Quality and hydrogeochemistry appraisal for groundwater in Tenth of Ramadan Area, Egypt

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ABSTRACT
Groundwater at Tenth of Ramadan area, Egypt, is the main source of water supply and it is ranked as high pollution risk area due to the high infiltration rate of the existing unlined oxidation ponds and the wastewater based-irrigation in the reclaimed desert. This investigation aims to evaluate groundwater quality and the spatial distribution of their ions, determine the chemical species (forms) of contaminated ions, and examine the process of water-rock interactions represented by the hydrogeochemical processes (ion exchange, dissolution, and precipitation) at Tenth of Ramadan area, Egypt. Eighteen water quality parameters were determined in triplicate samples collected from twelve wells in July 2017. Visual MINTEQ model was applied for geochemical speciation of cations, anions, trace and heavy elements in groundwater samples. The hydrogeochemical indices were used for investigating the quantity of changes in the chemical composition of groundwater. Outcomes revealed that the trend of spatial pollution for eleven water quality parameters is Site 3 > Site 1 > Site 2. The geochemical speciation indicated that Ca$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, F$^-$, HCO$_3^-$ and Fe$^{3+}$ are distributed as free ions. Hydroxides of Al$^{3+}$, Fe$^{3+}$ and carbonate of Pb$^{2+}$ are predominant. The free ions of cadmium are accessible within the absence of dissolved organic carbon (DOC). The results suggest that evaporation, dissolution, and precipitation play an essential control on the groundwater composition within the aquifer. The reverse ion exchange process is more effective than the ion exchange process in controlling the water composition for 58% of samples. Hence, groundwater requires more advanced treatment.

Introduction
Tenth of Ramadan (El Asher Men Ramdan) is one of the first new settlements that is accompanied by a large industrial area set on the fringes of the Eastern Nile Delta region (Figure 1). Industrial and domestic wastewater is somewhat arranged into unlined ponds east of the city. Another section of the city is employed in restricted irrigation. As the groundwater is used for the water supply of the city, the risk of pollution from the wastewater needs to be studied and monitored (El-Arabi, 1997). Monitoring of the physical and chemical parameters in groundwater is required for various destinations, i.e. to depict the chemical structure of groundwater and anthropogenic impacts on groundwater composition, to get an insight into the contribution of water-rock interactions, and to become attentive to spatio-temporal distribution of pollutants (El Gammal & Ibrahim, 2011; Ibrahim, Korany, Tempel, & Gomaa, 2019; Kumar, Ramanathan, Rao, & Kumar, 2006; Kumar and Singh, 2010; Quevauviller, Fouillac, Rath, & Ward, 2009).

Speciation of water quality variables offers information on the mobility and so bioavailability (which varies with the form) to living beings and furthermore their potential harming (Ekwere & Edet, 2012). Speciation of elements within the water system is extraordinarily reliant on the varied constituents of the water, specifically dissolved organic compounds (humic and fulvic acids), or inorganic species (CO$_3^{2-}$, HCO$_3^-$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$ and F$^-$) (Ibrahim, 2011). The organic and anionic species in water can easily interact with accessible metals and hence affect the metal speciation and transportation to the surrounding eco-system (Almas, Lombnaes, Sogn, & Mulder, 2006). The ability to perceive and measure the reactive chemical phases has been improved through computer-based programs for hydrogeochemical modeling, i.e. Visual MINTEQ (Ekwere & Edet, 2012; Gustafsson, 2007; Ibrahim, 2015). The model is able to consider the collaboration of cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$) with anions (Cl$^-$, SO$_4^{2-}$, NO$_3^-$, F$^-$, HCO$_3^-$, and CO$_3^{2-}$) with dissolved organic carbon (DOC) as a component of ionic strength, redox potential (Eh), temperature and pH.

Some previous work has been performed by (El-Arabi, 1997; El-Sayed, El-Aaassar, Abu El-Fadl, & Abd El-Gawad, 2012; Ibrahim, 2011; Taha, El-Mahmoudi, & El-Haddad, 2004) relating to groundwater quality issues.
in the investigation area. The previous studies indicated that groundwater at Tenth of Ramadan area, Egypt, is the main water supply and it’s ranked as high pollution risk area because of the high infiltration rate of the existing unlined oxidation ponds and also the wastewater based-irrigation in the reclaimed desert. However, no previous studies concerning the speciation of metal ions, spatial distribution, and saturation indices were done in the study area.

This research attempts to assess the groundwater quality and the spatial distribution of water quality parameters in three sites at Tenth of Ramadan area, Egypt, determine the chemical species of aluminum, cadmium, iron, lead, calcium, magnesium, potassium, sodium, chloride, sulfate, nitrate, bicarbonate and fluoride in groundwater using geochemical model (Visual MINTEQ), find out mineral saturation indices (SI) and appraise the water-rock interactions represented by the hydrogeochemical processes (ion exchange, dissolution and precipitation).

**Description of the study area**

Tenth of Ramadan, Cairo, covers a spot of more or less 100 Km² and is situated within the southeastern part of the Nile Delta, along the Cairo-Ismailia Desert road between Km 54 to 64 and geometrically lies between the longitudes 31° 39’ – 31° 49’ E and between the latitudes 30° 17’ – 30° 25’ N. Tenth of Ramadan includes two main parts. The first is an urban zone and two small industrial zones for small scale industries (north of Cairo-Ismailia road); and the second is a giant industrial zone for all types of industries, south of Cairo-Ismailia road (El-Arabi, 1997; Taha et al., 2004).

The geomorphology moreover geology of the investigation area has been considered by numerous authors. Among them are Shata (1965) and Shata and El Fayoumy (1970). These past investigations secured all the geomorphologic and geologic settings. Geomorphologic units within the investigation area embrace Bitter lakes moreover Isthmus plain within the east, El Ankabia – Iweibid structural plain in the south, while in the north embrace Belbies – El Tell El Kabier El Salhia plains, and in the West embrace Wadi El Tumilat depression and Desert dry drainage lines in West. The elevation of ground ascends from 12 m AMSL (Above Mean Sea Level) in the north to around 180 m AMSL in the south. The Tenth of Ramadan city is situated on the gravelly fluviatile plains. These plains involve the western area of the cultivated lands of the Nile Delta reaching out to Suez Canal (Khalaf & Gad, 2015).

The geology of the Tenth of Ramadan city is formed out of sedimentary rocks, which belong to Tertiary and Quaternary periods. Oligocene sands and gravels are well exposed at Gebel El-Hamza and Gebel Um El-Qamar unconformable excessively the Upper Eocene sediments. The outcrops of basaltic flows are seen at Gebel Um Raqm and El-Hamza. These basalts are unconformable underlyin the marine Miocene sediments. The Pliocene sediments are recorded in the subsurface sections (up to 250 AMSL). These are created out of rarely fossiliferous dark pyritic clay. The Quaternary sediments embrace a significant section of the investigation area. The old wadi deposits of the terraces of the large wadis within the southern section of the investigation area are formed of quartz sand, flint and quartize pebbles. The top soil of the investigation area comprises rounded gravel (Figure 2), (Awad, 2010).
Hydrogeologically, the southern section of the investigation area is complicated because of great changes in facies and geologic structure as shown in Figures 3 and 4. The Quaternary formation occupies an honest range of the northern part of the investigation area close to Ismailia canal. This aquifer consists of Pleistocene sand and gravel sediments, with a thickness of about 200 m. The aquifer in this area is considered unconfined. The lower section of the Quaternary aquifer constitutes the Plio-Pleistocene sediments of mixed shale, sand, and gravel (RIGW, 1980; RIGW/IWACO, 1998). The Miocene and Oligocene aquifers are directly present under the Quaternary aquifer deposits and appear within the southern sections of the area, as shown in Figure 3. The thickness of those formations may reach quite 200 m in the investigation area.

