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Spatial Variations of Major Ion Chemistry and Hydrogeochemical Processes of Groundwater, Menoufia Governorate, Egypt

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ABSTRACT

The current study is conducted to spatial distribution of major ions and hadrochemical properties of forty groundwater samples collected for one year (during 2017) from ten different Cities of Menoufia Governorate, Egypt. Samples for turbidity, pH, conductivity, TDS, total alkalinity, total hardness as well as major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, SO_4^{--}, CO_3^{--} and HCO_3^{-}) were determined. The results showed variations in the regional annual mean values of all the water quality parameters tested. All the groundwater parameters have lower values than those recorded by the Egyptian standard and WHO, less than the permissible limits. The major cations follow the trend: $Na^{+} > Ca^{2+} > Mg^{2+} > K+$, the domination of sodium and calcium ions in the groundwater is due to weathering of rocks. The major anions abundance followed the order $HCO_3^{-} > SO_4^{2-} > Cl^{-} > CO_3^{2-}$. In general, the ground water of Menoufia Governorate is suitable for drinking and agriculture purposes. The molar ratios of major ions of the groundwater revealed that the chemical composition of the groundwater samples was mainly influenced by carbonate weathering with a small contribution of silicate weathering.

INTRODUCTION

Ground water is found in the small spaces and cracks between rocks and other material such as sand and gravel. In recent years, for many of the world towns or cities, groundwater seems to be the only source of fresh water to meet domestic, agricultural, and industrial needs. Earlier studies reported the importance of hydrogeochemical studies of groundwater in a region (Sikdar *et al*., 2001). Hence, to utilize and protect valuable water resources effectively and predict the change in groundwater environments, it is necessary to understand the hydrogeochemical characteristics of the groundwater and its evolution under natural water circulation processes (Edmunds *et al*., 2006; Taheri and Voudouris 2008). The factors regulating groundwater quality in an area and to understand the sources of dissolved ions were studied and evaluated by Jalali (2009). The chemical compositions of the groundwater are dominated by Na^{+}, Ca^{2+}, HCO_3^{-} , Cl^{-} and SO_4^{2-}, which have been derived largely from natural chemical weathering of carbonates, gypsum and anthropogenic activities of fertilizer's sources. The abundance of major and minor ions is related mainly to rock/water interaction, the most important interactions are adsorption and mineral precipitation/dissolution (SubbaRao 2001; Kortatsi 2006; Herlinger 2007). The relationship between the major ions versus Cl concentration of water bodies and processes influence on the chemical composition are important factors because chloride is good indicator for mixing phenomenon (Somay *et al*.,2007). Two methods are used to describe the hydrogeochemical processes of groundwater, including the determination of typical hydrogeochemical ratios, which can be evaluate the dominant and origin processes of water resources (Zhu *et al*. 2007). In addition, the multivariate statistical analysis (Saleem *et al*. 2015; Purushothaman *et al*., 2014). Several processes such as sorption, redox reactions, ion exchange, and complexation are important of geochemical activities, which may alter its hydrogeochemistry and subsequently affect the quality of groundwater. The objective of the research paper is to examine each chemical parameter through mapping of the spatial variability and to study the different processes influence on the groundwater hydrochemistry.

MATERIALS AND METHODS

Description of Study Area

El-Menoufia governorate is 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 km^2 (981.99 sq mi). The study area occupies the southern part of the Nile Delta (Fig1). Menoufia Population represented about 4,366,000 (in January 2018). 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.

Sampling and measurements

Forty groundwater samples were collected during the year 2017. Sampling stations were chosen to cover ten different Cities of Menoufia Governorate (Fig. 1). After pumping out for 20 minutes to prevent nonrepresentative 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. Turbidity, pH, EC, TDS, total hardiness (TH), total alkalinity (T-Alk.), cations such as Ca^{2+}, Mg^{2+}, Na^+, K^+ and anions Cl^-, SO_4^{--}, CO_3^{--} and HCO_3^- were determined (APHA, 2005). Total alkalinity determination was carried out using the method recorded by Riley and Skirrow (1965). The pH values were 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).

