Groundwater Quality Assessment Using Water Quality Index and Multivariate Statistical Analysis Case Study: East Matrouh, Northwestern Coast, Egypt.

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Abstract

The groundwater quality deterioration is a global phenomenon due to the effect of contaminated surface water. This study covers the investigation of groundwater quality using the contamination indices, statistical analysis, and hydrochemical facies. Thirty-one water samples that representing the water resources in the study area were collected and analyzed for chemical compositions. There are two aquifers; Pleistocene and Miocene. From the obtained data, the electric conductivity (EC) values ranged from 8520 to 19410 µS/cm in Pleistocene aquifer. While in Miocene aquifer, it ranged from 4290 to 7920 µS/cm. The wide variation is due to interaction with aquifer rocks. The hydrochemical facies evolution diagram (HFE-D) indicated that the majority of samples belong to an intrusion phase; the Na-Cl facies represents the state of the aquifer and the remaining sample is scattered in the field of freshening. The dominance of average cations is about $Na^+ > Mg^{2+} > Ca^{2+} > K^+$, where the anion dominance average is in the imperative of $Cl^- > SO_4^{2-} > HCO_3^-$. Multivariate statistical techniques, such as cluster analysis (CA) and factor analysis (FA) showed contamination with heavy metal and fecal due to the influence of the sewage treatment plant. The spatial distribution of heavy metal pollution index (HPI), Ecological risk index (ERI) and pollution index of groundwater (PIG), in the southeastern portion of the research, revealed high values near the center and particularly in the northwest portion of the study region. It demonstrated that water in the northeast of the study area is likely to be influenced by heavy metal leaching from the water treatment plant.

Highlights

1- Assess the quality of surface and groundwater

2- Hydrochemical data are described for both groundwater and surface water samples.

3- Heavy metal pollution index is used for overall water quality determination

4- Cluster analysis is a statistical analysis used in grouping samples in clusters

5- hydrochemical facies diagram is used for the determination of seawater intrusion

1. Introduction

The north-west coast of Egypt is more sensitive to future sustainable development and this, on the other hand, depends primarily on the occurrence and maintenance of water resources (Ali et al. 2007). Due to the climate change, there have been insufficient precipitation on the north-western coast of Egypt for agricultural activity and residents have started drilling water wells (IPCC 2007). Surface waters are relatively inadequate, uniformly scattered or unsuited to human consumption in many coastal locations (Yidana and Yidana 2010). Further research have found that direct dumping into the surviving surface water bodies of various polluted materials from home, farming and industrial wastewater eventually pollutes them. (Edokpayi et al. 2017). Surface water also faces serious exposures to salinity due to sea backwater in coastal zones. (Vijay et al. 2011). The surface water is quite limited in the coastal zone because of the winter precipitations (**El Bastawesy et al. 2008**). Agricultural production may have several factors; however water is the most important factor **(**Oweis and Hachum 2003). Naturally, water can convey various heavy metals across diverse geological formations (Mohankumar et al. 2016). Biological activity, soil leaching, weathering and rock disintegration are many instances of natural processes that produce changes in the quality of groundwater (**Rao et al. 2020**). Appreciation of the water body's hydrochemistry exposes water to a variety of uses (Alexakis 2011; Gamvroula et al. 2013). The water quality index (WQI) approach aims to investigate and understand the status of water quality in a water body (Horton 1965; Brown et al. 1970). The WQI and multivariate statistical tools enable to manage water resources consistently (Bora and Goswami 2016). It aims to provide the water quality of a body a single value, which can help understand the quality of the water for various purposes (Smita et al. 2018). Other approaches, such as multivariate statistical methods such as (CA) and (FA), help to assess the spatial and temporal variants of water quality to identify potential factors affecting water quality (**Gamble and Babbar 2012**). The current investigation was shown with the objective of (i) Make an evaluation of ground and surface water, (ii) Estimate their drinking and irrigation appropriateness (iii) identify the state of aquifers for intrusion/freshening phases that occurs over time via using the hydrochemical facies evolution.

2. The Study Area

The study area is about 10 km away from Matrouh city. It is constrained by longitudes of 27^0 $15^/$ and 27^0 $25^/$E, latitudes of 31^0 $8^/$ and 31^0 $25^/$N with a total area of approximately 400 km^2. The study included three drainage basins; these basins from the northwest to the southeast are Wadi Samla, Wadi Khair, and Wadi Naghamsh with the area of 26, 36, and 116 km^2, respectively, Figure (**1**).

The sewage treatment plant in the study area at an altitude of approximately 60 m from sea level with a capacity of 25,000 m3/day. The plant has 14 oxidation basins used in aerobic and anaerobic treatment. The wastewater is treated and directed to three untreated dirt reservoirs used for water storage and tree forest irrigation. The wastewater treatment plant provides 9 million m3/year of water to irrigate 1000 acres of tree plantations. Groundwater interaction with polluted surface water can potentially put groundwater sources at risk; Different geochemical processes may affect ground water quality, including natural and anthropogenic activity.

North-western Egypt's summer is warmer (June, July and August) while winter is colder (December, January, and February) (UNESCO 1977). The average annual rainfall varies from 64 mm to 412 mm (CLAC 2015), with an average annual cumulative precipitation of 155mm. Evaporation rates vary with temperatures on the other hand, whereas in January the lowest evaporation rates (6.9 mm/day) were observed, while in September the greatest rate (8.8 mm/day) was observed (Egyptian Meteorological Authority 1996). Many authors have researched the geomorphology, hydrology, and geology of the coastal area of the northwest Mediterranean, (Raslan 1995; Masoud 2000; Barseem 2006; Mohamed et al. 2011).

3. Geomorphology, Geology And Hydrogeology

Geomorphologically, the northwestern Mediterranean coast is distinguished in three geomorphological units. These units were classified into the coastal plain, piedmont plain, and structural plateau (tableland), (Raslan 1995), Figure (**2**). The elevation is between the sea level and approximately l00m in costal and piedmont plains. There were coastal dunes, ribs and sand dunes in the coastal plain. At the foot of the structural plateau the Piedmont plain is growing. It has thick fine deposits of calcareous grounds derived from the alluvial deposits of various wadies.The main catchment region of the drainage line is the structural plateau (tableland). The construction of the plateau ranges from 100 to 175 m from the south to the north side of the Piedmont.

The geology of the area of study plays an important effect in groundwater occurrence and quality. The classifications of the studied area are mainly sedimentary from the Middle Miocenes to Quaternary eras (Raslan 1995). Marmarica formation is a characteristic element of the middle Miocene. The structure of the plateau and the Piedmont plain are formulated. The Quaternary deposits, which are alluvial deposits. In addition to being very calcareous, the deposits include mostly of sand, silt, and clay. As an Oolitic calcareous, Pleistocene sediments can be recognized. It comprises carbonate grains with quartz and fossil scattered grains. The rocks of the Middle Miocene are fractured in all the wadies and conducive for groundwater Figure (**3**).

Hydrogeological, The Pleistocene, and Middle Miocene aquifers are the foremost productive aquifers in the study area (Raslan 1995). The aquifer Pleistocene is composed of Oolitic calcareously. Either from a direct infiltration of the annual rainfall on site or by a deterioration of the portion of the tableland, ground water for this Oolitic calestone arises. The aquifer for the Middle Miocene is the Marmarica limestone. It includes alternate limestone and clay beds. Hydrogeological cross sections reveal that groundwater can be reflected from the precipitation, with rain dropping into the tableland and flowing to the Mediterranean Sea to the north. (**Yousif et al. 2014**). These aquifers are recharged by direct rainfall infiltrations and/or surface discharge. (Sewidan 1978; **NARSS 2005**).

4. Materials And Methods

Thirty-one water samples were collected during June 2019 from surface and groundwater points and chemically analyzed Figure (**4**). These samples are represented by 6 surface water samples and 25 groundwater samples. The analyses include the determination of TDS, pH, EC, the concentration of major ions Ca, Mg, Na, K, CO_3, HCO_3, SO_4, and Cl concentration of certain minor components including NO_3, PO_4, organic substance as chemical oxygen demand (COD), total organic carbon (TOC), biological oxygen demand (BOD), heavy metals and trace components as B, Fe, Pb, Co, Cr, Cu, Cd, Al, V, Sr, Zn, Mn, Mo, and Ni. The obtained chemical data are expressed in milligram per liter (mg/l) Table (**3 and 5**). Some parameters including pH, temperature, EC, CO_3, HCO_3, TOC, COD, and NH_4 were determined in situ using pH, EC meter, 3510 Jenway, UK, titrimetrically against sulphuric acid by neutralization method using Phenolphthalein as an indicator for CO_3 and Methyl orange as an indicator for HCO_3 and Compact photometer PF-12Plus. MACHEREY – NAGEL GmbH & Co.KG, Filter photometer with microprocessor control and auto-calibration; Wavelength range (340 – 860) nm, Automatic filter wheel with 7 interference filters, Xenon high-pressure lamp, respectively. The analyses include Ca, Mg, Na, K, SO_4, Cl, BOD and heavy metals were performed at the hydrogeochemistry department of Desert Research Center (**DRC**) according to the methods adopted by the United States Geological Survey (**Rainwater and Thatcher 1960**), (**Fishman and Friendman 1985**) and American Society for Testing and Materials (**ASTM 2002**).

4.1. Multivariate Statistical Analysis

All mathematical and statistical calculations were implemented using SPSS version 16.0 software was used for carrying out the statistical analysis of the data; the data sets were log-transformed to accommodate a wide range of parameters (**Matiatos et al. 2014**).

4.1.1. Cluster analysis

The objective of cluster analysis is to group a number of objects to such an extent that they are more similar to one another in the same group (called cluster) (**Otto 1998**).

4.1.2. Factor analysis

Factor analysis is a way used to analyze variability between observable and correlated variables as a result of a potentially lower range of variables termed factors (**Shrestha and Kazama 2007**).