The groundwater flow in Tenth of Ramadan area was primarily directed to the north-east plus east before the urbanization. The average groundwater heads vary from 6 to 16 m (AMSL). The groundwater salinity in the investigation area varies between 750 to 950 mg/l. Sources of groundwater recharge are see-page from Ismailia canal, return flow irrigation from the agricultural lands and seepage & leakage from the oxidation ponds. Groundwater abstraction takes place at a good field north-west of the city where 24 wells, with a maximum total discharge of about 40,000 m³/
day, are operated as a source of drinking water supply (El-Arabi, 1997).

**Materials and methods**

**Sampling**

A sum of 12 groundwater samples was gathered from 12 wells (3 sites) in July 2017 as mentioned in Table 1 and Figure 4. For QA/QC (quality assurance/quality control) triplicate samples were gathered from each well. Samples were gathered according to EPA (Environmental Protection Agency) guidelines (EPA, 2002). For each sample, three bottles were needed to perform the analysis. At each site, four wells were needed to collect groundwater samples from them, in light of the fact that the area of oxidation ponds contains just four wells. These water samples straddled the different geologic units inside the investigation area.

Site 1 (West); wells present in agricultural lands & close Ismailia canal, while site 2 (middle) represent groundwater from deep aquifer and site 3 (East); wells display in the area of unlined ponds.

In the field, the samples were gathered from every location in polyethylene bottles. One sample from every location was preserved by acidifying to pH 2 with 0.5 mL of concentrated HNO₃ acid for heavy & trace elements analysis. Calibrated PHT-027 water quality multi-parameter probe was used for field measurements (total dissolved solids (TDS), pH and redox potential (Eh)). Methods for preparation of Eh calibrator solutions can be found in Section 2580 A of Standard Methods for the Examination of Water and Wastewater APHA (2005). The samples were transferred to the Central Laboratory for Environmental Quality Monitoring (CLEQM) in a cool box with cooling elements in the city of El-Kanater for analysis.

**Reagents and quality assurance**

Analytical chemical grade and deionized water were utilized for preparing the standard solutions under a clean laboratory environment. Plastic bottles were cleaned through soaking in 10% HNO₃ solution, flushing with deionized water, furthermore drying in an oven. On the locations shown in Table 1, the plastic bottles were completely washed with aliquots of the sampled waters, prior to collection. Single standard solutions of Aluminum (Al), cadmium (Cd) iron (Fe) and lead (Pb) were gotten from Merck in concentrations of 1000 mg/L (Germany) for the preparation of calibration standards. The percentage of Recovery for

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**Table 1. Sampling sites and locations for the collected groundwater samples at Tenth of Ramadan area.**

| Sites         | North          | East          |
|---------------|----------------|---------------|
| Site 1 (West) | 30° 22’08”     | 31° 34’03”    |
|              | 30° 23’94”     | 31° 34’43”    |
|              | 30° 21’58”     | 31° 37’03”    |
|              | 30° 21’98”     | 31° 37’02”    |
| Site 2 (middle) | 30° 20’37” | 31° 38’83”    |
|               | 30° 20’39”     | 31° 39’16”    |
|               | 30° 20’41”     | 31° 39’36”    |
|               | 30° 20’43”     | 31° 40’18”    |
| Site 3 (East) | 30° 21’24”     | 31° 52’20”    |
|               | 30° 21’45”     | 31° 52’51”    |
|               | 30° 21’59”     | 31° 52’70”    |
|               | 30° 21’03”     | 31° 52’08”    |

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**Figure 4.** Sampling sites at Tenth of Ramadan (El Asher Men Ramdan) area.
the previously mentioned elements analyzed using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) varied between 90% and 106%. The measurements were repeated thrice; the calculated range, median, mean and Standard Deviation (SD) were reported.

**Water quality determination**

The parameters (pH, TDS, sodium, calcium, magnesium, chloride, sulfate, nitrate, fluoride, aluminum, cadmium, iron and lead) were chosen in consistency with the decree of the Egyptian National Guideline for drinking water, Minister of Health number 458 for the year 2007. Additionally to the previous parameters; potassium and Eh were measured to be used for Visual MINTEQ program input data.

Chemical analyzes were completed for all groundwater samples using the standard procedures suggested by APHA (2005). pH was measured at 25°C utilizing Info Lab meter. Alkalinity [Carbonate (CO$_3^{2-}$) & bicarbonates (HCO$_3^-$)] ions were determined titrimetrically against 0.2 N–H$_2$SO$_4$, utilizing phenolphthalein & methyl orange indicators, respectively. Total dissolved solids (TDS) were determined by evaporating a measured volume of filtered water sample to dryness at 105 ± 2°C, after that weighing the solid residue. Major anions; chloride (Cl$^-$), nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$) and fluoride (F$^-$) were estimated utilizing Ion Chromatography (IC). Major cations [sodium (Na$^+$), potassium (K$^+$), calcium (Ca$^{2+}$) and magnesium (Mg$^{2+}$)] were estimated utilizing inductively coupled plasma-optical emission spectrometry (ICP-OES), while heavy & trace elements [Al, Cd, Fe, and Pb] were estimated by ICP-MS. Dissolved organic carbon (DOC) was estimated utilizing DC-190 TOC (total organic carbon) analyzer, Tekmar Dohrmann with a non-dispersive infrared detector (NDIR).

**Programs utilized for interpretation and reporting**

Essential descriptive parameters (i.e. range, median, mean values & standard deviation (SD)), normality, homogeneity, Kruskal-Wallis and Mann-Whitney tests had been computed utilizing SPSS (Statistical Package for the Social Sciences), ver. 21, 2012 software (Fávero & Belfiore, 2019). Visual MINTEQ program was utilized for geochemical speciation of the variables (Gustafsson, 2007). Visual MINTEQ can do ion speciation using equilibrium constants from the MINTEQA2 database, solubility calculations involving solid phases, distribution of redox elements among their valence states (Fe$^{3+}$/Fe$^{2+}$) based on a specified Eh (Benjamin, 2015), organic complexation can be simulated using the Gaussian DOM (dissolved organic matter) described by Grimm, Azarraga, Carreira, and Susetyo (1991). The data of water samples, including temperature, pH, Eh (redox potential), DOC (dissolved organic carbon), cations, anions, and trace elements were inserted within the database of the geochemical equilibrium modeling program Visual MINTEQ version 3, so as to make input files. Chemical species of the variables and minerals saturation indices (SI) were acquired from the output file.

**Results and discussion**

**Groundwater chemistry**

Groundwater’s chemistry has predominantly been depended on the chemical structure of host rock. The outcomes from the groundwater analysis were utilized as a tool to recognize the processes and mechanisms influencing the groundwater’s chemistry from the examination area. Analytical outcomes are given in Table 2 for the sites. Comparing these results with Egyptian National Guideline for Drinking Water (2007) indicated that groundwater samples of site 1 and site 3 are unsuitable for drinking in light of the high concentrations of TDS, aluminum, cadmium, iron, lead, calcium, sodium, chloride, sulfate, nitrate, and fluoride. While groundwater samples of site 2 are suitable for drinking.

