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Evaluation of Groundwater Quality under Agricultural Land Use in the Sub-Catchment Area of Ras El-Ain

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Abstract

The evaluation of groundwater quality under agricultural land use and fertilizers' application was assessed by the physio-chemical parameters (20 parameters) of the springs of Ras El-Ain and 24 wells upstream. This study allows the investigation of chemical contamination reaching Ras El-Ain springs, an ecologically-rich site and part of Tyre Coast Nature Reserve, in addition to diverse well sites of mainly agricultural uses, located in the lower sub-catchment area of Ras El-Ain. The results of physio-chemical analyses show that their pH values are all alkaline, probably due to their rock exposure to Eocene Limestone (E); TDS and EC values are acceptable in all sites. 17 of the 26 sites are contaminated with Nitrite (NO_2^-), 15 of which are wells and the other two are Ras El-Ain springs (sites 24 & 25); all contaminated sites by (NO_2^-) exceed only the drinking water guideline by WHO, which entails restricted agricultural use for irrigation, and prohibiting water distribution for drinking and domestic purposes. Only sites (1) and (23) show very high Nitrate (NO_3^-) content, with site (1) exceeding both limits for drinking and irrigation water guidelines set by the WHO and FAO respectively, while site (23) exceeds only the limit for drinking water. The origin of contamination with Nitrate and Nitrite is agricultural fertilizers. Sites (20) and (21) are contaminated with Fluoride (F^-), exceeding only the drinking water limit. 15 sites (excluding Ras El-Ain springs) are contaminated with Bromide (Br^-), exceeding only the drinking water limit. No other ions or heavy metals' contamination were detected in the study sites. PCA statistical analysis shows that sites (1), (12), (20) and (22) are the most contaminated sites mainly with Nitrite, Nitrate, Fluoride and Bromide, primarily caused by over application of agrochemicals, proving the negative effect of unregulated agricultural land-use on groundwater quality.

Keywords

Agricultural Land Use, Agrochemicals, Contamination, Groundwater, Ras EL-Ain Springs

1. Introduction

Water is the most abundant environmental resource on Earth, and its accessibility is based on quality and quantity as well as on space and time. About 70% of the human body and almost 60% - 70% of plant cells are made up of water (Smith & Edger, 2006). Water is the most widespread substance on our planet: although in varying amounts, it is available everywhere and plays a crucial role in the environment and in human life (Igor, 1998).

Lebanon, with the highest amount of renewable water resources per unit area in the Middle East and 30% agricultural lands, is gradually suffering from climate change and water scarcity that has affected the availability of water for irrigation and agricultural production (Shaban, 2008). More than 50% of the Lebanese water sources are contaminated (Shaban, 2014). Hence, water quality deterioration is a prime striking challenge directly affecting the Lebanese population. Contamination in Lebanon is widespread, primarily due to the uncontrolled disposal of liquid and solid wastes from industrial, municipal, and agricultural sources.

This environmental situation put pressure on the physiochemical and biological health of surface and groundwater resources, and as a result, water quality became severely deteriorated, exceeding the international norms by many folds. Numerous studies have been conducted to assess water quality and identify pollution sources in Lebanon. However, these studies were often limited to specific pilot regions, particular water systems (*e.g.*, rivers, springs, aquifers), or focused on a single type of contamination (*e.g.*, chemical or biological).

Besides population increase, threatening and exploiting groundwater assets in Lebanon, water quality deterioration is being a vital and alarming trouble that deserves concern. Most water sources in Lebanon (>50%) are contaminated, more significantly the surface water sources. There were many investigations on water quality in Lebanon, wherein most sources displayed unacceptable pollution levels with respect to the international standards. For example, nitrate levels in some wells positioned in the central Bekaa plain surpassed 300 mg/L (Darwish et al., 2008a). While the microbiological tests of the Litani River confirmed a Total Coliform (TC) exceeding 100,000 c/ml and Fecal Streptococcus (FS) of 7000 c/ml in numerous localities. There is likewise the problem of heavy metals' contamination in lots of river sediments, and even in snowpacks, which upon investigation revealed anomalous values (*e.g.*, pH = 7.89; conductivity = 17.76 mS/cm; salinity = 11.22 ppm). Factors behind the quality deterioration in Lebanon's water are two main reasons: the lack of awareness and the shortage of suitable management.

Contamination is a critical threat occurring in groundwater resources in Lebanon. It implies plenty of factors, which include physiochemical and biological contamination, specifically in agricultural areas (Shaban, 2011). In Lebanon, the percentage of agriculture represented 59.5% of the total water demand in 2005 (Website 1). In the absence of plans for irrigation networks, new wells were added to the existing ones in the 1992-1995 period (Aquastat, 2008). Besides, extra fertilizer input and out-of-control disposal of refuse can lead to soil and groundwater contamination with nitrates and heavy metals (Darwish et al., 2005). In Lebanon, the main contaminants from agricultural activities are: 1) Fertilizers that are natural or synthetic substances, such as nitrogen and phosphorus; and 2) Pesticides that are usually toxic chemicals. Most farming practices are poorly controlled since farmers apply high doses of fertilizers and pesticides. Indeed, there are two cases: either fertilizers and pesticides residues enter the groundwater and contaminate it, or they are drained with agricultural runoff, so they flow on the surface and reach the basins directly (MoE, 2001).

The main objective of this study is to assess the impact of agricultural land use on groundwater quality in the lower sub catchment of Tyre region—south Lebanon.

2. Methods and Materials

2.1. Study Area

Our selected study area falls in Tyre district. Selected sites represent Ras El-Ain springs and wells located upstream in 9 surrounding villages of the lower subcatchment area of Ras El-Ain springs. The study sites are Ras El-Ain springs, and artesian wells used mainly for irrigation.

The area surrounding the wells is distinguished by vast fragile land, cultivated with different cultures and orchards. The wells are used mainly for irrigation and sometimes for the surrounding homes as drinking and domestic water.

Ras El-Ain is a place abound with immense springs, reservoirs and aqueducts 6 km south of Tyre, 77 km south of Beirut, in the South Governorate of Lebanon (**Figure 1**). The place lies in a green and fertile plain, about 1 km from the seashore. It is a popular touristic destination, owing to its artesian wells fed by underground springs and collected in stone reservoirs that have been conserved through the ages (Robinson & Smith, 1841). It has been the main source of water for ancient Tyre since the Phoenicians days. One of the reservoirs fed the arched aqueducts in the Roman period, which once stretched all the way to Tyre. Remains of these aqueducts, exhibiting tight and excellent masonry, with round arches and a continuous cornice above them, can still be seen (Robinson & Smith, 1841), and a short stretch of the original aqueduct is still used nowadays in Tyre waterworks.

Ras El-Ain is part of the best-preserved stretches of sandy coastlines in southern Lebanon. It has considerable spectacular and recreational value, and its artesian wells are an important heritage site that give rise to several valuable freshwater habitats. It is part of Tyre Coast Nature Reserve (TCNR), which was decreed in 1998 by the Ministry of Environment. The TCNR is within the best-preserved stretches of sandy coastlines in Lebanon. The terrestrial section is 3.5 km long and covers over 3.8 km^2 and is divided into three zones: Touristic (sandy beach), Conservation (core area), and Agricultural (Ras El-Ain), while the Marine zone's area is 113 km^2 (Yaacoub et al., 2011).

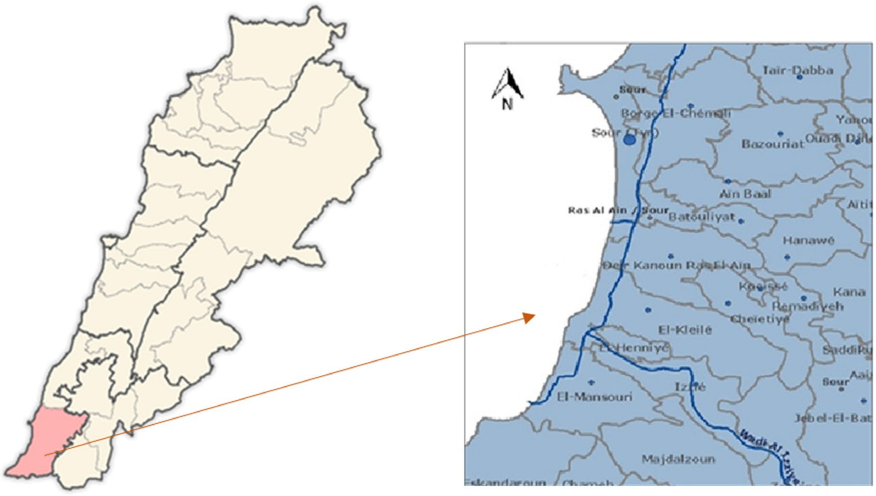

Figure 1. Study area: Ras El-Ain—Tyre district.

