HYDROGEOCHEMICAL EVALUATION OF THE GROUNDWATER WITHIN ABU JIR FAULT ZONE, HIT – KUBAISA REGION, CENTRAL IRAQ

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Key words: Hit, Abu Jir, Geochemical evaluation, Flow system, Groundwater, Iraq

ABSTRACT

The main theme of the study is to illustrate the groundwater quality in the hydrogeologic system within Abu Jir Fault Zone (Hit – Kubaisa region). The monitoring networks of the groundwater quality and water point locations were determined on the basis of the available previous information. The changes in the chemical composition of the all groundwater in the area were examined to get the spatial distribution of each parameter.

Three groups of factors that govern the groundwater quality in the studied area were determined:
- Mineralogy of the aquifer sediments.
- System of the dissolved load carrying and its relation with the water flow system.
- Hydro-geochemical processes (mixture, dispersion, enrichment and ionic exchange).

The main hydrochemical characteristics of the groundwater are presented in detail, regarding their concentration as space variations. The results show great dispersal of the data with dissymmetric distribution.

Special attention was given to ionic ratios, which facilitate the elucidation of the hydrochemical origin of these waters. The classification of the groundwater according to their hydrochemical facies enabled the definition of three main types with dominance of sodic and calcic chlorides, just like the connate water of marine origin and oil field waters mixed with water of meteoric origin. Besides, these waters are from fractured water bearing horizons of Fat'ha, Euphrates, Ana and Baba formations. More salty water could be observed in the discharge zone of deeper horizons in older formations than those of shallow horizons in formations of younger ages.

The physico-chemical parameters of spring waters indicate preferable factors that encourage the use of some of these springs in medical purpose.

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INTRODUCTION

The study of the groundwater quality is achieved in an area of about 2300 km². Physiographically, it is located within the low valleys region. To the west of Euphrates River, exactly in Hit – Kubaisa region, between the following coordinates (Fig.1):

Longitude 42° 15' – 42° 57'
Latitude 33° 15' – 33° 42'

Geomorphologically, the area is characterized by undulated plateau plain, gradually, elevated towards west from (50 – 200) m (a.s.l). Sissakian and Salih (1994) classified the geomorphic units into five types:
- Mesas and plateau (originated due to erosion factors with structural effect)
- Hills and pediment (originated due to erosional factors)
- Alluvial terraces, flood plains, depression and valley fill sediments (originated due to erosional and depositional factors).
- Karst, depressions and valleys (originated due to physical and chemical weathering).
- Sabkhas and salt crusts (originated due to climatic factors, such as temperatures and evaporation).

The climatologic factors are derived from meteorological station in Haditha, Ramadi and Rutbah, during long term period (1971 ~ 2000), which indicate that the investigated area is characterized by arid climate (Gharbi, 2005). The mean annual minimum and maximum temperatures range between (12.3 – 29.15)°C, the mean annual rainfall is 142 mm, ranges between (138.59 – 143.17) mm, and the mean annual evaporation is 106 mm, ranges between (100.1 – 113.3) mm.

Structurally, the studied area is located within the transitional zone between Stable and Unstable Shelves, including Abu Jir Fault Zone, which is characterized by Right-lateral Strike Slip Fault (Fouad, 2004).

The Stratigraphic section which represents the studied area is summarized in Table (1) (Hussien and Gharbi, 2007):

### Table 1: Sequence of geologic formations within the studied area

<table>
<thead>
<tr>
<th>Formation</th>
<th>Depth (m)</th>
<th>Age</th>
<th>Geologic Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary Fat'ha Euphrates</td>
<td>0 – 5</td>
<td>Quaternary Middle Miocene</td>
<td>Clay, sand, gravel</td>
</tr>
<tr>
<td></td>
<td>5 – 28</td>
<td></td>
<td>Gypsum, limestone, marls.</td>
</tr>
<tr>
<td></td>
<td>28 – 75</td>
<td>Early Miocene</td>
<td>Limestone, interbedded with marl and chalky fossiliferous limestone.</td>
</tr>
<tr>
<td>Anah</td>
<td>75 – 99</td>
<td>Late Oligocene</td>
<td>Chalky, brecciated, marly fossiliferous limestone.</td>
</tr>
<tr>
<td>Baba</td>
<td>99 – 149</td>
<td>Middle Oligocene</td>
<td>White consolidated dolomitic limestone.</td>
</tr>
</tbody>
</table>

**METHODOLOGY AND AIMS**

The groundwater quality of the hydrogeologic system is examined by 24 water points (springs) that represent the groundwater of different water bearing horizons within the studied area. Twenty-eight variables including hydraulic, physical and chemical components were used in this study to discuss and evaluate the groundwater quality for future Balneological studies as data base preparation (Agishi and Ohatsu, 1998). Nineteen chemical and mineralogical components were used in determination of the geochemical characteristics of sediments that can be benefited for future therapeutic and medical uses.