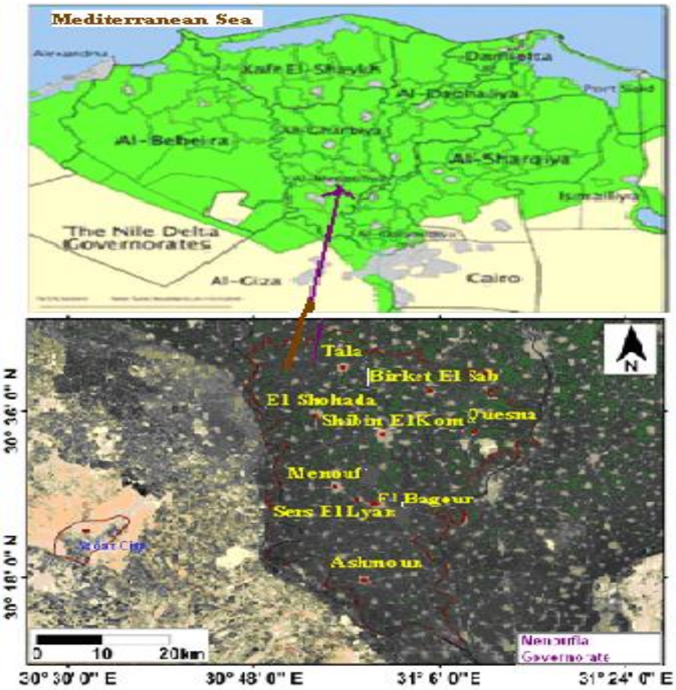

Fig. 1: Sampling Location of groundwater (2017)

Sodium and potassium (Na^+, K^+) were analyzed by flame photometry (Modal Jenway PFP 7), and by EDTA method titration for calcium and magnesium (APHA, 2005). Chloride (Cl^-) was determined by titration against standardized $AgNO_3$ (APHA, 2005). Sulfate (SO_4^{--}) was precipitated as barium sulfate and measured turbidimetrically (APHA, 2005). Carbonate and bicarbonate (CO_3^{--} 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). Portable Turbidity Meter (AMT 21).

Table1: Position of sampling locations

Code No.	Location	Lat.	Long.
I	Tala	30°40'46.19"N	30°56'34.09"E
II	Birket El Sab	30°38'19.45"N	31° 4'52.12"E
III	El Shohada	30°35'31.25"N	30°53'50.69"E
IV	Quesna	30°33'54.72"N	31° 9'28.47"E
V	Shibin El Kom	30°33'36.89"N	31° 0'28.40"E
VI	Menouf	30°27'57.78"N	30°55'50.22"E
VII	El Bagour	30°25'24.96"N	31° 2'14.14"E
VIII	Sers El Lyan	30°26'33.21"N	30°57'59.33"E
IX	Ashmoun	30°17'51.73"N	30°58'42.46"E
X	Sadat City	30°23'7.54"N	30°31'48.29"E

RESULTS AND DISCUSSION

Spatial variations of groundwater quality parameters:

The physico-chemical parameters of groundwater of Menoufia Governorate have been studied during 2017. Standards values as per Egyptian specification and WHO (2004) guidelines for water quality parameters are considered.

Turbidity and Hydrogen ion concentration (pH):

The pH of groundwater is important in defining the alkalinity equilibrium levels of carbon dioxide, bicarbonate, carbonate and hydroxide ions. The pH of most natural waters ranges from 6.5 to 8.5. The pH of the groundwater samples in the study area varies from 7.10 to 7.97, the spatial distribution of water samples pH does not show any significant variation during the periods of study. The pH shows a little variation from the south-western to the north-western part of the area. (Fig. 2).

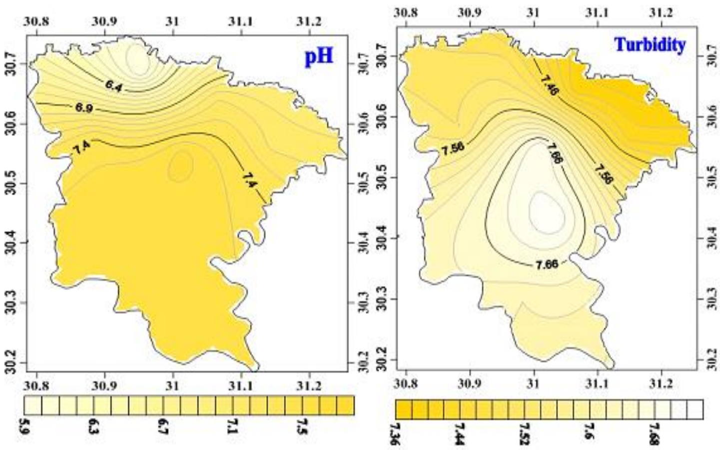

Fig. 2: Spatial distribution map of pH-Values and Turbidity (NTU) for Groundwater of Menoufia Governorate.