4.2. Pollution Indices

4.2.1. Heavy metal pollution index

Heavy metal pollution index, HPI is a comprehensive tool used for overall water quality determination, according to calculated weights of each metal; HPI was calculated according to (**Horton 1965; Mohan et al. 1996**). HPI is classified into five classes as following excellent extended from 0 to 25, good ranged from 26 to 50, poor ranged from 51 to 75, very poor ranged from 76 to 100, and unsuitable more than 100.

4.2.2. Nitrate pollution index

Nitrate sources in the groundwater are classified to point sources such as irrigation of land by sewage effluents and nonpoint sources such as densely populated sanitation and intense farming practices (**McLay et al. 2001**). The nitrate pollution index (NPI) for the water samples was determined by (**Spalding and Exner 1993**). The water quality according to NPI values was classified into five types: clean (unpolluted) ($NPI<0$), light pollution ($0<NPI<1$), moderate pollution ($1<NPI< 2$), significant pollution ($2<NPI< 3$), very significant pollution ($NPI > 3$).

4.2.3. Pollution index of groundwater

Drinking water quality can be assessed with the use of (PIG) **(Rao 2012)**, and were utilized successfully in several locations to monitor and evaluate variations in drinking water quality (**Rao et al. 2018; Rao and Chaudhary 2019**). In the current study the PIG values for each water sample were calculated using the standard limit of the World Health Organization (WHO 2017) prescribed for safe drinking water Table (**2**). PIG calculation involves four steps which determined according to **(Rao 2012)**. All the observed chemical variables in each sample of groundwater are determined in the PIG values. Thus, the effects of chemical pollution on the aquifer system are distinct.

4.2.4. Ecological risk index

In consideration of the pollution and toxic response factor, the potential ecological risk (ERI) index for the heavy metals analyzed has been quantitatively assessed. In this investigation, the ERI was estimated for each groundwater sample according to (**Bhutiani et al. 2017; Adimalla and Wang 2018; Taiwo et al. 2019**).

4.3. Hydrochemical facies evolution of groundwater

The Evolution Diagram for Hydrochemical Facies, proposed by **Gimenez FE(2010)** offers a convenient manner of recognizing the status of aquifers in temporal intrusion/refreshing phases, which is identified through the distribution of anion and cation levels in the square diagram Figure (5). Four heteropic facies are identified in this plot: Na-Cl (sea water), $Ca–HCO_3$ (fresh water) and Ca–Cl (water salinized with direct bases exchange).

5. Results And Discussion

5.1. Hydrogeochemistry

The hydrochemical data provides an overview of the physical-chemical parameters measured in the groundwater and surface water samples. The pH values ranged from 7.2 to 8.1 in the Pleistocene aquifer, from 7.1 to 7.6 in the Miocene aquifer and from 7.1 to 8.3 in surface water reflected that the groundwater and surface water samples are somewhat neutral to slightly alkaline. The electric conductivity(EC) values represent water's dissolved salt content and higher values typically reflect higher concentrations of ions in the water (**Prasanth et al. 2012**). The EC values ranged from 8520 to 19410 µS/cm in the Pleistocene groundwater, from 4290 to 7920 µS/cm in the Miocene groundwater and from 3970- 64410 µS/cm in the surface water. The EC value differences are attributable to the composition of the aquifer rocks. The total dissolved solids (TDS) values ranged from 5041 to 11741 mg/l in the Pleistocene groundwater, from 2360 to 4742 mg/l in the Miocene groundwater and from 2455 to 41958 mg/l in the surface water. Major ions are observed in Na+ and Cl− correspondingly as prominent cation and anion species in both the groundwater and surface water sample concentrations. The concentration of Na^+ varies from 1450 to 3500 mg/L in the Pleistocene groundwater, from 580 to 1380 mg/L in the Miocene groundwater, and from 740 to13400 mg/L in the surface water. The ionic concentration of Cl^- is highest among all the ions and the concentration of Cl^- in pleistocene groundwater is between 2211 and 6076 mg/L, in Miocene groundwater is between 951 to 2262 mg/L, and in surface water from 1054 to 20567 mg/L. Both the surface and the groundwater display significantly higher Na^+ and Cl^- concentrations, indicating that seawater most likely affects the water quality in the area under investigation and this indicates the mixing of groundwater with the matrix of marine aquifers. The concentration of K^+ shows the least variation with the range of 52 to 100 mg/L in the Pleistocene groundwater, from 32 to 55 mg/l in the Miocene groundwater and 28 to 600 mg/L in the surface water. In the Pleistocene groundwater, Ca^{2+} and Mg^{2+} concentrations range between 131 - 767 mg/L and 152 - 270 mg/L, respectively, also in the Miocene groundwater Ca^{2+} and Mg^{2+} concentrations range between 129 - 306 mg/L and 113-164 mg/L. Similarly, the concentrations of SO_4^{2-} and alkalinity vary from 344 to 2650 mg/L and 50 to 205 mg/L, in the Pleistocene groundwater, while in the Miocene groundwater ranges from 140 to1340mg/L and 135 to 275 mg/ L, in each case. The dissolving of marine sediments is the result of the high salinity of groundwater. Table (**3**), Figure (**6**).

A multi-rectangular hydrochemical facies evolution diagram (HFE) can be employed to determine the dynamics of seawater intrusion, considering the percentages of major ions, showing the intruding and freshening phases. Figure (7) shows that the majority of samples are appropriate for a phase of intrusion. The Na-Cl facies signifies the state of aquifer. The samples shown in HFE-D confirms the hypotheses regarding salinization with the exception of one sample (G1), is scattered in the field of freshening. The methodology of classification proposed in the present study takes into account that of **Gimenez FE (2010**).

5.2. Statistical analysis

5.2.1. Cluster analysis

Cluster analysis (CA) is a statistical analysis based on their similarity used in grouping samples in clusters and it is one of the most frequently used for evaluating the surface water effect on groundwater quality. The dendogram of two aquifers and surface water obtained by agglomerative hierarchical clustering are shown in Figures (**8and19**).Two dendrograms were produced which are certified to illustrate significant pollution. The diagram of CA calculated by using all detected parameters in water depend on chemical characteristics such as pH, EC, Ca, Mg, CO_3, HCO_3, Na, K, SO_4, Cl, BOD, TOC, COD, NO_3,NO_2, NH_4. The dendogram in Pleistocene was grouped by HCA into two groups Figure (**8**). Cluster 1 (C-1) contains 22samples (18 groundwater and 4 surface water); this cluster shows pollution and fecal contamination. Appearance of contaminated water at a sewage treatment plant in the study area, the remaining 2 samples, including two surface water is collective in cluster 2 (C-2). The variation of water quality parameters in cluster 1 of samples is presented in Figure (**8**) which indicated that the influence of sewage treatment plant on groundwater. In the Miocene aquifer, the dendogram also was classify into two clusters Figure (**9**). (C-1) includes 11 samples (7 groundwater and 4 surface water), (C-2) corresponding to surface water. The C-1 samples had substantially higher levels of water quality parameters, the predominance of the average cations being Na^+ > Mg^{2+} > Ca^{2+} > K^+ for both samples' clusters. The mean anion levels are in the category of Cl^- > $SO_4{}^{2-}$ > HCO_3.

5.2.2. Factorial analysis

The factor analysis was executed on 7 variables such as boron(B), strontium(Sr), biological oxygen demand(BOD), phosphorous(P), chromium(Cr), nickel(Ni) and total organic carbon(TOC) for the Pleistocene and Miocene groundwater, so that is identified the influence of surface water and treatment plant on groundwater. An eign value measures the relevance of the factor: the factors with maximum eign values are the most significant. Eigenvalues of 1.0 or larger are reflected significant values (**Shrestha and Kazama 2007**). Thus the classification for factor loads is 'strong,' 'moderate' and 'weak' which correspond to >0.75, 0.75-0.50 and 0.50-0.30 absolute loading values, respectively (**Liu et al. 2003**). Table (4) provides variable loads and explained variation and high loading values. The four factors of Miocene groundwater include more than 81.8 % of the total cumulative variance, and the three factors of Pleistocene groundwater include more than 71 % of the total cumulative variance respecting water quality data sets. The most significant parameters with strong positive factors in Miocene groundwater are B, Sr, BOD, Ni, and TOC and in Pleistocene groundwater are B, Sr, BOD, Ni, and TOC. Strontium and Boron with positive strong loading value have contributed as the most important parameters to changes in water quality in Miocene and Pleistocene ground water. This means that a significant amount of inorganic nutrients is caused by agriculture. The biochemical demands for oxygen, nickel and total organic carbon with strong factor loads are key parameters in the variability of water quality and it explains the fact that waste water and industrial wastewater enters the study area and causes significant pollution caused by the treatment plant. (**Pejman et al. 2009**).

5.3. Pollution indices

5.3.1. Heavy metal pollution index:

The mean concentrations were calculated to guess the heavy metal pollution index (HPI). Calculated index values and unit weightage values were listed in Table (**1**). In the current study, metals for example V, Cu, Mo, Cr, B, Fe, Cd, Mn, Ni, Pb, Al, and Zn were measured. The HPI for the study area is intended by integrating the mean concentration values of confirmed heavy metals. The particulars of the calculation are existing in Table (**8**). HPI is categorized into five classes; excellent (0–25), good (26–50), poor (51–75), very poor (76–100), and unsuitable (100). 72.2% of the Pleistocene aquifer samples is considered unsuitable for drinking purposes, 16.7% poor, 5.5% very poor, and the remaining samples5.5% is considered good, on the other hand, 71.5% of the Miocene aquifer samples is considered unsuitable for drinking purposes, and the remaining 28.5% is considered good. The results were assessed that in both aquifers (Pleistocene, Miocene), the heavy metal pollution index exceeds 100 in the majority of the samples. Wells are shown to be contaminated by heavy metals. It was estimated that the region of the research would be affected by heavy metal leakage from the water treatment plant, as shown in Figure (**10**). The water treatment plant has not treated the inorganic matters especially the heavy metals.

