population growth, particularly in rural areas, has increased the demand for water resources and created additional demand for infrastructure in the water sector, in recent years, the scarcity of rain has resulted from global warming, as well as the depletion of the Tigris River due to Turkey’s construction of numerous irrigation projects and large dams under construction (Alesso Dam) to the trend towards the use of other non-surface water resources. In Kirkuk province drilling wells has increased in recent times and use for various purposes as a result of frequent water outages, especially in the districts and areas of Kirkuk province or the lack of access to the water nets to them, and these areas rely on rain in agriculture, which its lack led to rely on groundwater also for watering. Therefore, it is necessary to conduct studies on the quality of water of other sources and their suitability for different uses and the formation of a data bank [1].

Groundwater is one of the most important sources of water in the world, which can be used for drinking, domestic work, irrigation and industry according to its specifications, especially in rural areas, it is important in areas with insufficient surface water to link the lives and activities of the population to their existence [2]. In areas where surface water is not available and is not affected by drought conditions that prevail in some years, sweet groundwater constitutes 30.1% of Sweet water on the surface of the earth, which is 100 times that of Sweet surface water [3].

Groundwater is characterized by a lack of suspended materials due to exposure to the filtration process as it passes through the pores of the soil, the presence of geological layers that isolate them from the weather conditions makes their temperature almost constant in summer and winter and does not
change more than several degrees, also characterized by a decrease or lack of dissolved oxygen concentration, and different salinity in the water by age and depending on the nature of her aquifer container [4].

The reasons of groundwater pollution include unsuitable solid waste disposal, landfill leachate, and wastewater [5]. Treatment of polluted landfill Leachate can be done by using aged refuse Biofilter medium [6].

There were many studies were conducted in Iraq and other countries on water quality using multivariate analysis, relationships among them and their variations [7]. Additionally, Shihab et al., (2013) studied the distribution of groundwater quality characteristics in selected areas in Ninevah governorate by using three dimensions contour maps. Shah et al., [8] analyzed the groundwater quality parameters of Makhmor area/ Northern Iraq using factor and cluster analysis, also they draw a classification map for groundwater quality of the area depending on the results of cluster analysis. Ahamad and Jawed [9] used wooden charcoal and sand to remove iron (II) from groundwater.

It is possible to use adsorption, electrocoagulation and chemical precipitation to treat the elevated concentrations of some studied parameters by using a new baffle plates electrochemical reactor [10].

The first goals of this research is to find the groundwater quality characteristics of a group of selected wells in the province of Kirkuk and indicate its validity for drinking, second, the find out the distribution of groundwater quality characteristics of the study area by using contour maps.

2. Materials and Methods

2.1. Study Area

The study area is located in Kirkuk province in northern Iraq between longitude (34° 00’ 00” - 36° 00’ 00”) and latitude (44° 00’ 00” - 45° 00’ 00”) and occupies an area of 1170 square kilometers and includes the southern part of Kirkuk province within the residential neighborhoods to the north in the district of Daqouq, the wells were chosen to cover the study area and in areas with different uses and hadn’t been studied previously, it included a number of wells within Daqouq district, as well as a number of them outside the jurisdiction within the villages of Daqouq (figure 1). The total number of selected wells was 14. The wells were deep and ranged between (95-245) meters, including the newly dug and the oldest drilling in 2004 (table 1) [11].

2.2. Samples Collection

The samples were collected once from each well every two months because the groundwater is isolated from the weather conditions and from December 2016 until April 2017. The well pump was operated for approximately 5 minutes to get rid of any effect of the pump on water quality and to ensure a sample of well water, this period was depended on the depth of the well, and then pH was measured immediately.

The samples were then taken to the laboratory in plastic bottles (2.25) liters and placed in the refrigerator (+4°C) then were acidified at pH below 2 using nitric acid for the rest of the tests. The water samples were analyzed in the laboratories of the Environmental Engineering Department/Tikrit University and the laboratories of the North Gas Company/testing and monitoring commission/Environment Department, according to the standard methods [12]. Three-dimensional contour maps were drawn using a program Statistica version 5.5 and based on the groundwater quality characteristics of the study area as well as the coordinates of wells extracted from the Google Earth program [7].
Table 1. General information about study area wells.

| Well | Name of well                          | Depth (meter) | Activity    |
|------|--------------------------------------|---------------|-------------|
| W1   | Al-mojama                            | 95            | Domestic    |
| W2   | old water project 1                  | 103           | Domestic    |
| W3   | old water project 2                  | 105           | Domestic    |
| W4   | Al-Ashayr                            | 110           | Domestic    |
| W5   | Al-Emam Zine El Abidine              | 107           | Domestic    |
| W6   | Al-Zahra district                    | 118           | Domestic    |
| W7   | Ashti district                       | 114           | Domestic    |
| W8   | Ghida                                | 210           | Agricultural|
| W9   | Al-Zarka                             | 218           | Agricultural|
| W10  | Ali Saray                            | 210           | Industrial  |
| W11  | Ishtar                               | 225           | Industrial  |
| W12  | Topazawa                             | 230           | Agricultural|
| W13  | Merkum                               | 217           | Agricultural|
| W14  | Suhail                               | 245           | Agricultural|

Figure 1. Area of the study and wells locations.

