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Assessment of Groundwater Quality through Hydrochemistry Using Principal Components Analysis (PCA) and Water Quality Index (WQI) in Kızılırmak Delta, Turkey

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Abstract: This study aimed to characterize the chemical composition and spatial distribution of groundwater in the Kızılırmak Delta of Turkey and to evaluate the suitability of groundwater in the Kızılırmak Delta for drinking water use through a Water Quality Index (WQI) assessment. Eleven water parameters, including nitrate (NO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), chloride (Cl^-), potassium (K^+), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), hardness (measured as $CaCO_3$), electrical conductivity (EC), and pH were analyzed to determine the water quality of each groundwater sample. The WQI was determined using the weighted arithmetic index method and the method specified by the Canadian Council of Ministers of the Environment (CCME). The spatial distribution of the result for all observation wells was plotted. Principal Component Analysis (PCA) was generated utilizing the analytical data from eleven selected samples. As a result of the study, according to the calculated WQI values, the water in most of the wells was not suitable for drinking purposes. The minimum Ca^{2+} concentration in the study area was 108,817 mg/L, and the maximum was 692,382 mg/L, which showed that the samples in all wells exceeded the WHO limit. The same situation is valid for Mg^{2+}, and the values vary between 100.383 and 5183.026 mg/L. From the spatial distribution of the water quality parameters it has been understood that the eastern part of the region is more suitable than the western part for drinking purposes. The results from correlation analysis showed the strongest positive correlation between Mg^{2+} and Na^+ and Na^+ and EC as 0.989. The present study shows that the groundwater of the delta, which has deteriorating water quality, should be treated before it is used for drinking water and protected from contamination hazards.

Keywords: groundwater quality; hydrogeochemistry; Water Quality Index (WQI); principal component analysis

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1. Introduction

Natural resources are indispensable for a country's development in every sense, and groundwater has a significant place among these resources regarding the water budget. Agricultural activities, the most essential tool for growth in many countries, lead to rapid pollution and even groundwater consumption [1,2]. Due to the gradual decrease in the availability and quality of groundwater resources recently, regular observation and hydrochemical evaluation of groundwater quality is necessary for sustainable development and strategic planning under this semi-confined aquifer.

Nowadays, stress on groundwater is increasing for many reasons, the most important of which are rapid population growth, unplanned industrialization, climate change, and climate variability. Groundwater sources are endangered by overuse, pollution, and inadequate development. This issue is more noticeable in regions where surface water sources are under stress and surface groundwater is used simultaneously [3,4]. For instance, water-intensive agricultural practices exist [5,6] water demand is rising [7], and surface water pollution is common in residential areas with inadequate water supply systems [8]. When groundwater is polluted, restoring and maintaining proper quality by removing contaminants from the source to protect public health and the environment is challenging. Therefore, it becomes necessary to regularly monitor groundwater quality and find ways to defend it from pollution [9].

Various natural and human-induced factors can detrimentally impact groundwater quality by introducing metals and nutrients. Natural sources of contamination include geothermal systems [10] and geological formations [11], while human activities such as mining, agriculture, and industrial or urban pollution also contribute to groundwater pollution [12]. Geogenic pollutants in groundwater primarily originate from natural geological processes such as the weathering of rocks and minerals, leaching of trace elements from soil and sediment, and interactions between water and geological formations [13]. Examples of geogenic pollutants include heavy metals like arsenic, lead, mercury, and fluoride; salts and ions like chloride, sulfate, and bicarbonate; hydrocarbons such as methane and petroleum compounds; and radionuclides such as radium and uranium, which can naturally occur in geological formations and be dissolved into groundwater [14]. The hydrochemical composition of groundwater is influenced by chemical interactions between water and minerals along its flow path, the mixing of different water sources, the chemical properties of recharged water, and the geochemical characteristics of the surrounding formations. These processes involve complex interactions between water and the geological materials through which it passes, shaping the overall chemical composition of groundwater [15]. These geogenic pollutants can pose risks to human health and the environment if present in groundwater at elevated concentrations [16].

Nowadays, hydrogeochemical processes have garnered increased attention [17] due to their valuable insights into the interaction between groundwater and the environment. The groundwater's hydrochemical properties, including both anions and cations, are predominantly dictated by the surrounding area's geology and the aquifer's characteristics [18,19]. Anions such as chloride (Cl^-), sulfate ($SO_4{}^{2-}$), and bicarbonate ($HCO_3{}^-$) may derive from the dissolution of minerals rich in these ions, such as halite, gypsum, and calcite, respectively. Similarly, cations such as Ca^{2+}, magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) are released into groundwater through the weathering and dissolution of minerals containing these elements, such as calcite, dolomite, feldspar, and mica [20]. These geogenic processes play a fundamental role in shaping the hydrochemical composition of groundwater.

In recent years, many researchers have paid great attention to studies on groundwater quality. An evaluation of the aquifer water quality due to seawater intrusion in the coastal region of the current study area was previously carried out by Fırat Ersoy et al. [21] and classified as non-consumable based on the groundwater permeability index, sodium adsorption rate, Na%, and Kelly Ratio (KR) values. Karakuş [22] studied the water quality of the Kızılırmak River and stated that portions near the Sivas city center and in the south of the province did not meet the standards for drinking water purposes. Samsunlu et al. [23] comparatively investigated the past and present status of the water quality of the Kızılırmak Delta. Demirci et al. [24] investigated the spatial distribution of saltwater intrusion on the northeastern coast of the Kızılırmak Delta.

Water quality management only readily provides an accurate overview of temporal and spatial trends in the global water quality in an aquifer, except for a few attempts to establish a comprehensive methodology that significantly consolidates data sources and makes them practical information. The WQI is a widely accepted indicator of water resource management and the quality assignment and classification of ground and surface waters [25,26]. Furthermore, the WQI combines the chemical and physical factors used to measure water quality into a single parameter [27,28]. The WQI was first developed by

Horton [29] based on a weighted arithmetical calculation. Afterward, other WQIs were created, such as the Oregon WQI [30], the Canadian WQI [31], the National Sanitation Foundation WQI [32], and the Weighted Arithmetic WQI Method (WAWQI) [33]. Combining the WQI with the Geographical Information System (GIS) to illustrate spatial variation in water quality and identify vulnerable sites assists in decision-making for sustainable groundwater management [34]. To demonstrate that groundwater is suitable for drinking, a WQI is utilized [34–38].

The simplicity of the computation and utilization of water quality indices such as the WQI has led to their widespread application in evaluating groundwater quality across a broad spectrum of landscapes and land use patterns. However, this method is a dimensionless numerical value that gives accurate results depending on multiple WQ parameters in more than one location. Many researchers [28,36,38] developed various WQI models based on the weighting and rating of different water quality parameters derived from the weighted arithmetic method. In recent years, groundwater quality assessment and monitoring have been done using the GIS and interpolation methods. It has proven a powerful tool for evaluating and analyzing spatial information in water resources [2,39]. Rabeiy [40] evaluated the quality of 812 groundwater samples from the central region of Upper Egypt (Sohag Governorate) regarding drinking and irrigation. The WQI converted the water parameter into a single indicator value representing the water quality level. The spatial distribution of the estimated values of each groundwater parameter is spatially modeled using the GIS. In the study by Singh and Noori [41] on 35 groundwater samples in Kabul, Afghanistan, water types, geochemical properties, quality, and the feasibility of the samples as drinking water were analyzed. Additionally, they used the GIS to model the spatial distribution of water quality with the parameters examined in the WQI calculation.

The Kızılırmak Delta is a RAMSAR site with international protection status and is an important wetland. In addition, agriculture and animal husbandry, the region's most important sources of income, are carried out in a significant part of the study area. For this reason, the delta's water resources are vital for economic and social activities. However, the fact that socio-economic activities, water use, and water quality directly affect each other reveals that a study on water quality is necessary for the region. Hence, conducting comprehensive studies to evaluate the groundwater quality and effectively communicating the findings to policymakers, managers, and water users is imperative. Also, it holds significant importance to analyze the hydrogeochemistry of the groundwater, assess the water quality, and understand the influencing factors in a given area to promote the sustainable utilization of groundwater reservoirs. From this point of view, a study, which is thought to contribute to the literature, was conducted for the following purposes in the Kızılırmak Delta, Turkey, which has the potential to be affected by salinity: (i) the chemical composition and spatial distribution of the groundwater are characterized, (ii) the sources of major ions present in the groundwater are identified, and (iii) the suitability of the groundwater in the Kızılırmak Delta for drinking purposes is evaluated, through a Water Quality Index (WQI) assessment. The study's findings provide further information on water quality assessment in the Kızılırmak Delta, and local governments can benefit from the study's results to develop sustainable groundwater management.