Available geological, climatological, hydrogeological information were used in research discussion. This information is derived from different references carried out since 1983 until 2007, mentioned wherever required. Furthermore, raw data included in the studied literature was considered as a helpful and beneficial for presentation and configuration of the data to get a better view for hydrochemical condition of springs, (Al-Ani, 1983; Ahmed, 1984; Mahmood et al., 2001 and Gharbi, 2005). Raw data is statistically treated to be more reliable for achieving maximum interpolation and extrapolation results in hydrogeological and hydrogeochemical interpretation.
HYDROGEOLOGIC CONDITIONS

The hydrogeologic conditions and the hydraulic characteristics of the water bearing horizons within the hydrogeologic system of Hit – Kubaisa region are explained in details by Hussien and Gharbi (2007). The hydrogeologic system is defined by the regional depositional basin of Middle Oligocene – Quaternary sediments. According to the properties of the formation sediments, the hydrogeologic system is divided into:

- **First Hydrogeologic Unit** (water bearing horizons of Quaternary sediments). This Unit is mainly composed of silt, sand, gravel, sandy gravel, and characterized by unconfined local extension of bank storage condition, exists along right side bank of the Euphrates River.

- **Second Hydrogeologic Unit** (water bearing horizons of Fat'ha Formation). These horizons are composed of porous limestone and fractured gypsum, which are characterized by semi-confined to confined condition of small extension.

- **Third Hydrogeologic Unit** (water bearing horizons of Euphrates, Anah and Baba formations). The horizons are composed of fractured, brecciated, fossiliferous, porous limestone and dolomitic limestone.

These horizons are characterized by unconfined condition in the exposed recharge area and semi confined to confined condition in the discharge area. The flow behavior regime and the groundwater movement, considering the regional and local structural phenomena, show general pattern of groundwater flow to the ENE direction, slightly deflected to NE and SE directions (Fig.2). According to the groundwater divide and flow direction, the studied area is divided into two districts. The first is in the northern part with groundwater velocity of about 0.030 m/ day, while the second is in the southern part with groundwater velocity of about 0.017 m/ day.

![Fig.2: Hydrogeologic Map of the studied area](Image)

(Geological Map: Sissakian and Salih, 1994 and Hydrogeological Map: Hussein and Gharbi, 2007)
The amount of groundwater inflow to the hydrogeologic system is $32.32 \times 10^6$ m$^3$/year, while the groundwater outflow from the system is $10.74 \times 10^6$ m$^3$/year, where the annual amount of the water discharge from springs, distributed in the studied area, within different hydrogeologic units is $21.58 \times 10^6$ m$^3$/year (Hussien and Gharbi, 2007).

**DISCHARGE OF SPRINGS**

The discharge amount of springs, within the studied area, ranges between (0.5 – 230) l/sec (Hussien and Gharbi, 2007). These springs are classified according to Todd (1970) as springs of low discharge flow (6$^{th}$ order) to high discharge flow (3$^{rd}$ order). Also these springs are distributed in four geographic groups, as shown in Table (2) that shows high discharge springs are located west and northwest of Kubaisa, with average discharge of about 65 l/sec (5616 m$^3$/year). Followed by springs located north and northeast of Kubaisa, with average discharge of 25.64 l/sec (2215 m$^3$/year). Springs of Hit – Ma'moora – Marij area, with average discharge of about 22.20 l/sec (1918 m$^3$/year) and the springs of south Kubaisa – Assforia area, with average discharge of about 17.75 l/sec (1533 m$^3$/year).

**Table 2: Discharge of springs within the studied area**

<table>
<thead>
<tr>
<th>No.</th>
<th>Group</th>
<th>Springs No.</th>
<th>Discharge Range (l/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Hit Springs</td>
<td>ST-1, ST-2, ST-3, ST4, SS-5, ST-6, ST-7, SS-8, ST-24</td>
<td>1 – 100</td>
</tr>
<tr>
<td>B</td>
<td>N – NE Kubaisa Springs</td>
<td>SS-10, SS-11, SS-12, SS-14</td>
<td>0.2 – 100</td>
</tr>
<tr>
<td>C</td>
<td>W – NW Kubaisa Springs</td>
<td>SS-15, SS-16, SS-20, SS-21, SS-22</td>
<td>0.5 – 230</td>
</tr>
<tr>
<td>D</td>
<td>South Kubaisa Springs</td>
<td>SS-9, SS-18, SS-19, SS-23</td>
<td>3 – 36</td>
</tr>
</tbody>
</table>

The variation in the springs discharge is related to the amount of the deformation in the water bearing horizons; due to the activity of faults and/ or activity of chemical weathering on the planes of fractures or joints (karstification), also due to the difference in the hydraulic gradients within areas. For more details refer to Hussein and Gharbi (2007). The discharge of the springs; No. SS-12, SS-14 and SS-16 is classified as of 6$^{th}$ order. Springs No. SS-7, SS-8, SS-9, SS-11, SS-19, SS-22, ST-2 and ST-3 classified as of 5$^{th}$ order. Springs No. ST-1, SS-5 and SS-21 classified as of 4$^{th}$ order and springs No. ST-4, ST-6, SS-10, SS-15, SS-18, SS-11 and SS-20 classified as of 3$^{rd}$ order.