Based on a synthesis of regional hydrogeological studies (Shaban, 2020a; UNDP-CEDRO, 2014; Darwish et al., 2008b; Dubertret, 1975), a clear understanding of the flow patterns and recharge mechanisms in the Ras El-Ain area of South Lebanon is critical for assessing the dynamics of groundwater contamination. This coastal region features a complex hydrogeological system dominated by karstified limestone formations, which exhibit high secondary porosity due to extensive fracturing and dissolution. Groundwater in Ras El-Ain predominantly flows along NE-SW trending strike-slip faults and inclined bedding planes that dip westward, enabling lateral subsurface movement from inland recharge zones—such as the Nabatieh Plateau—toward the coastal aquifers. The major fault systems, extending for over 10 kilometers, act as primary conduits for deep groundwater flow, transporting large volumes of water with limited natural filtration. Additionally, direct recharge occurs through fractured carbonate rocks, especially in areas where the overlying soil and vegetation are sparse, allowing precipitation to infiltrate rapidly. However, interbedded marly horizons can locally impede vertical infiltration, resulting in perched water zones. The interplay of karstification, fault-guided flow, and direct recharge increases the aquifer system's vulnerability to contamination. Pollutants from surface sources—such as agricultural runoff, wastewater, or chemical spills—can easily infiltrate through sinkholes, fractures, or unprotected wellheads, quickly reaching the groundwater table and discharging via the Ras El-Ain springs or through submarine groundwater discharge zones along the coastline. Therefore, a comprehensive understanding of the region's hydrogeological setting is essential for effective groundwater protection and sustainable management in this environmentally sensitive area.

2.2. Data and Methodology

The methodology is based on analyzing the impact of land use on water quality. Primary data were collected through direct sampling of water from wells after surveying the farmers. Data collected from farmers included the altitude of the land, depth of water in wells, amount of water pumping, type of cultivation and the fertilizers and pesticides used. The collected data are summarized in the following table (Table 1).

Table 1. Water and land use background data.

Sample	Location	Depth of water	Water pumping	Type of vegetation
Well 1	Abbasieh	40 m	6 inch	Banana, citrus, avocado, Annona
Well 2	Borj Echemali	80 m	6 inch	Banana, citrus
Well 3	Charnay	250 m	5 inch	Citrus, avocado
Well 4	Borj Echemali	250 m	6 inch	Banana, citrus
Well 5	Borj Echemali	250 m	6 inch	Banana, citrus
Well 6	Borj Echmali	250 m	6 inch	Banana, citrus
Well 7	Borj Echmali	250 m	6 inch	Avocado, citrus, Annona, litchi
Well 8	Borj Echemali	140 m	6 inch	Vegetables, banana, orange
Well 9	Bazouriye	450 m	6 inch	Citrus, avocado
Well 10	Bazouriye	200 m	5 inch	Banana
Well 11	Bazouriye	350 m	5 inch	Orange, lemon
Well 12	Bazouriye	160 m	6 inch	Citrus, vegetables
Well 13	Ain Baal	165 m	5 inch	Citrus, vegetables
Well 14	Ain Baal	250 m	6 inch	Citrus, banana
Well 15	Ain Baal	175 m	5 inch	Citrus
Well 16	Batoulay	250 m	6 inch	Citrus, vegetables
Well 17	Deir Qanon	180 m	5 inch	Banana, citrus
Well 18	Deir Qanon	180 m	5 inch	Citrus
Well 19	Deir Qanon	150 m	6 inch	Banana, citrus
Well 20	Qleileh	370 m	4 inch	Avocado, Annona, banana, orange
Well 21	Qleileh	150 m	5 inch	Avocado, Annona, banana, orange
Well 22	Qleileh	100 m	5 inch	Avocado, Annona, banana
Well 23	Qleileh	50 m	4 inch	Banana, citrus
Well 24	Tayr Debba	120 m	5 inch	Avocado, papaya, citrus

Concerning the sampling of water, the location coordinates of each site have been taken with a GPS. We have 24 wells located in villages in Tyre region. Locations of groundwater sample collection points are shown in the map below (Figure 2). The samples were taken from the direct source of water from 24 wells and the 2 springs of Ras El-Ain. The water samples (26 samples) were stored in cool boxes and transported to the laboratory (Doctoral School of Science and Technology at the Lebanese University) for subsequent analyses. At each sampling site, approximately 1000 ml of groundwater was sampled. The following parameters were analyzed in the laboratory: pH, EC, TDS, cations (Mg^{2+}, Ca^{2+}, Na^+, K^+), anions (NO_2^-, NO_3^-, F^-, Br^-, PO_4^{3-}, SO_4^{2-}, Cl^-) and heavy metals (Pb, Mn, Fe, Cu, Zn, Cr). Before conducting any analysis at the laboratory, all samples were filtered through a micro sterilized filter and poured into sterilized flacons.

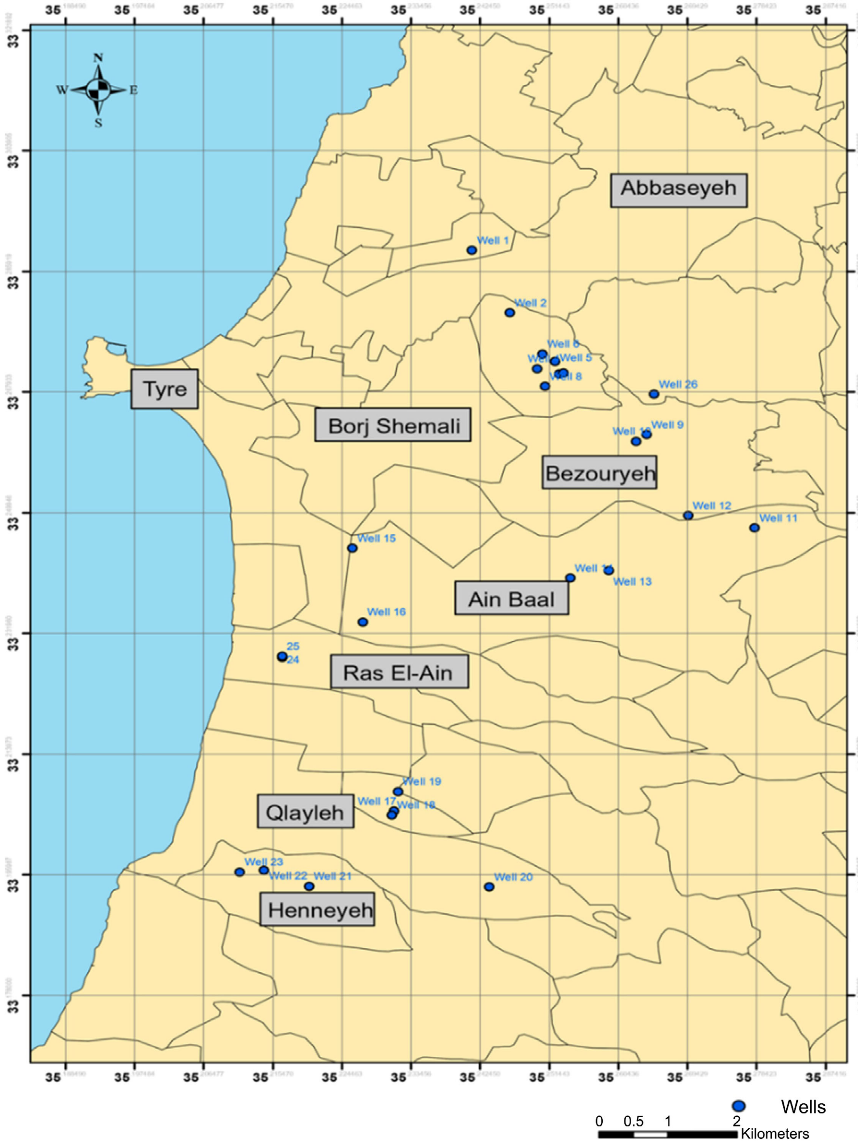

Figure 2. Locations of groundwater sample collection points.

