



Article Assessment of Hydrogeochemical Characteristics and Seawater Intrusion in Coastal Aquifers by Integrating Statistical and Graphical Techniques: Quaternary Aquifer, West Nile Delta, Egypt

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Abstract: The Quaternary aquifer in the western Nile Delta is threatened by seawater intrusion. Few studies have integrated diverse techniques for the assessment of seawater intrusion in this aquifer. The present study aims to determine the geochemical processes and impact of seawater intrusion on this aquifer. To accomplish this investigation, the integration of hydrogeochemical, statistical, multivariate statistical, and graphical tools were implemented on 75 groundwater samples and 5 soil samples. The physicochemical variables were analyzed using hierarchical cluster analysis (HCA), saturation index (SI), ionic ratios, ionic relationships, the seawater intrusion index (SWI) and the correlations among 16 hydrochemical parameters, to identify the influencing processes of groundwater quality in the study area. According to the statistical study, the groundwater is divided into four groups. Those are distributed, from north to south: Group1 (G1), Group2 (G2), Group4 (G4), and Group3 (G3). The samples of G1 and G2 are distinguished by Na-Cl chemical type. While G4 has two main ion associations, HCO₃-Ca-Mg and Cl-SO₄-Na, G3 is characterized by HCO₃-Cl-SO₄-Ca-Na type. The processes that affect the chemistry of the groundwater are the seawater intrusion, ion exchange, silicate and Ca-rich mineral weathering, and mineral deposition. G1 and G2 groups are primarily influenced by seawater incursion, evaporation, and the ion exchange mechanism. In addition, the weathering of silicate minerals has a substantial effect on G3 and G4 groups, resulting in the creation of carbonate minerals.

Keywords: coastal aquifers; seawater intrusion index; hierarchical cluster analysis; saturation index; ion exchange; GIS techniques

1. Introduction

Groundwater is a valuable natural resource that is essential for social and economic growth and human needs, especially in arid and semi-arid regions which suffer from shortage of precipitation and fresh surface water sources [1–3]. Aquifer rock material, climate conditions, and human activities in addition to seawater intrusion have a significant impact on groundwater quality and quantity in coastal aquifers [4–7].

Due to extreme use of the groundwater in coastal aquifers for industrial, agricultural, and urban expansion, seawater intrusion has come to be a global problem [8–11]. Climate change has raised atmospheric surface temperatures and melted ice caps, mountain glaciers, and polar ice sheets, which raises ocean and sea water levels, compounding the problem [12]. In addition, both the slope of the aquifer bed and the slope of the seaside influence the seawater intrusion; increasing the slope of the bed toward the sea will increase the interference [13]. Seawater intrusion hazard induces salinization of aquifers, reducing groundwater quality and causing a salinity hazard to the superimposed soils [14].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Globally, the coastal areas are occupied by about 20% of the world's population [12]. However, due to groundwater overexploitation to face the increasing water demand associated with population expansion and fast urban development, these locations are vulnerable to seawater intrusion. Future climate change and the resulting sea level rise are both predicted to worsen this vulnerability. Nevertheless, groundwater management becomes more complicated when all these elements come together.

Groundwater salinization threatens coastal fresh water supplies such as north Kuwait [15], Kish Island, Iran [16], Thriassion Plain and Eleusis Gulf, Greece [17], China [18], Spain [19], Bangladesh [20], Mexico [21], and others. Contamination by seawater has been studied in many coastal aquifers. The assessment of this phenomenon involves determining the spatial variation of physicochemical properties such as electrical conductivity (EC), total dissolved solids (TDS), seawater mixing and groundwater level, groundwater hydrochemical analysis, and geoelectrical methods such as resistivity and electromagnetic techniques [22–29]. Several studies have been conducted to simulate the seawater intrusion using different numerical techniques, including Sefelnasr and Sherif [30], Mabrouk et al. [31], Mabrouk et al. [32], Abd-Elhamid et al. [12], Abd-Elhamid et al. [13], Sarker et al. [20], Masoud et al. [33]. The Nile Delta aquifer is one of the largest fresh groundwater sources in the world. Researchers found that the seawater intrusion front in the Nile Delta aquifer moved inland more than 100 km from the Mediterranean shoreline [34–36].

Eventually, the complex process of seawater intrusion is influenced by, among others, shoreline geomorphology, hydrogeochemical reactions, biological processes, and aquifer dynamics. Saltwater intrusion, mostly in unconfined coastal aquifers, is the main cause of salinization [19]. In confined or semi-confined aquifers, complicated hydrogeological processes such as water–rock interaction and mixing with different water sources may impact groundwater quality and geochemical evolution [30].