**GROUNDWATER TEMPERATURE**

The average of the groundwater temperature for all the studied springs is $27^\circ$C and ranges between (22 – 34)$^\circ$ C. According to Laboutka (1974), the waters of the springs are classified as sub thermal to thermal waters.

The mean annual air temperature for 30 years is $20.5^\circ$C and ranges between (13.3 – 29.5)$^\circ$ C (Hussien and Gharbi, 2007). The correlation between the springs water temperature and air temperature shows no relation, which indicates that there is no direct effect of the climatic factors on the water of the springs, and there is a source of heat flow; transported with the moderately deep percolation that affects on the temperature of the springs water by $7^\circ$C more than the average air temperatures, which equals to 25% of the springs water temperature.
The variation in the temperature values of the spring waters that ranges between (22 – 34)°C is of high significance; according to the following statistical equation:

\[
\text{Significant level } \% = \left[ \frac{\text{max temp} - \text{min temp}}{\text{average temp}} \right] \times 100 \quad \text{(Ahmed et al., 1990)}
\]

\[
\text{Significant } \% = \left[ \frac{34 - 22}{27.4} \right] \times 100 = 44\%
\]

This result can not be neglected without interpretation; accordingly, the isotherm distribution map (Fig.3) explains the following:
- The regional phenomenon of the groundwater temperature within the studied area, shows increasing of the water temperature from the west to east (that coincides with the flow direction) initiated by 22°C and terminated by 34°C, except for a small local area with decreasing water temperature (about 2°C) in SS-13 and SS-14 water points.
- The groundwater temperature within Hit and surrounding area till south of Kubaisa ranges between (27 – 34)°C and is classified as thermal water, while the groundwater temperature to the north, northeast and northwest of Kubaisa ranges between (22 – 26)°C and is classified as sub thermal water.

**HYDROCHEMICAL CLASSIFICATION**

The water of the springs, in the studied area is classified according to the chemical constituents of major ions (Schoeller classification in Al-Hiti, 1985) as chloride group of two families, which are:
- Sodium – Chloride family, which is subdivided into two main water types:
  - Na > Mg > Ca; Cl > SO₄ > HCO₃
  - Na > Ca > Mg; Cl > SO₄ > HCO₃
- Calcium – Chloride family of: Ca > Mg > Na; Cl > SO₄ > HCO₃ water type
GENETIC CLASSIFICATION

The ratios $r_{Na} + r_{K}/ r_{Cl}, r_{Mg}/ r_{Cl}, r_{Ca}/ r_{Cl}, r_{SO_4}/ r_{Cl}$ and $r_{HCO_3}/ r_{Cl}$ are calculated from the chemical constituents data for the water samples of the springs, where $r$ represents the concentration in meq%.

The hydrochemical ratio values of the water samples of the springs are listed in Table (3).

<table>
<thead>
<tr>
<th>No.</th>
<th>Water type</th>
<th>$r_{Na}/ r_{Cl}$</th>
<th>$r_{Mg}/ r_{Cl}$</th>
<th>$r_{Ca}/ r_{Cl}$</th>
<th>$r_{SO_4}/ r_{Cl}$</th>
<th>$r_{HCO_3}/ r_{Cl}$</th>
<th>$r_{(Cl– Na)}/ r_{Mg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Spring water</td>
<td>0.55 – 0.95</td>
<td>0.11 – 0.49</td>
<td>0.07 – 0.57</td>
<td>0.06 – 0.3</td>
<td>0.01 – 0.33</td>
<td>0.09 – 2.4</td>
</tr>
<tr>
<td>2</td>
<td>Sea water</td>
<td>0.878</td>
<td>0.199</td>
<td>0.035</td>
<td>0.103</td>
<td>0.004</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>Oil field water</td>
<td>0.62</td>
<td>0.085</td>
<td>0.3</td>
<td>0.009</td>
<td>0.001</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The linear correlations of hydrochemical ratio values of the springs water (Table 3) show the followings:
- According to the genetic classification of the groundwater established by Sulin’s and Ivanov et al., in Collins (1975); the water of the springs is originated from connate fossil water of marine origin; mixed by the water of meteoric origin. The connate water exists in hydrostatic condition of deeper high pressure zone; mixed with hydrodynamic groundwater influenced by meteoric water infiltration.
- Hydrochemical ratios, such as $r_{Ca}/ r_{Cl}$ and $r_{SO_4}/ r_{Cl}$, indicate that the water of the springs is classified as oil field water; in bituminous springs, and similar to oil field water; in the rest of the springs, which is characterized by low salinity than the water of oil fields.