After the analysis of water sampling, the data were re-arranged for necessary statistical analysis using R statistical software. The methods used in the proposed research are described briefly in the following section. Empirical rule was used to assess the quality of groundwater sample data. The empirical rule states that approximately 95% of the measurements are within the interval of mean ± two standard deviation. In the present study, all the groundwater data were found within this limit. A total of six standard water quality indices, namely sodium absorption ratio (SAR), soluble sodium percentage (SSP), total hardness (TH), magnesium adsorption ratio (MAR), Kelly's ratio (KR) and total dissolved solids (TDS) were calculated from groundwater quality data. The following equations were used to calculate various groundwater quality indices:

1) $\text{SAR} = [\text{Na}]/(([\text{Ca}] + [\text{Mg}])/2)^{1/2}$

2) $\text{SSP} = ([\text{Na}] + [\text{K}]) \times 100)/[\text{Ca}] + [\text{Mg}] + [\text{K}]$

3) $\text{TH} = ([\text{Ca}] + [\text{Mg}]) \times 50$

4) $\text{MAR} = ([\text{Mg}] \times 100)/([\text{Ca}] + [\text{Mg}])$

5) $\text{KR} = [\text{Na}]/([\text{Ca}] + [\text{Mg}])$

6) $\text{TDS} = 0.64 \times [\text{EC} \times 10^6\ (\text{mmohs/cm})]$

The aim of these analyses was also to identify the origin of groundwater quality hazards. Furthermore, non-parametric Mann–Whitney test was conducted among the sets of groundwater quality data collected from different land use zones to decipher if there were any differences in groundwater quality due to land use.

3. Results and Discussion

3.1. Physicochemical Analysis

To assess the quality of water, it is critical to study its physicochemical parameters in order to be able to compare the results with standard values. The physicochemical parameters and heavy metals were compared with the WHO and FAO guidelines for drinking and irrigation water respectively. The relationship between the physicochemical parameters and heavy metals in the water samples were established using Pearson product correlation coefficient (r) at 1% level of significance. The mean values of different parameters and heavy metals' concentration is described below.

3.1.1. Conductivity (EC)

The EC values of selected sites are calculated from TDS values. The values were between (246 - 940) ms/cm, which are within the limit of WHO standards (1500 ms/cm) and FAO standards (3000 ms/cm). EC is a good measure of salinity hazard to crops. There is a very strong relationship between conductivity and mineralization (dissolved solids and minerals in water). The values of electrical conductivity of the tested samples are within the limits; therefore, all sites are of low-medium EC level, which is within the good salinity range.

3.1.2. Calcium (Ca^{2+})

The calcium in water samples in all sites ranges between 25.98 and 99.45 mg/L which is within the WHO and FAO limits. Hence, calcium concentration in water is within the desirable ranges in these sites.

3.1.3. Magnesium (Mg^{2+})

The magnesium concentrations in the studied sites range between 6.83 and 26.19

mg/L, it does not exceed the standards. Thus, no magnesium contamination was detected on these sites.

3.1.4. Sodium (Na^+)

The sodium concentrations at the sites do not exceed the limits of WHO and FAO, since their values range between 1.5 and 10.6 mg/L. No contamination by this element, and the water is suitable for irrigation and for drinking.

3.1.5. Potassium (K^+)

The measured values of potassium ranged between 0.06 and 0.43 mg/L, lower than those of the WHO (12 mg/L) and FAO (20 mg/L) drinking water and irrigation water standards. Therefore, potassium content in these sites is within its normal and acceptable limits.

3.1.6. Nitrite (NO_2^-)

The concentrations of nitrite exceeded the drinking and irrigation water limits specified by the WHO and FAO (0.05 mg/L) in the following sites: (1, 2, 3, 4, 6, 8, 10, 11, 12, 13, 14, 17, 19, 20, 21, 22, 24, and 25; Figure 3). Only two wells (20 and 23) had low amounts of nitrite (0.005 mg/L), while well 12 had the highest concentration (0.453 mg/L). High nitrite concentration in most of the studied sites proves the high use of nitrogen fertilizers, referring to agricultural land use.

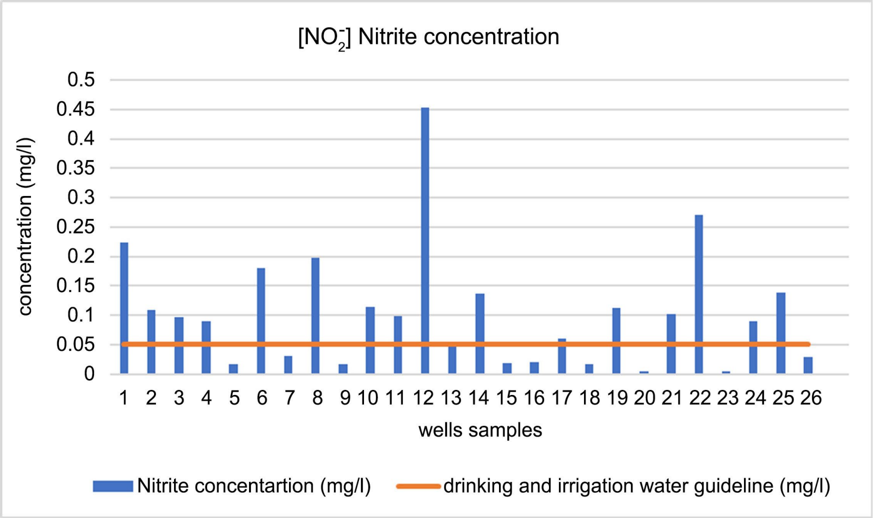

Figure 3. Concentration of nitrite in the studied wells.

3.1.7. Nitrate (NO_3^-)

The concentrations of nitrate in the studied wells show that only site 1 exceeds the limits of both WHO (40 mg/L) and FAO (70 mg/L) with a concentration of 75 mg/L, while sites 20 (2.33 mg/L) and 21 (1.01 mg/L) show the lowest nitrate concentrations. Site 23 (44.63 mg/L) exceeds the WHO limit for drinking water. The remaining sites comply with both guidelines, including Ras El-Ain sites (Figure 4). High nitrate concentrations in the majority of the sites also confirm their location in agricultural fields, and in turn their source from the excess use of nitrogen fertilizers associated with the agricultural land use.

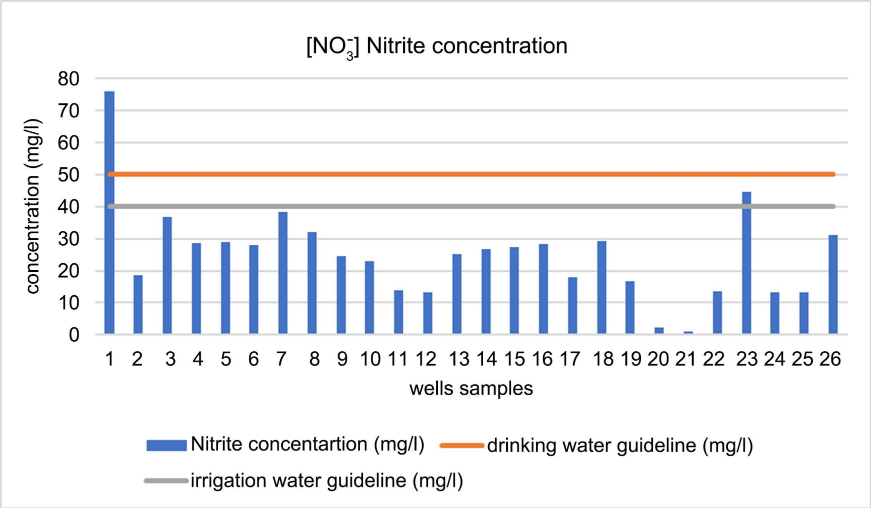

Figure 4. Concentrations of nitrate in the wells studied.