Turbidity is caused by suspended particles in the water, not dissolved minerals. Generally, the turbidity for all the groundwater samples showed wide variation, it ranged from 0.29 to 10.31 NTU. The spatial variation of groundwater turbidity in the study area showed significant variation during the periods of study. The turbidity values showed a greater variation from the north part to the south of the area (Fig. 2).

Spatial distribution of EC, TDS, Total Alkalinity and Total Hardiness:

EC and Total Dissolved Solids (TDS): In natural groundwater, TDS consists mainly of inorganic salts such as CO_3, HCO_3, Cl and SO_4 as well as major cations (Ca, Mg, Na and K) and small amount of organic matter and dissolved gases. The suitability of groundwater for drinking, domestic and irrigation purposes depends upon hadrochemical properties that are categorized with respect to TDS. Based on the classification given by WHO (2004), the groundwater samples of the study area fall in desirable for drinking, and useful for agriculture. The groundwater of the study area has TDS values from 147 to 699mgL^{-1}. The spatial distribution of TDS of groundwater samples is displayed in concentration maps (Fig. 3).

The lowest concentration is noticed in the south parts comparing with those recorded in the north area. The results of EC values revealed wide variation; its values ranged from221to 1048 µS/cm. The spatial variations of EC levels of groundwater samples were like the distribution of TDS (Fig. 3).

Total Hardiness: Total hardness of the groundwater is caused primarily by Ca and Mg; Ca and Mg enter the groundwater via the action of carbonic acid. As groundwater and carbon dioxide react, carbonic acid is produced and dissolves Ca and Mg from carbonate rocks (e.g. limestone, dolomite). The spatial distribution map of total hardness showed that the lowest concentration is noticed in the south, north and west of the study area, while the highest content was recorded at the north east of the study area at Birket El Sab and Quesna (Fig. 3).

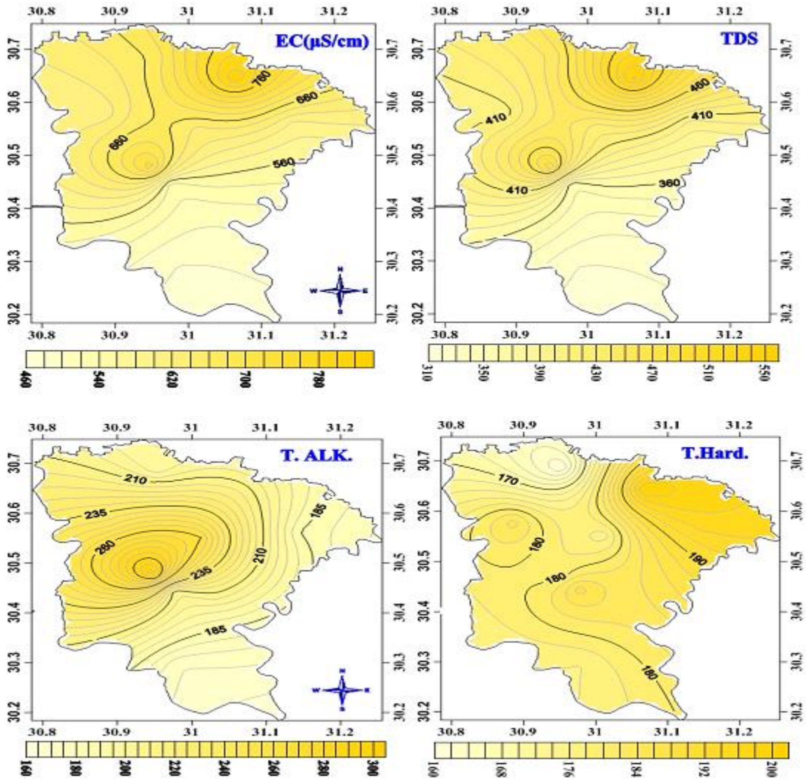

Fig. 3: Spatial distribution map of EC (µS/cm), TDS, Total Alkalinity and Total Hardiness (mgL^{-1}) for Groundwater of Menoufia Governorate