The hypothetical salts, which are also calculated from chemical constituents of the water samples of the springs (Table 4), indicate the same conclusion about the origin for the water of the springs in the studied area, where the presence of $CaCl_2$ and $MgCl_2$ associated with low percents of $CaSO_4$ and $MgSO_4$ concentrations, indicate the replenishment of the meteoric water to the hydrogeologic system of the connate water.

<table>
<thead>
<tr>
<th>Water type</th>
<th>KCl</th>
<th>NaCl</th>
<th>MgCl_2</th>
<th>CaCl_2</th>
<th>MgSO_4</th>
<th>CaHCO_3</th>
<th>CaSO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring water</td>
<td>1.3</td>
<td>28.5 – 76.45</td>
<td>8.4 – 33.3</td>
<td>0.0 – 26.1</td>
<td>0.0 – 19.47</td>
<td>1.1 – 17.5</td>
<td>2.8 – 24.8</td>
</tr>
<tr>
<td>Sea water</td>
<td>1.5</td>
<td>77.9</td>
<td>10.9</td>
<td>–</td>
<td>6.5</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Oil field water</td>
<td>1.5</td>
<td>60.0</td>
<td>8.5</td>
<td>29.0</td>
<td>–</td>
<td>0.1</td>
<td>0.9</td>
</tr>
</tbody>
</table>

HYDROCHEMICAL CHARACTERISTICS

The following characteristics were studied:

- **Acidity**

  According to the pH values of the water samples collected from the springs, which range from (6.8 – 7.7), the groundwater of the studied area is classified as slightly alkaline to slightly acidic water. The variations of the groundwater acidity, within the studied area are slightly significant, where the significant level percentage is equal to 12.5%. These variations are reflected in the acidity distribution map (Fig.4), as:

  - One anomaly of more than 7 pH between Hit and Kubaisa regions
  - Two anomalies of less than 7 pH in Hit and north of Kubaisa region

  These cases appeared due to the existence of different gases with different concentrations in the water of the springs such as CO$_2$ and H$_2$S.
The total hardness of the groundwater, in the studied area ranges between (855 – 7900) mg/l. According to the total hardness classification (Hem, 1970 and Todd, 1980), the groundwater is classified as very hard water.

The variations occur due to the concentration of calcium and magnesium and their hydrogeochemical behavior. The hardness in the groundwater is not controlled by the carbonate hardness class (carbonate content), but it is controlled by permanent hardness (non carbonate hardness).

The total hardness increases towards the flow direction, where water have been in contact with dolomite and limestone for long duration, which permits solving process of Ca and Mg from rocks forming the aquifers.

**Hydrogen Sulphide Gas (H$_2$S)**

The concentration of H$_2$S gas in the water samples of the springs is of high percent concentration; ranges between (16 – 81) mg/l; in Kubaisa region, and between (24 – 754) mg/l; in Hit region. The water of the springs, within the studied area is classified as Hydrogen Sulphide water, where the H$_2$S concentration exceeds the cutoff concentration (10 mg/l), as distinguished by Laboutka (1974).

The existence of H$_2$S in the groundwater of the studied area is attributed to the oil field water, especially in Hit and surrounding areas, where some brine water associated with petroleum, may contain several hundreds mg/l of dissolved H$_2$S, as mentioned in Hem (1970), according to the following reduction – oxidation reactions:
\[
\begin{align*}
\text{SO}_4^{2-} + \text{CH}_4 & \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O} \\
\text{HS}^- + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{S} + \text{OH}^- \\
\text{SO}_4^{2-} + 2\text{CH}_2\text{O} & \rightarrow 2\text{CO}_2 + 2\text{OH} + \text{H}_2\text{S}
\end{align*}
\]

The Hydrogen Sulphide distribution map (Fig.5) shows positive anomaly of H$_2$S concentration in Hit region that ranges between (100 – 250) mg/l, which indicates an upward H$_2$S gas leakage associated with hydrocarbon materials (tar), across weakness structural zone, while in the western parts, shows linear increase of H$_2$S concentration that ranges between (20 – 50) mg/l, towards the groundwater flow direction which reflects another low capacity of gas leakage in the north and northwestern parts of Kubaisa region.

![Fig.5: Distribution map of Hydrogen Sulphide](image)

**Carbon Dioxide Gas (CO$_2$)**

The concentration of CO$_2$ in the water samples of sulphide and sulphide – bituminous springs are of moderate concentration, and ranges between (11 – 32) mg/l and (44 – 366) mg/l, respectively. The water of the springs can not be classified as Carbon Dioxide water, according to Laboutka (1974), because the concentrations of CO$_2$ did not reach to the concentration cut off classification (500 mg/l).