Concerning other anions, no contamination by orthophosphate, sulfate, chloride or fluoride were detected in these sites.

3.1.8. Heavy Metals

The results showed that the heavy metals studied had very low or undetectable concentrations. These results are mainly attributed to the location of the study area far from the main influencers of such pollutants in groundwater such as dumpsites, industrial effluents, sewage water, *etc*.

3.2. Statistical Analysis of Groundwater Quality Indices

The water quality indices were calculated at all 26 sampling locations. Obtained results are summarized in Table 2.

Table 2. Summary of groundwater quality at 26 locations of Ras El-Ain subcatchment area.

Parameter	Min (mg/L)	MAX (mg/L)	MEAN (mg/L)	Std. dev (mg/L)
SSP	1.87	22.53	5.18	4.84
TH	1640.50	5785.50	3343.50	1019.43
MAR	12.08	34.84	21.35	4.85
KR	0.02	0.28	0.05	0.06
TDS	132.00	470.00	173.00	85.08
SAR	0.18	0.75	0.33	0.13

It was found that the average TH in the groundwater is very high. Some of other indices like TDS were also comparatively high in Ras El-Ain. The box plots of different groundwater quality indices are shown in Figure 5.

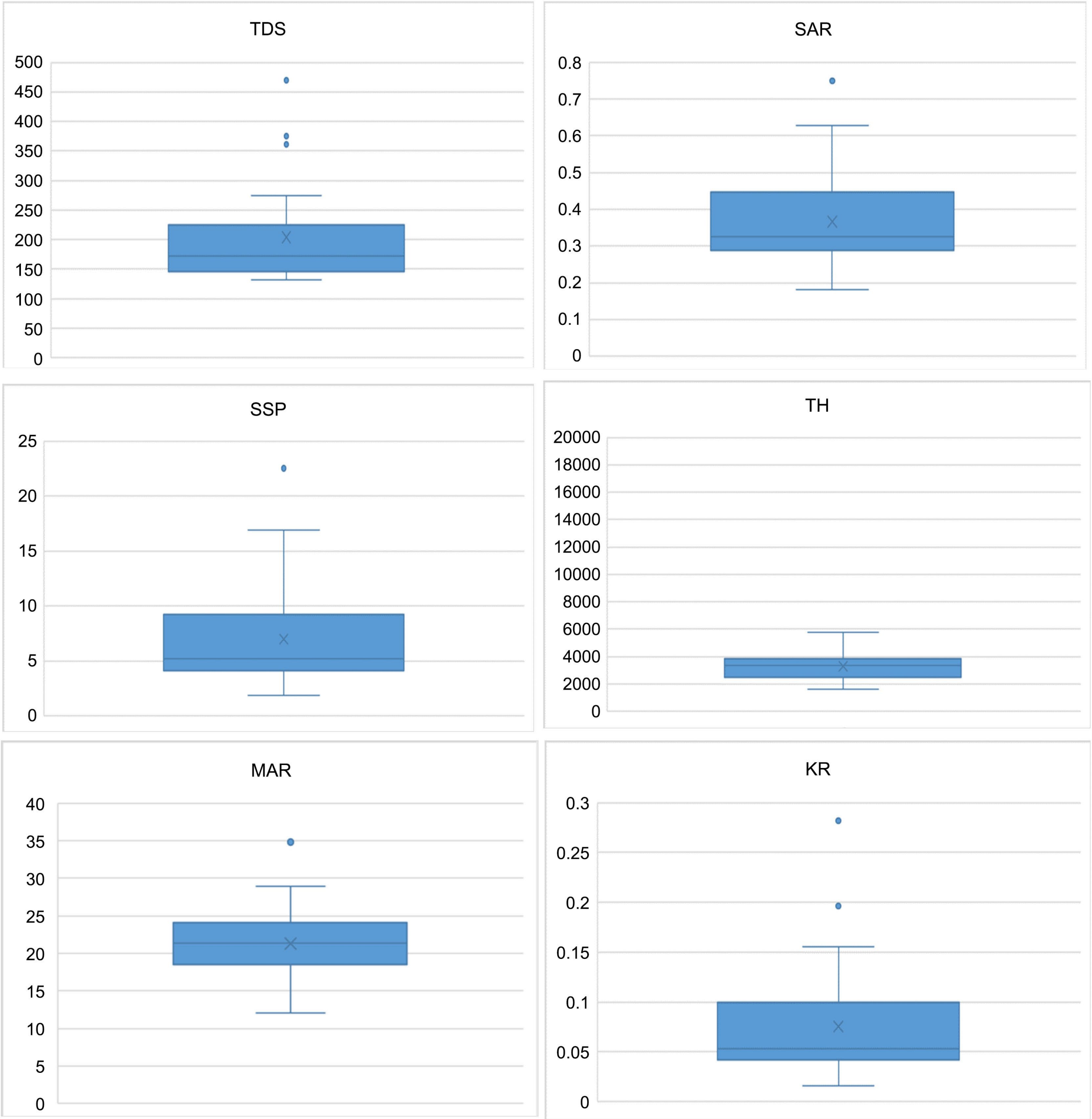

Figure 5. Box plots of different groundwater quality indices in the study area.

The box plots in the figure show a number of outliers in the positive direction for indices like TDS, SAR, MAR and KR. This indicates extreme values of these indices in specific locations. As the higher value of an index represents corresponding quality hazard, extreme values of these indices mean the presence of corresponding groundwater quality hazards in some locations of Ras El-Ain.

3.3. Multiple Regression and Correlation Analysis

The objective of this analysis is to make the diagnosis of the typology of the water of 26 sites through the physicochemical parameters by the principal component analysis and identify the most polluted site/s.

Principal Component Analysis (PCA) is a multivariate analysis method that aims to reduce the data from the higher dimensions to lower dimensional space without losing much information. The approach of PCA is to reduce the unnecessary features, which are presented in the data and is creating or deriving new dimensions (or also referred to as components). These components are a linear combination of the original variables. This way, PCA converts a larger number of correlated variables (i.e., breaks down the data) into a smaller set of uncorrelated variables. The principal component of a data set is the direction with the largest variance.

Based on Figure 6 & Figure 7, Axis 1 explains 29.3% of the total variation, it shows a positive correlation with SO_4^{2-} (r = 0.85), Na^+ (r = 0.85), Cl^- (r = 0.83), K^+ (r = 0.78), EC (r = 0.75) and Br^- (r = 0.67). Axis 2 explains 21.8% of the total variation, it is positively correlated with F^- (r = 0.86), Zn (r = 0.86), Mn (r = 0.73), and negatively correlated with NO_3^- (r = −0.67). Moreover, Axis 3 explains 10.2% of the total variation, it is negatively correlated with NO_2^- (r = −0.79) and positively correlated with PO_4^{3-} (r = +0.70).

Concerning the correlation between variables, the correlation circle visualizes graphically what we have already concluded: SO_4^{2-}, Na^+, Cl^-, K^+, and Br^- are closely correlated and represent the axis 1 of this positive side with EC and Cl^-, which are also correlated. Component 2 is mainly represented by F^- and Zn on its positive side which are strongly correlated. However, it is represented with NO_3^- on its negative side. The component 3 is mainly represented by PO_4^{3-} and Zn on its positive side and with NO_2^- on its negative side.

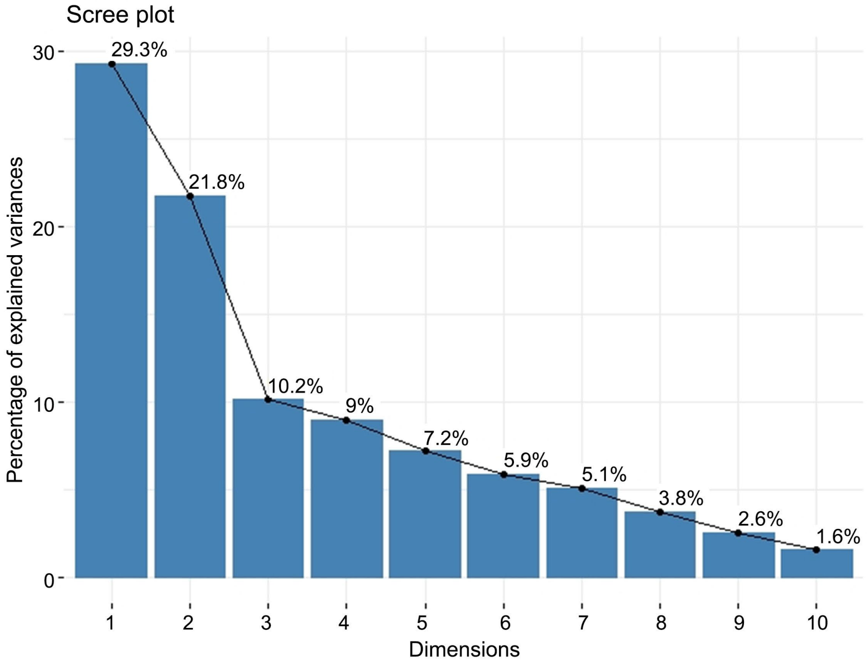

Figure 6. PCA results using R software.