Total Alkalinity: Alkalinity is a measure of the capacity of water to neutralize acids. It is primarily determined by the presence of carbonate, carbonates and hydroxides in water. These alkaline compounds in the water remove H^+ ions and lower the acidity of the water (increased pH). Spatial distribution map of alkalinity content showed obvious variations from the northern to the southern part of the study area, the high level was found in the middle area of study of Menouf and Sers El Lyan (Fig.3).

III.1.4. Spatial variation of HCO_3, CO_3, SO_4 and Cl:

Chloride (Cl^-): Cl^- in groundwater originates from both natural and anthropogenic sources. Cl^- content in groundwater samples was much lower than the permissible limits ($250mgL^{-1}$) as per WHO (2004). Cl^- concentrations in the study area have a wide range from 27 to $83.7mgl^{-1}$. The Spatial distribution map of Cl^- revealed that the lowest concentration is noticed in the south and north west at El Shohada and Ashmoun, while the highest content is at the north east of the study area at Birket El Sab and Quesna (Fig.4). The Cl^- is compatible with Na^+ in most of the groundwater samples due to geochemical coherence between Cl^- and Na^+. Both ions are controlled by extensive and intensive weathering of granite and gneisses that contain a lot of plagioclase, alkali amphiboles, micas apatite and fluorite minerals.

Sulfate (SO_4^{2-}): SO_4^{2-}concentration is possibly contributed by the type of precipitation and excess use of fertilizers in the study area. The sulfate in the groundwater during the period of study varied from 51.3 to $138mgL^{-1}$. The maximum permissible limit SO_4^{2-} was $250mgL^{-1}$(WHO 2004). The lowest value is at Tala, El Bagour and Sers El Lyanand the highest value at Birket El Sab and Quesna. SO_4^{2-} variation is comparable with that of all major cations and anions. Spatial distribution map of SO_4^{2-} content showed obvious variations from the northern to the southern part of the study area (Fig. 4).

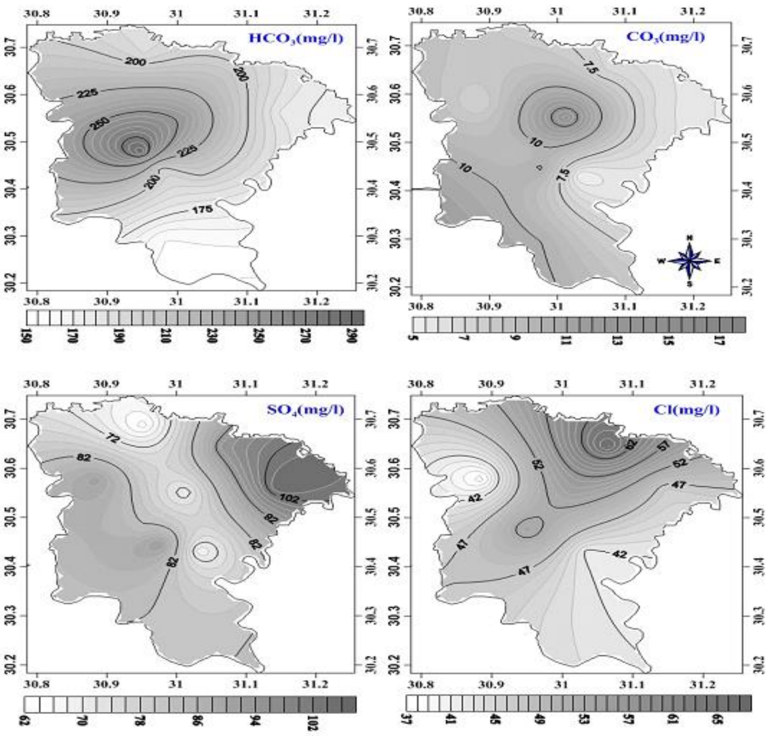

Fig. 4: Spatial distribution map of HCO_3^-, CO_3^{--}, SO_4 and Cl (mgL^{-1}) for Groundwater of Menoufia Governorate.