5.3.2. Nitrate pollution index:

Nitrate levels were ranged from 1 to 13.2 mg/L with an average of 4.03 mg/L in the study area. Nitrate was organized into three groups, 1) low (<20 mg/L), 2) medium (≥ 20 mg/L to <50 mg/L), and 3) high (≥50 mg/L). The concentration of nitrate in all the samples in the studied area is less than 20 mg/L. Five classifications of water have been determined according to NPI values: clean, light pollution, moderate pollution, significant pollution, and highly significant pollution, with NPI values of <0, 0-1, 1-2, 2-3, and >3, respectively. NPI is smaller than zero for all groundwater samples in the class clean Table (**8**).

5.3.3. Pollution index of groundwater:

The relative contribution of the pollutants from each ground water sample was evaluated in a Pollution Index (PIG) assessment. The chemical water quality (Ow) of pH and NO_3 of less than 0.1 Table (6) shows a low impact on groundwater contamination in the current study. Depends on the data in

Table (6), Pb and Fe had the greatest effect on sample water quality. This is evident in the values of Ow and PIG achieved. In this study the final PIG values were around 1.4 and 6.0. In five categories, the level of drinking water pollution is divided: PIG < 1.0 indicates insignificant pollution; 1.0–1.5 refers to the low pollution, 1.5-2.0 is moderate pollution; 2.0–2.5 signifies high pollution; and PIG > 2.5 shows very high pollution Table (**7**) (**Rao 2012; Rao et al. 2018; Rao and Maya 2019**). Based on this classification, 94.4% of Pleistocene water samples were found to be very high polluted, while the remaining samples, 5.6%, were highly polluted and unsuited for drinking. Nevertheless, Miocene aquifers include a very low pollution level of 14.3%, moderate pollution of 14.3%, high pollution of 28.6% and very high pollution of 42.8%. The highest anthropogenic input is probably found in the samples identified as unfit to drink and is observed from both the north and south regions of the study area Figure (11).

5.3.4. Ecological risk index:

For each heavy metals and water sample, the RI (potential ecological risk) was initially identified during the ERI evaluation. Table (**7**). According to (**Bhutiani et al. 2017**; **Adimalla and Wang 2018; Taiwo et al. 2019**), RI is divided into five, to reflect its impact on sample quality of heavy metal: RI < 40 (low potential risk), 40 ≤ RI < 80 (moderate potential risk), 80 ≤ RI < 160 (considerable potential risk), 160 ≤ RI < 320 (high potential risk), and ≥ 320 (very high potential risk). In the current study, depend on this classification; Cd poses moderate potential risks to sample G14, considerable potential risk index to samples G11, G13, G15, and G29, high potential risk index to samples G9, G16, G19 and G7, very high potential to sample G27. However, the samples G6, G13, G19, G1, G26, G27 and G29 have been found to be moderately at risk by Pb Table (**8**).

The final ERI values achieved from this analysis ranged from 10.9 to 388.3 Table (**8**). The ground water can be divided into four categories based on the ERI values: ERI < 150 (low risk), 150 < ERI (moderate ecological risk), 300 < ERI < 600 (considerable risk), and 276 > 600 (very high risk) (**Adimalla and Wang 2018; Taiwo et al. 2019**). According to this classification scheme, 66.7% of the Pleistocene aquifer samples have low ecological risk, 22.2% have moderate risk, and 11% are considerable risks. However, 42.8% of the Miocene aquifer has low ecological risk, 22.8% have moderate risk and 14.4% are a considerable risk Figure (**12**).

Conclusions

The hydrochemical data describes in the both of groundwater and surface water samples in the study area. The groundwater and surface water are somewhat neutral to slightly alkaline. Both the groundwater and the surface water display significantly higher Na^+ and Cl^- concentrations, indicating that seawater or leaching and dissolution of marine salts most likely affects the water quality of the study area. Two dendrograms were constructed by cluster. The Pleistocene aquifer; cluster 1 includes 22 samples (18 groundwater and four surface water), and the remaining includes two is combined in cluster 2. In the Miocene aquifer, cluster 1 includes 11 samples (7 groundwater and four surface water), cluster 2 corresponding to surface water which indicated the presence of contaminated water in the study area coming from a sewage treatment plant .The factor analyses were executed on seven variables for the Pleistocene and Miocene groundwater. The most significant parameters with strong positive factors in Miocene and Pleistocene groundwater are B, Sr, BOD, Ni, and TOC. Strontium and Boron have a positive substantial loading value as the highly significant parameters in Miocene, and Pleistocene groundwaters have a considerable amount of inorganic nutrients due to agricultural areas. The biochemical demands for oxygen, nickel and total organic carbon with strong factor loads are key parameters in the variability of water quality and it explains the fact that waste water and industrial wastewater enters the study area and causes significant pollution caused by the treatment plant. The majority of the groundwater samples are represented in an intrusion phase using the hydrochemical facies evolution diagram indicating the hypotheses about the salinization except for sample G1, which is dispersed in the field of freshening. All samples in the study area have nitrate levels of less than 20 mg/L belonging to the class clean. The final PIG, HPI and ERI values obtained from this study shows the presence of contaminated water in the study area upcoming from a sewage treatment plant. So that is identified the influence of surface water and treatment plant on groundwater. The heavy metal disposal from the treatment plant was most affected the groundwater in this area. The groundwater in the study area is unsuitable for drinking purposes because of the presence of a water treatment facility and is observed as being of high anthropogenic inputs.

Declarations

Declaration of interests

Ethics approval and consent to participate

'Not applicable'

Consent for publication

'Not applicable'

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

"The authors declare that they have no competing interests"

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Author contributions

All authors contributed to the study conception and design, Material preparation, data collection and analysis were performed by [RAE], [EZ], [HI], [EAS], [MMHK], [AME] and [MMS]. The first draft of the manuscript was written by [RAE] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Tables

Table (1) Unit weightage (Wi) and standard permissible value (Si) in mg/l according to Egypt Guidelines according to the Minister of Health decree Number (108) for 1995 and (458) for 2007.

Item	Egyptian 2007	W_i Egy
Al	0.1	0.01
B	0.5	0.009
Cd	0.003	0.60
Cr	0.05	0.04
Cu	2	0.0009
Fe	0.3	0.01
Mo	0.07	0.03
Mn	0.4	0.00
Ni	0.02	0.09
Pb	0.01	0.18
V	0.05*	0.04
Zn	3	0.0006

Table (2) Assigned weight (wi) and relative weight (Wi) of water quality parameters with their WHO (2017).

Parameter	unit	Relative weight (Rw)	Weight parameter (Wp)	WHO(2017) Stander limits
pH	-	3	0.0577	7
Na	mg/L	4	0.0769	200
K	mg/L	1	0.0192	12
Ca	mg/L	2	0.0385	75
Mg	mg/L	2	0.0385	50
Cl	mg/L	4	0.0769	250
HCO_3	mg/L	3	0.0577	250
SO_4	mg/L	5	0.0962	250
NO_3	mg/L	5	0.0962	50
Fe	mg/L	4	0.0769	0.3
Zn	mg/L	4	0.0769	3
Ni	mg/L	5	0.0962	0.02
Cr	mg/L	5	0.0962	0.05
Pb	mg/L	5	0.0962	0.01

Table (3) Summary of quality parameters in groundwater and surface water

Parameters	Groundwater									
	Pleistocene aquifer			Miocene aquifer			Surface water			WHO (2011) permissible limits
	median	Min	Max	Median	Min	Max	Median	Min	Max	
***pH**	7.6	7.2	8.1	7.4	7.1	7.6	7.7	7.1	8.3	**6.5 – 8.5**
***EC**	13543	8520	19410	6377	4290	7920	27895	3970	64410	**-**
TDS	7951	5041	11741	3678	2360	4742	17614	2455	41958	**1000**
Alkalinity	147	50	205	191	135	275	314	155	545	**600**
Cl^-	3885	2211	6067	1700	951	2262	8848	1054	20567	**250**
SO_4^{2-}	1090	344	2650	536	140	1340	2066	400	6000	**500**
Na^+	2250	1450	3500	966	580	1380	5702	740	13400	**200**
K^+	72	52	100	43	32	55	191	28	600	**-**
Ca^{2+}	348	131	767	185	129	306	380	74	879	**200**
Mg^{2+}	216	152	270	131	113	164	237	64	443	**150**

***pH is in numerical value, *EC is in μS/cm, all others are in mg/L.**

Table (4) The factor loadings value and explained variance of water quality parameters in Pleistocene and Miocene groundwater.

Miocene groundwater				
Parameters	**Factor 1**	**Factor 2**	**Factor3**	**Factor 4**
B	0.881	-.144-	-.069-	-.272-
Sr	0.831	-.392-	-.262-	-.158-
BOD	-.012-	0.786	-.351-	-.264-
P	0.375	0.663	-.126-	0.368
Cr	-.440-	-.499-	-.401-	0.218
Ni	-.032-	0.059	0.845	-.364-
TOC	0.432	-.010-	0.398	0.786
Total variance	28.395	21.213	17.780	14.436
Pleistocene groundwater				
Parameters	**Factor 1**	**Factor 2**	**Factor3**	
B	0.935	.004	-.120-	
Sr	0.918	-.148-	-.047-	
BOD	.021	0.857	.103	
P	.209	0.601	.594	
Cr	-.018-	-0.515-	.503	
Ni	-.025-	-.252-	0.773	
TOC	0.761	-.036-	.076	
Total variance	33.232	20.678	17.228	

Table (5) Heavy metals analysis for groundwater and surface water samples, all concentrations in part per million (ppm).