Understanding the hydrochemistry is essential for determining the groundwater quality and its suitability for various applications, and therefore, determining sound management options for this resource as well as efficient mitigation measures when required. Diverse statistical and graphical techniques, such as pattern diagrams and GIS, can also be used to characterize seawater incursion. However, evaluation of the groundwater chemistry in the region based on integration of hydrogeochemical methods, statistical analysis, and advanced geostatistical techniques is still weak. Such integration provides the means of investigating such complex coastal aquifers, and the results may function as the foundation for effective groundwater management.

The purpose of this study is to evaluate the anthropogenic impacts and saltwater intrusion on the geochemical constituents and processes governing groundwater in the study area. To achieve this objective, groundwater samples of soil and water were collected and analyzed. For organizing groundwater samples, managing this volume of data, and providing accurate interpretations, graphical representations of the data were accompanied by multiple statistical approaches and multiple indices.

2. Materials and Methods

2.1. Study Area

The study area is a part of the Northwest Rosetta branch. It lies between $30^{\circ}42'$ to $31^{\circ}28'$ N and $29^{\circ}45'$ to $30^{\circ}48'$ E (Figure 1). It is bounded to the north by the Mediterranean Sea, to the east by the branch of Rosetta, and to the west by El Nubaryia Canal. The study area has an arid to semi-arid climate with an average annual temperature of $30.4 \,^{\circ}$ C and an average annual humidity of 59% [37]. The rainfall ranges from 50 mm/a in the south to about 200 mm/a in the north. The evapotranspiration ranges from 1648 in the north to 1680 mm/y in the south [38]. Geomorphologically and hydrogeologically, the investigated area was subjected to different studies such as Allam et al. [39], Dawoud et al. [40], Morsy [41], El Fakharany and Hagran [42], and Salem et al. [43]. Young alluvial plains characterize the research region. It features a nearly elevated ground surface that ranges from -3 m (amsl) in the northwest to +6 m (amsl) in the southeast [41]. The area is

characterized by sand dunes, aeolian deposits that occasionally occupy the surface, brackish lakes, and water-logged areas that occur in several places [44]. The slope is very smooth, representing one meter per 10 km to the north direction [44,45]. The Quaternary aquifer is comprised of Mit Ghamr Formation on the bottom and Bilqas Formation on the top [43]. The Mit Ghamr Formation is made up of sand and gravel with clay intercalations of continental origin. The aquifer layer is semiconfined with a thickness reaches its maximum

continental origin. The aquifer layer is semiconfined with a thickness reaches its maximum near the Rosetta branch (about 850 m) and decreases rapidly towards the west, where it notably decreases near the El Nubaryia canal (<200 m) [36,46]. The Holocene-aged cap layer of the Bilqas Formation consists of clay and silt and is less than 20 m thick in the south and up to 50 m thick in the north. The Nile Delta aquifer system is recharged in the flood plain by infiltration from surface water (especially from irrigation systems), rainfall, and by leakage from subsurface drainage water in the cultivated lowlands [40]. Groundwater discharge takes place either naturally through the outflow into the drainage system, via evapotranspiration and groundwater baseflow, or artificially through direct well extraction, which is primary discharge component of the aquifer [47]. The groundwater level within the study area ranges from 1 m in the north to 4 m close to El Nubaryia canal. The general groundwater flow direction is from south to north and from southwest to northeast.



Figure 1. Location map showing the extent of the study area and the distribution of the collected water samples.

2.2. Sampling and Analytical Techniques

The study of the hydrogeochemical aspects of groundwater in the study area was mainly based on the results of the chemical analyses of 75 groundwater samples that were collected from the drilled wells during March, June, and October 2018 (Figure 1). In addition, five soil water samples were also collected from the subsoil drainage system and analyzed to estimate the origin of dissolved ions. The sampled wells have depths varying from 15 to 200 m. The chemical analyses were performed in the laboratory of the Geology Department, Faculty of Science, Tanta University, and in the Center of Scientific Research and Measurements, Tanta University. The analysis techniques are shown in Table 1. While water samples were being analyzed, a number of quality assurance and quality control procedures were carried out. The validation of analytical methodologies was accomplished by calibrating devices and assessing the precision of the samples being analyzed. Charge error balance (CBE) was calculated to ensure that the analytical error of the analyzed ions concentration in meq/L⁻¹ was accurate [48,49]. The CBE of every examined sample was

found to be within the permissible range of $\pm 5\%$. The obtained chemical data are listed in Table 2.