2. Materials and Methods

2.1. Study Area

This study was carried out in the Kızılırmak Delta located in the downstream area of the Kızılırmak Basin, between latitudes 41°44′ and 41°27′ N and longitudes 35°34′ and 36° 7′, with a total area of 103,537 hectares (ha) (Figure 1). Different climatic characteristics prevail in the interior and coastal areas downstream of Kızılırmak. In the coastal area, a typical Black Sea climate is observed. The average annual temperature in the study area is 13.7 °C; the hottest months are July and August, with 22.8 °C. The month with the lowest average temperature is January, with 5.7 °C. The annual average relative humidity is 74.9%. Total annual precipitation is 791.8 mm. The month with the highest precipitation is December (102.1 mm), and the month with the lowest precipitation is July (29.8 mm). The study area has fertile soil rich in content through the organic matter carried by the Kızılırmak River [42].

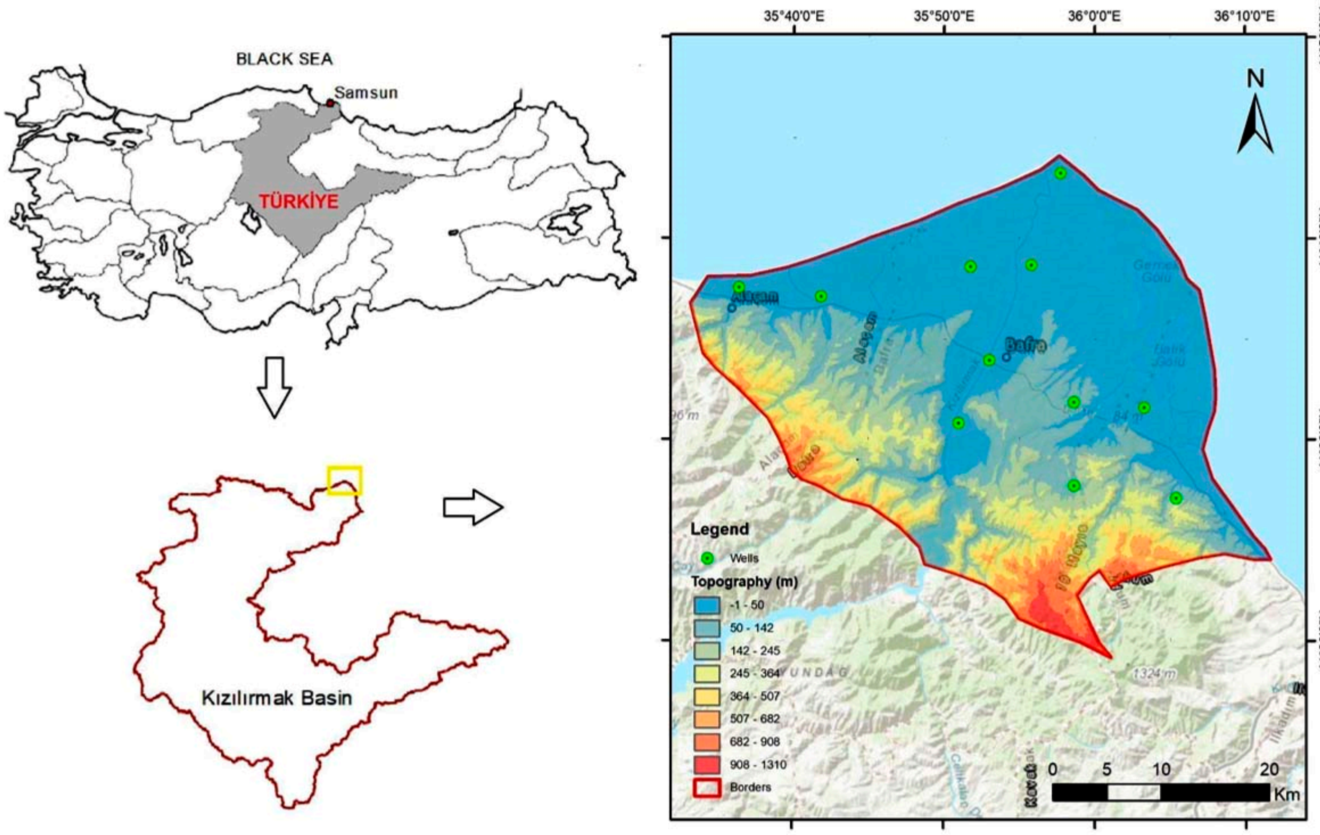

Figure 1. The location of the study area and observation wells used for groundwater samples.

Groundwater samples were obtained from eleven observation wells and analyzed for anions and cations. Locations of the wells in the WGS84 projection system for water quality monitoring are displayed in Table 1 and Figure 1. The samples were collected during different seasons and dates, and for the present study, the average values of each parameter were used.

Table 1. Water quality range [33].

WQI Level	Water Quality Status	Grade
0–25	Excellent water quality	A
26–50	Good water quality	B
51–75	Poor water quality	C
76–100	Very poor water quality	D
>100	Unsuitable for drinking	E

2.2. Geology and Hydrogeology of the Study Area

The Kızılırmak Delta was formed by the accumulation of fertile sediments carried by the Kızılırmak River. From the Black Sea to the inner regions, the area, which is primarily flat, gradually rises in steps. The formations seen in the delta are Mesozoic and Cenozoic (Eocene, Neogene) age volcanic, metamorphic, and fluvial deposits and Quaternary alluviums. The Upper Cretaceous flysch series are the oldest deposits widely distributed in the delta and represent the Mesozoic period. The delta is a plain consisting of a mixture of clay, silt, and sand spread over a wide area, following the Kızılırmak bed from the sea. Plio-Quaternary deposits primarily composed of clay, sand, and gravel are encountered on the slopes with the rise of the plain areas. The volcanics in the Flysch series consist of tuff layers and andesites [42,43].

The Kızılırmak Delta coastal region has many wells drilled in alluviums. The delta's primary aquifer is the alluvium unit on the river's banks and plains [43]. Groundwater is found near the surface in the alluvium, which is composed of silt, clay, gravel, and sand. These wells range in depth from 50 to 100 m and in flow rate from 1 to 60 L/s. The transmissivity coefficient in the coastal region of the Kızılırmak Delta varies between 18 and 8320 m^2/day, indicating that it is an unconfined aquifer. In the aquifer, groundwater flows in three directions: north, northeast, and northwest [21].

2.3. Data Acquisition

To evaluate the water quality, data on eleven observation wells (January–December 2016) (Figure 1) representing the study area's unconfined aquifer system were obtained from the General Directorate of State Hydraulic Works. Each well was pumped for a minimum of 15 min, after which the samples were collected and stored at 4 °C until the analysis. A portable multiparameter meter measured EC (electrical conductivity) and pH values. Hydrochemical parameters, including NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, K^+, HCO_3^-, SO_4^{2-}, and hardness (measured as $CaCO_3$), were analyzed using ion chromatography. Distilled water (used as blank samples) underwent parallel analysis to ensure quality control, and all measurements were duplicated. Method accuracy and quality control were verified by examining Standard Reference Materials (SRM). The suitability of the study area's groundwater for drinking water supply was evaluated using the ten groundwater quality parameters to reveal the groundwater quality index. Also, adding more parameters to the groundwater quality model would needlessly increase uncertainty, which is another reason to focus only on the most significant water quality parameters.

2.3.1. Determination of the Water Quality Index for Groundwater

The Weighted Arithmetic Index Method (WAIM) [33] was used to calculate the WQI. The calculation of the WQI utilized the weighted arithmetic method, which has been employed in several earlier studies [35,44–46].

This method is based on the following steps.

In the first step, for each parameter, a unit weight factor was calculated using Equation (1):

$$W_n = \frac{K}{S_n} \tag{1}$$

W_n is the unit weight factor, K is the constant for proportionality, and S_n is the standard desirable value of the nth parameter.

The following equation can calculate the K factor (Equation (2)):

$$K = \frac{1}{\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3} + \ldots + \frac{1}{S_n}} = \frac{1}{\sum \frac{1}{S_n}} \tag{2}$$

The sum of the weight factor calculation must equal 1.

