Impacts of hydrochemical processes on groundwater charcateristics in El-Dir area, West of Sohag City, Egypt.

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ABSTRACT

Groundwater is an essential resource for rural households and the public in El Dir, Sohag Governorate, South Egypt. Groundwater is used for drinking and irrigation in the larger settlements. The Pleistocene aquifer is considered the main groundwater source in the El Dir area due to suitable groundwater salinity. Geochemistry has been used to examine processes impacting groundwater quality and to investigate the recharge source(s), the extent of water-rock interaction, and the mechanisms of mixing processes. The main sources of groundwater recharge are the seepage from the River Nile and the surface water drainage system. According to the geologic environment, major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}) and nitrogen compounds (NH_4^+, NO_3^-) the shallow groundwater quality in the El Dir area has been deteriorated due to the regional extent of water-rock interaction, anthropological activity, and mixing processes. The majority of groundwater salinization is caused by silicate weathering, and the components, including Na^+, K^+, Ca^{2+}, and Mg^{2+} are mostly obtained from groundwater and aquifer lithology interacting (geogenic effect). Anthropological activities involve human activity, agricultural practices, and extensive uses of fertilizers. The mixing with wastewater infiltration leads to elevated nitrogen compounds in the Pleistocene aquifer. The groundwater in the El Dir area is suitable for agricultural uses; however, water treatment is crucial for human drinking to remove the impact of contamination with wastewater.

Introduction

In dry and semi-dry areas prone to water shortages, sustainable water management involves a greater understanding of the dynamic behavior of natural and anthropogenic pollutants, which influence the suitability of water quality and are considered a deciding factor for sustainable growth. In Egypt, Water is mostly obtained from the Nile River, which provides 94% of all renewable water resources (El-Din, 2013). Egypt faces water shortages, with 97 million people and 570 m3/year/capita of renewable water resources in 2018 (CAPMAS, 2019); this is less than the 1000 m³/capita/year threshold for water scarcity (Gleick, 2002). The local geological setting has a natural impact on the groundwater hydrochemistry and pollution levels (Banat and Howari, 2002; Banat et al., 2005; Edmunds and Shad, 2008; Embaby et al., 2016; Embaby and Ali, 2021, Othman et al., 2022; Abdel-Haleem et al., 2022) and the aquifer's lithological component (Howari et al., 2005; Howari, 2016; Embaby and Redwan, 2019; Mosaad et al., 2022).

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Besides anthropogenic considerations include agriculture (Wongsasuluk et al., 2014), industrial and disposal activities (Dong et al., 2015). Natural variables such as aquifer lithology, geological structure, recharge of water chemistry, geochemical reactions inside the aquifer, and the rate of groundwater movement from recharge to discharge areas along its passage all influence groundwater chemistry (Appelo and Postma, 2005).

This research provides approaches that could be useful to assess the main hydrogeochemical characteristics and hydro-chemical processes. As for determining minor and trace elements, heavy metals, and groundwater quality for varied objectives and determining the suitability rely on major or minor and trace elements are not covered in the current study.

2. Background

2.1. Study area and climate

Sohag Governorate, with a total size of around 6.546 k m², is located in the center of the Nile Valley, roughly 125 km long. Geographically, the study area is located 2 kilometers from the western Nile bank and 1 kilometer from the western desert borders. (Fig. 1a and 1b). Broad and flat terrains are the geomorphic characteristics of the settlements under study.

Sohag is situated in an area of North Africa that is dry and known for having cold winters and hot summers. The daily temperature is variable, and the yearly rainfall is only 1.18 mm (Allmetsat, 2021). Between December and May, the average monthly evaporation ranges between 96.1 and 325.5 mm (Egyptian Meteorological Authority, 2000). The region has a serious shortage of moisture influx and arid conditions, and the evaporation rate exceeds that of rainfall (Abu El-Magd, 2008).

2.2. Geological Setting

Many authors discussed the field of study, for example, Abu El-Magd et al., 2020, Omer 1996, Mostafa 1979, Omara et al. 1973, Othman et al., 2022; Abdel-Haleem et al., 2022. Stratigraphically, in this area of interest, the Nile Valley sediments consist mainly of an Oligiocene-Pliocene-

Quaternary Lower Eocene calystone series (Table 1). The lower Eocene sequence consists of Thebes Type, a thick calcareous with chert and nodules (Abotalib and Mohamed, 2013). The Thebes was identified as the main unit of limestone building in southern Egypt (Said, 1990).