Carbonate (CO3) and Bicarbonate (HCO3):

The spatial distribution of CO_3^{--} and HCO_3^-in the study area showed relatively high concentration at El Shohada, Shibin El Komand and Menouf (Stations III,V and VI), in the middle and southern west part of the study area (Fig. 4).The results showed considerable variation in the groundwater samples, it ranged from 2.4-26.4$mgL^{-1}$for $CO_3^{--}$and from 95.2- 429$mgL^{-1}$for HCO_3^-.According to the Egyptian standard and WHO (2004), with some exception, the groundwater samples have lower HCO_3^-than the permissible limits (300 mgL^{-1}).

Spatial Variation of Ca, Mg, Na and K:

Calcium (Ca^{2+}): The spatial distribution of Ca^{2+} showed high concentration at Birket El Sab and Quesna (Stations II and IV), in the northeast part of the study area (Fig. 5). The results showed considerable variation in groundwater samples ranged from 33.1-52.5 mgL^{-1}. According to the Egyptian standard and WHO (2004), all the groundwater samples have lower Ca^{2+} than permissible limits (200 mgL^{-1}).

Magnesium (Mg2+): Mg^{2+}sources in the groundwater is mainly derived from the process of ion exchange of minerals in rocks and soils by groundwater (Al Ahmadi ,2013). The levels of Mg^{2+}concentration may be influenced by rock weathering and controlled by precipitate process or seasonal variation. The concentration of Mg^{2+}in groundwater ranged between14.8and23.4 mgL^{-1}. The spatial distribution of Mg^{2+}in the study area showed slightly high content at Birket El Sab and Quesna (Stations II and IV) in the northeast part of the study area (Fig.5). According to the Egyptian standard and WHO (2004), the analyzed groundwater samples are suitable for drinking purposes, since the levels of $Mg^{2+}$are within the permissible limits (<150 mgL^{-1}).

Sodium (Na^+): Na^+ concentration between 34.6 and 108 mgL^{-1}, the levels of Na^+ content are suitable for drinking purposes, since the concentrations of Na^+ are within the permissible limits (<200 mgL^{-1}).The spatial distribution of Na^+ in the study area showed slightly high level at Birket El Sab and Quesna (Stations II and IV), in the northeast part comparing with the other sites of the study area (Fig. 5).

Potassium (K^+): The spatial variation of K^+ in the study area reveled similar distribution of the other cations, showed slightly high level at Birket El Sab and Quesna (Stations II and IV), in the northeast part (Fig. 5).Low range of K^+ was recorded in the present study, ranged from 0.30 to 1.80 mgL^{-1}. The concentrations of K^+ are within the permissible limits (<30 mgL^{-1}). In general, the spatial variation of Ca^{2+}, Mg^{2+}, Na^+ and K^+ concentrations are similar in their distribution for Groundwater of Menoufia Governorate (Fig. 5).

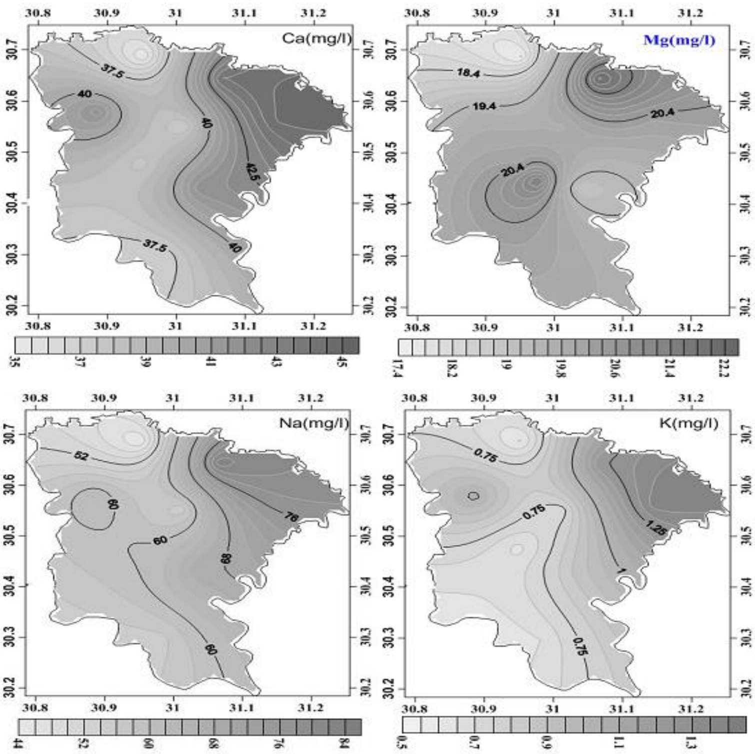

Fig. 5: Spatial distribution map of Ca, Mg, Na and K(mgL^{-1}) for Groundwater of Menoufia Governorate