Equation (3) calculates the sub-index (Q_n) value in the second step.

$$Q_n = \frac{V_n - V_0}{S_n - V_0} \times 100 \tag{3}$$

Q_n is the sub-index value on the parameter, the mean concentration of the nth parameter, S_n is the standard desirable value of the nth parameter, and V_0 is the actual value of the parameter in pure water (generally V_0 = 0 for most of the parameters except pH and Dissolved Oxygen (DO).

For the pH, Q_n must be calculated according to Equation (4).

$$Q_{pH} = \frac{V_{pH}}{s\tan dart_{pH} - 7} \times 100 \quad (4)$$

The third step involves computing the overall WQI using Equation (5). Calculating the overall water quality index involves a linear combination of the quality rating and the unit weight.

$$Overall WQI = \frac{\sum W_n \times Q_n}{\sum W_n} \quad (5)$$

The WQI values obtained were grouped into five categories based on the calculated WQI: excellent water quality (WQI < 25); good water quality (WQI 25–50); poor water quality (WQI 50–75); very poor water quality (WQI 75–100); and water unsuitable for drinking (WQI > 100) [33]. Table 1 shows all the categories of the WQI based on Brown, McClelland, Deininger, and O'Connor [33].

2.3.2. Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI)

The WQI, developed by the Canadian Council of Ministers of the Environment (CCME) in 2001, serves to simplify the presentation of intricate and technical water quality information. The WQI comprises three distinct factors, and comprehensive documentation is available (47).

Factor 1: F1 (Scope)

The scope evaluation determines the degree to which water quality guidelines are not met within the selected timeframe. This involves calculating the number of parameters for which the objective limits are not achieved. This methodology has been adapted from the British Columbia Water Quality Index. Equation (6) can find factor 1.

$$F_1 = \frac{Number\,of\,field\,\text{variables}}{Total\,number\,of\,\text{variables}} \times 100 \quad (6)$$

The number of field variables refers to parameters that exceed specified limits, while the total number of variables indicates the overall count of parameters studied.

Factor 2: F2 (Frequency)

The frequency of non-compliance (i.e., the number of times the measured or observed value falls outside the acceptable limits) indicates the proportion of individual tests that do not meet the objectives (termed "failed tests"). The formulation of this factor is taken directly from the British Columbia Water Quality Index. This value can be calculated using Equation (7).

$$F_2 = \frac{Number\,of\,field\,tests}{Total\,number\,of\,tests} \times 100 \quad (7)$$

Factor 3: F3 (Amplitude)

The amplitude reflects the extent to which the objectives are not achieved, representing the deviation of failed test values from their intended objectives. Its computation involves three steps. In the first step the "excursion" is calculated. An "excursion" refers to the number of instances in which an individual concentration exceeds (or falls below, in the case of a minimum objective) the intended objective and can be computed as follows: if the test value should not exceed the objective, the excursion is the difference between the test value and the objective; and can be calculated using Equation (8).

$$Excursion_i = \frac{Field\,test\,value_i}{Objective_i} - 1 \quad (8)$$

In instances where the test value should not be lower than the objective, the excursion can be calculated by using Equation (9).

$$Excursion_i = \frac{Objective_i}{Field\,test\,value_i} - 1 \quad (9)$$

In the second step to determine the total amount of non-compliance across individual tests, the excursions of each test from their respective objectives are summed up and divided by the total number of tests. This value is known as the normalized sum of excursions (NSE) and can be calculated using the following formula:

$$NSE = \frac{\sum_{i=1}^{n} excursion_i}{Total\,number\,of\,tests} \quad (10)$$

In the third step, F3 is calculated using an asymptotic function that scales the NSE from objectives to yield a value between 0 and 100.

$$F_3 = \frac{NSE}{0.01NSE + 0.01} \quad (11)$$

Finally, the CCME WQI can be found using the following formula: variations in each of the three components directly correspond to changes in the index.

$$CCMEWQI = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right) \quad (12)$$

where 1732 serves as a scaling factor and normalizes the obtained values to fall between 0 and 100, with 100 denoting the highest water quality and 0 indicating the lowest level of quality [47]. The classification of the CCMEWQI ranges is clearly stated in Table 2.

Table 2. Classification of CCME WQI ranges with descriptions Source [47].

Water Quality	CCMEWQI Value	Description
Excellent	95–100	Water quality is protected with a virtual absence of threat or impairment, conditions very close to natural or pristine levels.
Very good	89–94	Water quality is protected with a slight threat or impairment, conditions close to natural or pristine levels.
Good	80–88	Water quality is protected with only a minor threat or impairment; conditions rarely depart from natural or desirable levels.
Fair	65–79	Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable.
Poor (Marginal)	45–64	Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels.
Poor	0–44	Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels.

2.4. Principal Component Analysis (PCA)

The principal components present uncorrelated linear combinations of the original variables and explain the total variance of the original data [48]. In PCA, the correlation between all components is zero because the method generates all components to be orthogonal to each other. The first principal component explains most of the variation present in the original data [49].

The number of parameters is reduced by applying PCA, assuming a complete dataset containing k variables x_1, x_2, . . ., x_k measured on n variables. The component analysis is performed on the correlation matrix, so it can be assumed that each variable has a sample mean of 0 and variance of 1 without loss of generality. For a complete data set, any principal component is a linear combination, and all parameter variables can be written as in Equation (13):

$$y = a_1x_1 + a_2x_2 + \ldots + a_kx_k \quad (13)$$

The a_i (i = 1 to k) are constants [50].

The PCA procedure is implemented as follows:

i. First, the covariance/correlation matrix is calculated (here, the most appropriate data set to perform PCA is the one with the highest correlation between the individual indicators).
ii. Determine the number of principal components to be considered according to the percentage of variance they explain.
iii. Rotate the factors to improve their interpretation (this is done by maximizing the loading of individual indicators on individual factors) [46,51].

2.5. Hierarchical Cluster Analysis (CA)

Clustering is a statistical approach that facilitates the grouping of similar locations in various clusters based on distance criteria that characterize the parameters to be classified [52]. Principal Component Analysis (PCA) was the basis for performing Hierarchical Cluster Analyses (HCA), which quantified the degree of similarity between the samples. Factor scores from PCA were utilized in HCA as variables for statistical grouping. The aim of HCA is to find homogeneous subgroups of instances within a set of groups that maximize variation between groups while minimizing within-group variance. In the study area, wells with comparable chemical properties were categorized using HCA using the Ward method and Square Euclidean distance.

3. Results and Discussion

3.1. Hydrogeochemical Characteristics

Groundwater, essential for many uses, including agriculture and drinking water, is experiencing a decline in quality attributed to a mix of natural phenomena and human activities. For this reason, the assessment of groundwater quality is of immense importance to society [53]. In the study area discussed in this article, GW is used for drinking and irrigation purposes, which is why investigation into the water quality of this area is essential. All the parameters were compared according to concentrations in WHO drinking water standards. Table 3 shows the WQI values of the parameters used in this study for the eleven different wells considered and the value of each parameter according to WHO drinking water quality standards. The statistical analyses of groundwater quality parameters are shown in Table 4.

As seen from Table 3, except pH, most of the parameters of each well in the study area indicate that the GW in these wells is unsuitable for drinking water according to WHO standards. A necessary component for any application is the water's pH. According to the guidelines, a pH range of 6–9 is suitable for practically all applications [54].

The EC values of the samples examined fell within the range of 652 to 6112 µS/cm (with an average of 1762 µS/cm), suggesting that most of the groundwater in the area is more mineralized. Nearly all of the groundwater samples taken in the region were found to be not the acceptable limit of 500 µS/cm, as defined by the WHO [55]. It is known that sodium salts are found in all food and drinking water [40]. However, WHO has stated that concentrations above 200 mg/L taste unpleasant and are unacceptable. Among the samples obtained from the study area wells, the lowest sodium concentration value was determined to be 14.484 mg/L and the highest value was 1334.799 mg/L. It is seen that the sodium value obtained from five wells exceeds WHO standards. Most of these areas are located east of the studied area, in the region where the sea enters the delta (Figure 1).

Potassium is released into groundwater by weathering potassium-containing minerals in rocks and soils. Common minerals like feldspar, mica, and clay minerals are primary contributors to potassium in groundwater [56]. Agricultural activities are the predominant source of increased potassium levels in groundwater [44]. The maximum and minimum potassium values in the eleven wells in the study area were 25.02 mg/L and 1.95 mg/L, respectively, while the average value was 7.36 mg/L. It is seen that both the average potassium value and three of the wells exceed the WHO limit. It was determined that the potassium value was higher in the wells in the north of the delta than in other regions. Agricultural practices and the natural weathering of silicate minerals are likely the primary factors contributing to elevated potassium levels in the groundwater of the study area. Conversely, the lower potassium concentrations in the groundwater can be attributed to its binding with clay minerals and the greater durability of potassium-bearing minerals against weathering processes [57].