Groundwater samples from the three sites are somewhat slightly alkaline. According to TDS classification by Hem (1989), groundwater samples gathered from site 1 are named as slightly saline, while for site 2 are classified as freshwater and for site 3 are named as moderately saline. TDS acquires from the chemical interactions between geological materials and groundwater through which it flows. In site 2, the lower value of TDS might be ascribed to direct seepage from Ismailia canal (direct recharge from Ismailia canal) and dissolution of earth’s minerals (El-Sayed et al., 2012; Ibrahim, 2011). The high values of TDS in site 1 may be credited to the recharge of Pleistocene aquifer from Ismailia canal, irrigation process and leaching and dissolution of aquifer matrix (El-Sayed et al., 2012). The high concentrations of TDS in site 3 may be credited to the impact of evaporation and the marine sediments in aquifer matrix together with dissolution and leaching of minerals from agricultural, anthropogenic and industrial activities (El-Sayed et al., 2012; Taha et al., 2004).

Redox potential (Eh) is a measure of a water system’s ability to either release or gain electrons in chemical reactions (APHA, 2005). The essence of Eh measurement in water is to assess the corrosions of metals in drinking groundwater. The range of Eh in this study will not cause corrosion but may be considered in the normal range of 187–188 mV, 190–192 mV and 172–177 mV for sites 1, 2 and 3, respectively. Positive Eh in the samples demonstrated that these wells are oxidizing with appreciably high dissolved oxygen. The Eh values are similar to those
Table 2. Range, median and spatial variation in the mean values of physio-chemical parameters for the studied sites at \( P < .05 \) and the Egyptian National Guideline for Drinking Water (2007) included in the Table 2 for comparison.

| Parameters (Units) | Site 1 (4 wells) | Site 2 (4 wells) | Site 3 (4 wells) | P-value | Guideline for drinking water** |
|--------------------|----------------|----------------|----------------|--------|--------------------------|
| pH (dimensionless) | 7.29–7.53  | 7.35  | 7.37 \( ^{\circ} \pm 0.105 \) | 7.85–8.32  | 8.08  | 8.08 \( ^{\circ} \pm 0.205 \) | 7.23–7.58  | 7.39  | 7.39 \( ^{\circ} \pm 0.164 \) | 0.0001  | 6.5–9.2 |
| Carbonate (mg/L)   | <0.1     | <0.1 | <0.1 \( ^{\circ} \pm 0.0 \) | <0.1–5.67 | 1.67 | 2.3 \( ^{\circ} \pm 1.26 \) | <0.1–0.12 | 0.1025 | 0.103 \( ^{\circ} \pm 0.1 \) | 0.101   | - |
| Bicarbonate (mg/L) | 299–256  | 252.27 | 247.55 \( ^{\circ} \pm 12.46 \) | 173–205 | 187.67 | 188.63 \( ^{\circ} \pm 14.2 \) | 155–233 | 193.8 | 194.18 \( ^{\circ} \pm 36.6 \) | 0.0001  | - |
| TDS (mg/L)         | 875–4620 | 3045  | 2896 \( ^{\circ} \pm 105 \) | 579–729 | 669  | 669 \( ^{\circ} \pm 74 \) | 3992–7320 | 6041 | 5889 \( ^{\circ} \pm 1265 \) | 0.001   | 1000 |
| Eh (mV)            | 187–188  | 168  | 188 \( ^{\circ} \pm 0.46 \) | 190–192 | 191   | 191 \( ^{\circ} \pm 1.1 \) | 172–177 | 174   | 174 \( ^{\circ} \pm 2.5 \) | 0.012   | - |
| DOC (mg/L)         | 1.3–12.8 | 4.3  | 5.7 \( ^{\circ} \pm 5.2 \) | 0.4–0.8 | 0.6   | 0.6 \( ^{\circ} \pm 0.2 \) | 24.4–49.4 | 35.6 | 36.3 \( ^{\circ} \pm 11.5 \) | 0.0001  | - |
| Calcium (mg/L)     | 116–350  | 243  | 238.2 \( ^{\circ} \pm 96.61 \) | 36–48 | 42    | 42 \( ^{\circ} \pm 5.16 \) | 281–458 | 347.2 | 358.6 \( ^{\circ} \pm 89.39 \) | 0.001   | 350   |
| Potassium (mg/L)   | 6–12     | 7    | 8 \( ^{\circ} \pm 2.7 \) | 3–5    | 3.5   | 3.75 \( ^{\circ} \pm 0.95 \) | 16.2–21.4 | 18.6 | 18.7 \( ^{\circ} \pm 2.22 \) | 0.0001  | - |
| Magnesium (mg/L)   | 36.5–141 | 93.8 | 91.43 \( ^{\circ} \pm 48.77 \) | 16.8–39.5 | 20.1 | 24.12 \( ^{\circ} \pm 10.3 \) | 88.9–141.7 | 108.5 | 111.87 \( ^{\circ} \pm 26.73 \) | 0.01    | 150   |
| Sodium (mg/L)      | 104–1189 | 725  | 685.7 \( ^{\circ} \pm 564.5 \) | 140–195 | 167   | 167.5 \( ^{\circ} \pm 24.66 \) | 1153–1933 | 1485 | 1514.2 \( ^{\circ} \pm 23.29 \) | 0.002   | 200   |
| Chloride (mg/L)    | 172–2002 | 1045 | 1066.3 \( ^{\circ} \pm 873.9 \) | 149–259 | 195   | 199.78 \( ^{\circ} \pm 46.83 \) | 1518–3237 | 256   | 2467 \( ^{\circ} \pm 7564 \) | 0.003   | 250   |
| Sulfate (mg/L)     | 273–1200 | 600  | 668.8 \( ^{\circ} \pm 209 \) | 80–130  | 105   | 105 \( ^{\circ} \pm 10.3 \) | 850–1593 | 1238 | 1230.4 \( ^{\circ} \pm 188 \) | 0.003   | 250   |
| Nitrate (mg/L)     | 20–150   | 80   | 82.88 \( ^{\circ} \pm 26.47 \) | 12.5–20.2 | 5.65 | 8.215 \( ^{\circ} \pm 4.54 \) | 22–55 | 32.5 | 35.5 \( ^{\circ} \pm 6.9 \) | 0.024   | 45    |
| Fluoride (mg/L)    | 1.0–2.6  | 1.50 | 1.63 \( ^{\circ} \pm 0.68 \) | 0.45–0.8 | 0.6   | 0.6 \( ^{\circ} \pm 0.015 \) | 0.9–1.2 | 0.9  | 1.04 \( ^{\circ} \pm 0.29 \) | 0.043   | 0.8   |
| Aluminum (mg/L)    | 0.06–0.10 | 0.079 | 0.079 \( ^{\circ} \pm 0.016 \) | 0.04–0.06 | 0.05 | 0.05 \( ^{\circ} \pm 0.009 \) | 0.13–0.6 | 0.345 | 0.357 \( ^{\circ} \pm 0.211 \) | 0.012   | 0.2   |
| Cadmium (mg/L)     | 0.012–0.015 | 0.0135 | 0.0135 \( ^{\circ} \pm 0.0001 \) | 0.008–0.009 | 0.0085 | 0.0099 \( ^{\circ} \pm 0.0014 \) | 0.004–0.009 | 0.0055 | 0.006 \( ^{\circ} \pm 0.0024 \) | 0.0001  | 0.003 |
| Iron (mg/L)        | 0.164–0.349 | 0.2685 | 0.262 \( ^{\circ} \pm 0.083 \) | 0.082–0.218 | 0.1335 | 0.144 \( ^{\circ} \pm 0.06 \) | 0.458–0.874 | 0.648 | 0.658 \( ^{\circ} \pm 0.19 \) | 0.001   | 0.3   |
| Lead (mg/L)        | 0.001–0.004 | 0.0025 | 0.0025 \( ^{\circ} \pm 0.001 \) | 0.002–0.003 | 0.002 | 0.0022 \( ^{\circ} \pm 0.0001 \) | 0.006–0.011 | 0.0085 | 0.0085 \( ^{\circ} \pm 0.002 \) | 0.001   | 0.01  |

Data represented as mean ± SD (Standard Deviation) of 4 samples (collected from 4 wells). Different single letters (A, B, C) in the same raw for the mean values are significant (\( p < 0.05 \)).