Bounding limestone is known as the base of Thebes and the top of the Drunka group (Mostafa, 1979; Ahmed, 1980; Said, 1993; Omer and Issawi, 1998; Youssef, 2008). The base is the foundation for the two rock groups. The Thebes Formation is a local distribution with laminated calcareous columns with flint strips with a thickness of 30 m. The Thebes Formation is to the west of the village of El-Kawamil, where the Drunka Formation is formed accordingly.
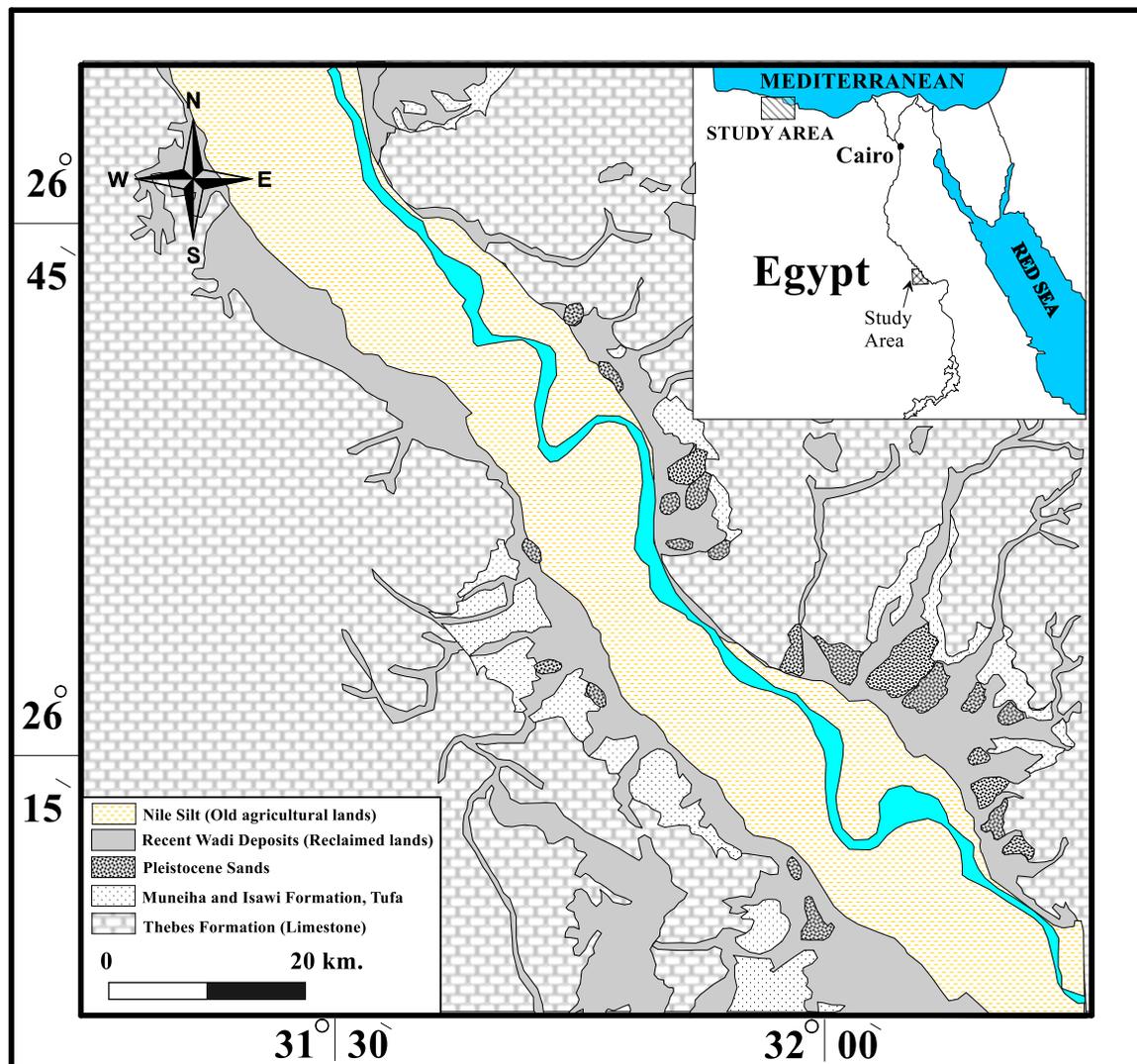
Fig.1a: Location and geological map of the study area Modefied after (CONOCO 1987 & Redwan and abdel Moneim, 2016), showing the location of wastewater treatment plant at Sohag (El-Dir).
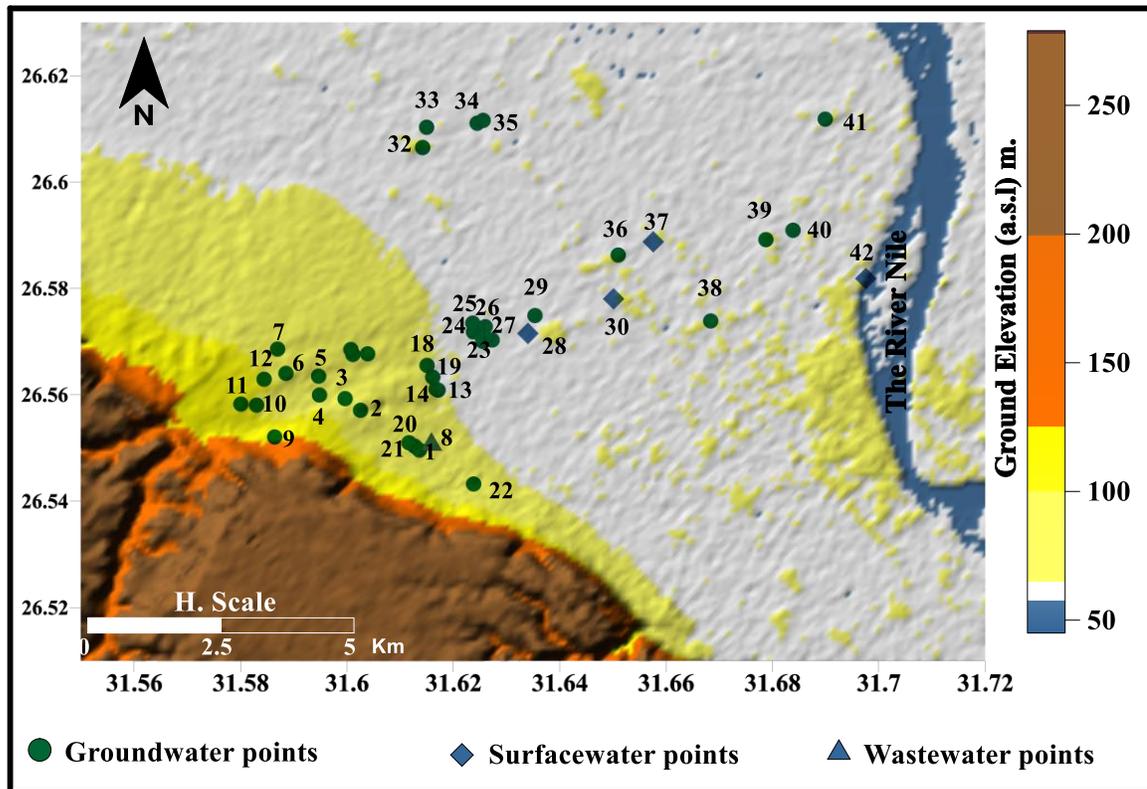
Fig.1b: El Dir Location map and well's location of study area

Table 1: Stratigraphic sequence of sediments in Sohag area (Abu El-Magd et al., 2020).

Age	Formation	Description
Pleistocene	Dandara	The fine sand-silt intercalations and accumulated at low-energy conditions (Omar and Isaac, 1998).
	Abbassia	The conglomerate consists of igneous rock pebbles, quartzite, and siliceous sandstones, is 2 - 20 cm in diameter, and is all set in a reddish-brown matrix (Said, 1981).
	Qena	Quartozose sands and gravels without fragments from igneous and metamorphic rocks (Said, 1981).
Late Pliocene/Early Pleistocene	Armant / Issawia	The carbonate facies in the middle zones and clastic facies in the lake margins (Said, 1971).
Early Pliocene	Madamud	Brown and gray bedded clays intercalated with thin beds of silt and fine sand lenses, and fluvial sediments made up of sand, silt, and mud intercalations (Mahran, 1993).
Oligiocene	Katkut Formation	Coarse clastic (Issawi, 2005)
Oligio-Miocene	Abu Retag Formation	Reddish-brown, coarse sediments mainly crop up on the lower hills of the western Eocene calcareous scars (Mahran et al., 2013).
Early Eocene	Drunka Formation	Snow-white color and massive bedding (Ahmed, 1980; Mostafa, 1979).
Early Eocene	Thebes Formation	Laminated limestone with flint bands with 30-meter thickness (Mostafa, 1979; Ahmed, 1980; Said, 1993; Omer and Issawi 1998; Youssef, 2008).

2.3. Hydrogeological setting

Qena Sands represents the aquifer is situated west of the old agricultural regions. The waste disposal site is located as shown in (Fig.2). The specific storage of the aquifer is 4.37×10^{-2}, and the horizontal hydraulic conductivity is 20.46 m/day (Abdel Moneim, 1999). The subsurface sediments' high vertical hydraulic conductivity contributes to groundwater pollution (El-Haddad and El-Shater, 1988, Youssef et al., 2011) due to hydrulic connections between the surface water bodies, including the oxidation bonds. The water-bearing layers range in thickness from 20 to 80 meters and generally grow eastward towards the Nile's ancient agricultural areas (Redwan and Abdel Moneim, 2016). The water depth varies between 5 and 25 meters (Abdel Moneim 1999). The aquifer is recharged through extra irrigation water seepage from neighboring ancient rural areas and post-Eocene accumulated water. Moreover, the groundwater flows in the northwestern direction due to irrigation land recharge and ground surface topography (Redwan and Abdel Moneim, 2016).
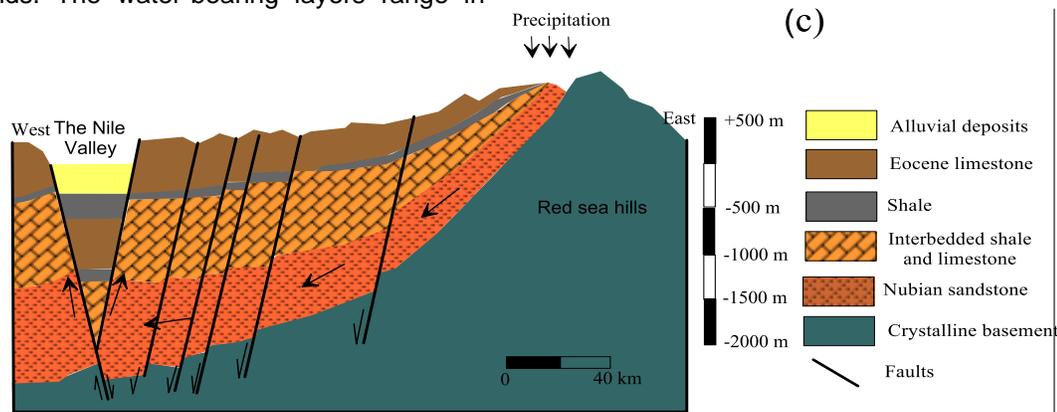
Fig. 2: General Hydrogeological cross section of Sohag area after (RIGW, 1993).