Calcium is released into groundwater through the weathering of calcium-containing minerals present in rocks and soils [58]. In addition, calcium-containing fertilizers, such as calcium carbonate (lime), can also be applied to agricultural fields to adjust the soil pH and improve the soil structure. However, overuse of these fertilizers may lead to Ca^{2+} ions leaching into groundwater. The minimum calcium concentration in the study area was 108.817 mg/L, and the maximum was 692.382 mg/L. According to the WHO limit, all wells in the study area exceeded the limit value. The increase in the calcium concentration in the groundwater can be attributed to both natural geological processes and human activities. Like the calcium concentration, the sodium concentration is more intense in the eastern part of the study area. The ion exchange reactions involving sodium and calcium frequently occur when freshwater mixes with saltwater. In cases where saline water infiltrates fresh groundwater, calcium is released from solid exchange surfaces in exchange for sodium in the groundwater. Conversely, when flushing out a saline aquifer with fresh groundwater, the opposite processes occur. While magnesium and potassium may also undergo exchange for sodium, their contributions are generally less significant. Cation exchange between exchange surfaces and groundwater thus regulates the proportions of sodium and calcium in saline groundwater [59].

Table 3. Groundwater water quality parameters of some wells in the Kızılırmak Delta.

			Parameters										
Stations	**X (m)**	**Y(m)**	**pH**	**EC**	**Na^+ (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**Mg^{2+} (mg/L)**	**HCO_3^- (mg/L)**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**Hardness**	**NO_3^- (mg/L)**
Well 1	41°31′51″	35°58′37″	7.12	1015	142.768	3.128	136.42	386.771	546.739	24.106	37.463	37.700	3.782
Well 2	41°27′41″	35°58′37″	8.5	1005	14.484	5.474	162.925	318.865	399.071	3.191	9.606	51.400	2.790
Well 3	41°30′48″	35°50′59″	7.7	1162	50.118	11.339	122.044	308.531	233.097	6.027	13.929	40.900	2.604
Well 4	41°33′55″	35°53′0″	7.6	1260	135.181	4.692	111.422	534.394	549.18	134.71	67.722	45.910	16.120
Well 5	41°37′31″	35°56′23″	7.4	672	19.771	2.346	129.859	128.432	369.781	24.106	39.865	36.710	<0.01
Well 6	41°38′34″	35°51′46″	7.5	1546	207.599	5.083	151.903	615.586	375.273	243.896	340.533	58.730	26.600
Well 7	41°42′53″	35°55′59″	7.5	2401	348.299	25.024	108.817	1778.851	685.865	383.215	475.497	87.410	31.000
Well 8	41°38′39″	35°55′47″	7.3	1950	229.67	7.429	205.811	863.592	487.55	311.96	400.09	80.600	50.900
Well 9	41°31′33″	35°3′16″	7	6112	1334.799	9.384	692.382	5183.026	732.85	638.1	1474.521	348.280	52.950
Well 10	41°37′5″	35°41′51″	7.4	652	17.243	1.955	118.036	100.383	371.002	28.006	37.944	32.890	17.110
Well 11	41°38′34″	35°51′46″	7.28	1606	187.598	5.083	130.26	1198.695	745.054	216.6	113.351	73.100	27.160
Average			7.5	1761	244.321	7.358	188.171	1037.921	499.587	183.083	273.684	81.239	23.102
WHO standard [55,60].			7.5	500	200	10	75	50	500	250	250	100	50

Table 4. Statistical analysis of groundwater quality parameters.

Parameters	Min	Max	Mean	Median	SD
pH	7	8.5	7.5	7.4	0.39
EC (μS/cm)	652	6112	1761	1403	1472
Na^+ (mg/L)	14.484	1334.799	244.321	165.100	359.281
K^+ (mg/L)	1.955	25.024	7.358	5.242	21.799
Ca^{2+} (mg/L)	108.817	692.382	188.171	130.030	171.762
Mg^{2+} (mg/L)	100.383	5183.026	1037.921	574.900	1394.753
HCO_3^- (mg/L)	233.097	745.054	499.587	488.700	160.746
Cl^- (mg/L)	3.191	638.100	183.083	81.350	199.711
SO_4^{2-} (mg/L)	9.606	1474.521	273.684	53.750	420.049
Hardness (mg/L)	32.890	348.280	81.239	55.065	86.441
NO_3^- (mg/L)	<0.01	52.950	23.102	16.616	18.845

The magnesium concentration was identified as one of the significant parameters among the major cationic constituents, with samples ranging from 100.383 to 5183.026 mg/L. It was noticed that all samples exceeded the desirable limit of 50 mg/L for drinking water, as set by the WHO [60]. Aquifers with naturally high concentrations of magnesium-containing minerals may also contribute to elevated magnesium levels in the groundwater. The high levels of Ca^{2+} and Mg^{2+} can be attributed to the lithological composition of the area and the presence of minerals such as calcite and dolomite, which are fundamental constituents of siltstone, a prevalent geological feature in the study region [61].

Sulfate in groundwater typically occurs in the form of soluble Ca^{2+}, Mg^{2+}, and Na^+ salts. There is a notable variation in the SO_4^{2-} concentration over time, particularly during rainfall infiltration and groundwater recharge [62]. Using sulfate-containing fertilizers such as ammonium SO_4^{2-} or potassium sulfate can also contribute to high SO_4^{2-} levels in groundwater. Over the past few decades, atmospheric deposition has emerged as a significant contributor of sulfate to soil, eventually permeating groundwater. Given the mobility of sulfate within soil, its introduction into the soil can consequently affect shallow aquifers as well [63]. The sulfate content in the groundwater samples ranged from 9.606 to 1474.521 mg/L, exceeding the WHO permissible limit of 250 mg/L at some stations (wells 6, 7, 8, and 9). The fact that these stations are within the region's borders where intensive agriculture is practiced may have increased the SO_4^{2-} value.

Bicarbonate in groundwater primarily originates from dissolved carbonate minerals like calcite and dolomite found in rocks and soil. As rainwater or surface water seeps through these carbonate-rich formations, it reacts with the minerals, releasing HCO_3^- ions into the groundwater [64]. Bicarbonate in groundwater is mainly derived from the carbonate minerals and CO_2 in the atmosphere and soil. At neutral pH, bicarbonate is the dominant ion [65]. An alkaline environment is created in the groundwater due to the reaction between the carbon dioxide in the soil and the minerals that form rocks. The HCO_3^- concentrations vary from 233.097 and 745.054 mg/L and exceed the permitted limit of 500 mg/L in some stations (wells 1, 4, 7, 9, and 11) [60].

Chloride originates from sodium chloride, which dissolves in water from rocks and soil. The presence of sodium chloride in water generally has minimal impact on its suitability unless it reaches concentrations that render the water non-potable or corrosive [61]. The chloride concentration of groundwater samples taken from wells in the study area varies between 3.191 and 638.100 mg/L. The maximum allowable concentration of Cl^- ions in drinking water is 250 mg/L. Water with chloride ion concentrations exceeding 250 mg/L tastes salty. A higher chloride concentration indicates a higher degree of organic contaminants, so chloride is an important parameter in assessing groundwater quality [66]. The spatial distribution of Cl^- is created via Arc-GIS 10.8.2 and given in Figures 2 and 3. Furthermore, it can be seen that this parameter is high in the eastern part of the study area. Sulfate is dissolved and leached from rocks containing gypsum, iron sulfides, and other sulfur-bearing compounds [9]. The groundwater hardness levels in the region varied between 32.890 and 348.280 mg/L (as $CaCO_3$), with an average value of 81.239 mg/L. Approximately 90% of the wells had hardness levels within the desirable 100 mg/L limit. The anionic and catatonic content of the groundwater was found to be $Mg^{2+} > HCO_3^- > SO_4^{2-} > Cl^- > Na^+$, as shown in Table 3.

