Monitoring and Assessment of hydrochemistry Properties of Groundwater, Menoufia Governorate, Egypt

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Abstract: The present study is an attempt to evaluate the hydrochemistry groundwater properties of Menoufia Governorate. A total of 40 groundwater samples were collected for the period of one year (January, April, July and October, 2017) from different Cities (Tala, Birket El Sab, El Shohada, Quesna, Shibin El Kom, Menouf, El Bagour, Sers El Lyam, Ashmoun, and Sadat City). Total depth of aquifers varied from 17 to 35 m. In this study, the concentration of major ions has been investigated in terms of temporal and spatial variations. The range and annual average values of Physicochemical parameters were: Ca2+ (3.03±1.66) for turbidity in NTU; 221-1048 (612±114) for conductivity (EC) in μS/cm, 147-699 (413.0±76.0) mg/l for total dissolved salts; 7.31-7.98 for pH, 100-437 (221±43) mg/l for total alkalinity and 146-220 (180.0±22.1) mg/l for total hardness. The concentration of major cations (range and average values in mg/l) were in the following order: Na+ (34.6-108.0, 61.9±12.94) > Ca2+ (32.3-52.5, 39.7±3.4) > Mg2+ (14.8-23.4, 19.8±1.5) > K+ (0.30-1.80, 0.85±0.31). The range and annual mean concentration (mg/l) of the major anions were arranged as the following order: HCO3− (95.18-429.5, 211.8±42.9) > SO42− (51.3-138, 82.3±15.3) > Cl− (27.0-83.7, 50.3±9.3) > CO32− (2.4-26.4, 9.82±4.0). Calcium is the dominant cation, while Bicarbonate dominates the anionic components of the groundwater. Piper diagram used to illustrate the relative concentrations of the major ions and to identify the water types of the groundwater in the study area, Ca-SO4 (calcium sulphate) was presented. Most of the groundwater samples of Menoufia Governorate revealed molar ration of Mg/Ca more than 0.5 and less than1.0, these may be indicated the equilibrium of water with both calcite and dolomite.

Keywords: Groundwater, hydrochemistry, Menoufia Governorate, piper diagrams

1. Introduction

The groundwater has become one of the most important sources of water for various human activities, there is an increasing dependence on groundwater resources in urban and rural regions. Thus, the quality and quantity of groundwater are continuously under threat. Gupta and Sarma (2016) showed that problems of decreasing groundwater table and deteriorating groundwater quality have become a common problem throughout the world. In semi-arid and arid regions of the world, most of the water demands are met by groundwater supplies as the factors of main population growth and climate change cause severe stress to surface water supplies in these areas (Edmunds et al., 2003; Kulkarni et al., 2015). The quality of groundwater is extremely controlled by two main factors; the first is natural processes such as movement of groundwater, soil/rock interactions with water, recharge water quality, and geology. The second important factor is anthropogenic activities, which are mainly represented urbanization with increasing exploitation of water resources, agricultural production and industrial growth (Helena et al., 2000; Chan, 2001). For these reasons, the study of groundwater quality assessment is important at spatial and temporal variations for managing this vital resource, especially in water-scarce regions. Many researches were done on the groundwater studies (RIGW, 2003; Abu Zeid and Rady, 1992; Hefny, 1992; RIGW/IWACO, 1999; Shata, 2001; Allam et al., 2002and El Tahlawi (2004, 2006). The chemical composition of Menoufia groundwater with respect to the major ion constituents (Ca2+, Mg2+, Na+, K+, Cl−, HCO3−, CO32− and SO42−), as well as total alkalinity, total dissolved salts and pH are important to water quality. The major ion composition reflects the various sources of dissolved material that affect on the groundwater systems.

The aim of the present work is to study the levels of the major ions of the groundwater in Menoufia Governorate in temporal and spatial trends during the period 2017, as well as to study the water types using piper diagram.