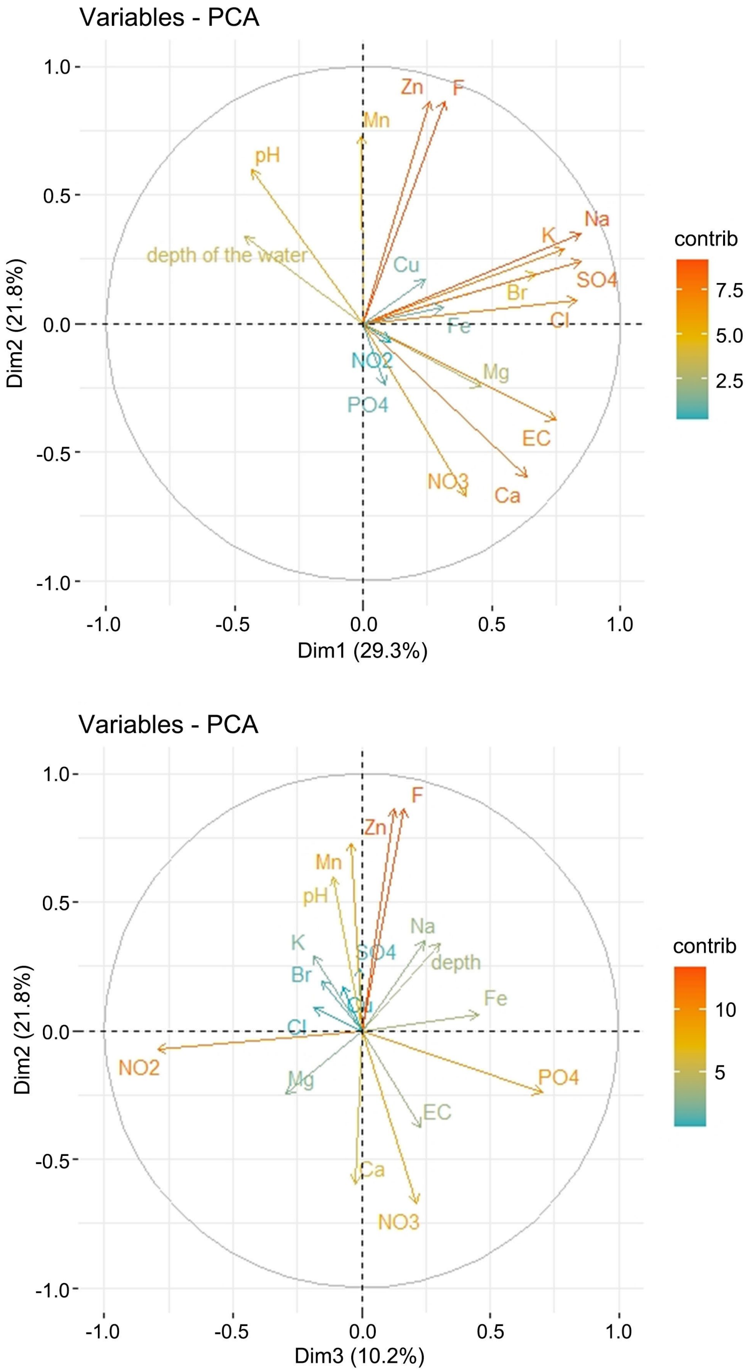

Figure 7. PCA Correlation circle axe 1 and 2 & 2 and 3.

	TDS	Na^+	Br^-	Ca^{2+}	Cl^-	F^-	K^+	Mg^{2+}	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Cu	Fe	Mn	Zn
TDS	1.000															
Na^+	0.572	1.000														
Br^-	0.277	0.680	1.000													
Ca^{2+}	0.693	0.299	0.124	1.000												
Cl^-	0.558	0.742	0.883	0.382	1.000											

Continued

F^-	−0.073	0.621	0.241	−0.258	0.216	1.000										
K^+	0.393	0.604	0.385	0.410	0.543	0.491	1.000									
Mg^{2+}	0.207	0.219	0.511	0.516	0.515	−0.120	0.250	1.000								
NO_2^-	−0.060	−0.139	0.156	0.000	0.166	−0.148	0.267	−0.005	1.000							
NO_3^-	0.623	0.134	−0.108	0.720	0.125	−0.394	0.224	0.190	−0.038	1.000						
PO_4^{3-}	0.254	0.172	0.087	0.077	−0.056	−0.120	−0.149	−0.143	−0.338	0.241	1.000					
SO_4^{2-}	0.537	0.735	0.445	0.381	0.589	0.499	0.920	0.217	0.181	0.342	−0.052	1.000				
Cu	0.246	0.357	0.146	0.046	0.157	0.133	0.230	−0.271	0.192	−0.006	0.204	0.173	1.000			
Fe	0.236	0.304	0.249	0.101	0.277	0.185	0.144	0.020	−0.299	0.065	0.183	0.222	−0.276	1.000		
Mn	−0.204	0.165	0.051	−0.311	0.059	0.549	0.231	−0.114	−0.138	−0.404	−0.240	0.102	0.189	0.092	1.000	
Zn	−0.108	0.542	0.187	−0.321	0.128	0.944	0.494	−0.161	−0.101	−0.454	−0.114	0.508	0.132	0.052	0.501	1.000

Additionally, the correlation matrix revealed several moderate negative correlations that provide important insights into groundwater quality dynamics in the study area. A significant inverse relationship was observed between TDS/EC and pH ($r = -0.50$), as well as Ca^{2+} and pH ($r = -0.53$), suggesting that increased mineralization and calcium concentrations are generally associated with more acidic conditions. This may reflect the dissolution of carbonate minerals or the influence of acidic contaminants such as nitrates. Similarly, nitrate (NO_3^-) showed a negative correlation with pH ($r = -0.49$), Mn ($r = -0.40$), and Zn ($r = -0.45$), indicating that higher nitrate concentrations could be linked to slightly lower pH and increased mobility of trace metals, possibly due to redox-sensitive processes or anthropogenic inputs like fertilizers. Additionally, Ca^{2+} and TDS/EC both showed a moderate negative correlation with well depth ($r = -0.56$ and -0.44, respectively), implying that shallow aquifers are more affected by surface-derived inputs and are more mineralized, possibly due to intensive agricultural activity and direct recharge in karstic zones. These findings highlight the hydrogeochemical sensitivity of the Ras El-Ain aquifer system, especially under agricultural land use pressures (Figure 7, Figure 8).

According to Figure 8, we notice that site 1 has a very high contribution (24.40); it influences the most axis 1, besides site 22 and 23 (18.09, and 13.23 respectively) and site 2 (10.57). Sites 20 and 21 influence the most axis 2 since they have the greater contribution (39.62 and 28.21 respectively) beside site 1 which has a limited impact on this component (8.20). Moreover, the site 12 influences the most axis 3 (21.05), followed by site 26 (20.87) and site 22 (16.05).

3.4. Discussion

The aim of this research was to study and analyze the impact of agricultural land use, specifically the application of fertilizers and agro-chemicals on the groundwater quality in the sub-catchment area of Ras El-Ain springs and the surrounding villages in Tyre region. Ras El-Ain springs make up part of Tyre Coast Nature Reserve (TCNR), the reason behind the choice to study a substantial site belonging to a protected area. Indeed, and based on this research, Ras El-Ain is the main water source in the area, providing the whole city of Tyre and its suburbs with domestic water. In addition, this source is to be an irrigation source for the entire Ras El-Ain agricultural lands, and the remaining part flows out into the sea, making an estuary and enriching the marine ecosystem with biodiversity. The rest of the sites are wells upstream Ras El-Ain, in the lower sub-catchment basin of the springs.