A positive linear correlation can be detected between CO$_2$ and H$_2$S gases in the water of the springs, where both concentrations increase in bituminous springs (Hit and surrounding area) than Sulphide springs (Kubaisa and surrounding area).

The existence of the carbon dioxide in the groundwater is attributed to the following reactions, especially, the water bearing horizons of limestone and dolomite:
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\[
\begin{align*}
H^+ + CO_3^- & \rightarrow HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O \\
\text{water} & \quad \text{limestone} & \quad \text{water} & \quad \text{(aq.)} & \quad \text{(aq.)} & \quad \text{(aq.)} & \quad \text{(L.)}
\end{align*}
\]

Finally, high discharge from the springs causes good condition for CO\textsubscript{2} escape off solution; as bubbles, where the concentration of CO\textsubscript{2} may be in equilibrium state under stable pressure. Accordingly, there is an observed variation in CO\textsubscript{2} concentration among water points that increases towards bitumen's springs in Hit region (Fig.6).

![Fig.6: Carbon dioxide gas distribution map](image)

**Nitrate (NO\textsubscript{3})**

The nitrate concentration in the water samples of the springs ranges between (10 – 35) mg/l. Linear correlation between NO\textsubscript{3} concentrations and the natural limit of its existence in the groundwater (45 mg/l) (Matthess, 1982) shows low NO\textsubscript{3} concentration, which is attributed to the natural upward leakage of the hydrocarbon component sources, where in the oxidation case of the nitrogen species (ammonia and ammonium) may be converted to nitrate, as shown in the following Redox reaction (involved in biologic process):

\[
\begin{align*}
NH_4^+ + 3H_2O & \rightarrow NO_3^- + 8e^- + 10 H^+
\end{align*}
\]

Oxidation of ammonium and ammonia to nitrate occurs wherever water of the springs is exposed to air, or mixed with infiltrated meteoric water, relatively saturated with dissolved oxygen.
• **Potassium and Sodium**

The concentrations of K\(^+\) and Na\(^+\) in the water samples of the springs, within the studied area range between (10 – 606) meq/l. The distribution map of K+Na concentrations (Fig.7) indicates the following phenomena:

- Generally, the concentration increases from the west to the east with the groundwater flow direction.
- A dilution case is observed in the western part of Kubaisa region, due to the replenishment process of rainwater and/ or surface runoff water through the intermittent valleys to the shallow water bearing horizons of Euphrates Formation. The high rate of springs discharge, in this region may clean the pores and cavities along the flow direction from the fossil water, which contain high percent of sodium and potassium concentrations.
- Obvious enrichment case is detected in Hit region, where the concentrations of Na+K increase abruptly from (50 – 606) meq/l within a distance not exceeding 7 Km, while the enrichment value of Na+K, in the western part increases from (20 – 50) meq/l within a distance that exceeds 15 Km. This means, there is an addition of Na+K concentrations from water of deep sources that passes across weakness fracture zones, restricted between Ma'moora village and Hit city.

![Fig.7: K+Na distribution map](image)

• **Calcium and Magnesium**

The concentrations of Ca+Mg in the water samples of the springs, within the studied area range between (20 – 155) meq/l. The presence of Ca and Mg ions in the groundwater may be due to the dissolution of Ca and Mg from limestone, dolostone and gypsum rocks, which form the aquifer.

The Ca+Mg distribution map (Fig.8) shows normal enrichment case for the Ca+Mg ions, which coincides with the groundwater flow direction. The enrichment value is 135 meq/l within a distance of about 25 Km. It indicates active hydrochemical process for dissolution of the rocks, such as dolostone and limestone that form the water bearing horizons. It also, indirectly affects the case of the groundwater, which is in active hydrodynamic case.
**Sulphate and Bicarbonate**

The concentrations of the sulphate and bicarbonate in the water of the springs, within the studied area range between (2.6 – 23.7) meq/l and (2.6 – 15.8) meq/l, respectively. The presence of the sulphate in the groundwater is due to the dissolution of the sulphate from leached secondary evaporates, such as, gypsum, which exists in soils and the brecciated limestone within Euphrates Formation. The presence of HCO$_3$ ion in the groundwater is due to the dissolution of the carbonates from limestone and dolomite, which form the aquifers productive rocks. The spatial distribution concentrations of the sulphate and bicarbonate, shows normal enrichment case that coincides with the flow direction of the groundwater, from west to east. The enrichment values for HCO$_3$ and SO$_4$ are 13.2 meq/l and 21.1 meq/l, respectively, for a distance of about 25 Km.