*: High value of SD indicated that the 4 wells at each site are different in physio-chemical compositions, and the symmetric or common factor in site 1; wells present in agricultural lands & close Ismailia canal, while in site 2; represent groundwater from deep aquifer and site 3; wells display in the area of unlined ponds.

**: Egyptian National Guideline for drinking water, No. 458, 2007.
obtained by Gbadebo, Taiwo, Ayedun, and Adeola (2012) in groundwater samples.

Median DOC concentrations were 4.3, 0.6, 35.6 mg/L at sites 1, 2 and 3, respectively. Besides, there is no guideline in comparing the data with drinking water Egyptian Law. It was observed that the higher concentrations of DOC in site 3 corresponds higher aluminum, iron, cadmium and lead concentrations (positive correlation was found \( r = 0.9, p < .01 \). These relations have not been observed in groundwater from site 1 and site 2. The degradation processes of soils organic matter are the source of many mineral compounds and new organic substances are leaching out of groundwater causing their pollution. These outcomes of these examinations demonstrated that soil organic matter decomposition and seepage of industrial wastewater from unlined ponds have a larger impact on wells of site 3 (El-Sayed et al., 2012).

The higher concentrations of calcium, magnesium, and sodium in site 1 and site 3 with regard to their concentrations in site 2 are attributed by Ibrahim (2011) and El-Sayed et al. (2012) to salt intrusion from deep aquifer, leaching of wastewater from agricultural activities in site 1 and leaching of industrial and domestic wastewater from oxidation ponds in site 3 additionally, to subsurface evaporation intercalated with water-bearing formation. The major cations distribution percentage regarding to total cations exhibited the following order (\( \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ \)), Figure 5. At sites 1, 2 and 3, sodium ion was generally dominant representing an average of 58%, 70% and 75%, respectively; calcium ion was next in abundance with an average of 29%, 18% and 18%, respectively. This may reflect the process of chemical weathering of silicates and therefore the common prevalence of calcium carbonate (Langmuir, 1997). At sites 1, 2 and 3, the third cation was magnesium with an average of 10%, 9% and 5%, respectively, and in the last order was potassium ion with an average of 1.2%, 1.6% and 0.9%, respectively. Potassium exhibited the lowest concentration levels relative to other cations. This can be common in natural waters as a result of its tendency to be fixed by clay minerals and precipitate within the formation of secondary minerals (Matheis, 1982).

The distribution percentage or abundance of anions with respect to total anions exhibited the following order (\( \text{Cl}^− > \text{SO}_4^{2−} > \text{HCO}_3^{−} > \text{NO}_3^{−} > \text{F}^− > \text{CO}_3^{2−} \)) for sites 1 and 3, while for site 2 demonstrated the next order (\( \text{Cl}^− > \text{HCO}_3^{−} > \text{SO}_4^{2−} > \text{NO}_3^{−} > \text{F}^− > \text{CO}_3^{2−} \)), Figure 5. The higher values of \( \text{Cl}^− \) at sites 1 and 3 are attributed to salt intrusion from a deep aquifer, leaching of wastewater from agricultural activities and oxidation ponds, respectively (Ibrahim (2011) and El-Sayed et al. (2012)). The variation of \( \text{HCO}_3^{−} \) and \( \text{SO}_4^{2−} \) concentrations reflect the intensity of participation of carbonic acid and sulfuric acid during weathering/dissolution process. The relative intensity of participation can be assessed from the C-ratio = \( \frac{\text{HCO}_3^{−}}{(\text{HCO}_3^{−} + \text{SO}_4^{2−})} \) ratio equivalent (Tarawneh, Janardhana, & Ahmed, 2019). In this investigation, the values of C-ratio of the groundwater samples gathered from sites 1, 2 and 3 vary from 0.14 to 0.39, from 0.51 to 0.65 and from 0.07 to 0.15, with average values 0.268, 0.588 and 0.116, respectively. These outcomes demonstrate that, value of 0.558 in site 2 suggests that coupled reactions (Equation (1)), involving carbonate dissolution and protons derived primarily from the oxidation of sulfate minerals, largely control both the concentration. The decrease of ratio in sites 1 and 3 refers to both the process control, but the sulfuric acid played relatively a major role in site 1 > site 3 during the weathering process.

\[
\text{Carbonate minerals} + \text{H}_2\text{SO}_4 \\
\rightarrow \text{Ca}^{2+} + \text{SO}_4^{2−} + \text{HCO}_3^{−} \pm \text{Mg}^{2+} + \text{H}^+ \tag{1}
\]

High values of nitrate were recorded at site 1 with concentration exceed the maximum allowable limit (50 mg/L \( \text{NO}_3^{−} \)) for drinking water. These values are attributed to agriculture activities and livestock wastewater (Mattas, 2009). For All sites, pH and nitrates have negative indirect correlation \( (r = −0.68, p < .05) \); in keeping with Kim, Rajmohan, Kim, Hwang, and Cho (2004), the supply of nitrates therein case is ammonium oxidation or aerobic decomposition of organic matter. The occurrence of fluoride in sites 1 and 3 with concentrations higher than the permissible limit may be attributed to multiple processes, including agricultural & industrial activities and water–rock interaction processes in the aquifer (Dhiman & Keshari, 2010).

The outcomes demonstrated that the prevalent salt is \( \text{NaCl} \), Figure 5; this reflects the marine origin of the water. The dominance of \( \text{Na}^+ \) and \( \text{Cl}^− \) (mill equivalent) in sites 1 and 3 implies that the groundwater is influenced by leaching and dissolution of marine salts with the original flow, while in site 2 showing that the origin of water was affected by meteoric water via leaching and dissolution process (El-Sayed et al., 2012). The dominance of \( \text{Ca}^{2+} > \text{Mg}^{2+} \) (mill equivalent) clarify the dissolution of calcite, which suggest that water moves in limestone or that marly limestone are rich with dolomite (Plummer, Jones, & Truesdell, 1976). The non-cyclic sulfate (NCS) was calculated from this formula (El Hinnawi, Frankfurt, & Abdel Mogheeth, 1972): NCS = (\( \text{Cl}^−/7.2 \) − \( \text{SO}_4^{2−} \)), where the unit is mg/L. The data affirm that all groundwater samples have been negative values of NCS indicates that the sulfate is of terrestrial origin.

The distribution percentage of the trace elements analyzed exhibited the relationship (iron > aluminum > cadmium > lead) for the three sites, Figure 5. The
high concentration of cadmium at site 1 was attributed by Taha et al. (2004) to the occurrence of pesticides employed in agriculture. The concentrations of aluminum, cadmium, iron & lead are higher than the standard limit at site 3, that was attributed by Taha et al. (2004) and Ibrahim (2011) to leaching of domestic & industrial (industrial sources; pigment industries, metal plating and stabilizers in plastic materials) wastewater from oxidation pond to the aquifer in that area in addition to crustal elements and corrosion product of well casing material (El Gammal & Ibrahim, 2017). Lead occurs in groundwater may be attributed to either the natural mobilization of lead or enriched from anthropogenic activities in the soil and, in some cases, mineral weathering (Buragohain, 2010).