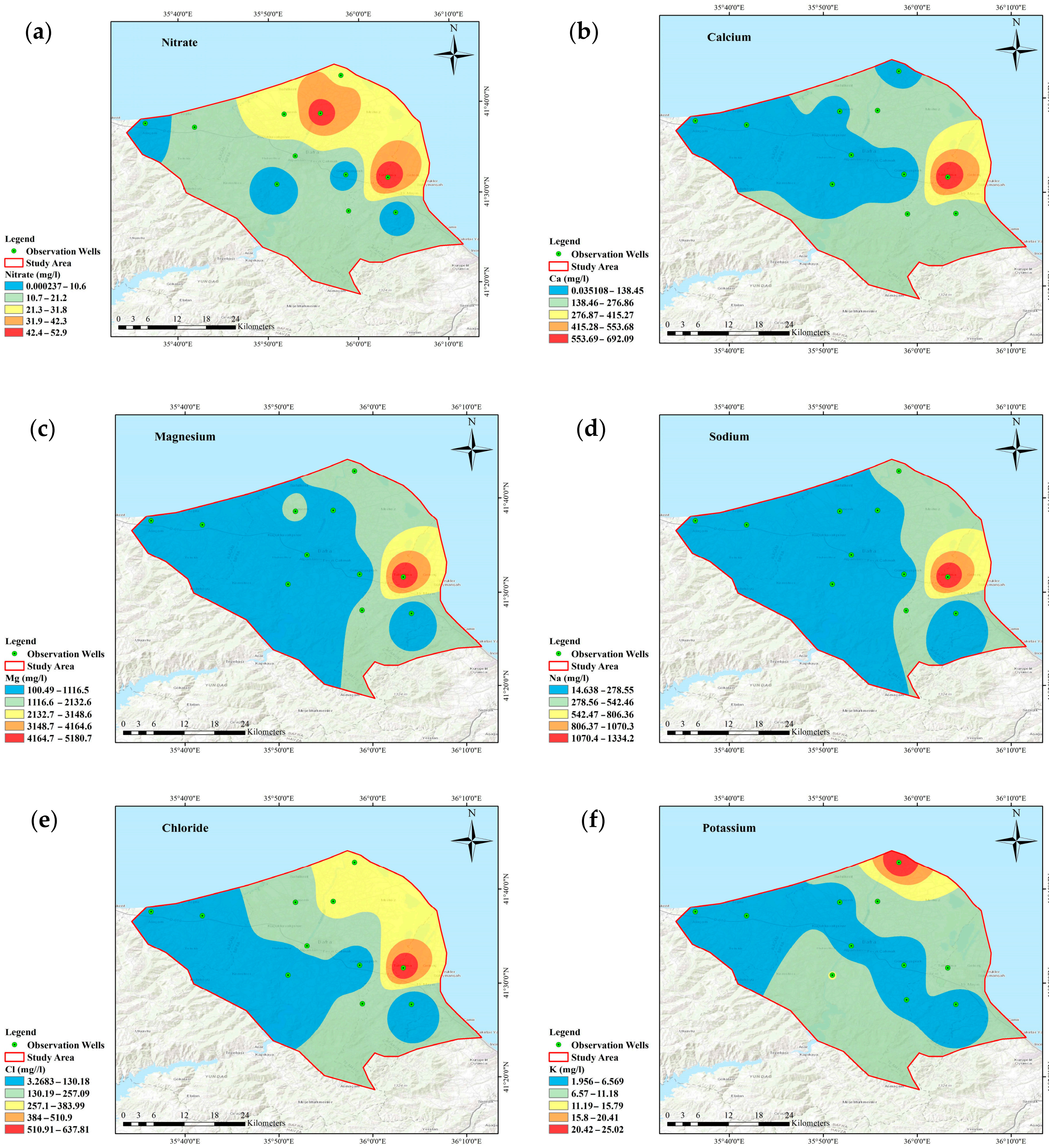

Figure 2. The thematic layer for each parameter of groundwater in the study area. (**a**) Nitrate (NO_3), (**b**) calcium (Ca^{2+}), (**c**) magnesium (Mg^{2+}), (**d**) sodium (Na^+), (**e**) chloride (Cl^-), (**f**) potassium (K^+).

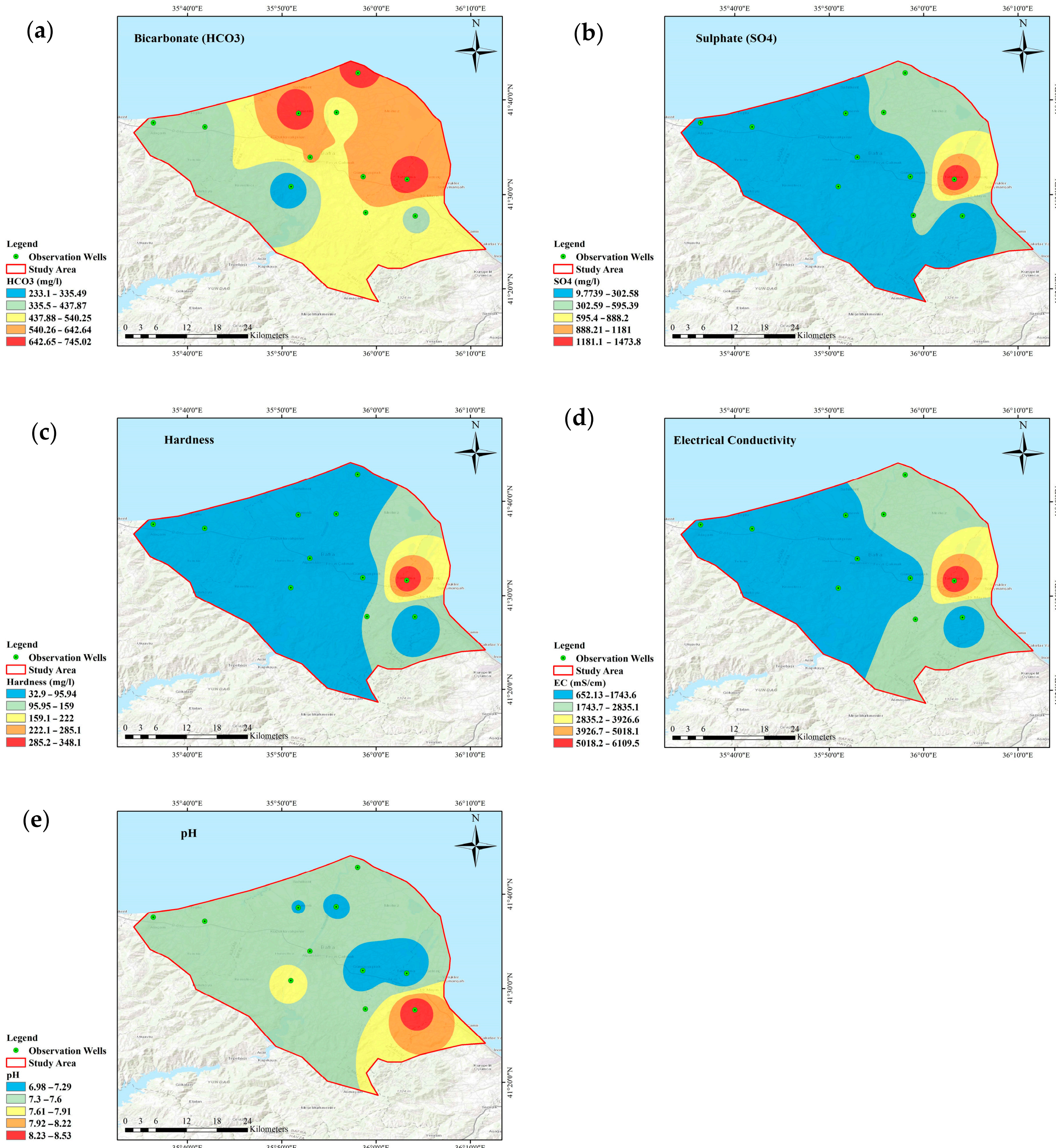

Figure 3. The thematic layer for each groundwater parameter in the study area. (**a**) Bicarbonate (HCO_3^-), (**b**) sulphate (SO_4^{2-}), (**c**) hardness ($CaCO_3$), (**d**) electrical conductivity (EC), (**e**) pH.