No.	Al	B	Cd	Cr	Cu	Fe	Mo	Mn	Ni	Pb	V	Zn
Pleistocene Aquifer (mg/l)												
G2	2.105	3.270	0.0191	<0.01	2.526	<0.006	<0.001	0 .1363	<0.002	0 .0482	0 .0335	<0.01
G4	0 .0991	2.757	<0.0006	<0.01	0 .0590	<0.006	<0.001	0 .0045	<0.002	<0.008	0 .0101	<0.01
G5	0 .0862	3.232	<0.0006	<0.01	0 .0761	<0.006	0 .0537	0 .0064	0 .0397	0 .0153	0 .0127	<0.01
G6	0 .2037	2.387	<0.0006	<0.01	0 .6749	<0.006	<0.001	0 .0146	<0.002	0 .1579	0 .0064	<0.01
G8	0 .1481	3.124	<0.0006	<0.01	0 .3304	<0.006	0 .0241	0 .0081	<0.002	0 .0858	0 .0291	<0.01
G9	0 .2854	1.947	0 .0204	<0.01	0 .9583	<0.006	0 .0296	0 .0184	<0.002	0 .3053	0 .0290	<0.01
G11	0 .0324	3.283	0 .0134	<0.01	0 .0012	<0.006	0 .1182	<0.002	<0.002	0 .0168	<0.0006	<0.01
G13	0 .3372	4.436	0 .0119	<0.01	0 .5047	0.0231	0 .0583	0 .0301	<0.002	0 .0889	0 .0071	<0.01
G14	0 .2011	3.696	0 .0072	<0.01	0 .5012	0.011	0 .0630	0 .0184	<0.002	<0.008	0 .0100	<0.01
G15	0 .0417	2.563	0 .0083	<0.01	0 .0265	<0.006	<0.001	0 .0030	<0.002	<0.008	0 .0142	<0.01
G16	0 .0653	2.844	0 .0212	<0.01	0 .0229	<0.006	0 .0171	0 .0036	0 .0311	<0008	0 .0086	<0.01
G17	0 .4775	2.244	<0.0006	<0.01	1.254	<0.006	0 .0140	0 .0803	0 .0269	<0.008	0 .0151	<0.01
G18	0 .0033	3.030	<0.0006	<0.01	0 .1263	<0.006	<0.004	0 .0034	0 .0109	0 .0764	<0.0006	<0.01
G19	0 .0707	4.540	0 .0270	<0.01	0 .0589	<0.006	0 .0615	<0.002	<0.002	0 .1642	0 .0284	<0.01
G21	0 .1093	3.849	0 .0171	0 .0371	3.369	<0.006	<0.001	0 .0240	<0.002	0 .2034	<0.0006	<0.01
G22	1.752	3.959	<0.0006	0 .0312	3.088	0 .0071	<0.001	0 .1416	0 .0070	<0.008	0 .0210	<0.01
G23	0 .0663	2.641	0 .0009	0 .0209	0 .0251	<0.006	<0.001	0 .0030	0 .0580	0 .0780	0 .0128	<0.01
G24	0 .2026	2.300	<0.0006	0 .0203	0 .6892	0 .0184	0 .1486	0 .0147	0 .0109	0 .0278	0 .0753	<0.01
Miocene Aquifer												
G1	1.748	0 .6449	9.434	0.0106	<0.01	0.0251	<0.0006	10.24	0 .1328	0 .0070	0 .0031	0 .2567
G3	1.643	0 .5168	1.112	<0.006	<0.01	0 .0266	<0.0006	11.30	<0.008	<0.002	0 .1097	0 .0354
G7	0.9865	0 .2093	1.007	<0.006	<0.01	0 .0214	0 .0247	12.38	<0.008	0 .0272	0 .0591	0 .0402
G25	2.126	0 .1062	0 .0545	<0.006	<0.01	0 .0088	<0.0006	5.484	<0.008	0 .0062	<0.001	0 .0113
G26	0.718	0 .0855	0 .2161	0.0131	0.025	<0.001	0 .0172	7.924	0 .0999	<0.002	0 .0475	0 .0040
G27	2.658	0 .1309	0 .0695	0.01	<0.01	<0.001	0 .0335	10.41	0 .1046	<0.002	<0.001	0 .0097
G29	1.858	0 .1352	0 .1247	<0.006	<0.01	0 .0127	0 .0154	10.24	0 .1328	0 .0070	0 .0031	0 .2567
Surfacewater												

No.	Al	B	Cd	Cr	Cu	Fe	Mo	Mn	Ni	Pb	V	Zn
S10	<0.01	0 .0404	0.02	<0.04	1.094	0 .1290	0 .0109	10.05	0 .2018	<0.002	0 .0109	0 .0080
S12	<0.01	0 .0172	0 .0056	0 .0517	9.222	0 .1924	0 .0653	26.55	0 .1156	<0.002	0 .0653	2.902
S20	<0.01	0 .0115	0 .0307	0 .3403	18.29	0 .1764	0 .0521	5.335	<0008	0 .0085	0 .0521	0 .4242
S28	<0.01	0 .0113	<0.0006	0 .0527	7.247	0 .2511	<0.001	Nil	<0.008	0 .0198	<0.001	0 .0687
Treatment plant (before)	<0.01	<0.001	0 .0094	0 .1763	1.777	0 .1094	0 .0568	2.739	<0008	0 .0163	0 .0568	0 .0786
Treatment plant (after)	<0.01	<0.001	0 .0014	0 .6108	2.682	0 .1085	<0.001	2.899	<0.008	<0.002	<0.001	0 .0553

Table (6) The overall quality (Ow) of the groundwater samples

No.	OW pH	OW Na	OW K	OW Ca	OW Mg	Ow Cl	OW HCO_3	OW SO4	OW NO3	OW Fe	OW Zn	OW Ni	OW Cr	OW Pb	∑OW
Pleistocene Aquifer															
G2	0.059	0.673	0.088	0.152	0.142	0.807	0.053	0.540	0.007	0.647	0.001	0.048	0.019	0.464	3.7
G4	0.059	0.731	0.091	0.344	0.200	0.949	0.037	1.020	0.011	0.015	0.000	0.048	0.019	0.077	3.6
G5	0.063	0.731	0.160	0.097	0.156	0.949	0.037	0.308	0.005	0.020	0.000	0.048	0.019	0.147	2.7
G6	0.066	0.558	0.083	0.111	0.127	0.743	0.038	0.250	0.005	0.173	0.000	0.048	0.019	1.519	3.7
G8	0.065	0.884	0.114	0.113	0.154	1.218	0.041	0.185	0.013	0.085	0.001	0.048	0.019	0.825	3.8
G9	0.065	0.654	0.112	0.084	0.158	0.680	0.041	0.577	0.002	0.246	0.001	0.048	0.019	2.937	5.6
G11	0.059	0.904	0.086	0.132	0.153	1.155	0.044	0.346	0.017	0.000	0.000	0.048	0.019	0.162	3.1
G13	0.062	0.980	0.128	0.126	0.198	1.329	0.038	0.280	0.016	0.129	0.000	0.048	0.019	0.855	4.2
G14	0.063	1.019	0.160	0.096	0.156	1.297	0.035	0.317	0.008	0.128	0.000	0.048	0.019	0.077	3.4
G15	0.061	1.000	0.106	0.180	0.179	1.518	0.034	0.281	0.008	0.007	0.000	0.048	0.019	0.077	3.5
G16	0.067	0.769	0.088	0.067	0.117	0.996	0.041	0.182	0.002	0.006	0.000	0.048	0.019	0.077	2.5
G17	0.060	0.634	0.088	0.129	0.132	0.981	0.037	0.133	0.023	0.321	0.000	0.048	0.019	0.077	2.7
G18	0.063	0.961	0.112	0.257	0.208	1.550	0.031	0.385	0.006	0.032	0.000	0.048	0.019	0.735	4.4
G19	0.065	1.057	0.160	0.178	0.186	1.582	0.023	0.327	0.007	0.015	0.001	0.048	0.019	1.580	5.2
G21	0.060	0.807	0.106	0.162	0.172	1.170	0.032	0.374	0.003	0.864	0.000	0.178	0.071	1.957	6.0
G22	0.063	1.346	0.160	0.258	0.206	1.866	0.037	0.466	0.002	0.792	0.001	0.150	0.060	0.077	5.5
G23	0.060	1.038	0.122	0.338	0.169	1.423	0.021	0.827	0.003	0.006	0.000	0.101	0.040	0.750	4.9
G24	0.060	0.827	0.104	0.394	0.186	1.297	0.013	0.750	0.003	0.177	0.002	0.098	0.039	0.267	4.2
Miocene Aquifer															
G1	0.059	0.223	0.080	0.157	0.126	0.293	0.038	0.516	0.018	2.418	0.001	0.048	0.019	1.278	5.3
G3	0.061	0.446	0.072	0.072	0.087	0.569	0.039	0.177	0.005	0.285	0.001	0.048	0.019	0.077	2.0
G7	0.063	0.231	0.051	0.066	0.090	0.387	0.034	0.054	0.002	0.258	0.000	0.048	0.019	0.077	1.4
G25	0.062	0.500	0.066	0.068	0.096	0.633	0.055	0.177	0.005	0.014	0.001	0.048	0.019	0.077	1.8
G26	0.059	0.223	0.058	0.105	0.096	0.419	0.069	0.061	0.014	0.055	0.001	0.120	0.048	0.961	2.3
G27	0.060	0.531	0.067	0.097	0.096	0.664	0.051	0.279	0.005	0.018	0.003	0.048	0.019	1.006	2.9
G29	0.061	0.446	0.088	0.098	0.116	0.696	0.042	0.181	0.007	0.032	0.001	0.048	0.019	1.127	3.0
Surface_water															
S10	0.068	0.285	0.045	0.038	0.049	0.324	0.032	0.154	0.006	0.082	0.000	0.048	0.019	1.941	3.1
S12	0.059	4.614	0.320	0.412	0.341	5.852	0.055	1.595	0.002	0.955	0.001	0.048	0.019	1.112	15.4
S20	0.068	5.152	0.960	0.451	0.321	6.327	0.044	2.309	0.002	0.162	0.001	0.048	0.019	0.077	15.9
S28	0.063	1.365	0.160	0.095	0.142	1.582	0.148	0.348	0.002	0.114	0.001	0.048	0.019	0.077	4.2
Treatment plant (before)	0.059	1.269	0.240	0.070	0.086	1.582	0.110	0.203	0.025	0.076	0.004	0.048	0.019	0.077	3.9
Treatment plant (after)	0.062	0.469	0.104	0.103	0.154	0.664	0.113	0.162	0.006	0.042	0.003	0.048	0.019	0.077	2.0