2. Materials and Methods

2.1 Area of study

El-Menoufia governorate one of the Middle Delta governorates in Egypt. The investigated area falls in the semi-arid zone. The total area covering an extent of 2543 km2 (981.99 sq mi). The study area occupies the southern part of the Nile Delta. This area is bounded by longitudes 30.99°E and latitudes 30.52°N. (Fig1). Menoufia Population represented about 4, 366, 000 (in January2018). It is generally hot in summer (37- 40 °C) and cool in winter (12-20°C). Rainfall occurs between December and February during the year; the average rainfall in the delta is very small and ranges from 25 mmyr−1 in the South and middle part of the Delta to 200 mmyr−1 in the North (RIGW, 1992). The main Nile Delta aquifer is formed by Quaternary deposits; it is considered as a semi-confined aquifer, it covers the whole Nile Delta. The Quaternary aquifer is covered by a thin clay layer, which leads to the characterization of this main aquifer as a semi-confined aquifer, the clay characteristics are spatially varying in the Nile Delta. The thickness of the clay layer varies from 5–20m in the south and the middle part of the delta, and reaches 50m in the north (Farid, 1980; Wilson et al., 1979 and Diab et al., 1997). The thickness and
lithological differences of the clay layer have a great effect on the degree of hydraulic connection between the ground and surface water (Saleh, 1980). The aquifer is continuously recharged by infiltration of irrigation water. The permeability ranges between 35 and 75 m/day and it decreases near the coastline due to increase in clay content. Shallow wells (<20m in depth) were dug near the household and groundwater were then pumped to the surface.

2.2 Sampling and measurements

A total 40 groundwater samples were collected seasonally in 2017 (January, winter; April, spring; July, summer and October, autumn). Sampling stations were chosen to cover the different Cities of Menoufia Governorate (Figure 1). After pumping out for 20 minutes to prevent no representative samples of stagnant or polluted water (Aris et al., 2010), the analyses were undertaken within 24 hours of the sampling operate. The bottles were rinsed using the groundwater to be sampled. The samples were taken and stored in the acid-washed polyethylene bottles (APHA, 2005). Also, the groundwater samples were filtered using membrane filter paper 0.45 μm (APHA, 2005; Zealand, 1998). The collected samples were kept at 4°C and transported to the laboratory. Groundwater samples for various physicochemical parameters were determined, which include Turbidity, pH, EC, TDS, total hardness (TH), total alkalinity(Talk), cations such as Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\) and anions Cl\(^{-}\), SO\(_4^{2-}\), CO\(_3^{2-}\) and HCO\(_3^-\). Determination of total alkalinity was carried out according to Riley and Skirrow (1965). The pH of the groundwater samples was determined using digital pH meter (Orion model 211 digital pH meter). Electrical conductivity (EC) and total dissolved salts (TDS) concentrations were measured using a conductivity probe TDS meter (model Hanna instruments HI 9635 Microprocessor conductivity / TDS meter). Classical methods of analysis were applied for the determination of the major cations by flame photometry (Modal Jenway PFP 7) for sodium and potassium (Na\(^{+}\), K\(^{+}\)) and by using the standard EDTA method titration for calcium and magnesium (Ca\(^{2+}\), Mg\(^{2+}\)). Chloride (Cl\(^{-}\)) was determined by titration against standardized AgNO\(_3\) (Mohr’s titration method). Sulfate (SO\(_4^{2-}\)) was measured by the turbidity method using the Digital Nephelo-Turbidity meter (132 model of Systronics). Carbonate and bicarbonate (CO\(_3^{2-}\) and HCO\(_3^-\)) were determined against standardized HCl (APHA, 2005). A global positioning system (GPS) Garment 12 was used for location and elevation readings (Table 1).

### Table 1: Positions of Sampling Location

<table>
<thead>
<tr>
<th>Code No.</th>
<th>Location</th>
<th>Lat.</th>
<th>Long.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Tala</td>
<td>30°40'46.19&quot;N</td>
<td>30°56'34.09'E</td>
</tr>
<tr>
<td>II</td>
<td>Birket El Sab</td>
<td>30°38'19.45&quot;N</td>
<td>31°4'52.12'E</td>
</tr>
<tr>
<td>III</td>
<td>El Shohada</td>
<td>30°35'31.25&quot;N</td>
<td>30°53'50.69'E</td>
</tr>
<tr>
<td>IV</td>
<td>Quesna</td>
<td>30°33'54.72&quot;N</td>
<td>31°9'28.47'E</td>
</tr>
<tr>
<td>V</td>
<td>Shubin El Kom</td>
<td>30°33'36.89&quot;N</td>
<td>31°0'28.40'E</td>
</tr>
<tr>
<td>VI</td>
<td>Menouf</td>
<td>30°27'57.78&quot;N</td>
<td>30°55'50.22'E</td>
</tr>
<tr>
<td>VII</td>
<td>El Bagour</td>
<td>30°25'24.96&quot;N</td>
<td>31°2'14.14'E</td>
</tr>
<tr>
<td>VIII</td>
<td>Sers El Lyan</td>
<td>30°26'32.21&quot;N</td>
<td>30°57'59.33'E</td>
</tr>
<tr>
<td>IX</td>
<td>Ashmoun</td>
<td>30°17'51.73&quot;N</td>
<td>30°58'42.46'E</td>
</tr>
<tr>
<td>X</td>
<td>Sadat City</td>
<td>30°23'7.54&quot;N</td>
<td>30°31'48.29'E</td>
</tr>
</tbody>
</table>