3. Methodology

3.1. Sampling procedures

The sampling techniques are implemented during sample collection and are established by the quantity of foreign academics (Claasen 1982; Barcelona et al. 1985). Grab, independent, discreteindependent, and discrete samples were taken from each physical site to get groundwater samples. The samples were physically collected during the field trip from a pump's flowing discharge line. Polyethelene 500 ml vials were used to collect the groundwater samples. They were stored in an icebox and subsequently a refrigerator at 4°C until they were transported to the Applied and Environmental Geochemistry Laboratory (EAG) at Sohag University and the Central Laboratory of Desert Research Center, Cairo, to undergo the necessary major, minor, and trace chemical analyses. The digital meters (WPA and Cole Parmer models) measured pH and electric conductivity (EC).

Ca^{2+}, K^+, and Na^+ concentrations were measured using a Jenway PFP7 Flame Photometer. The atomic absorption spectrophotometer (Perken Elmer 2380) measured the contents of iron, magnesium, and manganese. Chloride and HCO_3 were titrimetrically quantified (Richards, 1954; Jackson, 1973). The spectrophotometry identifies the nitrogen components (NH_4^+ and NO_3^-) and sulfate (Dewis and Freitas, 1970; DEWAS, 1980; and APHA, 1985). Parameters and different analytical approaches are summarized in Table 2.

Table 2: List of Chemical parameters and their test methods

	Parameters	Unit	Test Methods
1	pH	---	pH meter
2	Conductivity	ms/cm	Conductivity meter
3	Total dissolved Solids	mg/L	Digital conductivity meter
4	Chloride	mg/L	Titration
5	Calcium	mg/L	Flame Photometer
6	Sodium	mg/L	Flame Photometer
7	Potassium	mg/L	Flame Photometer
8	Magnesium	mg/L	FAAS
9	Chloride	mg/L	Titration
10	Sulfate	mg/L	Spectrophotometric
11	Bicarbonate	mg/L	Titration
12	Nitrate -Nitrogen ($NO_3 — N$)	mg/L	Spectrophotometric
13	Ammonia-Nitrogen ($NH3 — N$)	mg/L	Spectrophotometric

The quality assurance and quality control (QA/QC) of this study were assessed by carefully inspecting field blanks, duplicate samples, standards, and reagent blanks, as well as by computing each sample's charge balance, which must fall within 5% to be authorized by the authors.

4. Results and Discussion

4.1. Classification

The main ion concentrations were recorded on a diagram of discrimination proposed by Chadha (1999) in the groundwater of the El-Dir region. The diagram shows that most groundwater specimens are of the Ca^{2+} - Mg^{2+} - HCO_3^- form, and then the groups Na^+-Mg^{2+}-Cl^- and Na^+-Cl^- - Na_2SO_4 are just a few specimens (Fig.3).

4.2. Major ions chemistry

Hydro-chemical data of groundwater samples (Table 3). The pH varies from 6.7 and 8.6 and pH average is 7.4, which reflects slightly alkaline groundwater. The eastern portion of the research area is where the lower pH values are found, reflecting the proximity of the sampled wells to the ocean. The western portion of the research area's higher pH readings might point to places with favored recharge. Between 21°C and 30°C, the groundwater's temperature varies only slightly. The range of the Total Dissolved Solids is 150 to 242 mg/l, with a mean of 875 mg/l. These data demonstrate the significant variation in groundwater mineralization at the research site.

According to the coefficient of variation (CV), the spatial variability of the ions contents is remarkably large (50% CV 155%). The values of bicarbonate vary from 102 to 963 mg/l, chloride from 13 to 981 mg/l, sulfate from 4 to 1142 mg/l, nitrate from 0.02-32 mg/l, sodium from 12 to 359 mg/l, calcium from 22 to 287 mg/l, magnesium from 5 to 159 mg/l, potassium from 3 to 22 mg/l, and ammonia from 0.04 to 11.58 mg/l. The relative concentrations of the cations are Na^+, Ca^{2+}, Mg^{2+}, and K^+ and anions are HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-.

Pairwise relationships between the components were discovered using Pearson's correlation matrix (Swan and Sandilands, 1995). Correlation analyses between several groundwater parameters have been calculated in this work and are shown in Table 3. The correlation matrix Table 4. An instrument frequently used to determine the relationship between two variables is the correlation coefficient (R) (Kurumbein and Graybill, 1965; Mrazovac and Vojinovic, 2011).

EC and TDS positively correlate positively with Ca^{2+}, Mg^{2+}, Na^+, Cl^-, and SO_4^{2-} (R > 0.80). There is a strong positive correlation between Ca^{2+}- Mg^{2+} (0.9), Ca^{2+}-Cl^- (0.9), Ca^{2+}- SO_4^{2-} (0.69), Ca^{2+}-Na^+ (0.6), Na^+ - Cl^- (0.87), Na^+- SO_4^{2-} (0.66), Mg^{2+}- SO_4^{2-} (0.74), Mg^{2+}- Cl^- (0.56), Mg^{2+}- Na^+ (0.66), K^+-NH_4^{2-} (0.62), and Cl^--SO_4^{2-} (0.61) demonstrates that the sources of these parameters for the majority of the groundwater samples are different. The concentrations of these components tend to rise when the salinity of the groundwater rises. The ionic concentrations rising due to recharge water evaporation, seawater intrusion, and interactions between the groundwater and geological formations would be predicted to cause groundwater salinization.
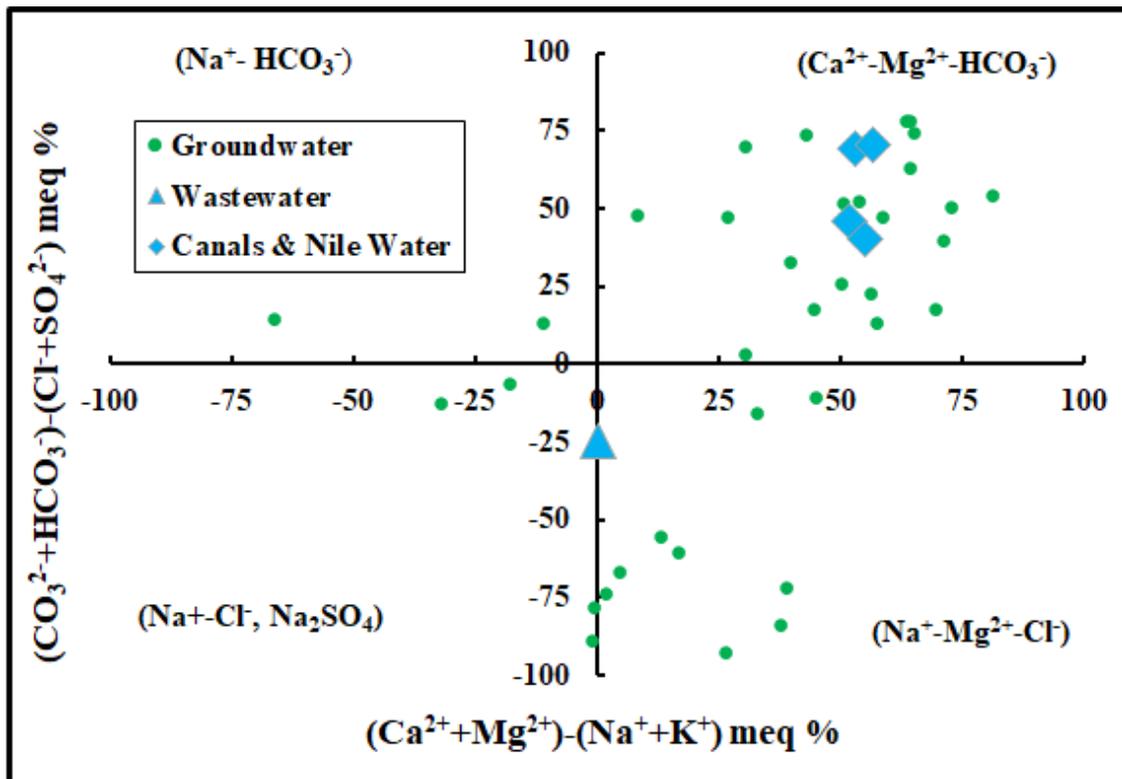
Fig. 3: Plots of the groundwater samples obtained on Chadha's rectangular diagram (1999).