In conclusion, groundwater quality deterioration at sites 1 & 3, may be attributed to the elevated concentration levels of cations (Na\(^+\), K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\)) and major anions (SO\(_4^{2-}\), NO\(_3^-\), F\(^-\) and Cl\(^-\)), has appeared in Table 2 and Figure 5, that may be related to the serious agricultural activities occurring in the area and domestic & industrial wastewater leaching from oxidation ponds.

**Spatial variation of water quality variables**

Spatial water quality variations are controlled by rock-water interacts on distinct subsurface flow paths (El Gammal & Ibrahim, 2017). Normality test (Fávero & Belfiore, 2019) demonstrated that the Shapiro-Wilk test showed significant values (p >0.05) for 18 water quality variables in the three sites. The null hypothesis was accepted that the examined water quality variables have normal distribution. Levene’s test (Fávero & Belfiore, 2019) is significant (p < 0.05) for all water quality variables except pH, potassium, nitrate and fluoride. So, the equal variance was not assumed for all variables except pH, potassium, nitrate, and fluoride had equal variance. In that case, the authors applied ANOVA, Kruskal-Wallis and Mann-Whitney (for comparisons between sites [(1, 2), (1, 3) and (2, 3)] tests on 17 water quality variables (Fávero & Belfiore, 2019). The authors found that the outcomes are the same in the tests utilized for comparison considering the data had normal distribution. ANOVA test demonstrated that the 17 variables showed spatial significant variation (p < 0.05), while carbonate exhibited non-significant variation (p > 0.05). For 17 variables, the null hypothesis was rejected (the sites are identical) and the alternative hypothesis was accepted (at least one site was different from the other two sites for each studied variable). Comparisons were utilized to figure out which pair of examined variables has significant impact. Multiple comparisons at two sites for 17 water quality variables indicated that:

- Evaluating the water quality variables at sites 1 and 2 exhibited that bicarbonate, Eh, TDS, DOC, aluminum, iron, lead, potassium, magnesium, sodium, chloride, and sulfate demonstrated no significant spatial variations (p > .05). Whereas all the remaining water quality parameters confirmed significant spatial quality variation (p < .05). These suggest that five parameters confirmed vast spatial variations among sites 1 and 2. These variations may come from leaching of agriculture wastewater at site 1.
- Assessing the water quality variables of site 1 with site 3 indicated that TDS, Eh, DOC, aluminum,
cadmium, iron, lead, sodium and potassium, showed significant spatial variation \( (p < .05) \). The alternate parameters (pH, bicarbonate, calcium, magnesium, chloride, sulfate, nitrate, & fluoride) of site 1 and site 3, showed non-significant spatial variation \( (p > .05) \). These variations can be ascribed to the leaching of industrial wastewater at site 3.

- For site 2 with site 3, the outcomes showed that bicarbonate, nitrate, and fluoride didn’t demonstrate any significant spatial variation \( (p > .05) \). While the rest of the water quality parameters demonstrated significant spatial quality variation \( (p < .05) \), indicating that 14 variables have different water resources. The variations might be ascribed to agriculture activities at site 1 and leaching of industrial and domestic wastewater from oxidation ponds in site 3.

- Finally, the sequence of spatial pollution for TDS, DOC, aluminum, iron, lead, calcium, potassium, magnesium, sodium, chloride, sulfate was site 3 > site 1 > site 2, while the trend for cadmium, bicarbonate, fluoride, and nitrate was site 1 > site 3 > site 2.

- In the end, pH, bicarbonate, TDS, Eh, DOC, aluminum, cadmium, iron, lead, calcium, potassium, sodium, magnesium, chloride, sulfate, fluoride & nitrate demonstrated significant spatial variation \( (p < .05) \) between the three sites and have different sources.

**Geochemical speciation of the studied elements**

Geochemical speciation of the studied elements: Speciation was accomplished to assess the forms of polluted ions and determine their mineral saturation index. The distribution of the various species is presented in Tables 3 and 4, while the saturation indices of minerals are exhibited in Table 5.

Calcium occurs in one oxidation state \( \text{Ca}^{2+} \) that is largely soluble in most varieties of natural waters. The dominant form of calcium in the studied samples is the free ions \( (\text{Ca}^{2+}) \) with 87.3%, 84.6% and 77.2% of the whole dissolved calcium, in site 1, site 2 and site 3 respectively. The prevailing inorganic species is calcium sulfate in site 1, site 2 and site 3, which account 7.07%, 11.45% and 21.44%, respectively. The free ions of sodium \( (\text{Na}^+) \) are the most soluble chemical species of sodium in groundwater and account about 99%, 98% and 95% of the whole dissolved sodium for site 1, site 2 and site 3, respectively. Complexes inorganic species demonstrate that 0.09% occurs as bicarbonate, 0.03% as sulfate and less than 0.002% as other anions. Potassium, look-alike sodium has only one important oxidation state and it tends to be soluble in most kinds of natural water. The result of potassium indicates that 94.61%- 99.4% exists as free \( (\text{K}^+) \), 0.23%- 2.57% as chloride, 0.41%- 2.77% as sulfate, and 0.02%- 0.06% as \( \text{KNO}_3 \). In a natural water system, dissolved magnesium occurs in the +2 oxidation state. Magnesium speciation in groundwater samples indicates that 89%, 86% and 72.4% of magnesium is in the free ionic form \( (\text{Mg}^{2+}) \) in site 1, site 2 and site 3, respectively. Inorganic species of sites account 0.192–0.332% occurs as fluoride, 1.28–9.22% as chloride, 5.75–17.35% as sulfate, 0.628–1.8% as bicarbonate, 0.045–1.24% as carbonate and as other anions as shown in Table 3. Comparison of these findings for calcium, sodium, potassium and magnesium with the previous study conducted by Obiefuna and Orazulike (2010) on groundwaters at Yola Area, Nigeria indicated there’s a match between the outcomes.

On the further hand, carbonate ion speciation for all sites, Table 3, showed that the main aqueous species is \( \text{HCO}_3^- > \text{H}_2\text{CO}_3 > \text{CO}_2 \) (relying on the pH). The combined metal carbonates will constitute only 2.7%, 2.9% and 9.1% of the aqueous carbon in site 1, site 2 and site 3, respectively, and thus don’t have any real effect on carbonate speciation. The sulfate speciation showed that the major aqueous form of sulfate is free sulfate ion \( (\text{SO}_4^{2-}) \). These inorganic species are in the order \( \text{CaSO}_4 > \text{NaSO}_4 > \text{MgSO}_4 > \text{KSO}_4 \) under a variety of conditions. The free ions of \( \text{NO}_3^- \) records the following range 97% – 99% of the overall dissolved concentration within the three sites. Chloride ion speciation in the three sites show that the major aqueous form is \( \text{Cl}^- \), which account more than 99%, 99% and 95% in site 1, site 2 and site 3, respectively. Fluoride ion speciation indicated that 94%, 92% and 80% of the whole species are in the form of \( \text{F}^- \) ion. These results are similar to those given by Falck, Quinn, Duffield, and Williams (1988).