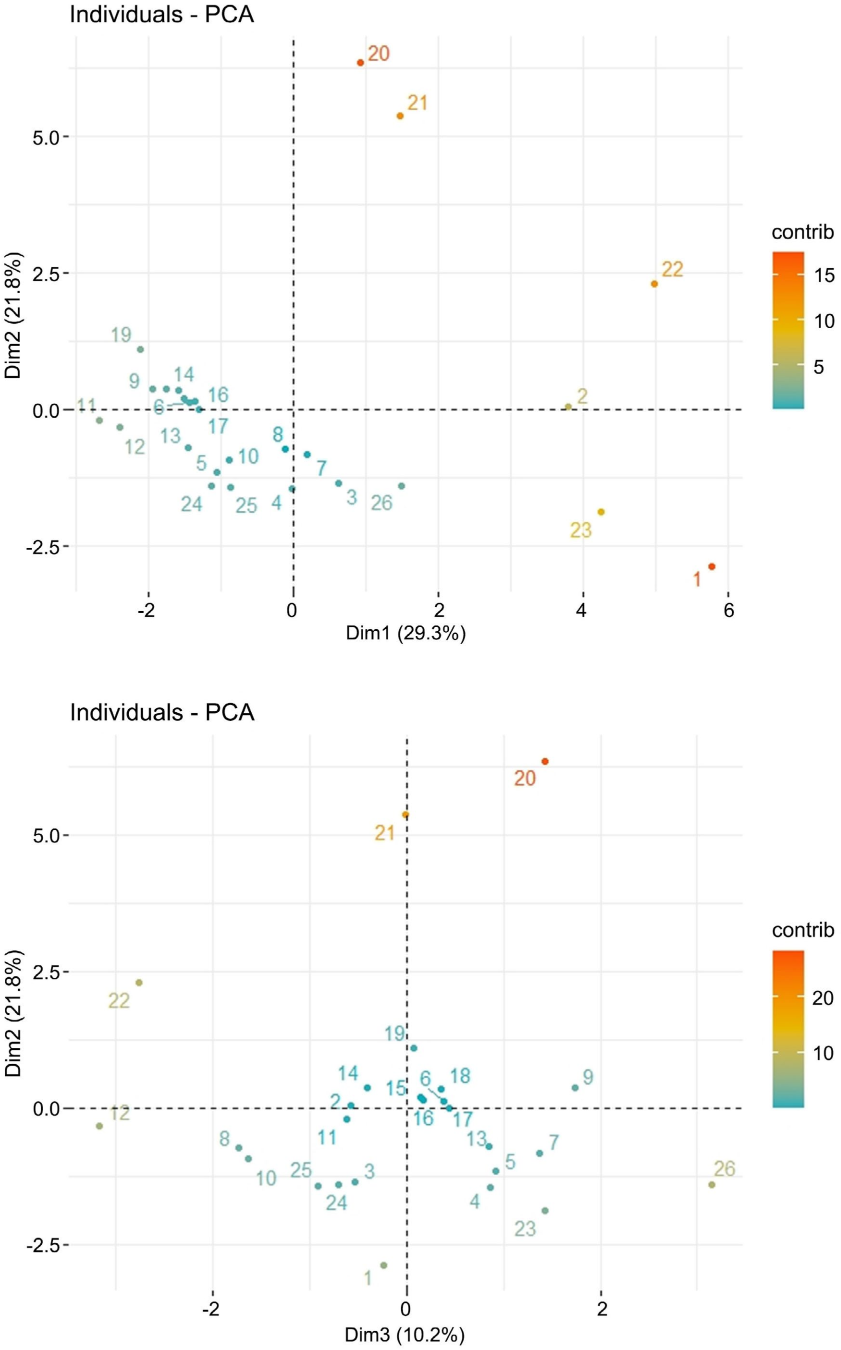

Figure 8. PCA individuals plot axes 1 and 2 & 1 and 3.

Table 3. Hydro-geological data of the sites.

Well #	Location	Depth of water	Rock exposure	Aquifer	Feeding zone	Remarks
Well 1	Abbasieh	40 m	Quaternary deposits (Q)	Quaternary Aquifer	Chabriha-Hamadieh and the surrounding	Unconsolidated sediments with permeable and porous zones due to faults intersection
Well 2	Borj Elchmali	80 m	Eocene Limestone (E)	Upper Eocene Aquifer	Ain Aoukali-Ain Al Qouahch-Khallet Etabel, Charniye, Tell ElQadi, Jouret Ezaitouni	Recharge from fractured carbonate rocks which are interbedded with marly horizons
Well 3	Charnay	250 m		Middle Eocene Aquifer		
Well 4	Borj Elchmali	250 m				
Well 5	Borj Elchmali	250 m				
Well 6	Borj Elchmali	250 m				
Well 7	Borj Elchmali	250 m				
Well 8	Borj Elchmali	140 m		Upper Eocene Aquifer		
Well 9	Bazouriye	450 m	Eocene Limestone (E)	Lower Eocene Aquifer	Daher El Hwar-Ma'arake and the surrounding	Groundwater flow along fault (5 km NE)
Well 10	Bazouriye	200 m	Eocene Limestone (E)	Upper Eocene Aquifer	Bir El Roujname and the surrounding	
Well 11	Bazouriye	350 m		Lower Eocene Aquifer	Aitit-Jabal Azzitoun the surrounding	
Well 12	Bazouriye	160 m	Senonian Marl (C_6)	Contact between E and C_6	Jbal Al Amoud-Wadi Ejilo-Ain Ba'al	Recharge from fractured carbonate rocks which are interbedded with marly horizons
Well 13	Ain Baal	165 m			Ain Ba'al-Jbal Al Amoud	
Well 14	Ain Baal	250 m	Eocene Limestone (E)	Middle Eocene Aquifer	Ain Ba'al and the surrounding	
Well 15	Ain Baal	175 m		Upper Eocene Aquifer	The area between Ain Ba'al and Batoyuay	
Well 16	Batoulay	250 m		Middle Eocene Aquifer	Batoyuay-Esemakieh and the surrounding	
Well 17	Deir Qanoun	180 m	Eocene Limestone (E)	Upper Eocene Aquifer	Malkiet Es Sahel Kniessh and the surounding	
Well 18	Deir Qanoun	180 m				
Well 19	Deir Qanoun	150 m				
Well 20	Qleileh	370 m		Lower Eocene Aquifer	Jouiya-Qala'at Echabike	Groundwater flow along fault (12 km NE)
Well 21	Qleileh	150 m		Upper Eocene Aquifer	Qleileh-Mazra't Nabi Amran	Recharge from fractured carbonate rocks which are interbedded with marly horizons
Well 22	Qleileh	100 m			To the southwest of Qleileh	
Well 23	Qleileh	50 m	Quaternary deposits (Q)	Quaternary Aquifer	Boustan Jouret Ettannout	Unconsolidated sediments
Site 24	Ras El-Ain 1	Spring		Cenomanian Aquifer	Nabatieh Plateau (El-Kfour-En-Nmayrieh-Ed-Douier-Insar)	Groundwater flow along a major fault system (exceeding 22 km NE)
Site 25	Ras El-Ain 2	Spring				
Well 26	Tayr Debba	120 m		Upper Eocene Aquifer	Wadi Es-Souida	Recharge from the valley sediments into the carbonate rocks

Based on the above, and concerning the wells water, wells for groundwater abstraction are tremendous in the coastal plain and in the foot slopes of the adjacent mountains. They are used mainly for agricultural purposes, and are almost shallow in depth, and this is the reason for their various distribution which is estimated at more than 1000 wells/km^2. The shallow wells are mainly dug in the Quaternary rock formation with less than 50 m depth from terrain surface. As for the higher altitudes in the mountainous region, groundwater is stored in the rocky lithology at exceeded depths. The current field survey has been carried out to investigate water quality in the coastal plain and the surroundings. Therefore, samples were selected from 24 wells and two from Ras El-Ain Springs (**Table 3**).