Table 3: Summary statistics of groundwater physical and chemical parameters. Ion concentrations and TDS are in mg/l. SD: Standard Deviation. CV: Coefficient of Variation

	TDS	pH	Ca	Mg	Na	K	NH$_4$	Cl	SO$_4$	NO$_3$	HCO$_3$
Maximum	2420.0	8.6	287.0	158.8	359.0	22.0	20.0	981.0	1142.0	32.0	963.0
Minimum	150.0	6.7	22.6	5.6	12.8	3.0	0.1	13.5	4.0	0.0	102.0
Mean	875.4	7.4	108.6	50.5	114.8	6.0	2.5	195.3	143.7	1.3	385.2
Standard Deviation	588.0	0.4	64.5	34.4	94.4	3.4	3.9	237.7	211.6	4.9	194.2
Coefficient variation	0.7	0.1	0.6	0.7	0.8	0.6	1.5	1.2	1.5	3.6	0.5

Table 4: Correlation matrix between chemical variables.

	TDS	pH	Ca	Mg	Na	K	NH$_4$	Cl	SO$_4$	NO$_3$	HCO$_3$
TDs	1.00	-0.61	0.83	0.80	0.84	0.18	-0.06	0.81	0.82	0.01	-0.07
PH		1.00	-0.61	-0.54	-0.51	-0.21	-0.10	-0.50	-0.34	0.07	-0.24
Ca			1.00	0.90	0.60	0.15	-0.08	0.75	0.69	-0.11	0.10
Mg				1.00	0.48	0.17	-0.07	0.56	0.74	-0.10	0.26
Na					1.00	-0.02	-0.09	0.87	0.66	0.11	-0.30
K						1.00	0.62	0.06	0.13	-0.09	0.06
NH$_4$							1.00	-0.03	-0.08	-0.08	-0.05
Cl								1.00	0.61	-0.02	-0.43
SO$_4$									1.00	0.01	-0.22
NO$_3$										1.00	-0.01
HCO$_3$											1.00

Combining the elements with the opposite sign's strongest relationships Cl$^-$ and Ca^{2+} (R = 0.9), Cl$^-$ and Na$^+$ (R = 0.87), and Cl$^-$ and Mg^{2+} (R = 0.56).

The Mg^{2+}- Cl$^-$ and Ca^{2+}- Cl$^-$ correlations are very strong, indicating that cation exchange can greatly impact groundwater composition. The evaporitic salts and agricultural activity may have contributed to the positive and significant correlations between sodium and sulfate (R = 0.66). Fertilizers based on potassium sulfate, ammonium sulfate, and ammonia sulphosphate can be used to supplement these elements (Achour and Bouzelboudjen 1998; Gouaidia et al. 2011; Ahmed et al., 2015; Eissa et al., 2019; Embaby and Ali, 2021). Sulfate indicates the evaporitic salts' contributions and magnesium have many strong and positive relationships (R = 0.74), sulfate and calcium (R = 0.69), and sulfate and sodium (R = 0.66) (Touhari et al., 2014). The high correlation between SO$_4^{2-}$ with Ca^{2+} (R=0.69), and Mg^{2+} (R=0.74) is important and indicates that the gypsum and Mg-sulfate minerals are partly derived by dissolution. While, HCO$_3^-$ with Ca^{2+} (R=0.10) and Mg^{2+} (R=0.26) reflects a poor correlation that the only source for such elements is not carbonate rock dissolution (calcite, dolomite).

4.3. Binary Diagrams

The processes that formed the groundwater structure that have been observed and the sources of the solutes may show dissolved species and their connection with each other (Singh et al., 2015; Ahmed et al., 2015). Na$^+$ produced from silicate weathering reactions typically interprets more than one Na$^+$ molar ratio (Meybeck, 1987; Zaghlool et al., 2018). Na$^+$/Cl$^-$ was often utilized to processes involving salinity and saline intrusions in semi-arid areas (Sami, 1992; Eissa et al., 2018). High levels of sodium and chloride in groundwater could be caused by the leaching of chloride salts or concentration processes by evaporation (Fig. 4).

The relationship Na$^+$ vs Cl$^-$ was frequently used to determine the salinity acquisition mechanism. The Na$^+$ vs. Cl$^-$ plot demonstrates not aligned samples with the line 1:1, but have a powerful correlation (R= 0.87) which suggests that Na+ and Cl-are not from the same source for the most portion. The Na+ and Cl- plot shows that most groundwater samples lie above the halite dissolution line. The additional Na$^+$ was most likely caused by the cation exchange of clay minerals and Ca^{2+} to adsorb clay minerals and Na$^+$ ions to escape later (Magaritz et al., 1981; Reda et al., 2022).
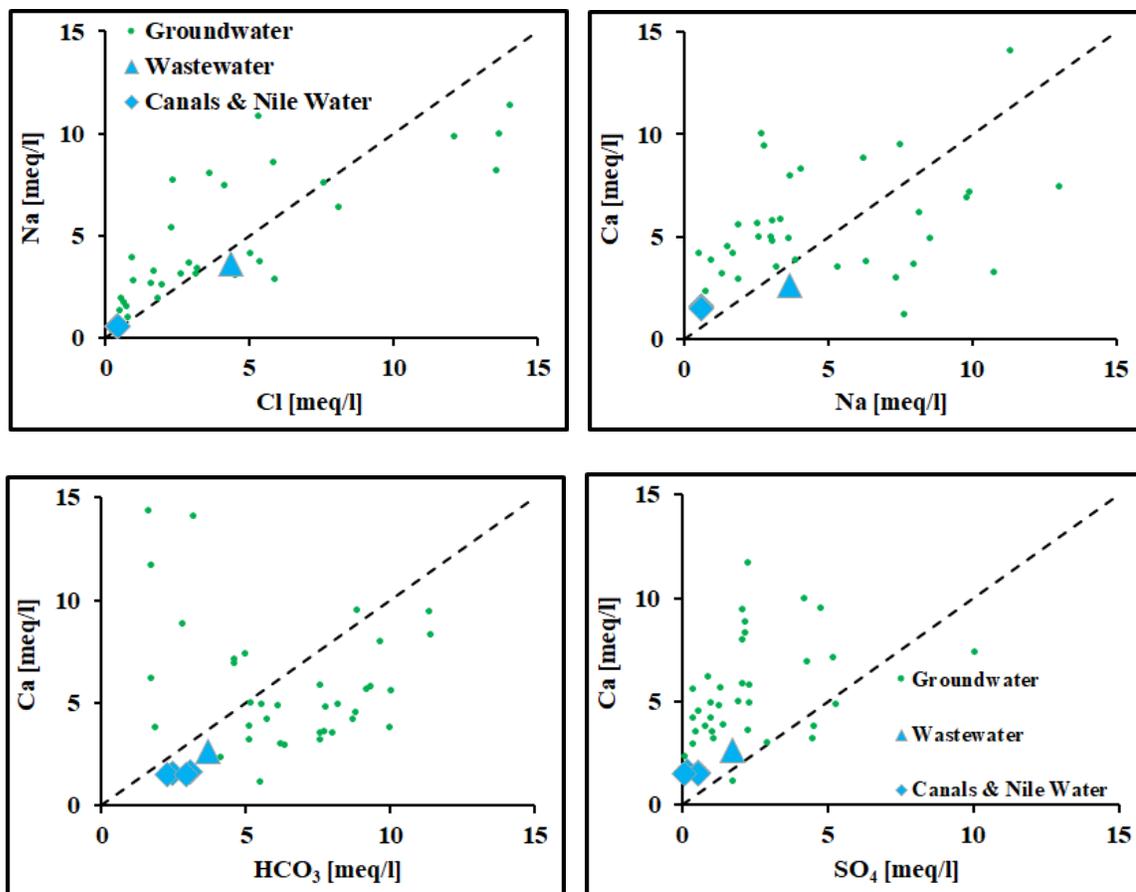
Fig. 4: Binary diagrams a) Cl^{2-} vs. Na^+; b) Na^+ Vs. Ca^{2+}; c) HCO_3^{2-} vs. Ca^{2+}.; d) SO_4^{2-} vs. Ca^{2+}.