The percentages of soluble aluminium species specified by the model are displayed in Table 4. The outcome revealed that the groundwater samples of site 1, site 2 and site 3 contain around 92.9%, 98.7% and 90.8% of the entire dissolved aluminium as \( \text{Al(OH)}_4^- \), respectively. The remainder (<10%) comprises from \( \text{Al(OH)}_3, \text{Al(OH)}_2^+, \text{AlF}_2^+, \text{AlF}_4^+ \) and \( \text{AlF}_3^- \). The negatively charged \( \text{Al(OH)}_4^- \) is dangerous because of the information recorded by Gardner and Gunn (1991) specified that the most dangerous aqueous species are the inorganic monomeric forms, these are the Al hydroxy species and \( \text{Al(OH)}_4^- \). Also, in line with Bi (2000), aluminium toxicity relies upon the form present in water instead of its total concentration. Free \( \text{Al}^{3+} \), aluminium hydroxide \( \text{Al(OH)}_3 \) and \( \text{Al(OH)}_2^- \) are believed to be the most lethal species while Al–fluoride complexes may mitigate toxicity while organically complexed aluminium are non-dangerous (Bi, 2000). Therefore, for site 3 (area of oxidation pond) the toxicity of \( \text{Al}^{3+} \) is serious,
while for sites 1 and 2, the toxic forms of Al concentrations are below the drinking water limit as appeared in Table 2.

Two species (Fe$^{2+}$ and Fe$^{3+}$) of iron are predominant within the range of the conditions examined; Table 4. The activities of Fe$^{2+}$ ions are superior to the activities of Fe$^{3+}$ ions within the three sites. The principal species ferrous ion (Fe$^{2+}$) is prevailing with log activities −7.1, −6.0 and −5.5 in site 1, site 2 and site 3, respectively. Chemical speciation of ferrous ions in groundwater samples collected from site 1, site 2 and site 3 indicated that the free ions (Fe$^{2+}$) account for 81%, 87% and 77%, respectively, while the inorganic species in the form of bicarbonate account for 16%, 8% and 20%, respectively. The outcome indicated that iron at site 3 is harmful and negatively affects living creatures. A previous study by Obiefuna and Orazulike (2010) on shallow groundwater at Yola Area, Nigeria demonstrated that 79.37% of Fe$^{2+}$ ions are available as a free ionic form that is analogous to the current study.

The second species is ferric ions (Fe$^{3+}$) showed log activities of −16.5, −15.8 and −15.6 for site 1, site 2, site 3, respectively. Ferric ions (Fe$^{3+}$) speciation in groundwater samples at site 1, site 2 and site 3 showed that 98%, 80% and 98% are in the form of Fe(OH)$^2_+$, respectively. The remaining ferric ions concentration are existing as Fe(OH)$_2$, Fe(OH)$_4^-$ and FeOH$^2+$ species. According to these computations, aluminum and ferric ions were mainly present as hydroxo complexes. These outcomes resemble those given by various specialists (Bradbury, Baeyens, & Alexander, 1990).

Table 4 showed that the higher level of cadmium is related to inorganic species in groundwater samples contain dissolved organic matter which is accessible as free cadmium species in the samples free from dissolved organic matter. At site 2, the free cadmium ions record 57.5%, while the inorganic species record 42.5% as chloride, carbonate and sulfate. Cd$^{2+}$ which is toxic and carcinogenic is immobile and if present in high concentrations may be adsorbed by clay, thus reducing its danger potential (Edet, Merkel, & Offiong, 2004). Under the current condition in site 2, Cd$^{2+}$ ions seem to be mobile. However, the contamination risks of the groundwater at this site from Cd contamination poses no issue, due to low Cd concentration (mean value 0.009 mg/L). The presence of cadmium as free ions is similar to Kamel (2011) investigation. At site 1 and site 3 the higher level of cadmium related to inorganic species which account 48.8% and 57.1%, respectively. The primary species was CdCl$^+$ which accounted for 12.7% of the total dissolved cadmium. These outcomes demonstrated that the species of cadmium at site 1 and 3 are not toxic to human beings, and its concentration at site 2 is less than the standard limit.

Table 4 showed that Pb$^{2+}$ accounted average value 7.84%, 13.97% and 11.74% of total dissolved lead for site 1, site 2 and site 3, respectively. While, the inorganic species accounted for 66.76%, 82.62% and 74.22% for site 1, site 2 and site 3, respectively. The predominant inorganic form is PbCO$_3$ which account for 80.3% of total dissolved lead concentration. The presence of lead in the form of PbCO$_3$ will restrict its mobility (Edet et al., 2004). While the rest of lead is accessible as an organic species and accounts the values 10.97%, <0.01% and 14.03% for site 1, site 2 and site 3, respectively. The previous study by Ekwere and Edet (2012) indicated that Pb and Cd are present as free ions and as series of other species in all the analyzed groundwater samples.

**Water-rock interaction processes**

Water-rock interaction processes are detected as follows:

*Detecting dissolution and precipitation reactions:*
Assessment of dissolution and precipitation reactions desires the outline of the mean mineral assemblage of the rocks inside that water, and additionally the identification of the chemical reactions accountable for the geochemical evolution of groundwater (Ibrahim et al., 2019). Saturation Indices (SI) are helpful to decide the equilibrium amongst water and minerals in the aquifer matrix. Saturation states come from a comparison of the ion activity product (activities in water samples) and solubility product (activities at equilibrium) (Appelo & Postma, 2005). SI helps in showing which minerals may be dissolving or precipitating into or from groundwater, dominant the groundwater structure or dominant the geochemical reactions. Mineral saturation states were calculated as a part of the output from the modeling program “Visual MINTEQ” (El Gammal & Ibrahim, 2017) the outcomes of saturation indices are found in Table 5.

The groundwater samples at the three sites are supersaturated concerning calcite, aragonite, magnesioferrite (MgFe$_2$O$_4$), gibbsite (Al(OH)$_3$), boehmite (γ-AIO(OH)), diaspor (α-AIO(OH)), ferrhydrate, goethite, hematite (Fe$_3$O$_4$), hercynite and maghemite. Groundwater samples at site 1 and site 2 are supersaturated with respect to K-Jarosite. The supersaturated with theses minerals recommends that these phases probably do not participate in chemical reactions and also the saturation index reveal that the precipitation of the former minerals. Carbonate oversaturation could be due to the excess input of Ca$^{2+}$ and Mg$^{2+}$ ions from silicate weathering processes. The saturation of groundwater with calcite refers to the phenomena known as a common-ion effect or common-ion driven precipitation (Langmuir, 1997). This phenomenon demonstrates that the Ca$^{2+}$ discharged by the dissolution of gypsum results in the precipitation of further calcite leading to supersaturated of groundwater with calcite. The high content of aluminum and iron oxides is credited to the weathering of silicate minerals that are accelerated by the acidic rain
Table 3. Major ions species (%) in the three sites studied.