Molar ratios of major ions:

Molar ratios of major ions have been utilized to attain the hydrogeochemical formation and process mechanisms of groundwater resources. Ca^{2+}/ Mg^{2+} ratio is normally used to assessment the source of Ca^{2+} and Mg^{2+} in the groundwater systems. The ratio of 1 indicates dissolution of dolomite, a ratio more than 1, indicates calcite contribution and a ratio greater than 2 elucidate dissolution of silicate minerals. All the groundwater samples of the study area have Ca^{2+}/Mg^{2+} ratio in the range from 0.92 to 1.51 (Fig. 6), demonstrate calcite and dolomite minerals dependable for Ca^{2+}/ Mg^{2+} contribution (Marghade *et al*. 2011; Singh *et al*. 2013; Murkute 2014).

The weathering and Ca enhancement processes exhibited by using the ratio of $(Ca^{2+} + Mg^{2+})$ / $(HCO_3^- + SO_4^{2-})$. If Ca^{2+}, Mg^{2+}, $HCO_3^-$and SO_4^{2-} ions are from the dissolution of dolomite, gypsum, and calcite, a 1:1 stoichiometry of $(Ca^{2+} + Mg^{2+})$ to $(HCO_3^- + SO_4^{2-})$ might occur (Singh *et al*. 2014). All the groundwater samples have ratio in the range from 0.24 to 0.70 (Fig. 6). The molar ratio also signifies that the sources of Ca^{2+} and Mg^{2+} were not only from carbonate since the ratio was not 1:2.

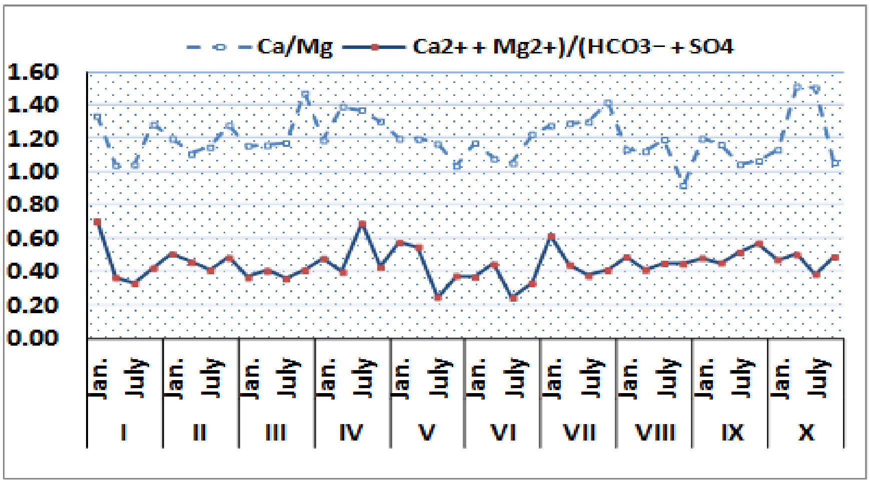

Fig. 6: Ca^{2+}/Mg^{2+} and $Ca^{2+} + Mg^{2+}) / (HCO_3^- + SO_4^{2-}$ratios.

The $(Na^+ + K^+)/Cl^-$ molar ratios in the analyzed ground water samples were greater than1, ranged from 1.03 to 5.59 (Fig.7), indicating that halite, as well as silicate weathering, such as potash plagioclase and sodium plagioclase were the source of Na^+ and K^+ ions (Lin *et al.*, 2016). If $Ca^{2+}$and HCO_3^-in the groundwater originate mainly from dolomite and calcite, the molar ratio of Ca^{2+} and HCO_3^-ions within the groundwater will be 1:2 and 1:4, respectively. $Ca^{2+}$and HCO_3^-molar ratio for some of the groundwater was between1:1 and 1:2, signifying that calcite was the only source of $Ca^{2+}$and HCO_3^-ions in the groundwater. Most of the groundwater samples had a molar ratio less than 1:2 (< 1:2), suggesting dolomite as the dominant sources of $Ca^{2+}$and HCO_3^-ions. All the groundwater samples have ratio in the range from 0.14 to 0.71 (Fig. 7).