3. Results and discussion
3.1. Electrical Conductivity (EC)
The results showed that there were differences in the electrical conductivity values between the wells of the study area, the W7 recorded the lowest rate of 700 μs/cm. The highest rate in W4 was 1600 μs/cm and 6 of these wells were more than 1000 μs/cm, Beyond the limits of the specifications of drinking water as water is safe to drink when the electrical conductivity of less than 1000 μs/cm [13]. Water with an electrical conductivity of more than 2500 μs/cm is also not potable. The high values of electrical
conductivity in the groundwater of the wells in the study area was because of the concentration of ions is increased due to the melting of gypsum, anhydrite and limestone rocks within Fatha formation which found within the composition of the feldspar and silica minerals [14].

3.2. Total Dissolved Solids (TDS)
For total dissolved solids, the highest value at W14 was 900 mg/L, while the lowest was at W3 and 430 mg/L (Table 2). All wells were within drinking water specifications [15] and [16]. The reason for the rise of dissolved solids (salinity) in the wells within the Fatha formation is attributed to the rocks of evaporators such as gypsum, anhydrite, and dolomite, which are rocks rich in minerals that are soluble in groundwater more than the wells located within Injana formation of sandstone and clay [17]. Belkhiri et al., [18] specified the concentration of total dissolved solids in drinking water with less than 1000 mg/L. It is noted that all studied wells have a total dissolved solids of less than 1000 mg/L.

3.3. pH
The results in table 2 shows that groundwater under study was equal to alkalinity (pH > 7) with pH values ranging between 7.5-8.3, with the highest value of pH in W14 and the lowest value in W10. It is noted that all values of pH recorded are among the standard specifications for drinking water [13], which is 5.5-9.2.

3.4. Calcium (Ca\(^{+2}\))
Table 2 shows differences in the concentration of calcium ion between the study area wells, with the lowest concentration in W2 and W9 with a concentration of 124 mg/L, and the highest concentration in W5 was 260 mg/L. This difference is due to the diversity of the incubator geological layers of groundwater between sand rocks in the Injana formation with very little content of the calcareous components, since only carbonate cement is responsible for the presence of this ion in groundwater located within this configuration [19] which led to a decline in values in the wells located within this Formation, while limestone and gypsum rocks work in Alfatha formation with water High level of calcium, As well as the carbonic cement materials made up of the marl rocks to raise the concentrations in wells within this formation [20]. The drinking water specification has determined the maximum concentration of calcium by 200 mg/L [13]. Therefore, only 6 of the studied wells had calcium concentrations within the allowable limits.

3.5. Magnesium (Mg\(^{+2}\))
The results of the analysis showed a difference in the concentration of magnesium ion between the water of the well in the study area. The lowest concentration of magnesium ion in W5 was at 12.15 mg/L and the highest rate was 92.34 mg/L in W1 (table 2). This difference maybe because of a difference in the Geological layers containing dolomite rocks that are responsible for magnesium within Alfatha formation and its absence in Ingana formation [21]. The World Health Organization (WHO) has determined the concentration of magnesium ion in drinking water at 150 mg/L. [15] therefore; all the wells of the study area are within the limits of the specification because magnesium concentration is less than 150 mg/L.

3.6. Chloride (Cl\(^{-}\))
The results of the analysis showed differences between the concentrations of chlorides in the wells studied, as in Table 2. The lowest concentration was 45 mg/L in W7 and the highest concentration was 410 mg/L in W13. This may be due to the difference in the amount of precipitation precipitated in groundwater according to the nature of the area, since this water is the source of the reached chlorides [22], as well as surface water, in both residential and agricultural areas, dissolves chloride salts and infiltrates into groundwater. Chlorides remain in their ionic state permanently because of their high solubility [23], as well as the effect of civil activity discharging water containing high concentrations of
chlorides [24, and 25]. 50% of the studied wells were within the drinking water specification of 250 mg/L or less [15].

3.7. Nitrate (NO\textsubscript{3}\textsuperscript{−})

There were differences in concentrations of nitrates between studied wells, and the lowest rate was not detected, in W1-W7 and W14 while the highest concentration was 0.01 mg/L in W11 and W13 (Table 2). The differences in nitrate concentrations between the wells of the study area may be due to different sources of organic or artificial fertilizers. Fertilizers are the main sources of nitrates, as well as water leaks from septic tanks and their mixing with groundwater. Nitrate is not related to the geological formation of water. All the wells under study are within drinking water specification for this ion because the concentration of nitrates is less than 45 mg/L as defined by Gray [13]. The increased nitrate concentration of 45 mg/L in drinking water causes childhood blueness [26].