| Species | Ions species | Site 1 | Site 2 | Site 3 | Species | Ions species | Site 1 | Site 2 | Site 3 |
|---------|--------------|-------|-------|-------|---------|--------------|-------|-------|-------|
| Calcium species (%) | Free ion | 87.27 | 84.56 | 71.01 | Free ion | 89.35 | 86.62 | 72.44 |
| Inorganic species | CaF\(^+\) | 0.06 | 0.03 | 1.99 | Inorganic species | Mg\(_2\)CO\(_3\)\(^+\) | 0.022 | <0.01 | <0.01 |
| | CaCl\(^-\) | 0.79 | 1.05 | 5.02 | | Mg\(_2\)OH\(^-\) | 0.045 | 0.017 | <0.01 |
| | CaSO\(_4\)(aq) | 7.07 | 11.45 | 21.44 | | Mg\(_2\)Cl\(^+\) | 0.32 | 0.192 | 0.215 |
| | CaHPO\(_4\)(aq) | 0.02 | 0.01 | 0.09 | | Mg\(_2\)CO\(_3\)S | 1.28 | 1.71 | 9.22 |
| | CaNO\(_3\)\(^+\) | 0.05 | 0.12 | 0.07 | | MgSO\(_4\)(aq) | 5.75 | 9.33 | 17.35 |
| | CaPO\(_4\)\(^-\) | 0.04 | <0.01 | <0.01 | | Mg\(_2\)CO\(_3\)S | 1.24 | 0.315 | 0.045 |
| | CaHPO\(_4\)(aq) | 0.02 | 0.01 | <0.01 | | MgHCO\(_3\)\(^-\) | 1.94 | 1.8 | 0.628 |
| | Ca\(_2\)CO\(_3\)\(^-\) | 2.36 | 2.19 | 0.76 | Organic species | <0.01 | <0.01 | <0.01 |
| | CaCO\(_3\)(aq) | 2.4 | 0.54 | 0.09 | Sodium species (%) | Free ion | Na\(^+\) | 99.26 | 98.91 | 95.15 |
| Inorganic species | Na\(^+\) | 0.22± | 0.28± | 0.74± | Inorganic species | NaCl(aq) | 0.228 | 0.329 | 2.58 |
| Potassium species (%) | Free ion | 99.36 | 98.88 | 94.61 | Inorganic species | NaSO\(_4\)(aq) | 0.314 | 0.586 | 2.00 |
| Inorganic species | KCl(aq) | 0.23 | 0.33 | 2.57 | Inorganic species | NaNO\(_3\)(aq) | <0.01 | 0.046 | 0.017 |
| | K\(_2\)SO\(_4\)(aq) | 0.41 | 0.76 | 2.77 | | Na\(_2\)CO\(_3\)(aq) | 0.05 | 0.022 | <0.01 |
| | KNO\(_3\)(aq) | 0.02 | 0.06 | 0.04 | | NaHCO\(_3\)(aq) | 0.134 | 0.134 | 0.066 |
| Organic species | <0.01 | <0.01 | 0.86 | Organic species | <0.01 | <0.01 | <0.01 |
| Carbonate ion (%) | Free ion | 1.21 | 0.35 | 0.24 | Fluoride ion (%) | Free ion | F\(^-\) | 94.45 | 92.43 | 80.00 |
| Inorganic species | CO\(_3\)\(^2-\) | 94.57 | 92.11 | 84.72 | Inorganic species | Al\(_2\)F\(_3\)(aq) | <0.01 | 0.06 | 0.09 |
| | H\(_2\)CO\(_3\)(aq) | 1.51 | 4.61 | 5.92 | | MgF\(_2\)(aq) | <0.01 | 0.04 | 0.14 |
| | MgCO\(_3\)(aq) | 0.31 | 0.10 | 0.14 | Al\(_2\)F\(_3\)(aq) | <0.01 | <0.01 | 0.02 |
| | Mg\(_2\)HCO\(_3\)\(^+\) | 0.54 | 0.67 | 1.66 | Mg\(_2\)F\(_2\)(aq) | 4.19 | 5.24 | 11.42 |
| | Ca\(_2\)CO\(_3\)\(^-\) | 0.71 | 1.45 | 4.52 | Ca\(^+\) | 0.77 | 1.59 | 4.39 |
| | Ca\(_2\)CO\(_3\)(aq) | 0.73 | 0.31 | 0.58 | Na\(_2\)F\(_2\)(aq) | 0.58 | 0.70 | 4.05 |
| | Na\(_2\)CO\(_3\) | 0.10 | 0.04 | 0.13 | Sulfate ion (%) | Free ion | SO\(_4\)(aq) | 85.37 | 79.8 | 65.49 |
| | Na\(_2\)HCO\(_3\)(aq) | 0.28 | 0.34 | 2.06 | Inorganic species | Mg\(_2\)SO\(_4\)(aq) | 5.30 | 5.61 | 6.39 |
| Nitrate ion (%) | Free ion | 99.64 | 99.39 | 97.33 | Inorganic species | CaSO\(_4\)(aq) | 7.10 | 12.1 | 17.61 |
| Inorganic species | NO\(_3\)\(^-\) | <0.01 | <0.01 | 0.011 | Na\(_2\)SO\(_4\)(aq) | 2.19 | 2.4 | 10.41 |
| | KN\(_2\)O\(_3\)(aq) | 0.19 | 0.40 | 1.32 | K\(_2\)SO\(_4\)(aq) | 0.04 | 0.04 | 0.03 |
| | Na\(_2\)NO\(_3\)(aq) | 0.17 | 0.20 | 1.34 | Chloride ion (%) | Free ion | Mg\(_2\)Cl\(^+\) | 0.22± | 0.28± | 0.74± |
| | Inorganic species | CaCl\(^+\) | 0.15± | 0.31± | 1.03± | Inorganic species | NaCl(aq) | 0.29± | 0.36± | 2.35± |

and groundwater temperature (Edet et al., 2004). The groundwater samples at the three sites are undersaturated concerning gypsum, fluorite, halite (NaCl), Cd(OH)\(_2\), Pb(OH)\(_2\), otavite and cerussite. Groundwater samples at site 3 are undersaturated with regard to K-Jarosite. The finding recommends that its soluble components are not limited by the mineral equilibrium. Hence, the dissolution of those minerals may well happen.

Gibbs plot, Figure 6, is utilized to interpret the impact of evaporation, water-rock interaction (rock dominance) and rainfall precipitation processes on groundwater geochemistry (Gibbs, 1970). Gibbs ratio is determined by utilizing the next Equations (2) and (3).

Gibbs ratio (for cation) = \( \frac{\text{Na}^+ + \text{K}^+}{(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})} \)  
(2)

Gibbs ratio (for anion) = \( \frac{\text{Cl}^-}{(\text{Cl}^- + \text{HCO}_3^-)} \)  
(3)

Figure 6 portrayed that the sampling points of sites 1, 2 & 3 occupy the transition zone among the rock–water interaction and evaporation zone. The rock dominance recommends that water–rock interaction is that the real supply of dissolved ions. As seemed in Figure 6, the moving of groundwater samples of sites 1 and 3 in the Gibbs field toward the evaporation dominance proposes an increase of Na\(^+\) and Cl\(^-\) ions and resulting in higher TDS as a result of water pollution, caused by the return flow after irrigation in site 1, infiltration of mixed (industrial and domestic) wastewater from unlined pond water in site 3.

In conclusions, evaporation, dissolution and precipitation could play a significant role in determining the water composition within the studied sites.

Detecting ion exchange reactions: The chloroalkaline indices (CAI and CAII) are widely used to assess the ion exchange reactions between groundwater and its host rock (Schoeller, 1967). The chloroalkaline indices are computed using Equations (4) and (5), whereas the concentrations of cations and anions are in meq/l.

Chloro – alkaline index[CAI] = \( \frac{\text{Cl}^- - \text{Na}^+ + \text{K}^+}{\text{Cl}^-} \)  
(4)

Chloro – alkaline index [CAII] = \( \frac{\text{Cl}^- - \text{Na}^+ + \text{K}^+}{\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-} \)  
(5)

The indices values (CAI and CAII) are positive indicating base-exchange reaction among which Ca\(^{2+}\) and Mg\(^{2+}\) ions present in groundwater react with clay minerals to
release Na⁺ and K⁺ ions. The indices values are negative that indicates reverse ion exchange reaction in which Na⁺ and K⁺ ions in the groundwater are exchanged with Mg²⁺ and Ca²⁺ ions to release Mg²⁺ and Ca²⁺ ions. Figure 7 confirmed that the two chloro alkaline indices (CA I and CA II indices) are negative values for 58% samples, which indicated that reverse ion exchange is observed. On the other hand, the ion exchange is dominant for 42% of samples; this could be confirmed as outcomes of two indices are positive values. The aquifer is much less impacted by the ion exchange process because of the sandy nature of this geological formation.