### Figure 1: Sampling Location of groundwater in the Study Area (2017)

3. Results and Discussion

3.1 Hidrochemical parameters characterization:

The quality of groundwater of the study area was assessed as per standard specification given by Egyptian Standards legisl and World Health Organization (WHO, 2004).

**Turbidity, pH, Conductivity, Total dissolved salts and Total alkalinity**

**Turbidity**

Turbidity is caused by suspended particles in the water, not dissolved minerals. Turbidity is measured optically by how much visible light can pass through a water sample. The acceptable and permissible limits are 1 and 5 NTU, respectively. The turbidity level in El Menoufia aquifers has changed dramatically, with more than five-fold at St. II increased from the recorded value at St. IX (Table 2 & Figure 2). This may probably due to the effect of particulate materials from the aquifer through runoff. With some exception, the turbidity in some groundwater samples was less than 1.0 NTU (turbidity units) in July and October, 2017. This is low, indicating fairly clear water. Generally, the turbidity for all the groundwater samples showed wide variation, it ranged from 0.29 to 10.31 NTU with annual mean value of 3.28±3.03 NTU; it is below the WHO standards (5 NTU).

**The pH-Values**

The pH of the groundwater gives an idea of the type and intensity of pollution. The pH of the water affects taste, corrosion, coagulation and disinfection processes. El...
Menoufia Governorate groundwater fall in the range from 7.11 at St. IV in October to 7.98 at St. X in January, 2017. The pH of groundwater was neutral to slightly alkaline, reflecting some extent of water–rock interaction within aquifers. This range of the pH value of the groundwater samples is definitely in the high end of the normal range; this may be due to active biological, which tends to raise water pH. The results showed slightly temporal variation in the pH values, ranged from 7.38±0.18 and 7.79±0.21 (Table 2& Figure 2). In general, the pH values of the groundwater in the present study were falling within the permissible limit.

Electrical Conductivity (EC)

Conductivity is the capacity of water to carry an electrical current and varies both with number and types of ions in a solution. In contrast, the conductivity of distilled water is less than 1μhmhos/cm. This conductivity depends on the presence of ions, their total concentration, mobility, valence and relative concentration and on the temperature of the liquid. Solutions of most inorganic acids, bases, and salts are relatively good conductors (Muthukumaravel et al., 2010). As shown in Table, EC values were in the ranges from 221 to 1048 μS/cm (annual mean; 612±204 μS/cm) The high EC value of groundwater may due to high amount of dissolved inorganic substances in ionized form (Saravanakumar and Ranjitkumar, 2011). The results of EC values revealed slightly increase at stations V and VI; its values were 1027 and 1048 μS/cm, recorded in July, respectively (Figure 2). The seasonal average values of EC fluctuated between 564±170 μS/cm in spring and 646±176μS/cm in winter with annual mean of 612±204 μS/cm(Table 2).

### Table 2: Spatial range, average ±SD, and annual mean of analytical results (in mg/l) of groundwater samples of the study area