Based on the detailed geological survey data of the wells and springs examined, the distribution of wells across different aquiferous rock formations is as follows:

- Quaternary = 2;
- Upper Eocene = 10;
- Middle Eocene = 7;
- Lower Eocene = 3;
- Contact between Lower Eocene/Cenomanian = 2;
- Cenomanian = 2.

The majority of surveyed wells are located within the Upper and Middle Eocene aquiferous rock formations, primarily composed of marly limestone. The depth to the water surface in the wells of the Upper Eocene Aquifer ranges between 80 meters and 200 meters, whereas it is approximately 250 meters for the Middle Eocene aquiferous rock formation. The primary sources of water feeding these wells can be categorized as follows:

- Unconsolidated sediments of alluvial and fluvial deposits with rock mixtures; therefore, permeable and porous zones are created. This is found mainly in the Quaternary Deposits Aquifer with shallow and limited (intermittent) groundwater storage.
- Direct recharge from fractured carbonate rocks which are interbedded with marly horizons that result with impermeable layers and then restrict the vertical movement of groundwater. This is almost found in the Upper and Middle layers of the Eocene Aquifer and sometime with the Lower layers of this formation, with limited to moderate groundwater storage. However, when water percolation through the fractured carbonate rocks reaches groundwater, it affects its quality by increasing its carbonate and other elements' content.
- Groundwater flows along faults that extend a few kilometers away from the location of the investigated wells. This is mainly the case of the Lower Eocene Aquifer and any other well dug into the Cenomanian Aquifer (not surveyed). Therefore, groundwater storage of this mechanism is often characterized by considerable volume of groundwater. **Figure 9** shows an example where groundwater flows along a fault alignment from a distance near Maarake region to the Lower Eocene Aquifer in well number 9.
- Groundwater flows along a major (almost exceeding 10 km) fault, usually transporting groundwater from the deep aquifers of the Nabatieh Plateau. This is a

well pronounced hydrogeological phenomenon in Southern Lebanon where strike-slip faults are trending in the NE-SW direction and groundwater seeps along these faults (with high permeability and porosity of faults' alignment), as well as along the inclined bedding planes which trend mainly to the west. Figure 10 shows an example of this phenomenon, where groundwater of Ras El-Ain Springs mainly seeps along faults extending from the Nabatieh Plateau to the coastal zone, and sometimes they extend to the littoral zone where submarine groundwater discharges (submarine springs) exist (Shaban, 2020b). Karstification, as the dissolution of carbonate rock, is another hydro-structure phenomenon which dominantly occurs in the limestone rocks in the area, and it is increased where the dolomite content exists with the limestone strata. Therefore, the karstified rocks show a number of carbonate dissolution aspects.

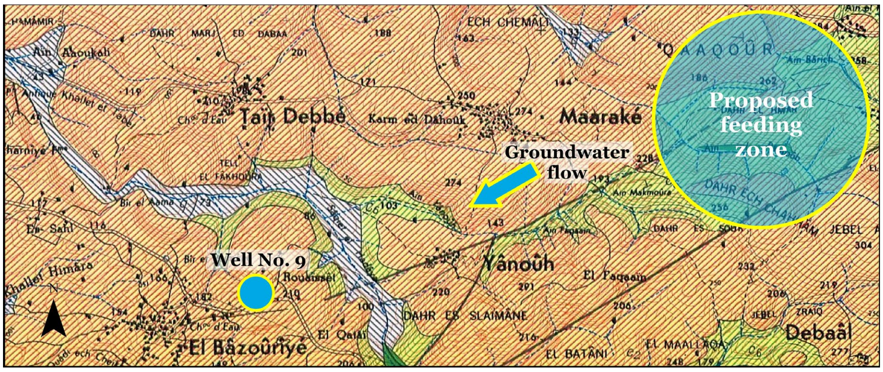

Figure 9. Example showing the flow of groundwater from a feed zone at a range from the source of groundwater (dug well).

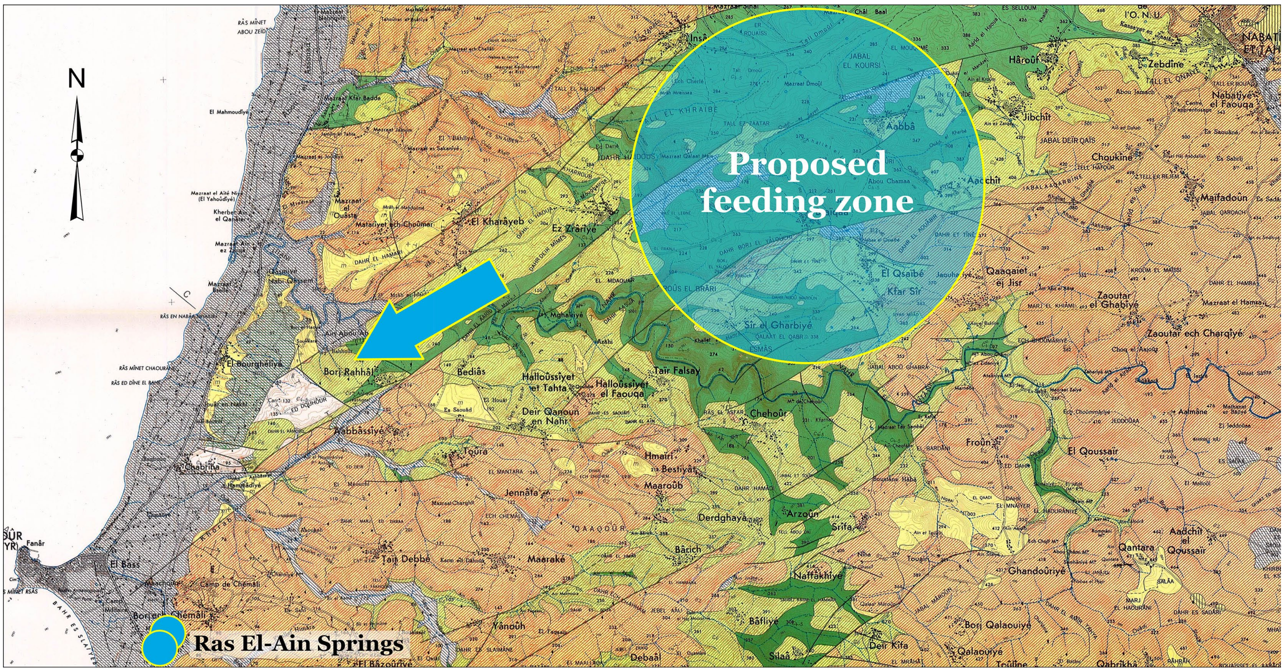

Figure 10. Example showing the flow of groundwater from a feed zone (Nabatieh Plateau) to the coastal zone where it is diffused and discharged at Ras El-Ain Springs.

The evaluation of the groundwater quality was based on the evaluation of water physio-chemical parameters (pH, EC and TDS) of the samples, their content of anions (NO_2^-, NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, Br^- and F^-), cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), and heavy metals (Pb, Cu, Cr, Fe, Mn, Zn).

The physical analysis of water shows that acceptable ranges of pH, electrical conductivity (EC) and (TDS), which are conform with the guidelines of WHO and FAO in all sites. Based on EC and TDS values, we concluded that water is not saline, and the water is acceptable at all sites for irrigation. pH values are also within the acceptable ranges of the WHO and FAO (slightly alkaline), except for sites (16), (18), (19) and (20) that exceeded those limits.

The chemical analysis of water shows that agro-chemicals' contamination was detectable in 17 sites with Nitrite (NO_2^-) including Ras El-Ain springs, in addition to two sites contaminated with Nitrate (NO_3^-). 15 sites indicated moderate contamination with bromide, and 2 sites only showed moderate contamination with fluoride.

No contamination with any other agro-chemical anions and cations, nor with any of the heavy metals was detected at any of the analyzed sites.

The main cause of pollution is clearly attributed to the intensive use of fertilizers as an important input in agricultural practices, especially nitrogen fertilizers that show in the form of nitrite and nitrate water content exceeding the acceptable FAO &/or WHO limits.