Parameter	Used Instrument	Analyzing Techniques	Analyzing Place
Electric conductance Ec (mS/cm)	Hach's Portable		
Total dissolved solids TDS (mg/L)	conductivity/ Total dissolved solids (TDS)		Field
Temperature (°C)		The typical analytical	
Hydrogen ion activity (pH)	Portable Consort pH Meter (Model p 314)	methods explained by HACH [50]	
SO_4 and NO_3	Hach's Direct Reading (DR/2000) Spectrophotometer		Department of Geology, Faculty
Cl and HCO ₃	Hach's Digital Titrator Model 16900-01		of Science, Tanta University
Na, K, Ca, Mg, Al, Ba, Fe, Mn, Sr, and Si	ICP (Inductive Coupled Plasma Optima 7000 DV)	EPA method 200.7 by USEPA [51]	Center of Scientific Research and Measurements, Tanta University

Table 1. The analyzing techniques of the measured parameters.

Table 2. Statistical analysis of the obtained hydrochemical data.

Parameter	Min	Max	Av	SD
TDS (mg/L)	190	27,680	3806.2	7001.4
EC (ms/cm)	0.38	55.3	7.1	12.3
pН	5.05	8.7	7.1	0.8
TH(mg/L)	25.93	3315	762.8	839.4
Ca (mg/L)	4.74	670	153.6	159.5
Mg (mg/L)	3.43	430	92.3	110.9
Na (mg/L)	37.98	9200	1156.7	2339.8
K (mg/L)	2.34	337.7	34.8	68.4
$HCO_3 (mg/L)$	13.02	394	222.6	74.1
$SO_4 (mg/L)$	0	2300	365.7	517.7
Cl (mg/L)	48	14,300	1844.1	3647.6
NO3 (mg/L)	0	202	22.9	36.6
Al (mg/L)	$9 imes 10^{-4}$	0.36	0.1	0.1
Ba (mg/L)	$12 imes10^{-5}$	15.39	0.3	1.7
Fe (mg/L)	$12 imes 10^{-5}$	34.56	1.1	4.1
Mn (mg/L)	$9 imes 10^{-4}$	2.853	0.5	0.5
Si(mg/L)	4.57	23.42	12.1	3.9
Sr (mg/L)	0.04	62.5	4.6	11.1

2.3. Cluster Analysis and Saturation Index (SI)

Multivariate statistical analyses were used to provide a quantitative measure of water quality parameters relative to each other and to estimate correlations between chemical parameters and groundwater samples [50–57]. Hierarchical cluster analysis HCA using Ward's linking method and squared Euclidean distance as a dissimilarity metric was used to group parameters by multivariate similarities.

The saturation percentage, specified as SI = log (IAP/Ks), defines the degree of mineral saturation in water. IAP is the ionic activity product of the proper ions, and Ks is the constant of saturation under a specific temperature. The equilibrium distribution of

minerals in an aqueous solution and the state of saturation is determined using the hydrochemical program PHREEQC Interactive Program [58]. An SI < 0 means that the mineral's groundwater is undersaturated. An SI > 0 indicates that the groundwater is supersaturated with this mineral phase and thus incapable of dissolving more of the mineral.

2.4. Seawater Intrusion Quality Index (SWI)

To identify the threat of seawater intrusion, Tomaszkiewicz et al. [59] created the groundwater quality index for seawater intrusion (GQI_{SWI}) (Equation (1)). This model translates the Piper diagram information $GQI_{piper (mix)}$ (freshwater seawater mixing index of Piper diagram) and the seawater fraction index GQI_{fsea} to create a new two-stage numerical indicator for seawater intrusion [59].

$$GQI_{SWI} = \frac{GQI_{piper(mix)} + GQI_{fsea}}{2}$$
(1)

The first stage included the calculation of $GQI_{piper (mix)}$ as follows:

$$GQI_{Piper(mix)}(meq/l) = \left[\frac{\left(Ca^{+2} + Mg^{+2}\right)}{Total \ cations} + \frac{\left(HCO_{3}^{-}\right)}{Total \ anions}\right] \times 50$$
(2)

The second stage involves computing the seawater fraction index GQI_{fsea} (Equation (3)) from the seawater fraction (f_{sea}) (Equation (4)). GQI_{fsea} was then used to classify the SWI. These values vary from 0 to 100, the fresher waters of which have lower values.

$$GQI_{f_{sea}} = (1 - f_{sea}) \times 100 \tag{3}$$

The following formula can be used to measure the seawater fraction (f_{sea}) [60]:

$$f_{sea} = \frac{m_{Cl(sample)} - m_{Cl(freshwater)}}{m_{Cl(seawater)} - m_{Cl(freshwater)}}$$
(4)

where m_{Cl} (sample) is the Cl concentration of the sample, m_{Cl} (seawater) is the Cl concentration of the Mediterranean Sea (603 meq/L), and m_{Cl} (freshwater) represents the Cl concentration of the freshwater (0.48 meq/L).