The high Na+ and Cl- the dissolution of halite and chloride salts may cause levels. Halite dissolution in water release Na^+ and Cl^- concentrations into the solution: NaCl → Na^+ + Cl^-

Moreover, the correlation is strong between sodium ion and sulfate ion (R=0.66) exhibiting the excess of sodium as a result of the dissolving of sodium sulfate minerals (Eq. 1) and most specimens lie above 1:1 (Fig.5a).

$Na_2HSO_4 + H_2O \rightarrow 2\,Na^+ + SO_4^{2-}$ (Eq. 1)
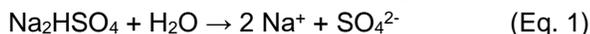
The negative correlation between pH and SO_4^{2-} (r = -0.34) reveals that the SO_4^{2-} component may result from biochemical reactions. The Na^+ and Cl^- correlation is strong (R=0.87) revealing the ion exchange process as shown in (Fig.5a). The relative abundance of K^+ in the clay minerals is probably considerably greater than Ca^{2+} or Mg^{2+} concerning the concentrations in groundwater. The high correlation between NH_4^+ and K^+ (R=0.62) may be explained due the attenuation of ammonium is mainly due to cation exchange and nitrification (biological oxidation) procedures in subsoils and groundwater (Buss et al., 2004). The effects of Ca^{2+} versus Na^+, Ca^{2+} versus HCO_3^- plots support these projected exchanges of cation (Fig.5b). The relationships and correlation between calcium and carbonate are not considerable (R=0.1), revealing that

calcite may not be the calcium source (Fig.5c). The majority of the plotted data reveals the depletion of calcium and magnesium. The later ions were connected to cation exchange with Na^+ and came from the weathering of carbonate minerals (Reddy and Kumar, 2010).

The positive correlation (Fig. 5d) with a coefficient of (0.69) between calcium and sulfates indicates all elements have the same origin. The points are dispersed over slope 1:1, this suggests that gypsum and/or anhydrite dissolution can be the source of the two ions (Bahir et al., 2018).

The correlation between calcium and magnesium is str ong (r=0.90), implying a similar geological formation (Fig. 5a). The strong correlation between sulfate and sodium, Sulfate and magnesium (R=0.66; 0.74) respectively, may occur as a result of the weathering of sodium sulfate and magnesium sulfate minerals (Fig. 5b and 5c). A large part of HCO_3^- is prognosticated to be formed due to the breakdown of carbonate rocks in the aquifer via the CO^{2-} enrichment cycle (Appelo and Postma 1996). The relationships and correlation between Magnesium and carbonate are not considerable (R=0.26) concluded that calcite may not be the calcium source (Fig. 5d).
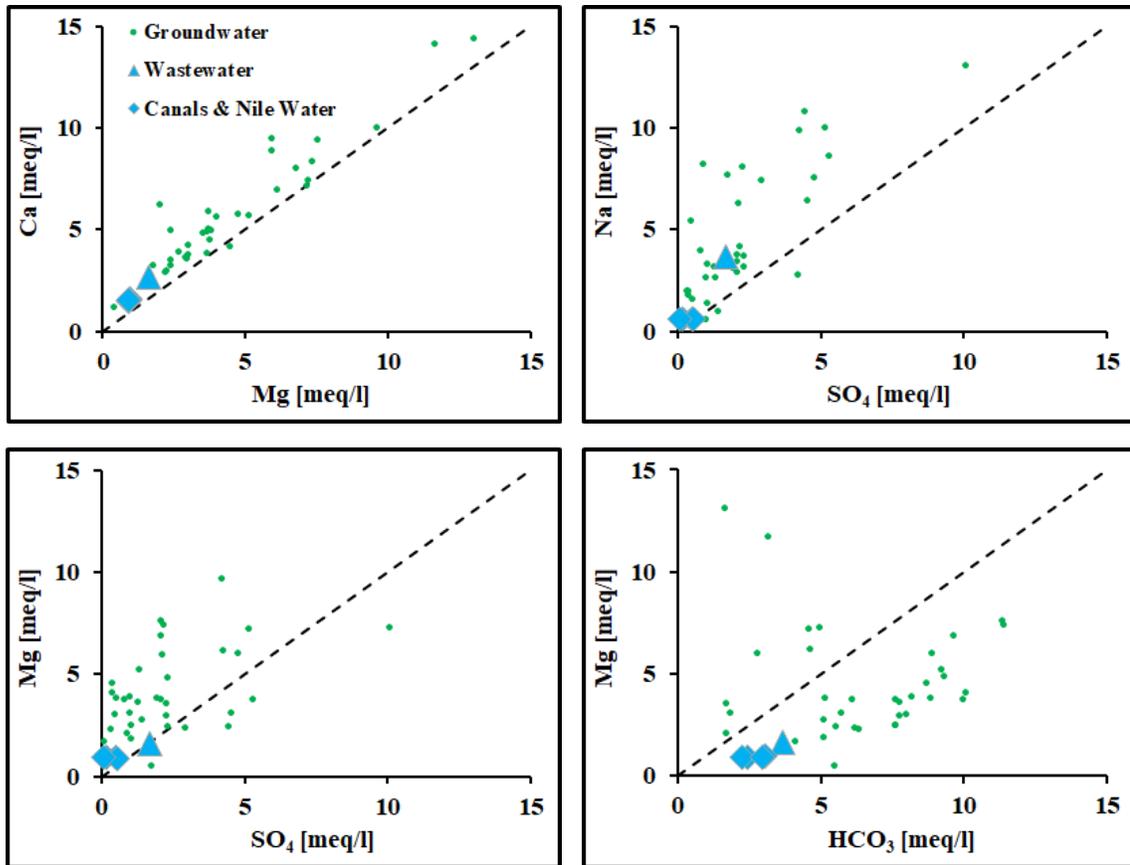
Fig. 5: Binary diagrams a) Mg^{2+} vs. Ca^{2+}; b) SO_4^{2-} vs. Na^+; c) SO_4^{2-} vs. Mg^2 d) HCO_3^{2-} vs. Mg^{2+}.