**Chloride (Cl)**

The concentration of the chloride in the water samples of the springs, within the studied area ranges between (31 – 636) meq/l. The distribution map of chloride concentration (Fig.9), indicates normal enrichment case for chloride concentration that coincides with the flow direction (west of Ma’moora village), with enrichment value of 20 meq/l. Also, abrupt significant change appears in the chloride concentration from 50 meq/l to 636 meq/l in the vicinity of Hit, this enrichment might be due to the mixing mechanism case of mechanical dispersion process from deep source through weakness fracture zones, between Hit city and Ma’moora Oasis. Also, concentration appears in the northwest direction of Kubaisa region. This source has local effect, where the chloride concentration is diluted towards the flow direction from 45 meq/l to 59 meq/l, as a result of dispersion mechanism with the regional groundwater movement.
The total dissolved solids in the water of the springs range between (2750 – 42820) mg/l. Normal extents of TDS values are present among the spring water points in the western part of the studied area, especially, to the west of Ma’moora Oasis, where the TDS values range between (2750 – 5400) mg/l, they are classified as slightly brackish to brackish water, according to the classification of Gorrel in Todd (1980). Large extents of TDS values are present in the eastern part of the studied area (Hit region), where the TDS values range between (5000 – 42820) mg/l, within a distance not exceeding 5 Km towards the flow direction. The groundwater is classified as salty to brine water. The TDS distribution map (Fig.10) shows abnormal enrichment in TDS values in Hit region. This abnormal phenomenon is attributed to the replenishment of the groundwater from upward leakage of oil field water across fractures zones of Abu Jir Fault.
Trace Elements

The concentrations of the trace elements (Cr, Co, Ni, Cu, Zn, Pb, Sr, Fe, Mn, Ba and Cd) in the water of Sulphide springs, which exist in the eastern part of the studied area (Kubaisa region) range between (0.01 – 0.03), (0.01 – 0.02), (0.01), (0.01 – 0.043), (0.01 – 0.1), (0.1 – 0.24), (7.1 – 13.6), (0.0 – 0.66), (0.02 – 0.06), (0.0 – 1) and (0.01 – 0.03) mg/l, respectively. The concentrations of the trace elements (Cr, Co, Ni, Cu, Zn, Pb, Sr, Fe, Mn, Ba and Cd) in the water of Sulphide – Bituminous springs, which exist in the eastern part of the studied area along the right bank of Euphrates River (Hit region) range between (0.02 – 0.07), (0.0 – 0.01), (0.0 – 0.01), (0.01 – 0.012), (0.08 – 0.3), (0.08 – 0.3), (0.1 – 0.31), (8.5 – 28.2), (0.19 – 1.16), (0.09 – 0.37), (0.0 – 0.5) and (0.01 – 0.04) mg/l, respectively. Generally, the concentrations of the trace elements in the Sulphide – Bituminous springs are relatively two to three times more than their concentrations in Sulphide springs.

The variations of the trace elements concentrations are attributed to the existence of hydrocarbon materials associated with the water of bituminous springs, where the hydrocarbons are characterized by intense ability to dissolve and leach the trace elements from solid materials (rocks). The concentrations of the trace elements in the water of Sulphide and Sulphide – Bituminous springs are within their natural limit in normal water, except for Pb, Sr, Ba and Cd concentrations that are slightly higher than the natural limits, where these elements are concentrated in the fossils forming limestone of the Euphrates Formation (Collins, 1975).

GEOCHEMISTRY OF SEDIMENTS

The recent sediments collected from the holes and canals of the springs in the studied area are predominantly composed of calcite, dolomite, gypsum, silica and clay minerals (montmorillonite, chlorite, palygorskite and kaolinite) (Al-Ani, 1983), with less amount of organic and bituminous materials, halite and traces of sulphide compounds.

The following minerals are originated from the aquifer beds of the studied area.
- Calcite and dolomite are originated from the limestone and dolomitic limestone of different formations in the studied area.
- Gypsum and halite are originated from the evaporates of Fat'ha Formation.
- Clay and opaque minerals, and silica are originated from the claystone, marl, marly limestone of Fat'ha and Euphrates formations and Quaternary sediments.
- Organic matter and sulphide compounds are originated from bituminous materials and gases associated with the groundwater of the water bearing horizons of the hydrogeologic system.

The chemical compositions of the sediments as oxide elements (conc. %) are shown in Table (5) (Al-Ani, 1983).

Table 5: Range and average concentrations of oxides of major elements in the sediments of the studied springs

<table>
<thead>
<tr>
<th>Oxide concentration (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>31 – 45</td>
<td>8 – 12</td>
<td>4 – 10</td>
<td>0.05 – 0.11</td>
<td>6 – 13</td>
<td>6 – 25</td>
<td>0.01 – 0.6</td>
<td>1 – 1.8</td>
<td>0.2 – 0.7</td>
</tr>
<tr>
<td>Average</td>
<td>37.8</td>
<td>10</td>
<td>6.4</td>
<td>0.07</td>
<td>9.1</td>
<td>14.3</td>
<td>0.03</td>
<td>1.4</td>
<td>0.52</td>
</tr>
<tr>
<td>Existence natural limit in shale</td>
<td>15.62</td>
<td>15.11</td>
<td>6.74</td>
<td>0.11</td>
<td>2.48</td>
<td>3.09</td>
<td>1.29</td>
<td>3.2</td>
<td>0.77</td>
</tr>
</tbody>
</table>