The difference in hydrochemistry between seawater and freshwater was classified by concentrations of anions and cations. Indeed, the freshwater is defined by an abundance of calcium and bicarbonate, while the seawater is classified by its dominance of chloride and sodium [61]. The concentration of chloride is the base which determines the mixing of these two types of water, which is clarified by the conservative presence of anions [62].

3. Results and Discussions

3.1. Hydrochemical Characteristics and Spatial Distribution

The hydrochemical characteristics of groundwater are discussed with respect to the study area and according to the results of water samples chemical analysis. As shown in Table 2, the groundwater pH values range from slightly acidic (5.05) to slightly alkaline (8.7) averaging 7.1. The differences in pH values are primarily due to the aquifer–rock interaction and the distance from the sea [63]. Based on the classification of Winslow and Kister [64], 53%, 21%, 15%, and 11% of the groundwater samples are fresh, slightly, moderately, and very saline water, respectively (Table 3). The EC of groundwater in the study area ranges from 0.38 to 55.3 mS/cm with an average of 7.1 mS/cm (Table 2). TDS levels range from 190 to 27680 mg/L, averaging 3806.2 (Table 2). The Rosetta branch and many irrigation canals nearby produce fresh to slightly salty water in the southern and central study area. Near irrigation canals, Nile water seepage dilutes groundwater. Figure 2 shows that seawater incursion increases salinity northward, where the shore is 30 km away.

Water Class	Salt Concentration (mg/L)	No. of Wells	%
Fresh	>1000	40	53
Slightly saline	1000-3000	16	21
Moderately saline	3000-10,000	11	15
Very saline	10,000–35,000	8	11
Brine	<35,000	-	-

Table 3. Classification of water according to Total Dissolved Solids [64].



Figure 2. Spatial distribution of TDS across the study area.

As demonstrated in Figure 3a–c, Ca, Mg, and Na concentrations were lowest in the south and center regions and rose northward. It is largely seawater interference. The southern and central parts may have lower cations due to Nile water seepage and irrigation.

Figure 3d shows that the concentration of bicarbonate increases from south and northwest towards the central parts. Bicarbonates are introduced to natural water through recharging with meteoric water and interaction with sediments rich in either carbonate minerals or organic matter. The dissolution of $CaCO_3$ or the decay of organic matter increase in the presence of CO_2 leading to the formation of more soluble bicarbonate [65]. SO_4 and Cl spatial distributions showed that they have almost the same pattern. The lower values are located in the south and increase towards the north (Figure 3e,f). Such distribution patterns could be related to seawater intrusion effect.

Figure 4a–f shows Al, Mn, Ba, Fe, Sr, and Si spatial distribution maps. Al concentration increases southward and decreases northward (Figure 4a). Mn is highest in the northeast and declines westward to its minimum at El Nubaryia Canal (Figure 4b). Ba, Fe, and Sr have similar distributions. The concentration increases northeastward from the south (Figure 4c–e). Si levels are higher in central areas from northeastern to southwestern directions and lower along the western boundary (Figure 4f).



Figure 3. The spatial distribution maps of major ions.



Figure 4. The spatial distribution maps of minor ions.

3.2. Hydrochemical Classification

3.2.1. Cluster Analysis

Based on the HCA procedures, four groups were identified. Figure 5a shows that G2, G3, and G4 are related, but G1 samples are distinct. This is primarily due to their

occurrences in the south and center of the study area, which are relatively located far from the sea. On the other hand, G1 is located in the northern region near to the sea, thus, its chemical composition was significantly affected by the seawater.



Figure 5. (a) Dendrogram shows the grouping of the groundwater samples into four groups depending on the major ion concentrations in milliequivalents per lite and (b) Scholler diagrams characterizing the chemical type for samples groups.

Table 4 shows the mean hydrochemical data values for each sample group to explain their features. Figure 6 depicts group dispersion by location.

Parameter	G1	G2	G3	G4
TDS mg/L	22,686.75	6486.4	597.94	1829.1
Ca meq/L	26.09	14.27	4.24	5.37
Mg meq/L	30.12	14.97	2.57	5.94
Na meq/L	329.78	82.24	5.51	19.17
K meq/L	5.18	0.72	0.17	0.56
HCO ₃ meq/L	3.42	187	3.49	3.95
$SO_4 \text{ meq/L}$	29.71	13.94	2.92	5.93
Cl meq/L	332.59	92.92	5.6	20.91
Si mg/L	12.63	12.89	11.31	10.59
Al mg/L	0.09	0.03	0.01	0.00
Ba mg/L	0.12	3.11	0.13	0.24
Fe mg/L	0.25	10.01	0.55	1.47
Mn mg/L	0.49	1.55	0.49	0.88
Sr mg/L	0.80	28.01	1.97	6.14

Table 4. The average composition of the hydrochemical parameters of the four groundwater sample groups.