Table (7) Groundwater classification based on the PIG and ERI

Quality index	Range of values	Classification	% of samples in category Pleistocene aquifer	% of samples in category Miocene Aquifer
PIG (Subba Rao et al. *2018*)	< 1.0	Insignificant pollution	---	---
	1.0 – 1.5	Low pollution	---	14.3
	1.5 – 2.0	Moderate pollution	---	14.3
	2.0 – 2.5	High pollution	5.6	28.6
	> 2.5	Very high pollution	94.4	42.8
ERI (Bhutiani et al. 2017; Taiwo et al. 2019)	< 150	Low ecological risk	66.7	42.8
	150 < ERI < 300	Moderate ecological risk	22.2	42.8
	300 < ERI < 600	Considerable ecological risk	11.1	14.4
	> 600	Very high ecological risk	---	---

Table (8) The potential ecological risks (RI) and heavy metals pollution index (HPI) of the groundwater samples

Sample	RI (Cd)	RI (Cr)	RI (Cu)	RI (Fe)	RI (Mn)	RI (Ni)	RI (Pb)	RI (Zn)	∑RI	HPI	NPI
Pleistocene Aquifer											
G2	191	0.2	0.015	8.42	0.341	0.5	24.1	0.011	224.6	516.0	-0.705
G4	6	0.2	0.015	0.20	0.011	0.5	4	0.003	10.9	32.6	-0.86
G5	6	0.2	0.015	0.25	0.016	9.925	7.65	0.004	24.1	64.8	-0.875
G6	6	0.2	0.015	2.25	0.0365	0.5	78.95	0.002	88.0	305.0	-0.67
G8	6	0.2	0.015	1.10	0.020	0.5	42.9	0.010	50.7	175.1	-0.95
G9	204	0.2	0.015	3.19	0.046	0.5	152.65	0.010	360.6	968.4	-0.565
G11	134	0.2	0.015	0.00	0.005	0.5	8.4	0.000	143.1	307.5	-0.595
G13	119	0.2	0.05775	1.68	0.075	0.5	44.45	0.002	166.0	412.3	-0.78
G14	72	0.2	0.0275	1.67	0.046	0.5	4	0.003	78.4	170.2	-0.79
G15	83	0.2	0.015	0.09	0.0075	0.5	4	0.005	87.8	185.2	-0.95
G16	212	0.2	0.015	0.08	0.009	7.775	4	0.003	224.1	457.2	-0.39
G17	6	0.2	0.015	4.18	0.201	6.725	4	0.005	21.3	53.2	-0.84
G18	6	0.2	0.015	0.421	0.0009	2.725	38.2	0.000	47.6	158.2	-0.825
G19	270	0.2	0.015	0.196	0.005	0.5	82.1	0.009	353.0	843.9	-0.925
G21	171	0.742	0.015	11.23	0.06	0.5	101.7	0.0002	285.2	723.1	-0.95
G22	6	0.624	0.0178	10.293	0.354	1.75	4	0.007	23.0	73.2	-0.93
G23	9	0.418	0.015	0.084	0.008	14.5	39	0.0043	63.0	189.7	-0.92
G24	6	0.406	0.046	2.297	0.037	2.725	13.9	0.0251	25.4	81.2	-0.54
Miocene Aquifer											
G1	6	0.2	0.0265	31.447	0.642	1.75	66.4	0.0121	106.5	288.2	-0.865
G3	6	0.2	0.015	3.707	0.089	0.5	4	0.0082	14.5	45.5	-0.645
G7	247	0.2	0.015	3.357	0.101	6.8	4	0.003	261.5	530.2	-0.86
G25	6	0.2	0.015	0.182	0.028	1.55	4	0.014	12.0	34.2	-0.81
G26	172	0.5	0.03275	0.720	0.010	0.5	49.95	0.008	223.7	530.9	NPI
G27	335	0.2	0.025	0.232	0.024	0.5	52.3	0.043	388.3	864.1	-0.815
G29	154	0.2	0.015	0.416	0.016	0.5	58.55	0.017	213.7	524.6	-0.705

Figures

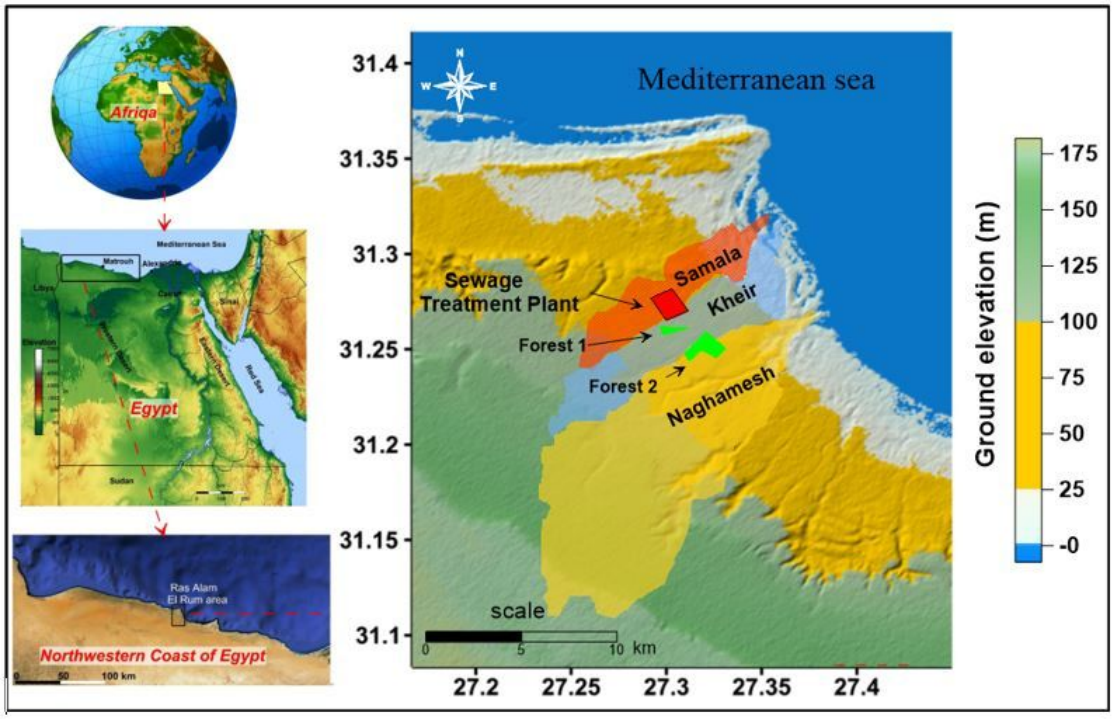

Figure 1

Location map of the study area.

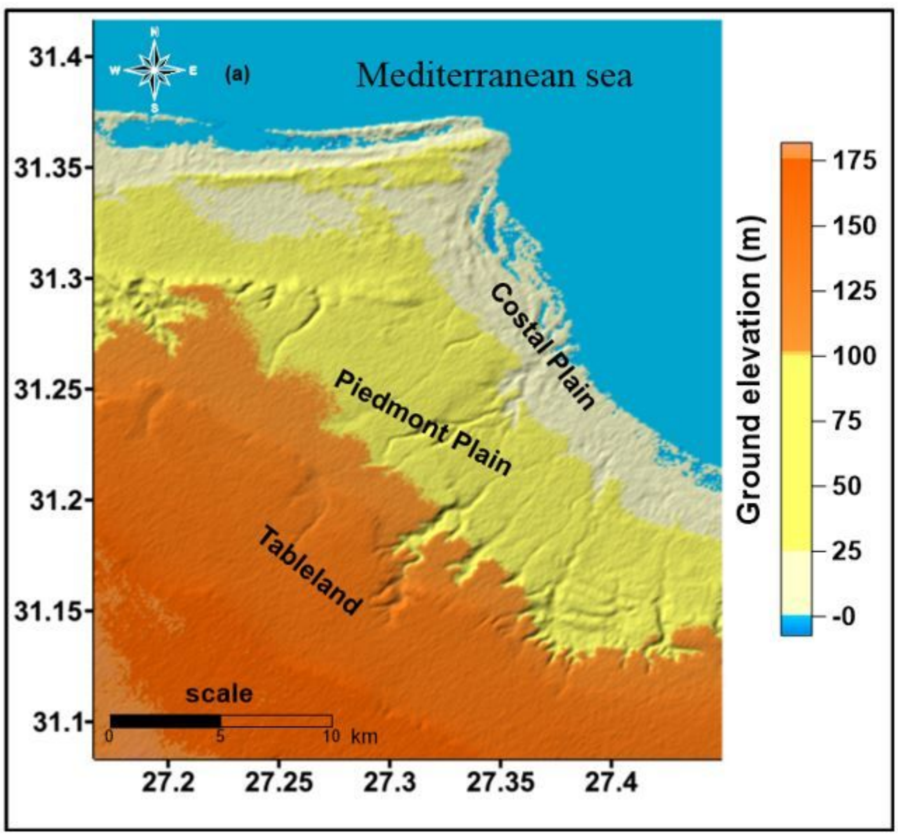

Figure 2

Geomorphological map of the study area.