3.8. Sulphates (SO\textsubscript{4}\textsuperscript{2−})

In the analysis of sulphates concentrations in the wells of the study area, the difference in concentrations was as in table 2, and the lowest average was 40 mg/L in W1 and the highest 690 mg/L in W11. The differences between the sulphate concentrations between the wells of the study area due to the diversity of geological layers that incubate water between gypsum rocks containing gypsum and anhydrite in Alfatha formation which responsible for sulphates, to sand rocks in the Injana formation with very little of calcareous rock content [7]. 50% of the wells in the study area exceeded the limit for drinking water according to the World Health Organization of 250 mg/L [15].

3.9. Lead (Pb)

The difference in concentration of lead between the wells of the study area as in Table (2). the lowest rate was not detected in W1-W3 and the highest rate of 2.2 μg/L, in the well W13. All studied wells were within drinking water limits (Lead concentrations less than 10 μg/L), according to the World Health Organization [15]. Concentrations of lead in the groundwater in areas with industrial activities, particularly mining, have increased. 0.7-62.8 μg/L in China's heavily mined Shenzhen region [22].

3.10. Cadmium (Cd)

There were differences in cadmium concentrations between the wells of the study area as in Table 2 and the lowest average was 0 μg/L in W1, W2, W3, W5, W6 and W7 and the highest rate of 0.7 μg/L in W13 All studied wells were within the drinking water specification of 5 μg/L or less [22].

3.11. Zinc (Zn)

Table 2 shows differences in the concentration of zinc between the wells of the study area the lowest rate of 1.2 μg/L was in W2 and the highest 12 μg/L in W13. The highest concentration of zinc allowed in drinking water is 3000 μg/L [15]. All the wells in the study area had zinc concentrations of less than 3000 μg/L. In comparison with the areas where this element was studied globally, namely the Shenzhen region of China, in a study of groundwater in these areas, zinc concentration was ranging from 0.01-585 μg/L, which may be due to a large number of industrial activities in these areas [22].

4. Distribution of water quality characteristics in the study area using contour maps.

Three-dimensional contour maps were plotted for each water quality characteristic to identify their distribution and direction in the study area based on the coordinates of wells and concentration. Figure 2 shows the high values of electrical conductivity in the north-east direction, which is the Ashhi region, and the south west, which is the area of Al-mojama district within the study area, while its values decreased in the middle of the region. As expected, due to the association of total dissolved solids with electrical conductivity, the increase of total dissolved solids were in the same directions that increased the conductivity values as in figure 3. The figure shows that the total dissolved solids decline was more
severe in the direction of the south-east of the study area in the areas of Daqouq, as the values of total dissolved solids decreased below 1000 mg/L [14].

Table 2. Some of the characteristics of the study area wells.

| well | EC (μs/cm) | TDS (mg/L) | pH | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | Cl⁻ (mg/L) | NO₃⁻ (mg/L) | SO₄²⁻ (mg/L) | Pb (µg/L) | Cd (µg/L) | Zn (µg/L) |
|------|------------|------------|----|-------------|-------------|-----------|-------------|-------------|-----------|-----------|-----------|
| W1   | 850        | 480        | 7.6 | 172         | 92.3        | 80        | N/A         | 40          | 2.5       | 0.3       | 2         |
| W2   | 800        | 460        | 7.8 | 124         | 89.9        | 90        | N/A         | 80          | 1.1       | 0.2       | 1.2       |
| W3   | 900        | 430        | 7.9 | 240         | 24.3        | 115       | N/A         | 55          | 2         | 0.4       | 1.5       |
| W4   | 750        | 510        | 7.8 | 212         | 21.8        | 130       | N/A         | 75          | 0.9       | 0.2       | 2.2       |
| W5   | 760        | 550        | 7.7 | 260         | 12.1        | 75        | N/A         | 80          | 0.92      | 0.5       | 5.3       |
| W6   | 810        | 490        | 7.7 | 220         | 31.5        | 60        | N/A         | 95          | 0.3       | 2         | 2.4       |
| W7   | 700        | 650        | 7.9 | 232         | 29.1        | 45        | N/A         | 110         | 0.7       | 0.5       | 3         |
| W8   | 1000       | 710        | 8.0 | 212         | 26.8        | 320       | 0.001       | 470         | 1         | 0.4       | 5         |
| W9   | 1300       | 730        | 7.8 | 124         | 20.1        | 300       | 0.005       | 490         | 1.2       | 0.5       | 6.6       |
| W10  | 1400       | 820        | 7.5 | 168         | 29.1        | 330       | 0.008       | 530         | 1.4       | 0.5       | 6.5       |
| W11  | 1630       | 500        | 8.2 | 144         | 26.8        | 400       | 0.01        | 690         | 2         | 0.6       | 10.5      |
| W12  | 1200       | 680        | 7.8 | 192         | 22.8        | 320       | 0.008       | 510         | 1         | 0.5       | 6         |
| W13  | 1450       | 880        | 8.0 | 232         | 26.8        | 410       | 0.01        | 650         | 2.2       | 0.7       | 12        |
| W14  | 1500       | 900        | 8.3 | 200         | 67.2        | 260       | N/A         | 410         | 0.9       | 0.1       | 2         |