Scholler's diagram is commonly used to correlate many of the chemical water compositions. The average hydrochemical data of the four groups (Table 4) are plotted on the semi-logarithmic diagrams (Figure 5b). The samples of G1, G2 and G4 have Na–Cl water type (Na > Ca > Mg > and Cl > SO₄ > HCO₃) with an average TDS values 22,686.7 mg/L, 6486.4 mg/L and 1829.1 mg/L, respectively. The spatial distribution of G1, G2 and G4 (Figure 6) indicated that these groups are influenced by seawater intrusion, while G3 samples have Na–Cl (Na > Ca > Mg and Cl > HCO₃ > SO₄) water type and lower concentrations of TDS (average 597.9 mg/L) and ions compared to the other groups. G3 is distributed in the southern part of the study area and its origin might be related to direct seepage from the irrigation canals.



Figure 6. Spatial distribution map of the groundwater samples groups.

3.2.2. Piper's (Trilinear) Diagram

The collected samples were plotted in the trilinear diagram [66] (Figure 7) according to the HCA classification (Figure 5a). In most groundwater samples, Na is the major cation and Cl is the main anion. Generally, the samples of G1, G2 and G4 were plotted on sub-area 7 (Figure 7) indicating primary salinity character, where NaCl and Na₂SO₄ salts dominate the chemical properties. This is largely due to the impact of seawater intrusion and soil salinity. Most samples of G4, which occupied the southern parts, are located in sub-area 9 (Figure 7) indicating that none of the cation–anion pairs exceeds 50%. In the right triangle, samples of G3 and 4 show an increase in concentrations of either SO₄ or HCO₃ and decrease of Cl. In the lift triangle, due to ion exchange process, concentrations of Ca and Mg increase in groups 3 and 4 and Na decrease [67].



Figure 7. Piper diagrams show the hydrogeochemical characters of the studied groundwater. Samples are labeled according to their HCA groups shown in Figure 5a.

3.2.3. Statistical Ions Classification

Figure 8 shows sample group ion-association dendrograms. Na, Cl, and TDS in groundwater samples from groups G1 and G2 (Figure 8a,b) show seawater intrusion in the northern section of the research area (Figure 6). Assuming G3, HCO_3 –Cl– SO_4 –Ca–Na is the major ion association in the southern region, indicating freshwater origin and evaporation (Figure 8c). Figure 8d demonstrates ion-association in group four samples. HCO_3 –Ca–Mg-minors and Cl– SO_4 –Na showed that freshwater impacted by seawater intrusion and exchange processes is widespread. Al, Mn, Ba, Fe, Sr, Si, and NO₃ are linked in a short distance, suggesting a shared origin that may affect fertilizer or water–rock interactions (Figure 8).



Figure 8. Dendrograms show the ion-associations in sample groups.

3.3. Saturation Index (SI)

Table 5 shows the statistical summary of dissolved mineral saturation indicators. The dissolved minerals were classified into five different groups: carbonate, sulphate, chlorides, oxides, and silicate minerals. Detected carbonate minerals include aragonite, calcite, dolomite, and witherite. Unlike groups 1, 2, and 4, group 3 is saturated with aragonite, calcite, and dolomite. All groups are undersaturation with respect to witherite. As the investigated aquifer is composed of clastic sediments, production of bicarbonate ion is due to the formation of CO_2 from decay of the organic matter (Equation (5)) [60]. Such conditions could lead to saturation conditions in the southern part where group 3 samples are located but the unsaturation conditions in groups 1, 2, and 4 might be related to carbonate minerals deposition where the increase in sulfate and chloride minerals due to seawater intrusion in the northern parts is accompanied by deposition of the carbonate minerals [36,68].

$$CO_2 + H_2O \rightarrow H_2CO_3 + H \rightarrow HCO_3^- + H$$
(5)

$$SO_4^{-2} + 2C + 2H_2O \rightarrow H_2S + 2HCO_3$$
 (6)

The studied groundwater is mostly unsaturated with respect to anhydrite and gypsum minerals, whereas most of G3, which is located in the southern part of the area, was saturated with respect to barite. Hydrochemical studies of major and trace elements made by Drevaliene et al. [69] showed that the probable barium source in groundwater is the

dissolution of witherite. According to Table 5, all four groups of groundwater samples showed an undersaturation state with the dissolved chloride minerals (Halite and Sylvite).