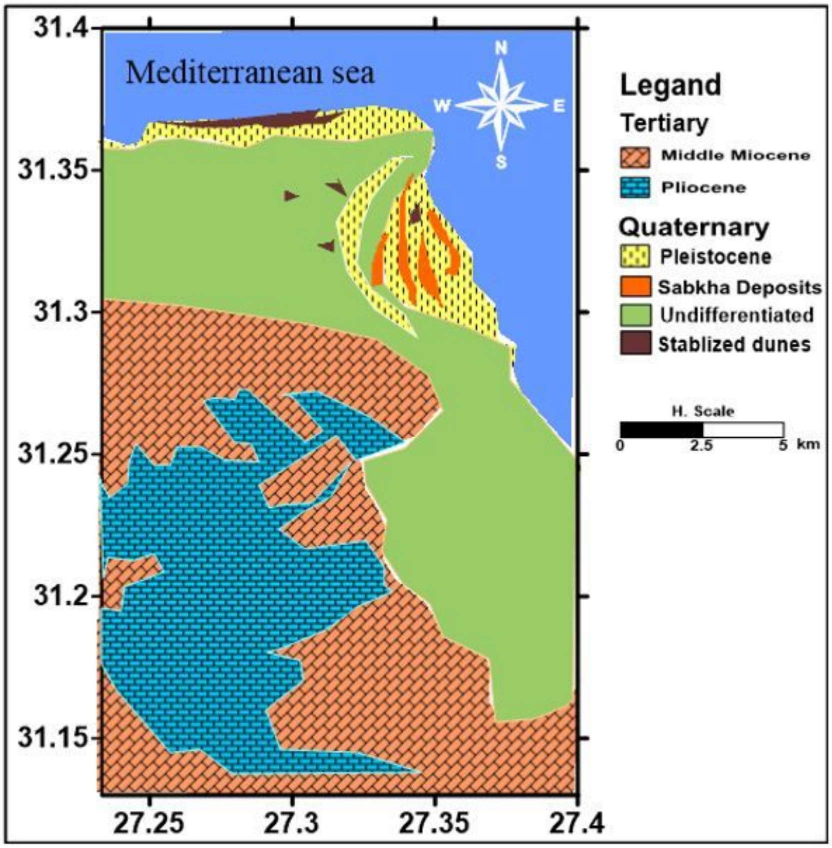

Figure 3

Geological map of the study area.

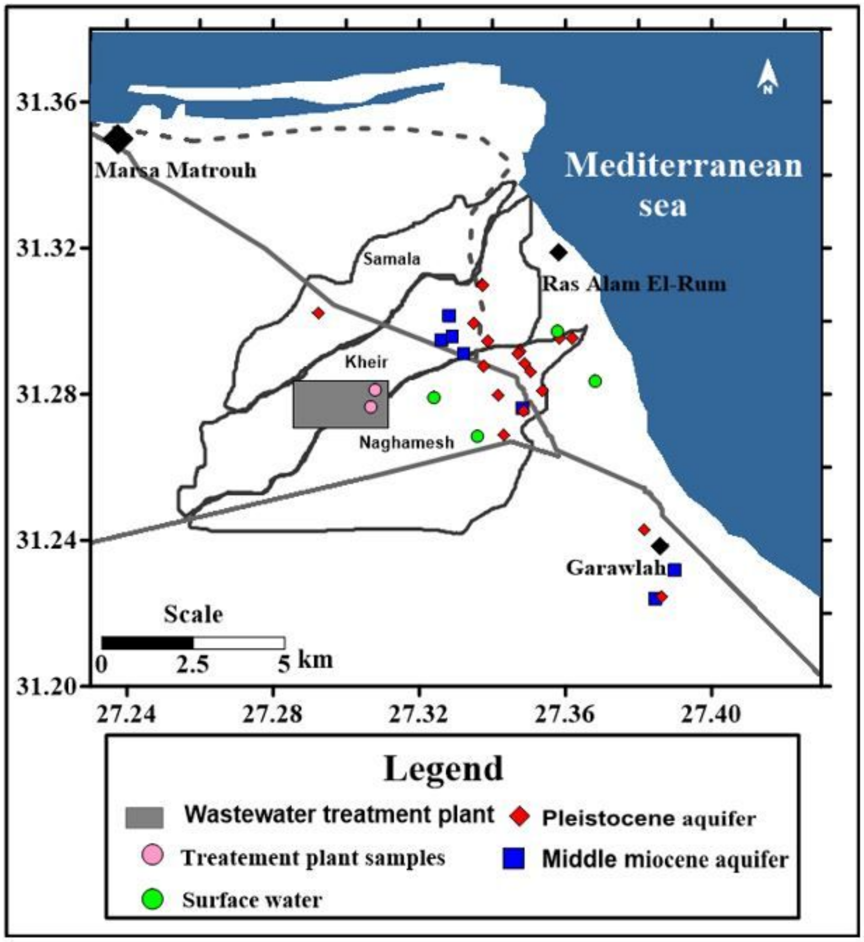

Figure 4

Map of sampling points of the area under investigation.

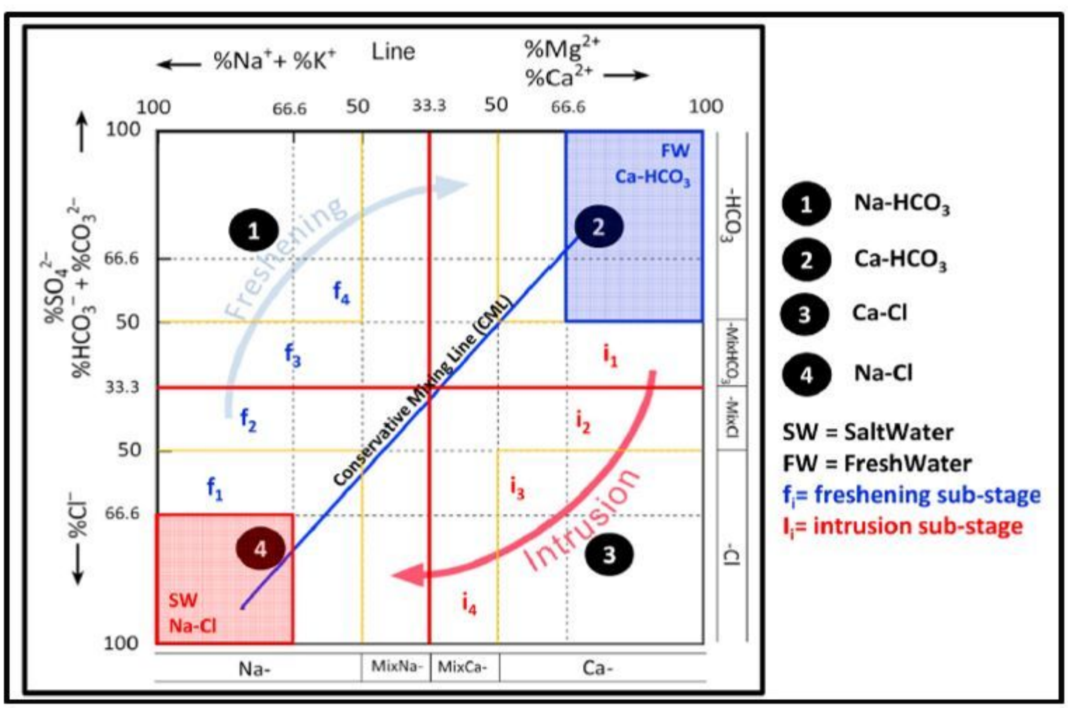

Figure 5

Hydrochemical facies evolution of groundwater

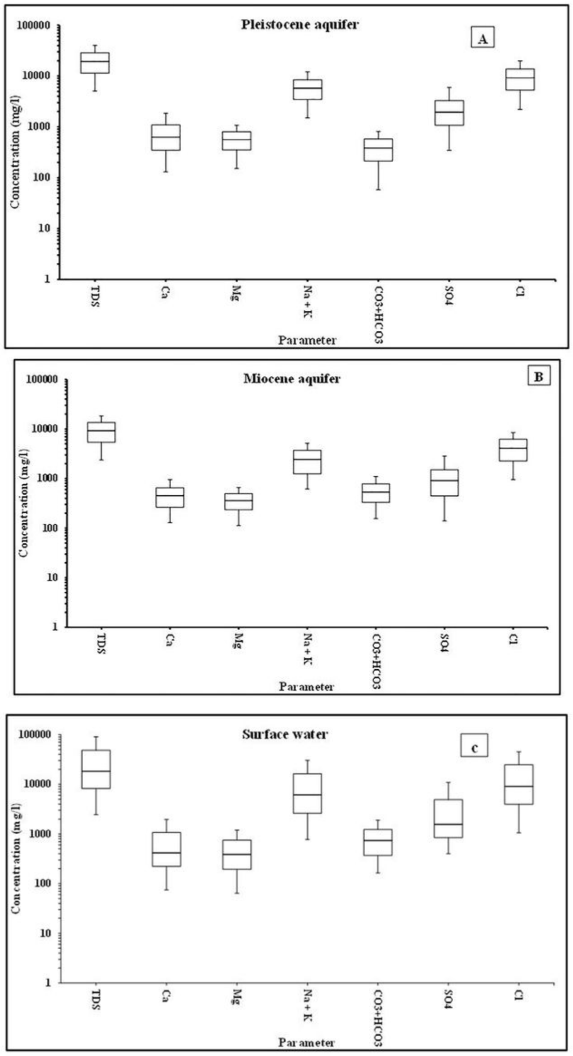

Figure 6

Box plots of (TDS, Ca,Mg, Na+K, CO3+HCO3, SO4, Cl),(A) in Pleistocene aquifer ,(B)in Miocene aquifer and (C) in surface water samples of the study area. All concentrations are given in milligram per litre (mg/l).