Large quantities of nitrates are also generated from organic waste produced by agricultural livestock and urban sewage, potentially reaching groundwater reservoirs. Particularly in areas with intensive feedlots, livestock waste significantly contributes to excess nutrients entering the environment. While concerns regarding the pollution of both surface waters and aquifers due to increased use of mineral fertilizers are supported by observed correlations linking fertilizer application to nitrate leaching [67], pinpointing the direct impact of fertilizer application on water nitrate content is challenging. Nitrate concentrations in groundwater can vary significantly across different locations, even when uniform farm management practices are employed [68]. The study area is a RAMSAR area with international protection status and is an important wetland. Agriculture and animal husbandry are carried out in this study area. Animal waste, plants, and remaining animals go through ammonification in the soil, generating ammonia that is then converted to nitrate by Nitrosomonas and Nitrobacter bacteria [9]. Nitrogen released through weathering has a significant impact on soil and water quality. Additionally, denitrification significantly impacts how much nitrogen is released during the weathering process of bedrock, which affects the amount of nitrate in groundwater [9,69]. According to the study by [70], approximately 25% of the nitrogen applied to agricultural ecosystems leaches into water resources. However, there are significant uncertainties about the time of transfer of agriculturally applied nitrogen from topsoil to groundwater. This uncertainty arises from a deficient mechanistic understanding of the impact of different nitrogen transformations in the soil [71].

Nitrate pollution is a critical anthropogenic variable impacting groundwater quality [72]. Their overabundance or accumulation due to human activities can harm water quality, health, and environmental sustainability. When it exceeds the WHO's allowable limit of 50 mg/L for nitrate, its higher concentration generally poses health risks [73,74]. The study area's concentration ranges from <0.01 to 52.498 mg/L (Table 3). Overall, the low nitrate concentration in the assessed area is likely a result of a combination of factors, including organic agricultural activities, natural processes, land management practices, and geological conditions. Since this region has international protection status, attempts are made to protect an important wetland and ecosystem health. For this reason, projects are being carried out by the Ministry of Agriculture and Forest regarding organic farming. In addition, ecosystem-based solutions are being implemented to remove nitrate and nitrite pollution from soil in this region. Therefore, except for two wells (wells 8 and 9), nitrate concentration was found below WHO limit values (50 mg/L).

3.2. Groundwater Quality Mapping/Spatial Distribution Pattern

This study evaluated the quality and pollution status of water samples collected from eleven underground wells in the Kızılırmak Delta. The results of the chemical parameters of the groundwater samples taken from the Kızılırmak Delta are given in Table 5. The result of the analysis parameters was plotted on the thematic map for all observation wells using ArcGIS 10.8.2, as shown in Figures 2 and 3. The present study utilized the Inverse Distance Weighted (IDW) interpolation technique, which has proven to be a proficient method for producing spatial distribution maps by spatially interpolating groundwater quality parameters. The closest specified locations were considered when calculating the weights, allocated to different parameters at each location based on distance. As seen in Figures 2 and 3, the contour maps of the groundwater quality parameters were created with a spatial distribution pattern. The pH distribution pattern indicates the presence of alkaline groundwater in the northeast region of the Kızılırmak Delta, the NE (Figure 2a). The groundwater's Ca^{2+} and Mg^{2+} ions came from the rock formations in the study area, which contains Ca and Mg leaching (Figures 2 and 3). Weathering and erosion of these rocks release calcium and magnesium into soil and water systems. The concentration of calcium and magnesium in water can vary depending on geological factors, such as the composition of underlying rocks and soils. They are naturally present in dissolved form, contributing to water hardness.

Table 5. GIS-based WQI index values of each monitoring well according to Brown et al. [33].

Stations	GIS-Based WQI	Remarks
Well 1	69.14688	Poor
Well 2	200.0549	Unsuitable
Well 3	144.0467	Unsuitable
Well 4	143.5819	Unsuitable
Well 5	66.03841	Poor
Well 6	157.0077	Unsuitable
Well 7	367.2081	Unsuitable
Well 8	184.5786	Unsuitable
Well 9	772.5291	Unsuitable
Well 10	63.94814	Poor
Well 11	211.5382	Unsuitable

To summarize, it is obvious from Figures 2 and 3 that the water quality in the west of the region is insufficient for drinking water and irrigation purposes. When the figures are examined, it can be clearly seen that high levels were also obtained for HCO_3^- and NO_3^- in the wells in the north of the region. It can be said that the samples obtained from the east of the region are useful for drinking water and irrigation.

3.3. GIS-Based Groundwater Quality Index

3.3.1. GIS-Based Groundwater Quality Index by Brown et al. [33]

Eleven groundwater parameters, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, K^+, HCO_3^-, SO_4^{2-}, hardness ($CaCO_3$), EC, and pH, were analyzed to evaluate the groundwater quality of eleven different wells in the study area for drinking and irrigation purposes. These wells are monitoring wells, and these parameters are measured during different seasons of the year. Two types of GIS-based WQI calculators were applied to the study area data, and each method was discussed in the method section of Brown et al. [33]. The results shown in Table 6 show that most of the wells have low-quality water for drinking purposes.

The calculated result of the WQI for each well shows that most of the water of the well is not suitable for drinking purposes. It exceeds the water quality rating as per Brown, McClelland, Deininger, and O'Connor [33]. Among these monitoring wells, well 10 has a low water quality index of 63.948, but all other wells have E-grade water quality, which is unsuitable for drinking purposes. These exceeded the limit of the WQI for these wells due to the high concentration of different parameters in the groundwater; For instance, in Well 1, Na^+ and Mg^{2+} concentrations were higher than the WHO standards for drinking water. Well, 9 had the highest GIS-based WQI (772.529), indicating the lowest water quality at the site, which is attributed to elevated levels of Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and $CaCO_3$, as detailed in Table 5. Figure 4 shows the plotted map of the WQI for all eleven sites based on the Brown et al. [33] WQI method.

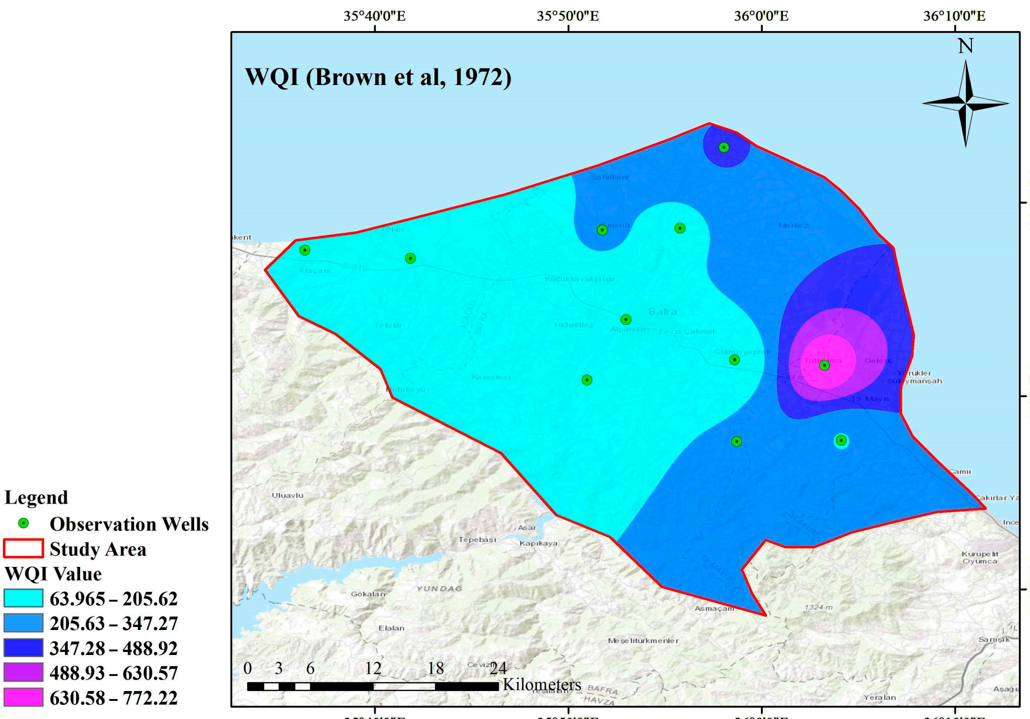

Figure 4. Plotted map of WQI for eleven wells based on WQI method [33].

Table 6. CCME WQI index values of each monitoring well developed by the Canadian Council of Ministers of the Environment (2001).

Stations	CCME WQI	Remarks
Well 1	77.728	Fair
Well 2	70.306	Fair
Well 3	62.884	Fair
Well 4	62.880	Fair
Well 5	77.731	Fair
Well 6	62.878	Fair
Well 7	40.577	Poor
Well 8	48.027	Marginal
Well 9	32.887	Poor
Well 10	77.728	Fair
Well 11	70.278	Fair

3.3.2. CCME WQI

As indicated in Figure 5, the northeast side of the Kızılırmak Delta site has lower water quality than the southwest side. The northeast part of the study area is influenced by the high concentrations of Na^{+}, Mg^{2+}, Ca^{2+}, SO_4^{2-}, and $CaCO_3$, which have decreased the water quality and made it unsuitable for drinking purposes. On the other hand, the CCME WQI method is applied for the same groundwater parameters in the study area.