	No.	Aragonite	Calcite	Dolomite	Witherite	Anhydrite	Gypsum	Barite	Halite
	Min	-1.7	-1.6	-2.7	-8.4	-1.3	-0.9	-2.5	-3.1
	Max	0.2	0.3	1.0	-3.6	-0.4	0.0	2.5	-2.2
G1	Av	-0.7	-0.6	-0.8	-5.5	-0.7	-0.4	-0.1	-2.7
	SI > 1%	12.5	25	25	0	0	0	57.2	0
	SI < 1%	87.5	75	75	100	100	100	42.8	100
	Min	-1.9	-1.7	-3.1	-8.6	-2.2	-1.9	-2.7	-4.2
	Max	1.1	1.2	2.5	-3.7	-0.8	-0.6	-0.7	-3.8
G2	Av	-0.5	-0.4	-0.5	-6.0	-1.4	-1.1	-1.5	-3.9
	SI > 1%	40	40	40	0	0	0	0	0
	SI < 1%	60	60	60	100	100	100	100	100
	Min	-1.1	-1.0	-1.9	-6.4	-3.8	-3.5	-4.2	-7.2
	Max	1.2	1.3	2.6	-1.8	-1.1	-0.7	0.7	-5.4
G3	Av	0.4	0.5	0.9	-2.9	-2.1	-1.8	-0.2	-6.3
	SI > 1%	84.90	87.90	87.9	0	0	0	63.7	0
	SI < 1%	15.10	12.10	12.1	100	100	100	36.3	100
	Min	-1.9	-1.7	-3.4	-8.0	-3.8	-3.5	-3.3	-7.1
	Max	0.8	0.9	1.7	-1.8	-1.2	-0.8	1.2	-4.4
G4	Av	-0.8	-0.6	-1.1	-5.2	-2.1	-1.8	-1.2	-5.4
	SI > 1%	22.6	25.9	22.6	0	0	0	25.9	0
	SI < 1%	77.4	74.1	77.4	100	100	100	74.1	100
	No.	Sylvite	Hematite	Pyrolusite	Albite	Anorthite	K-feldspar	Kaolinite	Quartz
	Min	-4.6	-2.7	-1.8	-4.4	-12.1	-4.3	-1.8	0.1
	Max	-3.7	16.5	2.9	0.1	-4.3	0.6	4.8	0.7
G1	Av	-4.0	10.6	0.7	-2.2	-7.7	-1.6	1.3	0.4
	SI > 1%	0	87.5	0	25	0	25	50	100
	SI < 1%	100	12.5	100	75	100	75	50	0
	Min	-5.7	1.7	-0.4	-2.9	-8.4	-2.9	1.1	0.1
	Max	-4.9	20.3	0.4	-1.7	-5.1	-1.1	1.7	0.5
G2	Av	-5.4	9.7	0.1	-2.5	-6.9	-2.2	1.4	0.3
	SI > 1%	0	100	0	0	0	0	100	100
	SI < 1%	100	0	100	100	100	100	0	0
	Min	-7.9	5.5	-0.2	-3.8	-6.6	-2.6	0.7	0.1
	Max	-6.4	20.3	2.1	0.1	-0.7	1.3	5.8	0.5
G3	Av	-7.1	15.0	1.1	-1.0	-2.2	0.1	3.6	0.3
	SI > 1%	0	100	0	5.8	0	79.5	100	100
	SI < 1%	100	0	100	94.2	100	20.5	0	0
	Min	-7.6	1.1	-0.6	-4.6	-9.6	-3.8	0.5	-0.1
	Max	-4.9	21.2	2.7	-0.6	-1.6	0.0	6.4	0.5
G4	Av	-6.4	11.4	0.5	-2.9	-6.5	-2.0	1.7	0.2
	SI > 1%	0	100	0	0	0	0	100	88
	SI < 1%	100	0	100	100	100	100	0	12

Table 5. Dissolved minerals saturation indices.

G1, G2, G3, and G4 are undersaturated with respect to pyrolusite but most of them are saturated with hematite (Table 5) due to the reductive dissolution of Fe and Mn. The dissolution of Fe and Mn oxides in the aquifer is at the cost of the oxidation of organic matter [70,71], and the bicarbonate will increase. The reaction Equations (7) and (8) are as follows:

$$CH_2O + 2MnO_2 + 3H^+ = 2Mn^{2+} + HCO_3^- + 2H_2O$$
(7)

$$CH_2O + 4Fe(OH)_3 + 7H^+ = 4Fe^{2+} + HCO_3^- + 10H_2O$$
(8)

The encountered dissolved silicate minerals are albite, anorthite, K-feldspar, kaolinite, and quartz. Groundwater samples are undersaturated with albite and anorthite. Most of G1, G2, and G4 are in the undersaturation state with K-feldspar but G3 is mostly saturated with this mineral. G2, G3, G4, and most of G1 are saturated with quartz and kaolinite (Table 5). Following Hosono et al. [72], incongruent dissolution reactions of silicate weathering in the study area can be hypothesized by following Equations (9) and (10):