If we coincide these results of active individuals with the results of the active variables, we observe:

- Site 1 is located on the positive side of axis 1 far from the center; so, we conclude that it has the highest concentrations of NO_3^-, Ca^{2+}, SO_4^{2-} and the highest value of EC. Second comes site 23 which has a high concentration of NO_3^-, Ca^{2+}, Cl^-, Mg^{2+} and a high value of EC; then we observe site 22 which has the highest concentrations of Br^-, Cl^- and a high concentration of SO_4^{2-}.
- Sites 20, 21 are on the positive side of axis 2 far from the center, which indicates that they have the highest concentrations of F^-, Zn, and Mn but the lowest concentrations of NO_3^- since their location is opposite to this variable.
- Sites 12 and 22 are in the negative side of axis 3, hence they are characterized by the high concentration of NO_2^- and the lowest concentration of PO_4^{3-} (concentration null) since they are located to the opposite side of the impact of this variable (**Figure 11**).

Although detailed records of site-specific fertilizer and pesticide application rates were not available during this study, existing literature and national assessments provide insights into typical usage patterns under similar agro-climatic and cropping conditions in Lebanon. According to the FAO and the Ministry of Agriculture of Lebanon, nitrogen-based fertilizers (urea and ammonium nitrate) are commonly used at rates ranging from 120 - 200 kg/ha/year in intensive vegetable and cereal production systems, particularly in the southern Bekaa and South Lebanon regions (FAO, 2016; MoA & FAO, 2014). Similarly, pesticide application—

including insecticides, herbicides, and fungicides—can reach up to 20 - 30 kg of active ingredient per hectare per year, especially in open-field vegetables and citrus crops, which are prevalent in the Ras El-Ain sub-catchment.

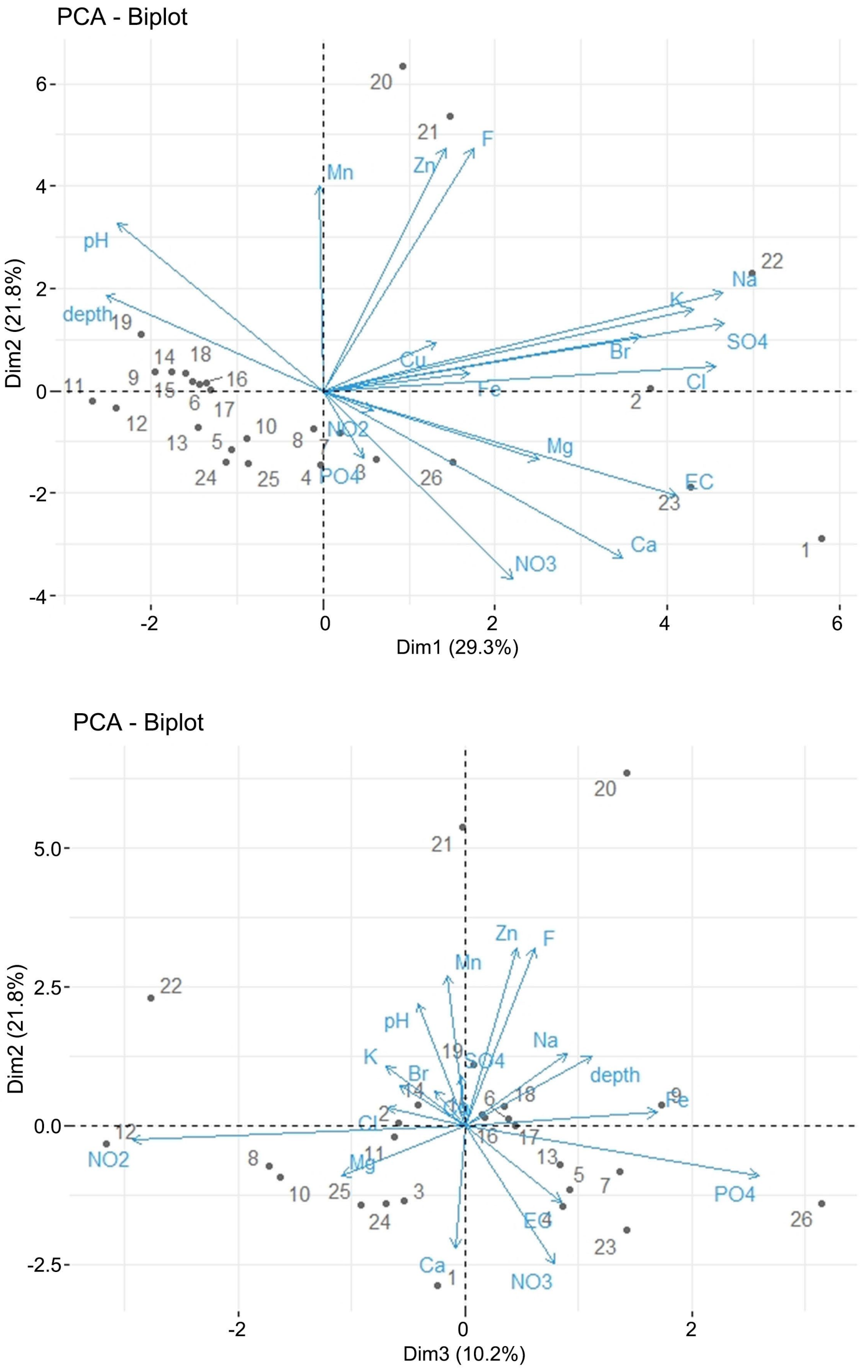

Figure 11. PCA biplot axes 1 and 2, 2 and 3.

The lack of precise regulation and monitoring of chemical inputs in many smallholder systems contributes to over-application and misuse, often exceeding recommended dosages (Saadeh et al., 2012). This significantly increases the risk of nitrate leaching, heavy metal accumulation, and pesticide residues in shallow groundwater, especially in karstic and fractured aquifer systems such as those in Ras El-Ain, where percolation can be rapid and direct.

Therefore, even in the absence of measured input rates, the known intensity of agricultural practices in the region—combined with the hydrogeological vulnerability—strongly supports the observed correlation between land use and groundwater contamination.

4. Conclusion and Recommendations

In this study, we presented the hydrogeological background of the area under study. We sampled and analyzed water taken from 24 well sites with dominant agricultural land use for irrigation purposes, in addition to the two springs of Ras El-Ain. These chosen sites are of particular importance due to the extensive anthropological agricultural practices.

The presence of high concentration of nitrite at Ras El-Ain springs alerted the need for agricultural paradigm shift towards more sustainable practices, especially since they fell within a nature reserve with distinguished ecosystems rich in biodiversity. Furthermore, due to the toxicity of this element and the risks it has to human health, it should be prohibited to use this water source for drinking and restrict its use for irrigation. However, it is expected that water resources will continue to be threatened over the next decade, which is why the conservation and sustainable management of all water sources, including the remarkable Ras-El-Ain springs, deserves our utmost efforts by constituting a model for sustainable watershed and natural resources management. This site, in addition to the whole groundwater resources, deserves to be protected and restored to ensure their sustainability.

The absence of heavy metals from all the analyzed water samples reflected the fact that no source of leachates leading to this type of contamination existed in the area, like dumpsites, sewage or industrial effluents.

The PCA statistical analysis aimed to reduce the data from higher dimensions to lower-dimensional space while preserving essential information. The results indicated that sites 1, 12, 20, and 22 are the most contaminated with nitrate, nitrite, fluoride, and bromide. Additionally, the analysis revealed a negative correlation between water depth and both EC and Ca^{2+}, with a weak negative correlation with other parameters. This suggests that the concentration of dissolved minerals and chemicals decreases with increasing depth in aquifers, supporting the inference of anthropogenic influence on these parameters through agricultural land use. To enhance the quality of Ras El-Ain's water and the studied sub-catchment, it is imperative to increase awareness among local communities about the challenges affecting water resources and the necessity of conservation for sustaining their livelihoods. Additionally, reducing the use of pesticides and fertilizers through scientific and vocational support provided to local farmers, coupled with stringent law enforcement, is essential for preserving water quality. Furthermore, raising awareness about the risks associated with excessive use of fertilizers and pesticides and providing best practices guidelines regarding these agro-chemicals, including the appropriate amounts, types, and timing for optimal crop production and ecological conservation, is crucial.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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