4.4. Hydrogeochemical processes

4.4.1. Ion exchange

Important geochemical processes called ion exchange reactions produce Ion concentrations in groundwater. It might be located by examining the interaction between Na^+ and Cl^- ions. Ion exchange reactions are indicated by an increase or decrease in Na^+ around the Cl^- ion (Rajmohan and Elango 2004, Salama 1993), where Na^+ is discharged into the groundwater but $Ca2+$ is maintained in the aquifer material. The enriched Na^+ concentrations to Cl^- in the examined samples (Fig. 6) provide proof of an ion exchange reaction, The Na^+ and Cl^- correlation is strong (R=0.87), and all points above Line 1:1, revealing the ion exchange process. Na^+/Cl^- molar ratios in groundwater samples varied from 0.92 to 23.75.

Na^+/Cl^- molar ratio is greater than or equal to 1, which reveals silicate weathering has taken the position of the ion exchange process as the primary mechanism.

Calculations of the Chloro-Alkaline Index (CAI) can also be used to achieve the process of ion exchange (Schoeller, 1977);

CAI = [C1 (Na^+ + K^+)/C1$^-$]. In meq/l, all values are expressed.

When the aquifer material contains Na^+ and K^+, a negative CAI index value suggests ion exchange of Ca^{2+} or Mg^{2+} in groundwater. The CAI values range from -0.30.83 to 0.06; most samples have a negative value.

4.4.2. Evaporation

Gibbs diagrams can support this assertion, which plot TDS against $Cl^-/(Cl^-+HCO_3^-)$ to reveal the natural mechanisms (Gibbs, 1970;). Rainfall, rock weathering, evaporation, and participation dominance are natural processes governing groundwater chemistry. The rock-water interactions are prevalent and greatly impact regulating groundwater chemistry. The whole samples plotted in the zone of rock-water interaction reveal, according to Gibbs diagrams (Fig. 7). Gibbs diagrams (Gibbs, 1970) reflect that the interactions between rocks and water are common and greatly impact how groundwater chemistry is regulated.

4.4.3. Silicate weathering process

Ion ratios aid in defining the water origin and detecting the hydrochemical processes involving pollution, mixing, and ion exchange. Most samples have rCa^{2+}/rMg^{2+} ratios greater than one, indicating evaporate dissolution as gypsum and anhydrite or ion exchange. However, less than one values signify magnesium-rich minerals' dissolution, including amphiboles and pyroxenes (Ahmed, 2015).
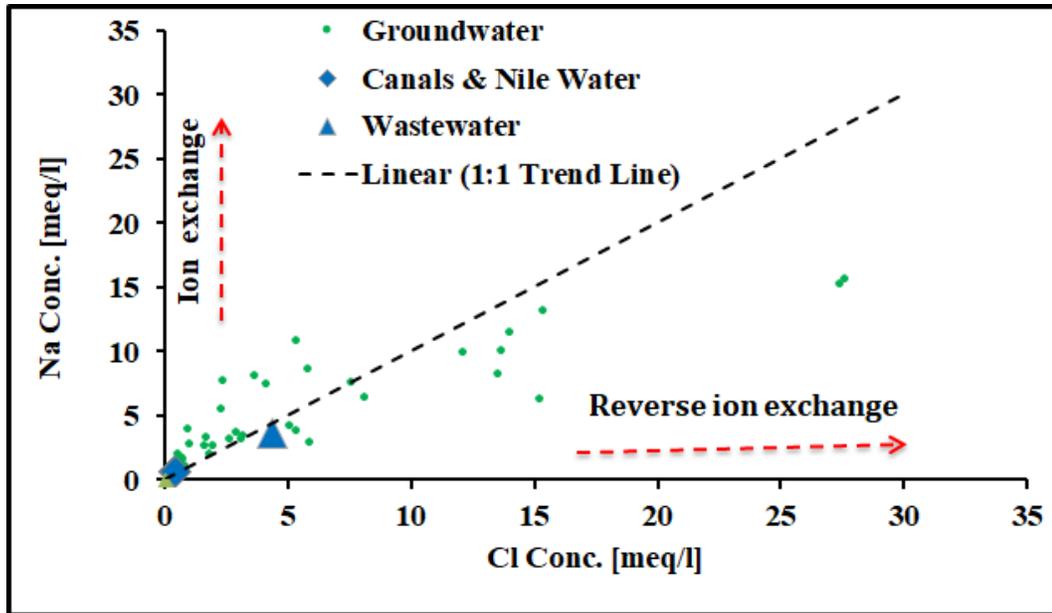
Fig. 6: Dominance of ion-exchange process in the study areas as indicated by Na^+-Cl^- plot.
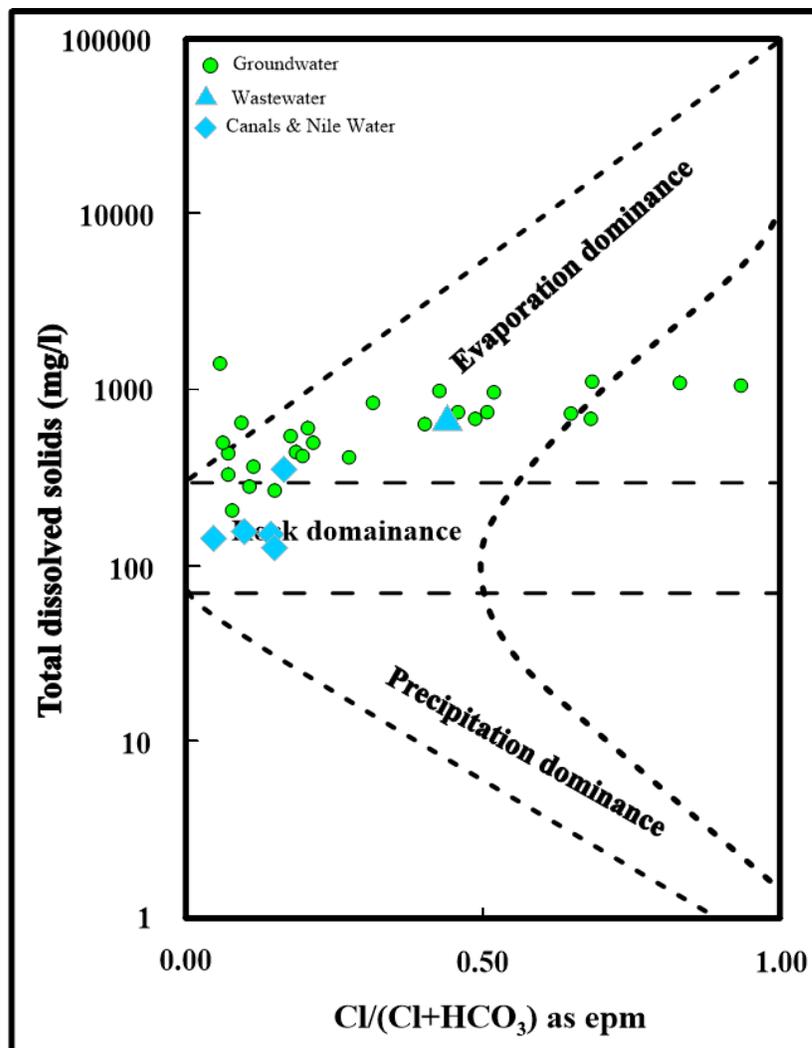
Fig. 7: Gibbs diagram showing the dominant geochemical processes in groundwater of the study area, TDS vs. Cl^-/(Cl^-+HCO_3^-).