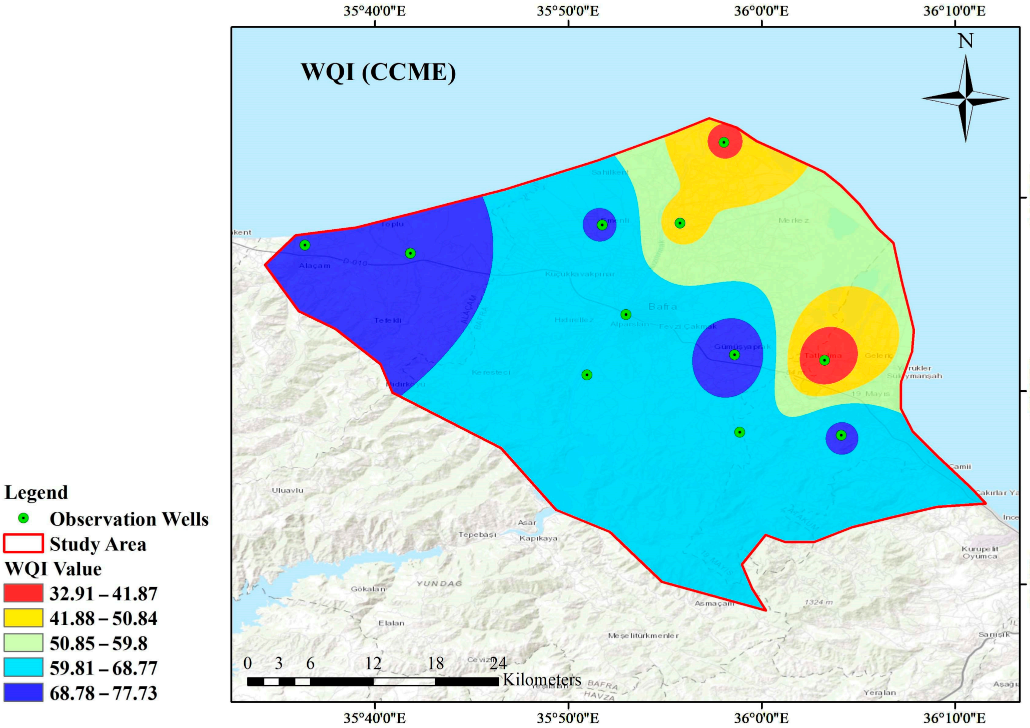

Figure 5. The water quality index map for the study area, based on the CCME method.

As indicated in Table 6, most sites have fair or lower than fair water quality or poor or marginal water quality, which is unsuitable for drinking purposes. As shown in Table 6, these types of water quality in the CCME method are usually or almost always threatened or impaired and cannot be suitable for drinking purposes. As indicated in Figure 5, only two sites have low water quality, which is in the range of 32.9 to 41.87, defined as poor grade, and other sites have a fair and marginal grade, which are the lowest water quality grades for drinking purposes.

Additionally, some studies [9,75–78] have used various WQIs to draw attention to the variations in the spatial-temporal classification of water sources. This context also includes calculations using a variety of arithmetic and logarithmic indexes. According to the findings, the indices are generally successful in accurately classifying water quality levels.

3.4. Principle Component Analysis (PCA)

Principal Component Analysis (PCA) is a statistical technique for reducing the number of multi-index data [52,79]. PCA and Cluster Analysis (CA) are the most widely used multivariate statistical methods of environmental samples. PCA is used for data reduction and reveals a few representative factors in analyzing relationships between identified variables. This study used PCA and CA to assess the accuracy of analytical data and analyses. The component analysis technique performs classification by comparing grouped data by measuring either similarity or distance between them. The objectives of CA analysis are to group similar components [80]. A groundwater quality study was performed in 2016 using PCA with varimax rotation and Kaiser normalization component values. PCA was generated utilizing the analytical data from 11 selected samples. It is a method of statistical analysis used to reduce the size of a multi-index data set. Eleven parameters were used, and two components with eigenvalues greater than one were identified (Figure 6). To comprehend the groundwater parameter structure, Figure 6 shows screen plots utilized to calculate the number of PCs. For the groundwater quality data, the overall variation for PC1 and PC2 was 70.50% and 11.49%, respectively. A highly positive loading of the K^+ physicochemical characteristic was indicated by the factor (PC2) in the data set. All of the physicochemical characteristics were low positively loaded (except pH), according to the factor (PC1) in the data sets. The varimax rotated method factor loadings from the PCA results are shown in Table 7. PCA indicates whether a positive or negative relationship exists. A value approaching 1 indicates a significant relationship between the parameter and the PC. A value greater than 0.75 indicates a strong correlation. It was found that the values in the range of 0.5 to 0.74 were closely related [52]. Table 7 illustrates the processes that the factor loadings have been used to interpret.

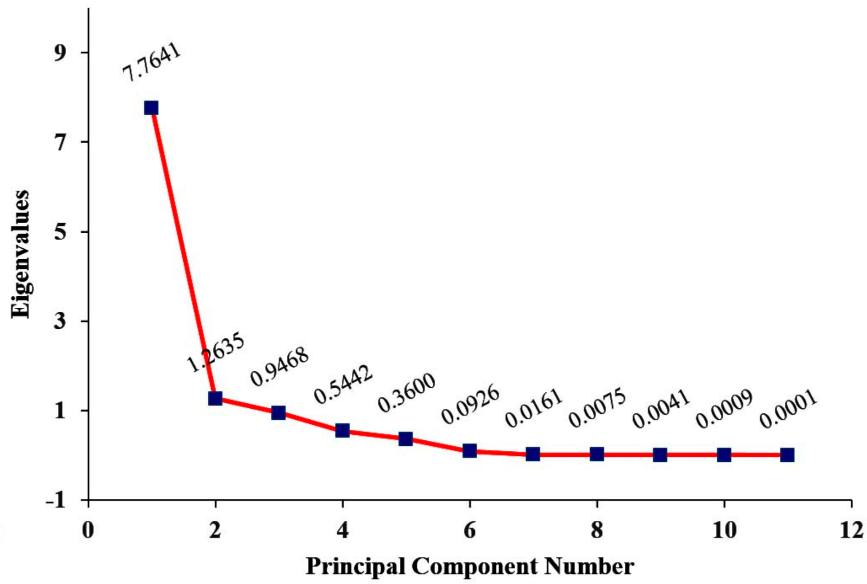

Figure 6. Screen plot of the characteristic eigenvalues used in principal component analysis.

Table 7. Varimax rotated method factor loadings from PCA.

Variables	Component Matrix	
	PC1	PC2
pH	−0.18876	0.15442
EC	0.35053	0.16871
Na^+	0.35206	0.09999
K^+	0.02028	0.79085
Ca^{2+}	0.31866	0.23649
Mg^{2+}	0.35237	0.09261
HCO_3^-	0.24332	−0.11207
Cl^-	0.3326	−0.23585
SO_4^{2-}	0.34852	−0.0826
$CaCO_3$	0.34591	0.15731
NO_3^-	0.28371	−0.38469
Eigenvalues	7.764	1.26353
Variability (%)	70.50	11.49
Cumulative (%)	70.50	82.07

Figure 7 illustrates the relationships between PC1 and PC2, contributing the most to the overall variance. The variables given in Figure 7 are all represented by a vector, and the vector's direction and length indicate each variable's contribution to the two principal components. It can be said that PC1, on the horizontal axis, has positive coefficients for K^+, Ca^{2+}, EC, hardness, Mg^{2+}, Na^+, SO_4^{2-}, HCO_3^-, Cl^-, and NO_3^- but negative coefficients for pH. For PC1, it can be said that vectors directed to the right side of the axis have a positive effect, while those directed to the left side have a negative effect. PC2, on the vertical axis, has negative coefficients for SO_4^{2-}, HCO_3^-, Cl^-, and NO_3^- and positive coefficients for pH, K^+, Ca^{2+}, EC, hardness, Mg^{2+}, and Na^+ (Table 8).