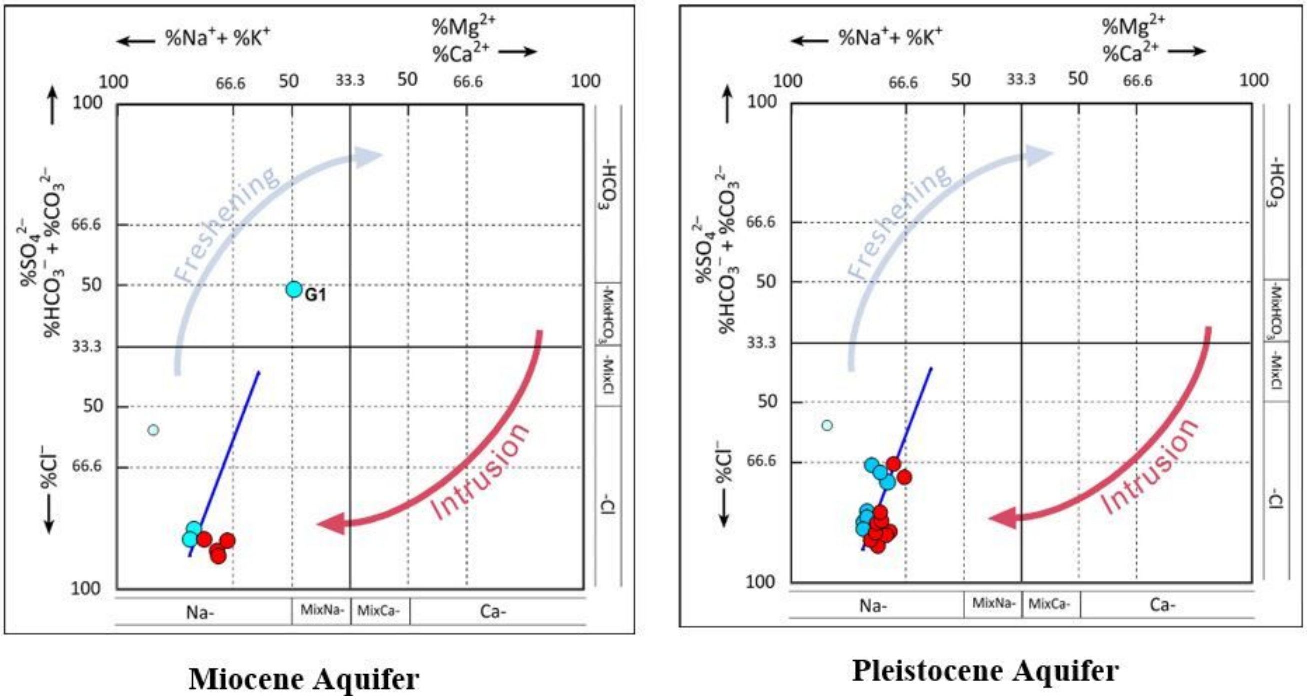

Figure 7

Hydrochemical facies evolution (HFE) diagram in groundwater of Pleistocene and Miocene aquifer.

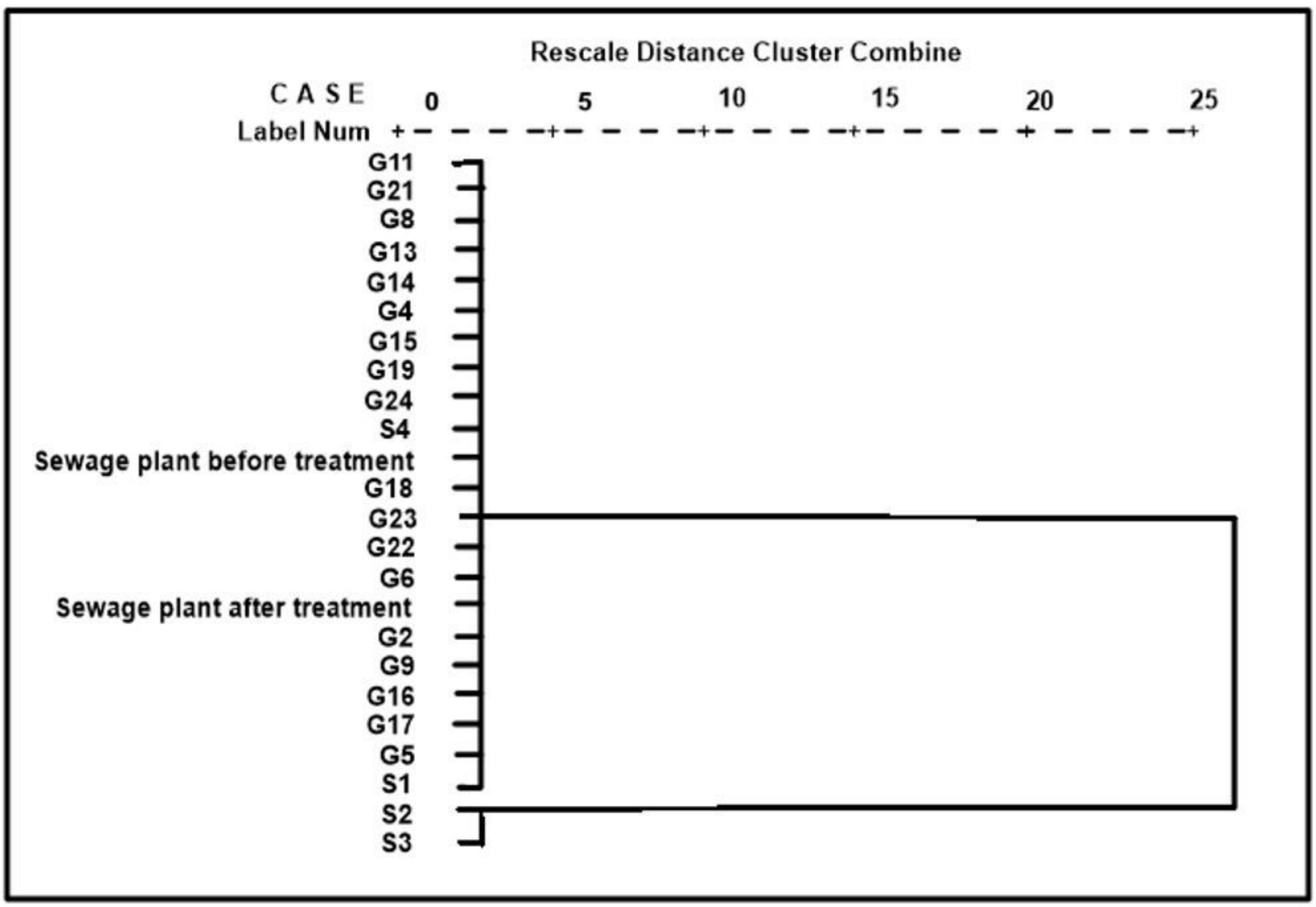

Figure 8

Dendrogram of the Pleistocene groundwater.

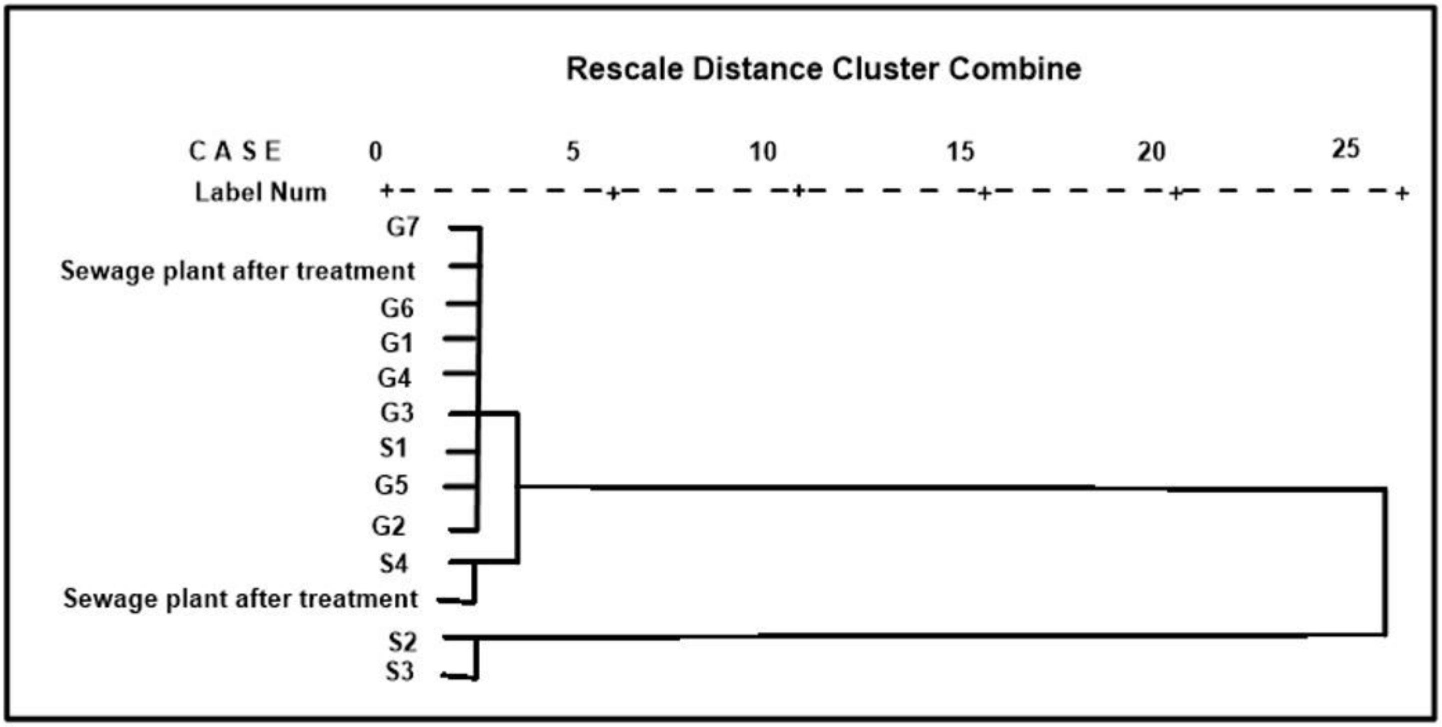

Figure 9

Dendrogram of the Miocene groundwater.