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Annual mean</th>
<th>WHO 2004</th>
<th>Egyptian legend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>0.29-9.68</td>
<td>1.29±0.3</td>
<td>0.6-9.88</td>
<td>0.87-5.47</td>
<td>±3.28</td>
<td>±3.03</td>
<td>5</td>
</tr>
<tr>
<td>pH</td>
<td>7.31-7.98</td>
<td>7.74±0.23</td>
<td>7.79±0.21</td>
<td>7.7±7.97</td>
<td>7.1-7.6</td>
<td>±</td>
<td>6.5-8</td>
</tr>
<tr>
<td>EC (μS/cm)</td>
<td>440-890</td>
<td>439-931</td>
<td>221-1048</td>
<td>431-922</td>
<td>612.0±204.0</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>TDS</td>
<td>293-593</td>
<td>293-621</td>
<td>147-699</td>
<td>287614</td>
<td>408.0±136.0</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>Total H.</td>
<td>146-216</td>
<td>154-211</td>
<td>157-220</td>
<td>154-219</td>
<td>181.0±22.3</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>Total Alk.</td>
<td>100-263</td>
<td>175-256</td>
<td>112-437</td>
<td>165-283</td>
<td>219.0±38.0</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>Cl</td>
<td>34.8-54.5</td>
<td>27-75</td>
<td>27-83.7</td>
<td>41.7-79</td>
<td>50.0±13.9</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>51.3-109</td>
<td>54.1-127</td>
<td>56.1-134</td>
<td>55.2-138</td>
<td>82.3±15.3</td>
<td>250</td>
<td>400</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>4.8-16.8</td>
<td>2.4-26.4</td>
<td>2.4-19.2</td>
<td>5.4-15.6</td>
<td>9.8±4.0</td>
<td>250</td>
<td>400</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>95.2-246</td>
<td>154-246</td>
<td>109.8-429</td>
<td>154-274</td>
<td>211.8±43.0</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>Na⁺</td>
<td>34.6-108</td>
<td>38.2-93.4</td>
<td>37.696.6</td>
<td>36.1-94.8</td>
<td>62.2±21.6</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.32-1.68</td>
<td>0.33-1.72</td>
<td>0.30-1.8</td>
<td>0.33-1.65</td>
<td>0.86±0.46</td>
<td>30</td>
<td>75</td>
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<tr>
<td>Ca²⁺</td>
<td>33.6-48.8</td>
<td>33.1-49.4</td>
<td>32.3-51.2</td>
<td>32.8-52.5</td>
<td>39.80±8.85</td>
<td>200</td>
<td>75</td>
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<tr>
<td>Mg²⁺</td>
<td>15.1-22.9</td>
<td>14.8-23.1</td>
<td>15.2-23.4</td>
<td>15.4-23.4</td>
<td>19.70±2.68</td>
<td>150</td>
<td>50</td>
</tr>
</tbody>
</table>
Total dissolved salt (TDS)
TDS is a measure of the concentration of the materials dissolved in the groundwater. TDS values are changed when ions are introduced to water from salts, acids, bases, or hard water minerals. A total dissolved salt (TDS) is a measure of salinity that can have an important effect on the taste of drinking-water. The palatability of water is generally considered to be good with a TDS level less than 600 mg/l. Drinking water becomes significantly unpalatable at TDS levels greater than 1000 mg/l. The groundwater of the study area had the lowest content of TDS (147 mg/l) at station IV in July, while the high level of TDS concentration (699 mg/l) was found at station VI at the same season in July. The seasonal average values of TDS concentration ranged from 376±113 mg/l in spring season to 430±117 mg/l in winter season (Table 2 & Figure 2). The acceptable and permissible limit is 500 and 2000 mg/l, respectively (Dohare et al., 2014). The TDS values in the study area lower than those reported by (Shankar et al., 2008), their values of TDS reached to 4100 mg/l. The permissible limit of TDS in the drinking water is 1000 mg/l (WHO 1993).

Total alkalinity (T-Alk.)
It is a total measure of the substances in water that have acid neutralizing ability. It protects or buffers against pH changes. Alkalinity comes from rocks and soils, salts, certain plant activities, and certain industrial wastewater discharges (detergents and soap-based products are alkaline). If an area’s geology contains large quantities of calcium carbonate (CaCO₃, limestone), water bodies tend to be more alkaline. Alkalinity (as CaCO₃) is not a pollutant. Commonly occurring materials in water that increase alkalinity are carbonate, phosphates and hydroxides. In the present study, the absolute values of total alkalinity fluctuated between 100 mg/l at station I in January and 437 mg/l at station VI in July. The seasonal average values of total alkalinity varied between 181±50 mg/l in winter and 260±109 mg/l in summer season (Table 2 & Figure 2).