The Na$^+$/Ca^{2+} ratio in most samples suggests an excess of Na$^+$ because sewage effluent pollutes groundwater and fertilizers increase soil salinity. Na$^+$/Ca^{2+} and Mg^{2+}/Ca^{2+} diagrams distinguish between silicate, limestone, and dolomite dissolution (Fig. 8). Groundwater features are mostly derived from silicate weathering, as seen by the groundwater samples' tendency to cluster around the silicate pole. Groundwater and aquifer lithology interacting (geogenic effect) is the main source of key elements, such as (Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+}). It involves agricultural practices, anthropogenic activities, and the weathering of silicate minerals through infiltrating wastewater in the Pleistocene aquifer. The interaction of

aquifer lithology and groundwater is the main source of key elements. It includes agricultural practices, anthropogenic activities, and the weathering of silicate minerals through infiltrating wastewater in the Pleistocene aquifer (Gedamy, 2015). Na$^+$, Mg^{2+}, and K$^+$ ions are added to the groundwater by the geochemical processes at a higher rate than Ca^{2+} (Stallard and Edmond 1983; Sarin et al. 1989). Na$^+$/Ca^{2+} ratio is varied from 0.13 to 6.8 (average: 1.05) and Ca^{2+}/Mg^{2+} from 0.91 to 3.34 (average: 1.4). This result confirms that Na$^+$ ions predominate over Ca^{2+} ions in the groundwater samples. Ca^{2+} + Mg^{2+} were less important to groundwater chemistry than Na$^+$ + K$^+$.
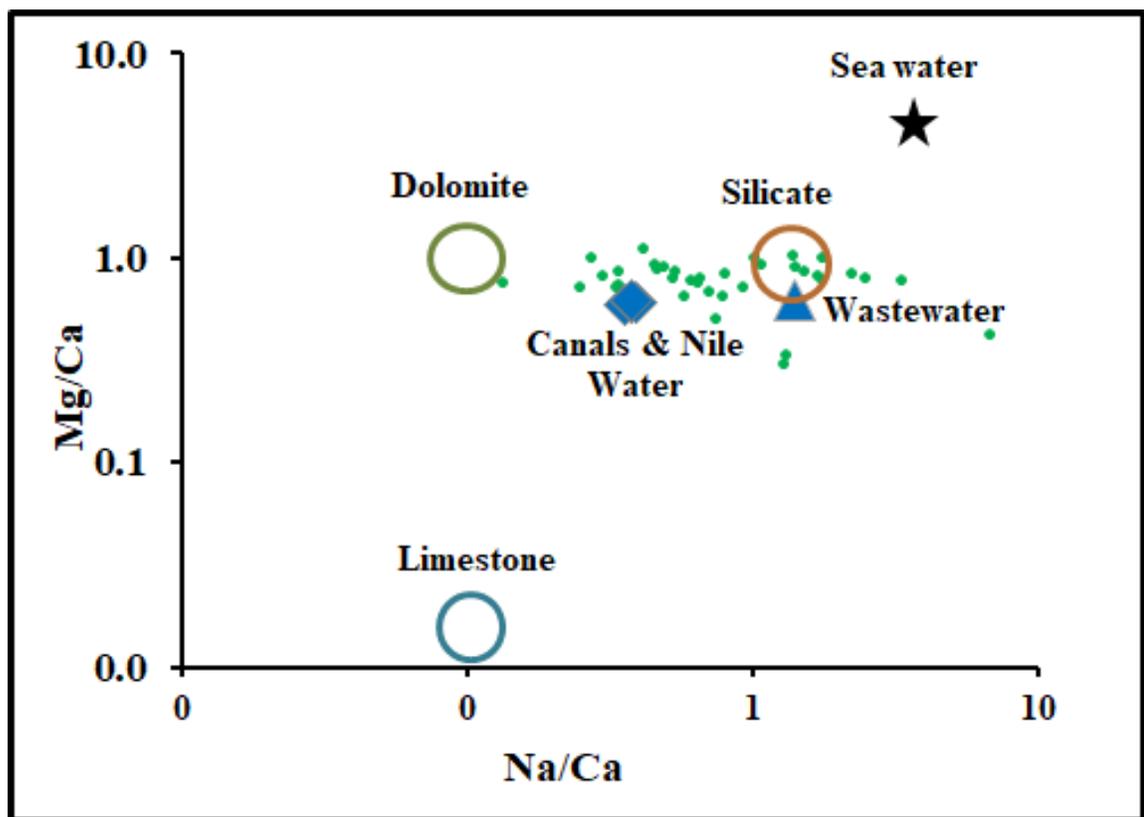
Fig. 8: diagram of Mg^{2+}/Ca^{2+} and Na$^+$/Ca^{2+}

All of the groundwater samples deviate from the 1:1 halite dissolving line, as seen by Cl$^-$ levels plotted against Na$^+$ (Fig. 7). Domestic wastewaters and agricultural activities commonly have Na$^+$/Cl$^-$ ratios (> 1.0), varied from 0.92 to 23.75, which is a classic sign of anthropogenic origin (Jones et al., 1999; Vengosh et al., 1999). Na$^+$/Cl$^-$ ratios >1.0 in all groundwater samples may result from anthropogenic contamination.

The Ca^{2+}/Mg^{2+} ratio was used to identify the sources of Ca^{2+} and Mg^{2+} ions in groundwater, (Maya and Loucks, 1995). Ca^{2+}/Mg^{2+} ratio is equal to 1, it indicates that dolomite is dissolving, and when it is greater than 2, it indicates that silicate minerals are releasing Ca^{2+} and Mg^{2+} ions into groundwater (Katz et al., 1998). Groundwater

ranged from 0.91 to 3.34 (average=1.4), with most samples above 1 and below 2 indicating calcium ion precipitation as carbonates that result in a decrease in Ca^{2+} values or an ion exchange process, while some samples show ratios greater than 1, a magnesium ion increase caused by an ion exchange with sodium ions.

4.4.5. Carbonate/silicate weathering

The (Ca^{2+}+Mg^{2+}) and (HCO$_3^-$) diagram distinguishes the leaching of calcite, dolomite, and silicate minerals (SenthilKumar and Elango, 2013). Most groundwater lies near and below the aquiline 1:1 indicates that Nile Valley's excess bicarbonate caused by bicarbonate seeping from the margins of the desert as well as recharging from the Nile River and canals (Fig. 9). The (Ca^{2+}+Mg^{2+}) against