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The chemical composition of the sediments of the studied springs is compared with their natural existence limits (Turkian and Weddephol, 1961). The comparison shows the followings:

- The concentration percent of titanium, potassium, sodium, manganese, iron and aluminum oxides are less or within their existence limits in shale and clays.
- The concentration percentages of magnesium, calcium and silica oxides are more than their existence limits in shale, because the mother rocks of these components, in the studied area are dominantly limestone, dolomite, marl, silt and clay of Fat'ha and Euphrates formations and Quaternary sediments. While some increase of SiO$_2$ in these sediments is attributed to additional chemical deposition from the slightly acidic water of the springs after overflow of the water to the surface across spring holes, exposing to the atmosphere.

The chemical precipitation of the silica occurs due to the following reactions:

$$\text{Al}_2\text{SiO}_5(\text{OH}) + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$$

\text{kaolinite} \quad \text{acidic condition} \quad \text{silicic acid}

$$\text{H}_4\text{SiO}_4 \leftrightarrow \text{SiO}_2 + 2\text{H}_2\text{O}$$

\text{Silicic acid (aq)}

The trace elements concentration (ppm) of the sediments of the studied springs is listed in Table (6).

Table 6: Ranges and averages of the trace elements concentration (after Al-Ani, 1983)

<table>
<thead>
<tr>
<th>Trace elements (mg/l)</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
<th>Sr</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td>80.5</td>
<td>16.4</td>
<td>129.7</td>
<td>74.2</td>
<td>117.2</td>
<td>2.9</td>
<td>107.5</td>
<td>609.7</td>
<td>32353</td>
<td>462</td>
</tr>
<tr>
<td><strong>E.N.L. (shale)</strong></td>
<td>100</td>
<td>20</td>
<td>95</td>
<td>57</td>
<td>80</td>
<td>0.3</td>
<td>20</td>
<td>450</td>
<td>47000</td>
<td>850</td>
</tr>
</tbody>
</table>

The comparison of the trace elements concentrations with their natural limits in shale (Krauskopf, 1967) shows:

- Enrichment in the concentrations of Ni, Cu, Zn, Cd, Pb due to the increase of the trace elements precipitation mechanisms as sulphide compounds in reduction condition.
- The concentration of strontium is higher than it is natural existence, because these sediments are mainly originated from the limestone and dolomite of high Sr percentage, which represent the mother rocks of soils, in the studied area.
- The concentrations of Fe, Mn, Cr, Co elements are lower than their natural limits, because these elements become solvable and easily leached from sediments, in the case of acidic reduction environment, where, the water of the spring transports these trace elements as dissolved loads.
CONCLUSIONS AND DISCUSSION

• The mount of the springs discharge varies from low discharge rate (0.5 l/sec) to high discharge rate (230 l/sec); it is classified as of third to sixth order springs, respectively. These variations in the springs discharge are attributed to the variations in the amount of deformation that occur in the water bearing horizons.

• The groundwater temperature increases towards the groundwater flow direction from the west to the east. The correlation between air and spring waters temperatures shows that there is no direct effect of climatic factors on the groundwater temperature, but there is a source of heat flow from moderately deep sources.

• The groundwater temperature within Hit and surrounding area, including the area south of Kubaisa, ranges between (27 – 43)°C, and is classified as thermal water, while the groundwater temperature north and northwest of Kubaisa ranges between (22 – 26)°C, and is classified as sub thermal water.

• The groundwater is hydrochemically classified as chloride group of two families. These are:
  - Na – chloride family
  - Ca – chloride family
  
  The Na – chloride family is subdivided into the following water types:
  1- Na > Mg > Ca; Cl > SO₄ > HCO₃
  2- Na > Ca > Mg; Cl > SO₄ > HCO₃

  The Ca – chloride family is of the following water type:
  Ca > Mg > Na; Cl > SO₄ > HCO₃ water type

• According to the genetic classification; the groundwater is originated from connate fossil water of marine origin; mixed by the water of meteoric origin, where the connate water exists in hydrostatic condition; mixed with hydrodynamic groundwater influenced by infiltration of the meteoric water.

• According to the hydrochemical ratios, the groundwater is classified as oil field water, in bituminous springs and similar to oil field water, in the other springs, which are characterized by lower salinity as compared to oil fields water.

• The salts that can be segregated from the groundwater after evaporation process under natural condition are KCl, NaCl, MgCl₂, CaCl₂, MgSO₄, CaHCO₃ and CaSO₄. The concentrations percentages range between (1.3 – 6.3) meq%, (28.5 – 76.45) meq%, (4.8 – 33.3) meq%, (0.0 – 26.1) meq%, (0.0 – 19.47) meq%, (1.1 – 17.5) meq% and (2.8 – 24.8) meq%, respectively.