Total Hardness (TH)
Hardness is the sum of polyvalent metallic ions in water. Calcium and magnesium are the principal components, and hard waters are most common in groundwater, especially when derived from limestone, dolomite or chalk aquifers. Hard water can be unacceptable to consumers and can form scale deposits on pipes, basins, pots and hot water heaters (scale formation increases at higher temperatures). In contrast, soft water can lead to corrosion of metal pipes and elevated levels of heavy metals such as cadmium, copper, lead and zinc in drinking water. The taste threshold for the calcium ion is in the range of 100–300 mg/l and probably lowers for magnesium. The maximum calcium and magnesium concentrations were 52.5 and 23.4 mg/l July. The mean value of total hardness lies in acceptable value (200 mg/l) and is lower than the Permissible limit (600 mg/l) prescribed by WHO (2011). The total hardness during the period of study ranged from 146 in January to 220 mg/l in July with annual mean value 180.91±22.32 mg/l (Table 2 & Figure 2).

4. Distribution of Major Ions Concentrations
4.1 Calcium and Magnesium (Mg²⁺ and Ca²⁺)
A source of Magnesium in the groundwater is mainly derived from the process of ion exchange of minerals in rocks and soils by water. The concentration of Mg²⁺ in the groundwater may be influenced by rock weathering. Ca²⁺ and Mg²⁺ are important parts of drinking water and are of both direct and indirect health significance. A certain minimum amount of these elements in drinking water is desirable since their deficiency poses at least comparable health risk. Based
on the available data, the desirable minimum of Mg$^{2+}$ and Ca$^{2+}$ can be estimated to be > 10 mg/l and > 20-30 mg/l, respectively. The Ca$^{2+}$ plus Mg$^{2+}$ are the dominant cations increased than Na plus K in groundwater in the study area. Spatial and temporal variability are shown in Table 2 and Figure 3. Ca$^{2+}$ showed considerable variation in groundwater samples in the study area. The concentrations of Ca$^{2+}$ ranged from 32.30 mg/l in July at St. I to 52.50 mg/l in October at St. III, with annual mean content of 39.80 ± 5.85 mg/l. The results of Mg$^{2+}$ concentration ranged from 14.80 mg/l in April at St. X and 23.40 mg/l in July at St. II and station IX in October with annual mean value of 19.70 ± 2.68 mg/l. Temporal variability of the average concentration was between 39.3 ± 5.0 mg/l in winter and 40.2 ± 6.9 mg/l in autumn for Ca and from 19.4 ± 2.4 mg/l in winter to 19.9 ± 2.8 mg/l in summer season for Mg$^{2+}$. A relatively lower concentration of Ca$^{2+}$ and Mg$^{2+}$ is detected in all the samples collected from Menoufia Governorate groundwater. The levels of Ca$^{2+}$ and Mg$^{2+}$ concentration is below from 4 to 5 times comparing with the permissible limits (the permissible limits are 200 and 100 for Ca$^{2+}$ and Mg$^{2+}$ respectively).

Sodium (Na$^{+}$) and Potassium (K$^{+}$): Na$^{+}$ and K$^{+}$ are alkaline metals commonly occurring in natural environment. Na$^{+}$ in drinking water normally presents no health risks, as about 99 percent of the daily salt intake is from food and only about one percent from water. However, elevated sodium in groundwater may be considered a health concern for those on a salt restricted diet. Individuals on a low sodium diet due to a high blood pressure or other medical problems are often restricted to water containing less than 20 mg/l of sodium (Sayyed and Bhosl (2011)).

Figure 3: Spatial and Temporal Variation of Major Ions (Cations and Anions) Concentration for Groundwater of Menoufia Governorate

K$^{+}$ is an essential element and is present in all animal and plant tissues. The sources of potassium are likely due to silicate minerals, orthoclase, microcline, hornblende, muscovite and biotite in igneous and metamorphic rocks and evaporate deposits gypsum and sulphate release considerable amount of potassium into groundwater. Although concentrations of potassium normally found in drinking-water are generally low and do not pose health concerns, the high solubility of potassium chloride and its use in treatment devices such as water softeners can lead to significantly increased exposure.

Table 2 and Figure 3 showed the temporal and spatial variation of Na$^{+}$ and K$^{+}$ concentrations. Min., Max. and mean annual Na$^{+}$ content ranged from 34.6 to 108.0 mg l$^{-1}$ and K$^{+}$ was in the range of 0.30 - 1.80 mg l$^{-1}$ with annual mean (0.86 ± 0.46 mg l$^{-1}$), the concentration is lower 77 times than the permissible level. On this period of study, the results obtained for Na$^{+}$ and K$^{+}$ concentrations displayed greater variability. The proportions between Na$^{+}$ and K$^{+}$ concentrations fluctuated within the range between 46 and 125 in July. The highest Na/K coefficient values reached more than 100 in January at station I and in October at stations V, VII and VIII and in April and July at Station X (high Na$^{+}$ concentrations and distinctive decrease in K$^{+}$ content).