 $2NaAlSi_{3}O_{8} (Albite) + 2CO_{2} + 11H_{2}O \rightarrow Al2Si_{2}O_{5}(OH)_{4} (Kaolinite) + 2Na^{+} + 2HCO_{3}^{-} + 4H_{4}SiO_{4}$ (9)

 $CaAl2Si_2O_8 \text{ (Anorthite)} + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 \text{ (Kaolinite)} + 2Ca2^+ + 2HCO_3^-$ (10)

3.4. Hydrogeochemical Processes Ions-TDS Relationships

• Gibbs diagram

Gibbs diagrams show the groundwater chemistry's main natural process. It shows how rock weathering, mineral precipitation, and evaporation affect groundwater chemistry [73]. High concentration of Ca^{2+} and HCO_3^- reveals rock–water interaction. On the other hand, the presence of high concentration of Na⁺ and Cl⁻ indicates evaporation processes or seawater intrusion [74,75]. TDS concentrations are plotted against the weight ratios of Na/(Na + Ca) for cations (Figure 9a) and the weight ratios of Cl/(Cl + HCO₃) for anions (Figure 9b). The major processes governing groundwater chemistry are evaporation/seawater intrusion and rock interaction. Most G3 samples have dissolved HCO₃ and Ca via water-rock interaction. Evaporation and seawater intrusion supply Na and Cl to Groups 1, 2, 4, and soil water.



■ G1 ● G2 ◆ G3 ▲ G4 ▲ Soil water

Figure 9. Gibbs diagrams illustrate (**a**) TDS concentrations are plotted against the weight ratios of Na/(Na + Ca) for cations and (**b**) the weight ratios of $Cl/(Cl + HCO_3)$ for anions. Concentrations of TDS and ion are in mg/L.

• TDS vs. Ca, Mg, Na + K, Cl, HCO₃, and SO₄

2

TDS vs. Ca, Mg and Na + K relationship (Figure 10a–c) are very strong ($r^2 = 0.9, 0.9$, and 0.9, respectively, Table 6). For TDS relationships with Ca and Mg, samples were plotted under the mixing line which indicate ion-exchange process due to seawater intrusion, where Na replaces either Ca or/and Mg as shown in Equations (11) and (12). TDS vs. Cl relationship shows a very strong correlation ($r^2 = 0.9$, Table 6, Figure 10d). For the relationships between TDS and Na + K and Cl, most plotted groundwater samples are clustered along the irrigation water–seawater mixing line suggesting that the variance in concentrations of theses ions is due to the mixing between irrigation canal water and seawater. TDS vs. HCO₃ (Figure 10e) showed weak inverse relationship ($r^2 = -0.1$, Table 6), which means that freshwater seepage is not only the primary source of dissolved carbonates but may also be the reason for the weathering of silicate minerals. as shown in Equations (11) and (12) [76].

$$2Na^{+} + Ca - X_{2} \rightarrow 2Na - X + Ca^{2+}$$
 (11)

$$2Na^{+} + Mg - X_{2} \rightarrow 2Na - X + Mg^{2+}$$
 (12)

where x is an ion exchanger.



Figure 10. The relationships between Total Dissolved Solids (TDS) and the concentrations of (**a**) Ca, (**b**), Mg, (**c**) Na + Ca, (**d**) Cl, (**e**) HCO₃, and (**f**) SO₄.

	TDS	EC	Ca	Mg	Na	К	HCO ₃	SO ₄	Cl	NO ₃	Al	Ba	Fe	Mn	Si	Sr
TDS	1															
EC	0.9	1														
Ca	0.9	0.9	1													
Mg	0.9	0.9	0.9	1												
Na	0.9	0.9	0.8	0.9	1											
K	0.6	0.6	0.5	0.6	0.7	1										
HCO ₃	0.1	0.1	0.2	0.1	0.1	0.1	1									
SO_4	0.6	0.6	0.5	0.7	0.6	0.7	0.0	1								
Cl	0.9	0.9	0.9	0.9	0.9	0.7	0.1	0.6	1							
NO_3	-0.1	-0.1	-0.1	0.0	-0.1	0.1	0.0	0.1	-0.1	1						
Al	-0.2	-0.2	-0.2	-0.3	-0.2	-0.1	-0.1	-0.1	-0.2	-0.1	1					
Ba	0.5	0.5	0.4	0.4	0.5	0.4	-0.1	0.5	0.4	-0.1	-0.1	1				
Fe	0.4	0.4	0.4	0.4	0.5	0.4	-0.1	0.5	0.4	-0.1	-0.1	0.9	1			
Mn	0.1	0.1	0.2	0.1	-0.1	-0.1	0.2	-0.1	0.1	-0.2	-0.1	0.1	0.1	1		
Si	0.1	0.1	0.1	0.1	0.1	0.0	-0.1	0.1	0.1	-0.2	0.3	0.1	0.1	0.2	1	
Sr	0.5	0.5	0.6	0.6	0.5	0.6	-0.1	0.6	0.5	0.1	-0.2	0.9	0.9	0.1	0.1	1

Table 6. Correlation matrix between physico-chemical parameters in groundwater.