From the outcomes, almost 42 % of samples display positive results with the Base Exchange reaction among Na⁺, K⁺, Mg²⁺ and Ca²⁺ ions. High base-exchange reaction within which alkali earth elements are exchanged for Na⁺ (in case of HCO₃⁻ > Mg²⁺+Ca²⁺) can be called to as base-exchange softened water, while Na⁺ ion is exchanged for the alkali earth (in case of Ca²⁺+Mg²⁺ > HCO₃⁻) can be called to as base-exchange hard water (Jeewanandam et al., 2012). In this study, 42% of samples are Base Exchange hard water due to the precipitation process.

### Conclusions

In general, elevated concentrations of TDS, aluminum, cadmium, iron, lead, calcium, sodium, chloride, sulfate, nitrate and fluoride were observed in groundwater at site 1 and site 3, according to Egyptian National Guideline for Drinking Water (2007). Spatial water quality variation exhibited that 17 elements showed significant (P < .05) spatial distribution. The investigation discovers in the light of model calculations that Fe²⁺, Na⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻, NO₃⁻, F⁻ and HCO₃⁻ are highly soluble and consequently will be bioavailable at the pH ranges of the studied wells. The outcome reveals that these free ions at such level (site 1 and site 3) would be accessible for uptake by plants, animals and humans. It is

### Table 4. Aluminum, cadmium, lead, ferric and ferrous species (%) in the three studied sites.

| Minerals                  | Site 1 (%) | Site 2 (%) | Site 3 (%) |
|---------------------------|------------|------------|------------|
| Aluminum species          | AIOH⁺⁺      | 0.01       | <0.01      | 0.21       |
| Al(OH)₃⁺                  | 0.68       | 0.04       | 1.69       |
| Al(OH)(aq)                | 4.96       | 1.22       | 4.48       |
| Al(OH)₆⁻                  | 92.9       | 98.7       | 90.8       |
| AlF⁻                     | 0.05       | <0.01      | 0.12       |
| AlF₃⁻                    | 0.88       | <0.01      | 2.63       |
| AlF₃(aq)                  | 1.33       | <0.01      | 2.69       |
| Al₄⁻                     | 0.24       | <0.01      | 0.33       |
| Organic species           |            |            |            |
| Cadmium species           | Cd²⁺       | 34.28      | 57.51      | 20.65      |
| Inorganic cadmium species | CdOH⁻      | 0.37       | 0.41       | 0.02       |
| Cd(OH)(aq)                | 0.03       | 0.05       | <0.01      |
| CdOH₂⁻                   | <0.01      | 0.03       | 0.02       |
| CdCl₂⁻                   | 48.79      | 19.00      | 57.10      |
| CdCO₃⁻                   | 5.64       | 0.36       | 13.26      |
| CdSO₄(aq)                 | 7.28       | 4.86       | 6.29       |
| CdSO₄(2)²⁻                | 0.60       | 0.06       | 1.05       |
| Organic species           |            |            |            |
| Ferric species (%)        |            |            |            |
| Pb(CO₃)²⁻                 | 0.04       | 0.04       | 0.02       |
| PbOH²⁻                   | 0.05       | 0.12       | 0.01       |
| PbCl₂⁻                   | 2.42       | 3.75       | 0.56       |
| PbF₂⁻                    | 1.08       | 13.61      | 0.37       |
| PbClO₄(2)²⁻               | 0.01       | 0.27       | <0.01      |
| Organic species           |            |            |            |
| Ferrous species (%)       |            |            |            |
| FeHCl₂⁺                   | 98.0       | 80.0       | 98.0       |
| Fe(OH)(aq)                | 1.10       | 4.84       | 1.06       |
| Fe(OH)₆⁻                  | 0.69       | 15.03      | 0.83       |
| FeOH⁺⁺                    | 0.04       | 0.01       | 0.05       |
| Pb(CO₃)²⁻                 | 10.75      | 2.50       | 11.74      |
| Inorganic ferric species  | Fe(OH)⁺⁻    | 81.0       | 87.0       | 77.0       |
| FeOH⁺⁻                   | 0.93       | 3.08       | 0.90       |
| Fe(OH)(aq)                | <0.01      | <0.01      | <0.01      |
| Fe(OH)₆⁻                  | 0.05       | 0.07       | 0.06       |
| FeOH⁺                    | 0.19       | 0.12       | 0.19       |
| FeOH⁺⁻                   | 0.39       | 0.19       | 1.12       |
| FeSO₄(aq)                 | 16.0       | 8.0        | 20.0       |
| FeHPO₄(aq)                | 0.06       | 0.14       | 0.02       |
| FeHCO₃⁻                   | 1.80       | 2.25       | 0.96       |
| Organic species           |            |            |            |

### Table 5. Saturation index (dimensionless) for minerals in groundwater studied.

| Minerals                  | Mean (dimensionless) ± SD (standard deviation) |
|---------------------------|-----------------------------------------------|
| Aragonite (CaCO₃)         | 0.44 ± 0.34                                   |
| Boehmite (γ-AlO(OH))      | 0.39 ± 0.26                                   |
| Calcite (Ca₃)             | 0.58 ± 0.34                                   |
| Diaspore (α-AlO(OH))      | 2.05 ± 0.33                                   |
| Dolomite (CaMg(CO₃)₂)     | 0.83 ± 0.92                                   |
| Ferrhydrite (SiFeO₃.9H₂O) | 4.96 ± 0.38                                   |
| Fluorite (CaF₂)           | −1.19 ± 0.19                                  |
| Gibbsite (Al(OH)₃)        | 2.90 ± 3.16                                   |
| Goethite (FeO(OH))        | 10.05 ± 5.09                                  |
| Hematite (Fe₂O₃)          | 13.92 ± 6.99                                  |
| Hercynite (FeAl₂O₄)       | 3.50 ± 2.29                                   |
| Maghemite (FeO₄)          | 11.09 ± 1.96                                  |
| Magnesioferrite(MgFe₂O₄)  | 17.03 ± 5.97                                  |
| Gypsum(CaSO₄.2H₂O)        | −1.87 ± 0.03                                  |
| Halite(NaCl)              | −6.01 ± 0.10                                  |
| K-Jarosite (KFe₄(OH)₆)    | 0.24 ± 0.28                                   |
| Cadmium hydroxide (Cd(OH)₂) | −5.15 ± 0.66                                |
| Lead(II) hydroxide (Pb(OH)₂) | −1.71 ± 0.42                                |
| Otavite (CdCO₃)           | −0.53 ± 0.34                                  |
| Cerussite (PbCO₃)         | −1.40 ± 0.10                                  |
additionally profoundly conceivable that such conditions may have a negative health impact since their concentrations exceed the permissible limits for drinking purposes. The groundwater samples are supersaturated (SI>0), as for goethite, hematite, ferrihydrite, gibbsite, aragonite, boehmite, diaspore, hercynite, maghemite, magnesioferrite, calcite, dolomite & K-jarosite and undersaturated with regarding to gypsum, fluorite, halite (NaCl), Cd(OH)$_2$, Pb(OH)$_2$, otavite and cerussite. The outcomes of the saturation index exhibited that dissolution and precipitation are influencing the groundwater composition in the study area. The process water-rock interaction (evaporation, dissolution, precipitation, ion exchange and reverse ion exchange) is impacting the aquifer quality of the study area. In view of the results of this study, proper design and implementation of wells are highly recommended to reduce water treatment costs and considering water treatment technologies as desalinization.

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