Chloride (Cl$^{-}$), Sulfate (SO$_{4}^{2-}$) and Bicarbonate (HCO$_{3}^{-}$): Cl$^{-}$ in groundwater originates from both natural and anthropogenic sources. The high Cl$^{-}$ content in drinking water may indicate possible pollution from human sewage,
animal manure or industrial waste (Shahata and Mohamed, 2015). The desirable limit for chloride is 250 and 1000 mg l\(^{-1}\) in permissible limit. The mean concentration of Cl\(^{-}\) in the study area (50 ±13.87 mg l\(^{-1}\)) was lower than the desired limit of 250 mg l\(^{-1}\) with a maximum value 83.7 mg l\(^{-1}\) at station II in July and the minimum value 26.95 at station III in April (Table 2 and Figure 3). The current results showed that the chloride concentration in all samples didn't exceed the permissible limit prescribed by USEPA, WHO and the Egyptian standards which is 250 mg l\(^{-1}\) (WHO, 2004; USEPA, 2009).

SO\(_4^{2-}\) concentration is possibly contributed by the type of precipitation and excess use of fertilizers in land cultivation. Natural water contains sulphate ions and most of these ions are also soluble in water. Many sulphate ions are produced by oxidation process of their ores, they also present in industrial wastes. SO\(_4^{2-}\) in drinking water can cause a noticeable taste above concentrations of about 250 mg l\(^{-1}\). In the absence of oxygen and free chlorine, bacteria can convert sulfate to hydrogen sulfide, which causes a distinctive “rotten-egg” odour at concentrations as low as 0.05 mg l\(^{-1}\). Desirable limit (acceptable level for sulphate is 200 mg l\(^{-1}\) and the permissible limit 400 mg l\(^{-1}\). The results of SO\(_4^{2-}\) variations in the study area are shown in Table 2 and Figure 3. A wide range of fluctuations in SO\(_4^{2-}\) content of Menoufia Governorate groundwater could be found (51.30–138.0 mg l\(^{-1}\)). In the present study, the average value of SO\(_4^{2-}\) was found within desired limits (200 mg l\(^{-1}\)). The highest values more than 100 mg l\(^{-1}\) were observed at station IV in January, April and July (ranged; 109-134 mg l\(^{-1}\)), at station VIII in July (102 mg l\(^{-1}\)), and at station III (138 mg l\(^{-1}\)) in October 2017. Temporal distribution of SO\(_4^{2-}\) concentration ranged between 79.5±20 mg l\(^{-1}\) in winter and 86±27 mg l\(^{-1}\) in autumn and the annual mean SO\(_4^{2-}\) content was 82.3±15.3 mg l\(^{-1}\) (Table 2). Use of large amount of fertilizer and pesticide is the main source of non-point pollution which increases the concentration of SO\(_4^{2-}\). The distribution of the SO\(_4^{2-}\) content levels in groundwater samples indicated that it was accepted with the standards and guideline limits (WHO, 2011 and USEPA, 2009).

The bicarbonate (HCO\(_3^{-}\)) was the dominant anion, the concentration of HCO\(_3^{-}\) showed spatial variation, due to the existence of carbonate rock in the recharge area which varied from a minimum of 95.0 mg l\(^{-1}\) at station I in January to a maximum of 430 mg l\(^{-1}\) at station VI in July. Temporal variability of the average concentration was between 8.0±6.0 mg l\(^{-1}\) in summer and 11.8±8.2 mg l\(^{-1}\) in spring for CO\(_3^{2-}\) and from 171.6±46 mg l\(^{-1}\) in winter to 252.8±107 mg l\(^{-1}\) in summer season for HCO\(_3^{-}\) (Table 2 and Figure 3). The annual mean content of CO\(_3^{2-}\) and HCO\(_3^{-}\) were 9.82 ±4.0 mg l\(^{-1}\) and 211.8 ±43 mg l\(^{-1}\) respectively.