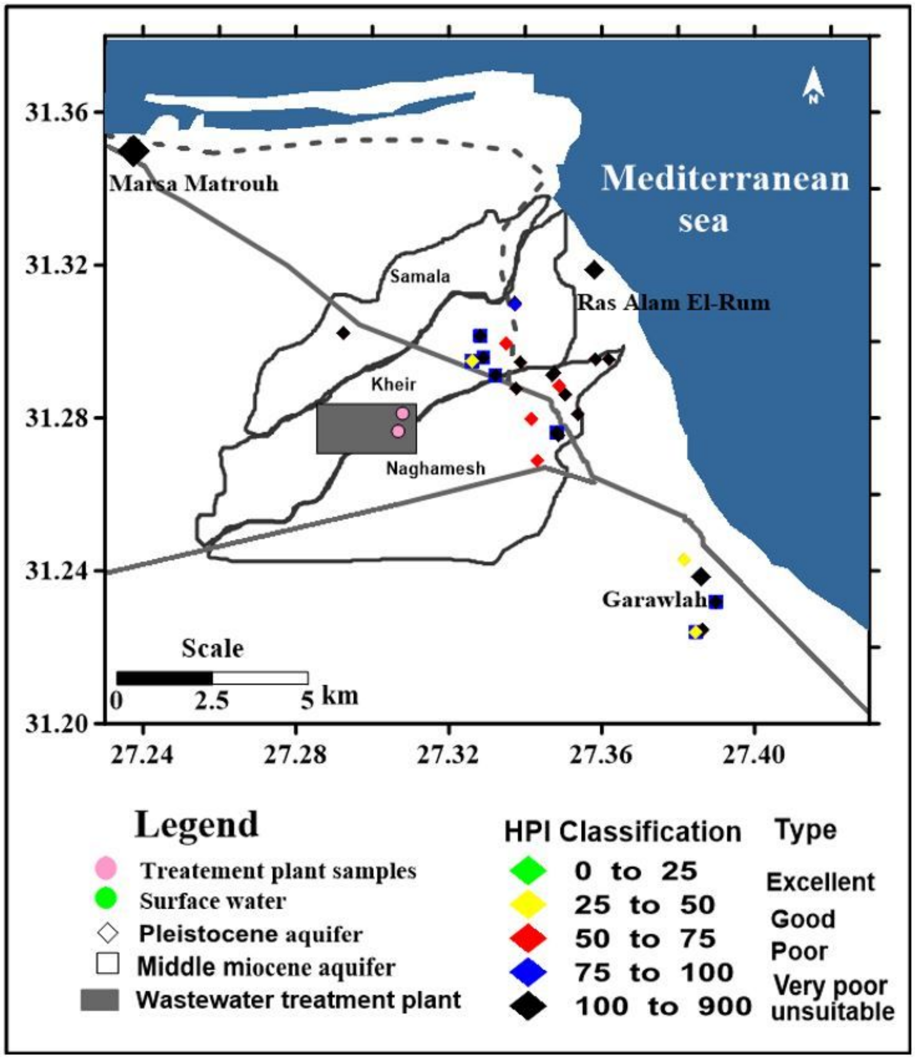

Figure 10

Heavy metals pollution index classed map of groundwater samples in the area under investigation.

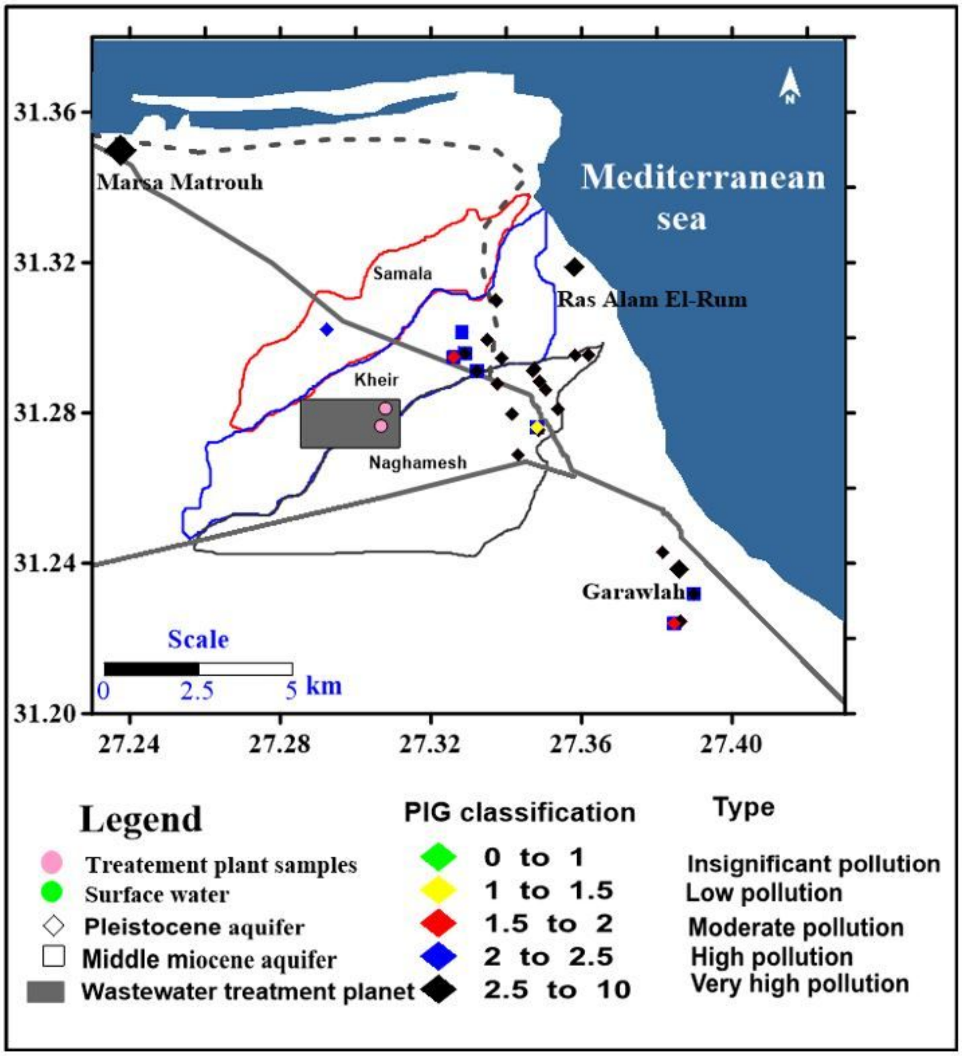

Figure 11

Pollution index classed map for the groundwater samples in the study area.

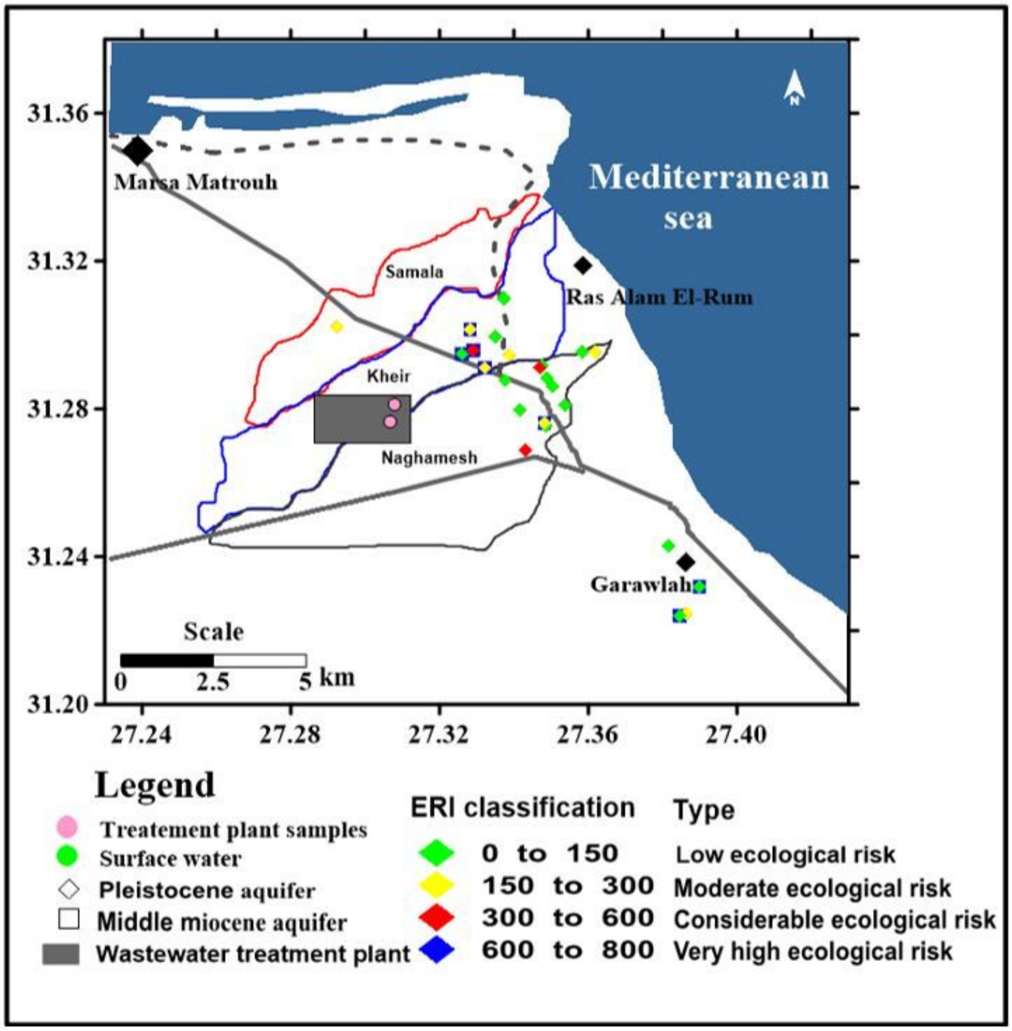

Figure 12

Classed map of Ecological risk index of the studied groundwater in Pleistocene and Miocene aquifer.

Supplementary Files

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- graphicalabstract.docx