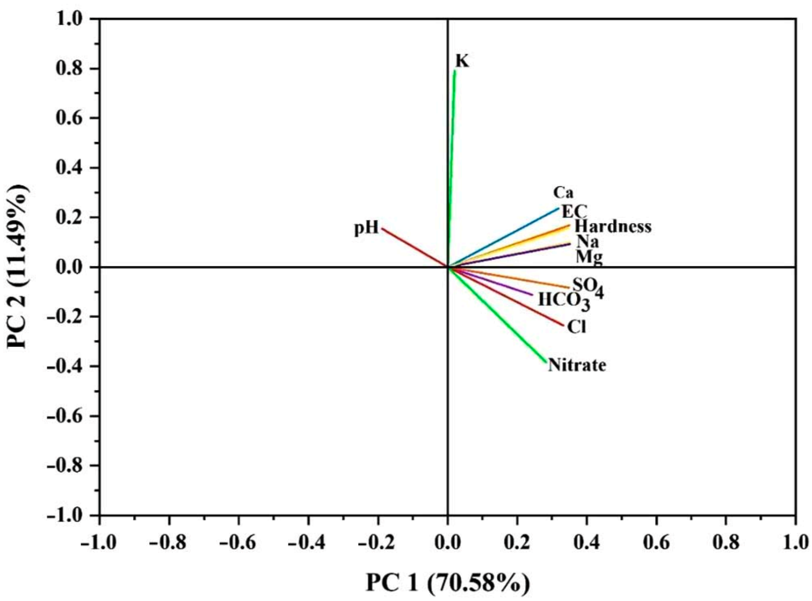

Figure 7. The 2D plot of PC1 and PC2.

Table 8. Correlation matrix of groundwater quality parameters.

	pH	EC	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	$CaCO_3$	NO_3^-
pH	1	−0.436	−0.488	−0.054	−0.296	−0.443	−0.468	−0.470	−0.448	−0.411	−0.469
EC		1	**0.989**	0.197	**0.928**	**0.987**	0.605	0.854	**0.944**	**0.985**	0.678
Na^+			1	0.099	**0.918**	**0.989**	0.610	0.855	**0.960**	**0.988**	0.673
K^+				1	0.164	0.101	0.078	−0.116	−0.080	0.129	−0.210
Ca^{2+}					1	**0.902**	0.383	0.711	0.873	**0.962**	0.577
Mg^{2+}						1	0.669	0.871	**0.950**	**0.982**	0.679
HCO_3^-							1	0.680	0.547	0.563	0.566
Cl^-								1	**0.933**	0.810	0.911
SO_4^{2-}									1	**0.939**	0.793
$CaCO_3$										1	0.636
NO_3^-											1

3.5. Hierarchical Cluster Analysis (HCA)

Hierarchical cluster analysis used groundwater samples from different classes. The dendrograms have several clusters, each with one or more variables. Clusters were selected based on the diagram of the dendrogram in Figure 8 to facilitate understanding. They can be divided into two main groups based on the geochemical parameters of the variables as well as the outputs of the cluster tree (Figure 8). Cluster analysis and the derived dendrogram based on eleven parameters illustrated that sampling sites are ordinated into five groups: group 1 included pH, EC, Na^+; group 2 included Mg^{2+}, hardness; group 3 included SO_4^{2-}, Ca^{2+}, Cl^-; group 4 included Na^+, HCO_3^-; and Group 5 included K^+. Extreme values in the data sets are sensitive to the clusters. The similarity between PCA factors and HCA clusters supports the PCA-suggested dominating processes; the similarities among the parameters and their distribution facilitated an understanding of the impact of water quality. According to CA analysis, the most representative variable was EC, while the least representative variable was pH.

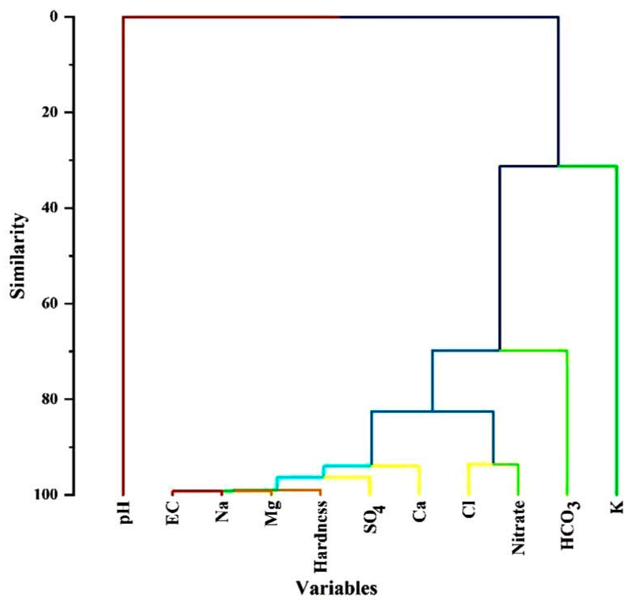

Figure 8. Dendrogram resulting from the hierarchical cluster analysis of groundwater samples.

The clusters impact extreme values in the data sets. The similarity between PCA factors and HCA clusters supports the dominating processes suggested by PCA. Therefore, incorporating physicochemical variables into the PCA to evaluate groundwater quality is a flexible and useful method that offers fresh insights and a remarkable performance.

3.6. Correlation Coefficient Matrix Analysis

The relationship between two variables is usually determined using the correlation coefficient. In this study, the relationship of eleven parameters with each other was determined via the correlation coefficient and is given in Table 8. In the correlation analysis, the Pearson correlation method was used. The correlation values between the parameters were within the 95% confidence interval. The bold prominences when r values were more than +0.75 are strongly correlated. A correlation coefficient close to 1 or −1 indicates a strong relationship between two parameters, while a correlation coefficient of zero indicates no relationship [52]. The results show that a highly positive correlation is observed between Na^+ and EC (0.98), Ca^{2+} and EC (0.92), Mg^{2+} and EC (0.98), $SO_4{}^{2-}$ and EC (0.94), $CaCO_3$ and EC (0.98), Ca^{2+} and Na^+ (0.91), Mg^{2+} and Na^+ (0.98), $SO_4{}^{2-}$ and Na^+ (0.95), $CaCO_3$ and Na^+ (0.98), Mg^{2+} and Ca^{2+} (0.90), $CaCO_3$ and Ca^{2+} (0.96), $SO_4{}^{2-}$ and Mg^{2+} (0.95), $CaCO_3$ and Mg^{2+} (0.98), $SO_4{}^{2-}$ and Cl^- (0.93), and $CaCO_3$ and $SO_4{}^{2-}$ (0.93). It was observed that while K^+ showed a low correlation with all other parameters, pH showed both a negative and low correlation.

4. Conclusions

This study aimed to analyze the chemical composition and spatial distribution of groundwater within the Kızılırmak Delta of Turkey. It also sought to assess the suitability of the groundwater in the Kızılırmak Delta for drinking water purposes by conducting a WQI evaluation. Samples were collected from eleven wells for analysis. Eleven key water parameters, comprising $NO_3{}^-$, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, K^+, $HCO_3{}^-$, $SO_4{}^{2-}$, hardness (measured as $CaCO_3$), EC, and pH, were scrutinized to gauge the quality of each groundwater sample. The WQI was computed using the weighted arithmetic index and the CCME methods. In this study, the chemical composition and spatial distribution of the groundwater in the Kızılırmak Delta of Turkey were characterized, the WQI was determined, and the relationships between the parameters were analyzed using the PCA method.

- The WQI value was high due to the high values of Ca^{2+}, Mg^{2+}, and $SO_4{}^{2-}$ in some wells, indicating that the groundwater has the potential for salinization.
- A low nitrate concentration was observed in this region. The reason is a combination of factors, including suitable agricultural activities, natural processes, land management practices, and geological conditions. In addition, since this region has international protection status, an important wetland and ecosystem health are also being protected.
- Approximately 90% of wells had hardness levels within the desirable 100 mg/L limit. The low hardness may be because the hardness level decreases when mixed with groundwater and surface water or other sources with lower hardness. Another reason is that groundwater with a short residence time may need more contact with minerals in the aquifer to accumulate significant hardness.
- According to the WQI values, most wells' water is unsuitable for drinking and use. On the other hand, the CCME WQI method indicated that most sites have fair or lower than fair water quality or poor or marginal water quality, which is also unsuitable for drinking purposes.
- Based on the spatial distribution of the water quality, it is estimated that the region's western part is inadequate for drinking water and irrigation in the Kızılırmak Delta.
- The correlation coefficient determined the relationships between the groundwater parameters, and the highest correlation was between Mg^{2+} and $CaCO_3$.

The present study shows that the delta's groundwater, which has deteriorating water quality, should be treated before it is used for drinking water and protected from contamination hazards.

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