Note: values listed in red font have strong positive correlation, blue font have intermediate positive correlation, values listed in green font have weak correlation.

On the other hand, TDS–SO₄ (Figure 10f) have a strong relationship ($r^2 = 0.7$, Table 6). The origin of sulfates is not linked to the trend of surface water–seawater mixing but possibly related to soil origin, especially in low salinity water. The relationships between TDS vs. Ba, Fe and Sr (r^2 equals 0.5, 0.4, and 0.5, respectively, Table 6) showed intermediate correlation, on the other hand it showed weak relationships with Al, Mn, and Si (r^2 equals –0.2, 0.1, and 0.1 respectively, Table 6). Figure 10a–f shows that plotted soil water samples and indicates that the soil hydrochemical processes are very effective in the hydrochemical characteristics of the studied low salinity groundwater (G3 and G4) where it acts as an important origin of the dissolved ions.

3.5. Seawater Intrusion Quality Index (SWI)

In ArcGIS 10 framework, the calculated GQI_{SWI} results are transformed into a map using a kriging interpolation function. The GQI_{SWI} value varies from 17.8 to 82.3 as shown in Figure 11. According to Table 7, the groundwater of the study area is classified into saline, mixed, and fresh water. The coastal area in the northern parts has low values and reflects the salinization of groundwater.



Figure 11. *GQI*_{SWI} in the study area.

Wator Trees	GQI _{SWI} Base	ed on Worldwi	Typical GQI _{SWI}		
water type	Min	Max	Mean	Min	Max
Fresh water	73.5	90.1	82.7	75	100
Mixed groundwater	47.8	79.9	63.4	50	75
Saline groundwater	4.8	58.8	27.5	10	50
Seawater	3.1	9.2	5.8	0	10

Table 7. *GQI*_{SWI} ranges [77].

4. Conclusions

In this work, the seawater intrusion and the processes governing the groundwater of the Quaternary aquifer of the Nile Delta were assessed using hydrochemical analysis in conjunction with several multivariate statistical methods and graphical approaches. It was concluded that groundwater chemistry is influenced by the evaporation process, seawater intrusion, ion exchange process, dissolution and weathering of Ca-rich minerals, and weathering of silicate minerals. The groundwater samples are divided into four groups in accordance with HCA, which were identified as G1, G2, G3, and G4. G1 and G2, which are found in the northern regions near to the Mediterranean Sea, are primarily controlled by the evaporation process and seawater intrusion. High Cl and Na concentrations and low HCO₃ concentrations mostly serve to demonstrate this. Additionally, seawater intrusion is joined by another process such as cation exchange where Na replaces Ca and/or Mg. On the other hand, in the case of G3 and G4, the weathering of silicate minerals led to the development of carbonate minerals. Most of the groundwater samples from the four groups included more calcium than HCO₃ and SO₄; this is mostly because calcium-rich minerals dissolve and weather.

Climate change and its parameters, sea-level rise, extensive groundwater pumping to meet various needs, land-use changes due to population growth and urbanization, changes in rainfall patterns, and reduced groundwater recharge all threaten saltwater intrusion coastal aquifers.

Since the coastal aquifer in the Nile Delta is responsive to climate change and groundwater extraction, sustainable water resource management is needed to protect it from saltwater intrusion. This research provides a useful assessment tool for seawater intrusion variability in coastal aquifers. The results can improve understanding of present and future saltwater intrusion in the investigated area and provide specific adaptive keys. As a response to the aquifer stresses, adaptation styles to any of the given hazards or challenges may be designed. Thus, the adaptation in the case of the Quaternary aquifer in the Nile Delta should be transformational, where changes in the fundamental attributes of a system (especially pumping) must be adopted. This may not preclude combining different adaptation strategies or using biodiversity and environmental services as part of an adaptation plan. Constant monitoring of the saline interface is essential for maintaining the aquifer's equilibrium and determining the most effective aquifer management strategy. An assessment study for the saltwater intrusion under different climate and anthropogenic activities is still needed for the aquifer.

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