**Ionic Ratio**

The relation of total Ca\(^{2+}\)+Mg\(^{2+}\) to total alkalinity indicated the weathering of carbonates within the aquifer in the area (Figure 4). Moreover, the molar ration of Mg/Ca (Figure 5) in the collected groundwater samples provides further information on water-rock interaction in the area. The Mg/Ca is a useful parameter providing the lithological composition of carbonate rock through which the water sample circulated (Mayo and Loucks, 1995). A ratio Mg/Ca = 1 is for dissolved water from dolomite; in contrast, a ratio Mg/Ca = 0 is for dissolved water from pure calcite. A ratio Mg/Ca of 0.5 indicates the equilibrium of water with both calcite and dolomite. Most of the groundwater samples of Menoufia Governorate revealed molar ration of Mg/Ca (Figure 5) more than 0.5 and less than 1.0, these may be indicated the equilibrium of water with both calcite and dolomite. A Ca\(^{2+}\)/Mg\(^{2+}\) ratio, greater than 2, may represent the dissolution of silicate minerals into the groundwater (Katz et al., 1997).

![Figure 4](image-url)  
**Figure 4:** Calcium and magnesium versus total alkalinity in (m mole l\(^{-1}\)) in Menoufia Governorate Groundwater
The geochemical classification of groundwater is based on ion relationships, the most common are the trilinear diagram of Piper (1953). This diagram illustrates the trend of geochemical evolution of groundwater through mixing with other sources and through water-rock interaction. The diagram consists of two triangles, one for cations and the other for anions and a diamond shape field for representing the overall chemical character of the plotted data. The classification is based on the percentage of milli-equivalent per liter of the major anion (HCO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$ and Cl$^-$) and major cations (Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$). Piper's trilinear diagram for groundwater wells consequently show that chemical composition of groundwater diamond field revealed that most of water chemical compositions are plotted.

For Menoufia Governorate groundwater samples, the cationic strength was observed as Na$^+ >$ Ca$^{2+} >$ Mg$^{2+} >$ K$^+$ with percentages in the range of 46.56%, 29.36%, 14.18%, and 0.5-1.0%, respectively. The dominant elements of the groundwater are quite different in the study area. The anions dominances of the groundwater samples were observed as HCO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ > CO$_3^{2-}$, and the ratio as percentages are 53-66%, 19-32%, 10.18% and 2.5%, respectively. The main cations are Na$^+$, Ca$^{2+}$ and Mg$^{2+}$, and main anions are HCO$_3^-$ and SO$_4^{2-}$ in the groundwater of the study area. Piper trilinear diagram, which was conceived by Hill (1940) and improved by Piper (1944), is a widely used tool to understand the hydrochemical regime and facies classification of groundwater and surface water (Ray and Mukherjee 2008; Otero et al., 2005). Sample points with similar hydrochemistry tend to cluster together in the diagram. The diamond-shaped field showed that alkaline earths exceed alkalis and strong acids exceed weak acids for all the groundwater samples. There is a slightly difference in point distribution between the groundwater samples in the diagram. The composition of elements implies weathering of carbonate minerals is the primary controlling factor. However, hydrochemistry of shallow groundwater is affected by evaporation, because relative high proportion of Na$^+$ and SO$_4^{2-}$, a higher proportion of HCO$_3^-$ which are shown in the triangular field. This behavior is the consequence of NaHCO$_3$ and CaSO$_4$ precipitation under evaporation.

The evolution of groundwater geochemical data can be understood from the plot of Piper diagram (Figure 6). From the present data, some information was obtained; the contents of Cl$^-$ are low for all groundwater samples, whereas the concentrations of SO$_4^{2-}$ and HCO$_3^-$ are high with diversity degrees for groundwater collected from different aquifers. The cations also have the similar character with the anions. The most groundwater samples from Menoufia City aquifer were characterized by the high contents of Na+, and the anions are dominated by the SO$_4^{2-}$ or HCO$_3^-$. Whereas, the groundwater samples from Quaternary aquifer have higher contents of Ca$^{2+}$ and Mg$^{2+}$. Piper’s trilinear diagram for groundwater aquifers consequently show that chemical composition of groundwater diamond field revealed that most of water chemical compositions are plotted in two fields (field 9 and field 5), those reflect Ca-HCO$_3$ and Mg-HCO$_3$ water type in the study area (Figure 6). In generally, the plot of Piper diagram has been divided into three subfields, viz. 1 (Ca–HCO$_3$ type); 2 (mixed Ca–Na–HCO$_3$ type) and 3 (mixed Ca–Mg–Cl type). The majority of the groundwater samples are concentrated in Ca–HCO$_3$ facies indicating the dominance of freshwater recharge into the aquifers.