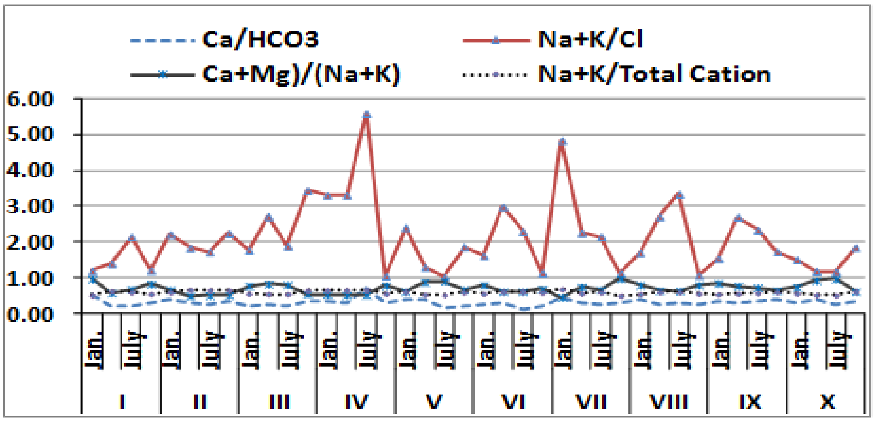

Fig. 7: Ca/HCO_3, Na+K/Cl, (Ca+Mg)/(Na+K) and Na+K/Total Cation Ratios

A high ratio of$(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$, ranged from 0.46 to 0.98 and $(Na^+ + K^+)$/total cation demonstrate ranged between 0.50 and 0.69 that the chemical composition of the groundwater samples were mainly influenced by carbonate weathering with a small contribution of silicate weathering (Fig. 7). The plot of Ca^{2+}+ Mg^{2+}/Cl^- ratio revealed that salinity decrease with increase in Ca^{2+}plus Mg^{2+}, and this phenomenon can be ascribed to ion exchange (Fig.8). Ca^{2+}+ Mg^{2+}/ HCO_3^- plot (Fig. 8) revealed a horizontal trend line, signifying that Ca^{2+}+ Mg^{2+}/HCO_3^-ratio does not alter during the increase of HCO_3^-.Thus, the contribution of Ca^{2+}+ Mg^{2+} and

$HCO_3^-$are from different sources. Enrichment of $HCO_3^-$and depletion of Ca^{2+}+ Mg^{2+}may be attributed to cation exchange.

Gibbs plot Application

Gibbs plot is used to interpret the effect of hydrogeochemical processes such as precipitation, rock–water interaction and evaporation on groundwater geochemistry (Boateng *et al*. 2016). Gibbs plots are indicated by the variation diagrams of TDS against the ratios (Na^++K^+) / Na^++K^++Ca^{2+}) and TDS against Cl^- / (Cl^- + HCO_3^-) for both cations and anions groups. These plots provide very good genetic information about the composition, origin and distribution of the dissolved constituents in groundwater. The major natural mechanisms controlling surface and groundwater chemistry are due to rock dominance, evaporation dominance or precipitation dominance (Gibbs, 1970). The groundwater samples of the study area are plotted on Gibbs diagrams (Fig. 9).