• The water bearing horizons are characterized by:
  - Slightly acidic to slightly alkaline water, where pH values range from 6.8 to 7.7. The pH values show that the groundwater is suitable for different uses.
  - Very hard water, where the total hardness of the groundwater ranges between (855 – 7960) mg/l. The hardness is controlled by permanent hardness (non carbonate hardness), which increases towards the groundwater flow direction, where water have been in contact with dolomite and limestone for long time.
  - High percentage of H₂S concentrations range between (16 – 81) mg/l, in Kubaisa region and between (24 – 754) mg/l, in Hit region. The existence of H₂S in the groundwater is originated from the oil field water, where the concentration of H₂S increases in the case of water associated with bitumen; accordingly, the groundwater might be classified as Hydrogen Sulphide water.
- Moderate concentration of carbon dioxide ranges between (11 – 32) mg/l and (44 – 366) mg/l in sulphide and sulphide – bituminous springs.

- Low nitrate concentrations range between (10 – 35) mg/l. These concentrations are less than their natural existence in the groundwater (45 mg/l), originated from natural upward leakage of hydrocarbon components sources.

- The chemical constituent's concentrations of the groundwater represented by major ions \((K^+, Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} \text{ and } HCO_3^-)\) are attributed to:
  - The dissolution mechanisms that occur on the mineral compositions of the sediments.
  - Chemical constituents of connate fossil water of marine origin.
  - The mixing mechanisms between deep oil field water and the shallow meteoric groundwater.
  - The chemical constituent's distribution in the studied area shows increase in their concentration towards the groundwater flow direction, due to the convection transport process, synchronized with the groundwater velocity.

- The main phenomenon that obviously appeared, as abrupt increase of major ions concentrations between Ma'moora and Hit region, along side the western bank of Euphrates River, where the mechanical dispersion process plays as main factor for groundwater mixing, is resulted from irregular tortuous flow across weakness fracture zones.

- According to the TDS concentrations, the groundwater is classified as slightly brackish to brackish water in the area west of Hit region, while the groundwater in Hit region is classified as salty to brine water.

- The concentrations of the trace elements (Cr, Co, Ni, Cu, Zn, Pb, Sr, Fe, Mn, Ba and Cd), in the water of bituminous springs are relatively more than their concentrations in the other springs. The concentrations of the trace elements are within the natural limits of their existence in natural waters, except for Pb, Sr, Ba, and Cd that increase towards the flow direction, also with the existence of hydrocarbon materials, which are associated with the water of the springs.

- The distribution of the trace elements concentrations shows the same phenomenon that was observed in the major ions distribution, such as the abrupt increase limit of their concentrations within Hit region, due to the tortuous flow resulting from the pressure variations between water bearing horizons (Upward Leakage).

- The sediments at the surroundings of the studied springs are composed of calcite, dolomite, gypsum, silica, clay minerals (e.g. montmorillonite, chlorite, palygorskite and kaolinite), organic and bituminous materials, halite and traces of sulphide compounds. The average concentrations of the oxides of the major elements (SiO\(_2\), Al\(_2\)O\(_3\), MnO, CaO, Na\(_2\)O, K\(_2\)O and TiO\(_2\)) are (37.8, 10, 6.4, 0.07, 9.1, 14.3, 0.03, 1.4, and 0.52) %, respectively, while the remaining 20% represents the organic materials, sulphide compounds and ignited residue.

- The average concentrations of the trace elements in the springs sediments (Cr, Co, Ni, Cu, Zn, Cd, Pb, Sr, Fe, and Mn) are (80.5, 16.4, 129.7, 74.2, 117.2, 2.9, 107.5, 609.7, 32353 and 462) mg/l, respectively. These concentrations show enrichment in the concentration of Ni, Cu, Zn, Cd, pb and Sr, due to the precipitation process; according to the Redox potential (Eh) reaction.

- The groundwater of the hydrogeologic system is unsuitable for domestic, human drinking use, swimming and recreational purposes, also unsuitable for building and industrial purposes. But, it can be used for agricultural purposes for tolerant plants, in case of the presence of permeable soils.
• All hydro-geochemical parameters that are earned from this research (groundwater and sediments quality) might be used for comparison and preferring among the water of the springs for Balneo-therapeutic studies.

RECOMMENDATIONS

- This study finds that it is necessary to perform full water chemical analyses for the water points, which help us in choosing the best springs that can be used for medical therapy.
- The existence of H$_2$S and CO$_2$ gases, NO$_3$ and strontium in the most of water points give an evidence for future hydrocarbon exploration, especially, in the area located west and northwest of the studied area (Muhiwir Depression).

REFERENCES