Figure 4 shows the decrease in pH in the groundwater from the east to the west in the study area. The decline was more severe in the southern part of the study area, while the highest values were in the south-east direction of the village of Ghida and towards Kirkuk- Bagdad Street. Figure 5 shows a sharp increase in the value of the Total hardness as we move south in the study area towards the Daqouq- Kirkuk road. The highest values were recorded in the south-west, which includes areas near Al-Zahra neighborhood within the study area; While Total hardness recorded a high decline in the west of the study area [14].

![Figure 2. Contour map for electrical conductivity of groundwater in the study area.](image-url)
Figure 3. Contour map for total dissolved solids of groundwater in the study area.

Figure 4. Contour map for pH of groundwater in the study area.

Figure 6 shows the concentration of calcium ions in the groundwater towards the western part of the study area, and in the direction of the Kirkuk-Baghdad road, as shown in figure 6, while no changes were recorded in calcium ion towards the north-south axis, Values for the ions include wider areas than in total hardness.

Figure 7 shows that the lowest concentration of magnesium ions in groundwater was recorded in the northeastern part of the study area and increased westward to reach the highest value in the village of Ghida. The values of this ion are then decreased from the above-mentioned area to the north in the areas of Ali Saray and Topazawa [14].

Figure 8 shows the increase of chloride ion concentrations in the south east direction of the study area, which includes the northern section of Ashti district and Daqouq district center, and the concentrations decrease in the north of the study area.
Figure 5. Contour map for Calcium ion of groundwater in the study area.

Figure 6. Contour map for Magnesium ion of groundwater in the study area.

Figure 9 shows that the concentration of nitrates in the groundwater increases if we move south towards the study area, in the Ishtar region. Nitrates decrease in the westward direction to reach the lowest levels in the areas near Al-Zahra and Ashaer areas. This is due to the low population activity in these areas. Lack of septic tanks, which are the main source of nitrates. Figure 10 shows the increase of sulphate concentrations to the south in the western part of the study area, which includes the village of Markum and the village of Suhail. The reason is that the geological formations of these areas contain large amounts of gypsum and anhydrite (Alfatha formation), which dissolve easily in water [8], sulphate concentrations decrease sharply towards the east, especially in the southern part of the study area.

Figure 11 shows the increase of lead concentrations to the south of the study area and less severe eastwards. This can be attributed to the lack of vegetation cover and civil installations in these areas and thus the leakage of large amounts of rainwater and the pollutants it carries with it [8]. Figure 12 shows the increase of cadmium concentration to the north, at Al-Zahra, Ashti, and Daqouq districts [27]. This can be attributed to the effect of vegetation as in lead [28, and 29]. The concentration of zinc is increased to the south-west axis of the study area, which includes Al-Zahra and Daqouq districts, as well as the north-east direction, in the areas of Ashti district [8]. The change in the concentration of zinc was slightly towards the northwest-southeast axis in the vicinity of Suhail village (figure 13).
Figure 7. Contour map for Chloride of groundwater in the study area.

Figure 8. Contour map for Nitrate of groundwater in the study area.

Figure 9. Contour map for Sulphate of groundwater in the study area.
Figure 10. Contour map for Pb ion of groundwater in the study area.

Figure 11. Contour map for Cd ion of groundwater in the study area.

Figure 12. Contour map for Zn ion of groundwater in the study area.
5. Conclusion
The results obtained from the physical and chemical tests and the trace elements of water samples taken from several wells from the Daqouq district in Kirkuk governorate can be reached with the following conclusions:

The groundwater in the district of Daqouq of the province of Kirkuk is valid as a source for drinking purposes with some of the treatments.

The groundwater in the district of Daqouq of the province of Kirkuk is valid as a source for irrigation crops directly.

Geological formations and their containment of gypsum, anhydrite, and carbonic rocks have played a major role in the deterioration of groundwater quality in the study area.

For all characteristics, the study area was differences in the characteristics of groundwater quality in wells.

The three-dimensional contour maps that were drawn based on the characteristics of the well water quality and its characteristics showed a clear image of the distribution of the qualitative characteristics of the groundwater in the region.

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