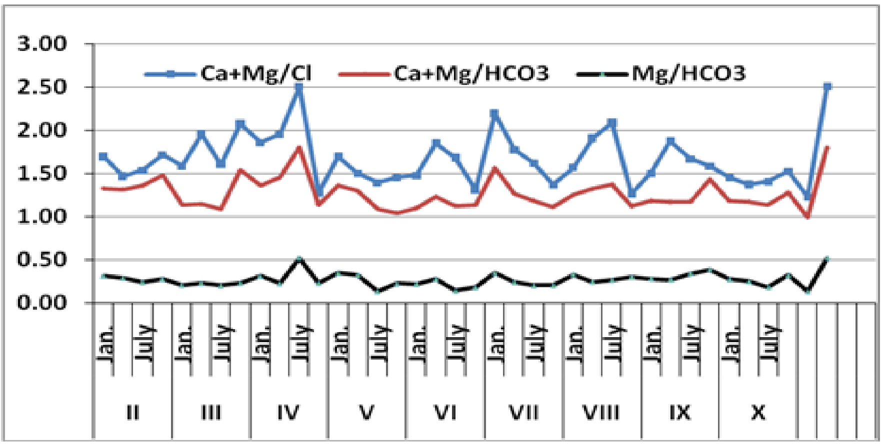

Fig. 8: Ca+Mg/Cl, Ca+Mg/HCO_3 and Mg/HCO_3Ratios

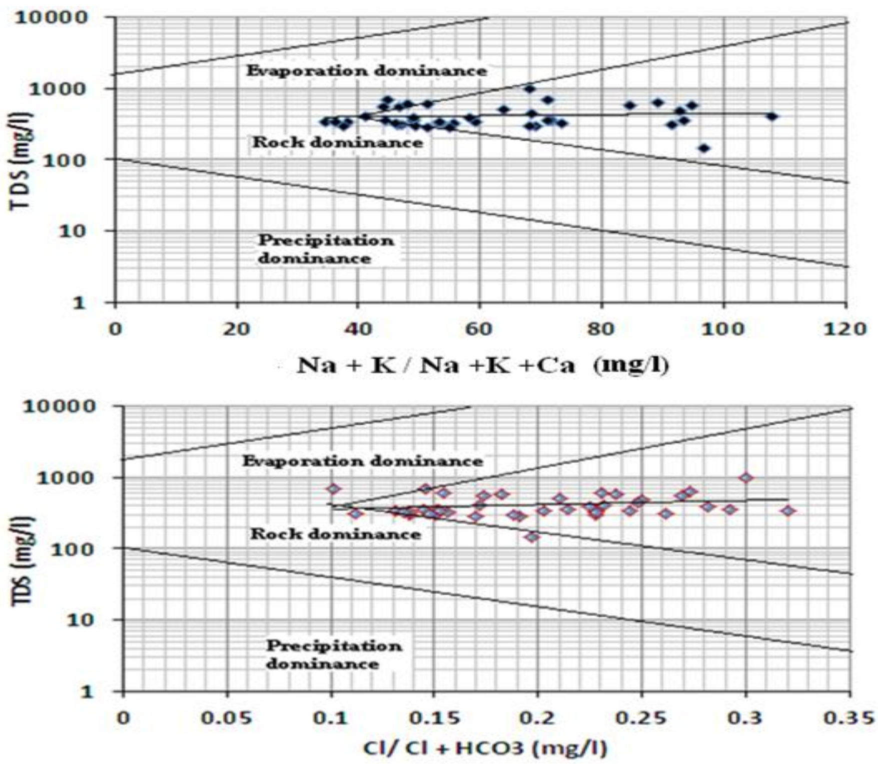

Fig. 9: Gibbs plots explain groundwater chemistry and geochemical process in the study area.

To understand controlling mechanisms, according to Gibbs classification most groundwater samples are fall under rock dominance province. Alkali (Na^{+} + K^{+}) content is higher in many samples collected during the period of study at a given amount of TDS (147-699 mgL^{-1}). The groundwater samples of the area on the plot TDS versus {Cl^{-}/Cl^{-} +HCO_3^{-}} show similar variation with that of cation diagram (Fig. 9). However, the samples are shifted from right to left fields due to less Cl^{-} content and high concentration of HCO_3^{-}. The rock-water interaction may play a major role in the groundwater chemistry of the study area (Sugreeva *et al*., 2010).

CONCLUSION

Fourteen chemical parameters were selected to examine the situation of groundwater quality in Menoufia Governorate, south of Nile Delta of Egypt. This is done by collecting representative water samples. The spatial distribution maps showed the pattern of each parameter in the groundwater of the study area. The concentration of chemical parameters is shown in different parts of the horizontal distribution levels of the parameters. The major ions of ten groundwater samples were analyzed at different locations. The average values of all physiochemical 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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