(HCO_3^- + SO_4^{2-}) plot reflects that most groundwater samples are above and below the aquiline 1:1. The results reveal the increase of (SO_4^{2-} + HCO_3^-) over (Ca^{2+} + Mg^{2+}) in most of the samples; moreover, samples above the aquiline 1:1 revealed that calcite is not the source of calcium and magnesium (Fig. 10).
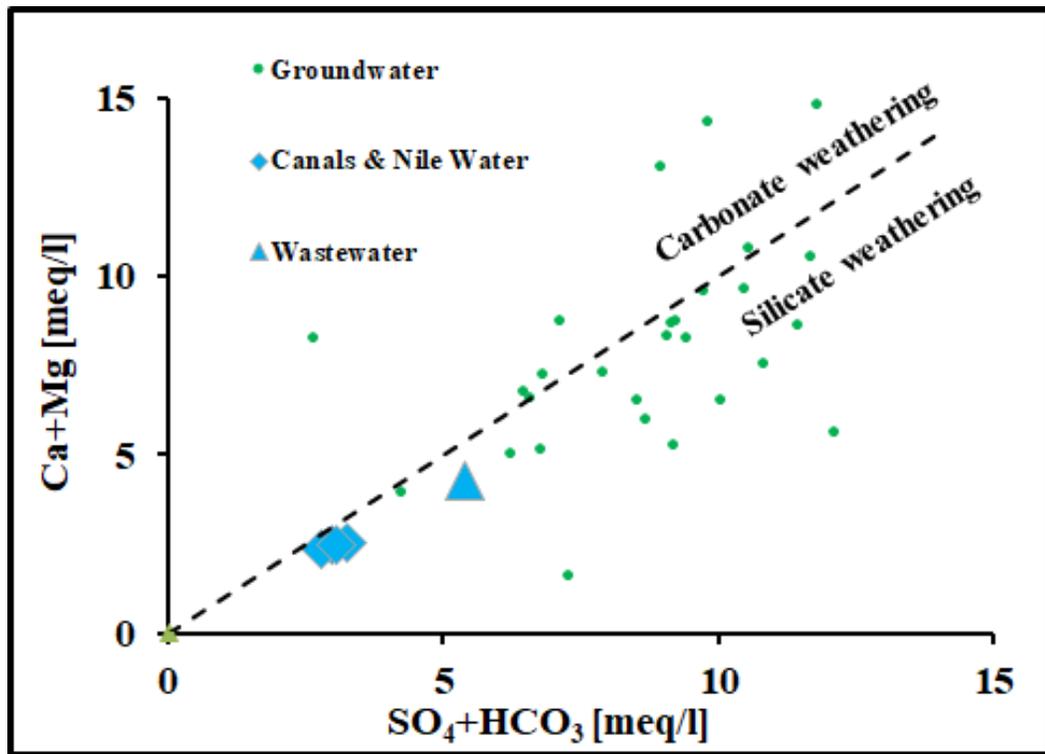
Fig. 9: Plot of [Ca^{2+}+Mg^{2+}] vs. [HCO_3^-+SO_4^{2-}].
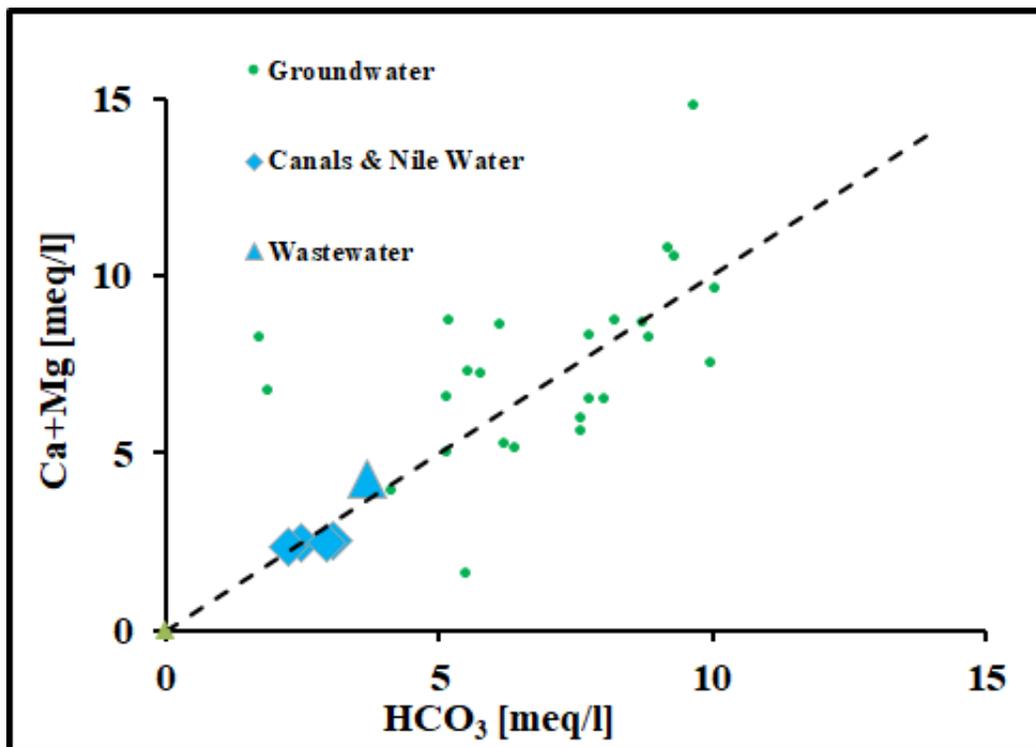
Fig. 10: Plot of [Ca^{2+}+Mg^{2+}] vs. [HCO_3^-]

4.4.6. Anthropogenic activity

Nitrate is a major environmentally responsible pollutant, commonly produced from agricultural fertilizers, air pollution, human and animal wastes, bio-burden,bio-burden, and synthetic N (Jeong, 2001; Xiao and Liu, 2002). Ammonium (NH_4^-) and nitrate (NO_3^-) are the two main pollutants in both surface water and groundwater (Böhlke et al.,2006; Brauns et al., 2016; Zhang et al., 2014). Leaking sewage pipes, chemical combination spills under industrial operations, and fertilizer leaching are some of the causes (Di Lorenzo et al., 2012; Best et al., 2015; Yang et al., 2016; Roehrdanz et al., 2017; Caschetto et al., 2018). Possibly from wastewater treatment facilities, septic tanks, and sewage systems, leaks are the main contributors to decreased groundwater quality, which mostly creates nitrogen compounds as pollutants (Ahmed and Ali, 2011). Two nitrogen species, nitrates and ammonia, were detected. The NO_3^- level have an average (1.35), vary between 0.02 to 32 mg/L, indicating that home and industrial wastewater has been contaminated by nitrogen fertilizers, nitrite oxidation, and nitrification of ammonia nitrogen (El Morhit, 2013 and Taouil, 2013). The overuse of nitrogen fertilizers during agriculture and anthropogenic activities mainly causes the relatively high NH_4^+ content in groundwater (Gedamy, 2015). Low NH_4^+ levels in the groundwater will be caused by the substantial oxidation of NH_4^+ to NO_3^- (Gedamy, 2015). Ammonium varies from 0.04 and 11.58 mg/L, with 1.30 as a mean value. Because of the decomposing organic matter in the groundwater may have occurred naturally or as a result of artificial sources. The potassium concentrations in groundwater ranged from 3-22 mg/L with an average of 1.30 mg/L showing the potential for sewage and fertilizer pollution of groundwater (Choi, 1988; Gedamy, 2015).

Conclusion

To identify the hydro-geochemical factors that regulate the groundwater chemistry of the research site, groundwater samples from El Dir area, 2 km apart of Sohag city, Egypt, were collected for this study. The shallow aquifer in El Dir village has a low concentration of dissolved ions, which suggests recent recharging from the Nile River. Contrarily, the deeper aquifer in the settlement has a comparatively higher dissolved ions content. Groundwater dominance types are Ca^{2+} - Mg^{2+} - HCO_3^-, and Na^+-Mg^{2+}-Cl^- indicating freshwater types. The statistical correlation study shows that cation exchange and mineral dissolution/precipitation are the main governing forces affecting the geochemistry of groundwater. However, Silicate weathering and rock water interaction are the main processes controlling groundwater characteristics. The dissolved major ions in groundwater samples show strong relationships between Mg^{2+}- Cl^- and Ca^{2+}- Cl^- postulate that cation exchange can also significantly impact groundwater composition while the cation exchange shows negatives value for most samples. The wastewater seepage leads to increase of NH_4^+, NO_3^-, and K^+ reveals the contamination from the sewage plant, domestic wastewater, and fertilizers.

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