Figure 5: Molar ratio of magnesium to calcium (mmole l$^{-1}$) in Menoufia Governorate Groundwater

Figure 6: Piper’s diagram showing the general hydrochemical change of urban groundwater (N= 40) in Menoufia City
4.2 Correlation Matrix

The correlation matrix allows us to distinguish several relevant hydrochemical relationships. As shown in Table 3, the contents of sodium, potassium, calcium and magnesium are positively correlated to sulfate with correlation coefficients of 0.759, 0.764, 0.754 and 0.694, respectively. These values indicate the interdependence of the sulfate ion and the major ions in the groundwater in Menoufia governorate. Also, a strong positive correlation was found between the total hardness and the major cations Na⁺, K⁺, Ca²⁺ and Mg²⁺ with correlation coefficients of 0.935, 0.855, 0.924 and 0.865, respectively. The correlation between Na⁺ and K⁺, Ca²⁺, Mg²⁺ showed correlation coefficients of 0.873, 0.854 and 0.823, respectively. It can also be deduced that for most of the groundwater samples these parameters originate from a common source. There is a positive correlation of Ca²⁺ with Mg²⁺ in the groundwater of the area. The positive correlation between Ca²⁺ and Mg²⁺ (0.607) is attributed to the precipitation of aragonite, dolomite and calcite (Appelo and Postma, 1996). Precipitation takes place during the cation exchange process. The results revealed lower concentration of Ca²⁺ compared to Na⁺, indicates the cation exchange process that occurs naturally into the aquifer system.

| Table 3: Correlation Coefficient Matrix of Groundwater Samples of the Study Area |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| EC          | TDS             | Total hard.     | Total Alk.      | Cl  | (SO4) | HCO3       | TOC  | Na             | K   | Ca   | Mg   |
| 1.000       | 1.000           | 1.000           | 1.000           | 1.000 | 1.000 | 1.000      | 0.997 | 0.241          | 0.006 | 1.000 | 1.000 |
| Tds         | 1.000           | 0.902           | 0.536           | 0.962 | 0.491 | 0.087      | 0.113 | -0.109         | 1.000 | 0.166 | 1.000 |
| Total hard. | 0.902           | 1.000           | 0.911           | 0.927 | 0.268 | 0.411      | 0.113 | -0.012         | 0.759 | 0.167 | 0.607 |
| Total Alk.  | 0.536           | 0.911           | 1.000           | 0.529 | 0.530 | 0.102      | 0.200 | 0.180 -0.018   | 0.764 | 0.014 | 0.655 |
| Cl          | 0.962           | 0.268           | 0.102           | 0.529 | 0.530 | 0.102      | 0.200 | 0.180 -0.018   | 0.764 | 0.014 | 0.655 |
| (SO4)       | 0.491           | 0.411           | 0.102           | 0.529 | 0.530 | 0.102      | 0.200 | 0.180 -0.018   | 0.764 | 0.014 | 0.655 |
| HCO3        | 0.087           | 0.411           | 0.097           | 0.529 | 0.530 | 0.102      | 0.200 | 0.180 -0.018   | 0.764 | 0.014 | 0.655 |
| TOC         | 0.113           | 0.112           | 0.146           | 0.113 | 0.112 | 0.146      | 0.080 | 0.078          | 0.085 | 0.164 | 0.779 |
| Na          | -0.011          | -0.011          | -0.105          | -0.011 | -0.011 | -0.105      | -0.085 | 0.178          | 0.865 | 0.162 | 0.779 |
| Ca          | -0.011          | -0.011          | -0.105          | -0.011 | -0.011 | -0.105      | -0.085 | 0.178          | 0.865 | 0.162 | 0.779 |
| Mg          | 0.164           | 0.162           | 0.865           | 0.164 | 0.162 | 0.865      | 0.085 | 0.178          | 0.865 | 0.162 | 0.779 |

5. Conclusion

Monitoring of the groundwater quality of Menoufia Governorate, south of Nile Delta of Egypt is done by collecting representative water samples. Physicochemical characteristics and the major ions of ten groundwater samples were analyzed at different locations. The average values of all physicochemical parameters and major cations and anions were found within the permissible limits of the WHO and Egyptian limits guideline for drinking water.

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