

Groundwater quality assessment using principal component analysis and hierarchical cluster analysis in Alaçam, Turkey

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ABSTRACT

This study assessed groundwater quality in Alaçam, where irrigations are performed solely with groundwaters and samples were taken from 35 groundwater wells at pre and post irrigation seasons in 2014. Samples were analyzed for 18 water quality parameters. SAR, RSC and %Na values were calculated to examine the suitability of groundwater for irrigation. Hierarchical cluster analysis and principal component analysis were used to assess the groundwater quality parameters. The average EC value of groundwater in the pre-irrigation period was 1.21 dS/m and 1.30 dS/m after irrigation in the study area. It was determined that there were problems in two wells pre-irrigation and one well post-irrigation in terms of RSC, while there was no problem in the wells in terms of SAR. Piper diagram and cluster analysis showed that most groundwaters had CaHCO₃ type water characteristics and only 3% had NaCl as the predominant type. Seawater intrusion was identified as the primary factor influencing groundwater quality. Multivariate statistical analyses to evaluate polluting sources revealed that groundwater quality is affected by seawater intrusion, ion exchange, mineral dissolution and anthropogenic factors. The use of multivariate statistical methods and geographic information systems to manage water resources will be beneficial for both planners and decision-makers.

Key words: Alaçam town, multivariate statistical techniques, Piper diagram, seawater intrusion

HIGHLIGHTS

- Multivariate statistical analysis was used to evaluate the groundwater quality.
- According to the Piper diagram, 83% of the groundwater was of the CaHCO₃ type in both periods.
- The effect of seawater was observed in some wells located 4 km inland from the sea in the post-irrigation period.
- Seawater intrusion has been detected in coastal areas.
- Well number 28 should not be used for irrigation purposes.

INTRODUCTION

Groundwater is used for irrigation, drinking and domestic uses. It is a natural and limited source of water. Groundwater also plays an important role in both the ecosystem and economy of developing countries like Turkey (Twarakavi & Kaluarachchi 2006; Arslan 2013). In places where most agricultural water needs are supplied from groundwaters, water quality assessment is crucial for sustainable use of these resources in irrigations. Groundwater quality largely depends on hydro-chemical processes realized through regional hydrogeological and anthropogenic activities under saturated and unsaturated soil conditions (Kazakis *et al.* 2017). Besides, chemical processes between the soil and aquifer minerals, up-down water flow within the soil profile and flowing duration continuously influence groundwater quality. As well as such natural processes, anthropogenic factors including excessive irrigation and leakage of harmful substances from unconsciously fertilizer-treated soil surface also negatively affect groundwater quality. Additionally, excessive groundwater withdrawals for irrigation from deep aquifers bring groundwater to upper layers or surfaces. Such withdrawals result in seawater intrusion into groundwater in coastal zones and thus end up with groundwater salination and pollution (Boniol 1996).

Irrigation water quality is one of the most crucial problems affecting plant production. The good quality of irrigation water used in agricultural production will lead to an increase in crop yield with proper water management and soil applications

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(Aravinthasamy *et al.* 2020). Hence, effectively monitoring and evaluating the quality of groundwater is required to ensure sustainability in agricultural production in especially coastal aquifers. Different irrigation water quality indexes such as EC, SAR, RSC, %Na and MR are widely used to determine the suitability of groundwater for irrigation (Masoud & Ali 2020; Sunkari *et al.* 2020). Khanoranga & Khalid (2019) used quality criteria such as sodium adsorption ratio (SAR), residual sodium carbonate (RSC), sodium percentage (Na%), permeability index (PI) and magnesium hazard (MH) to determine the suitability of groundwater for irrigation in Pakistan. Singh *et al.* (2020) evaluated the suitability of groundwater quality for irrigation in the Punjab region of India. The study results determined that 5% of the samples in the whole area were 'harmful' in terms of %Na and RSC and 100% of them were in the 'unsuitable' class according to MR values. Kamaraj *et al.* (2021) conducted a study to determine the suitability of groundwater in coastal aquifers in South India for irrigation and determined that 56% of the samples by %Na and 5% by SAR were unsuitable for irrigation.

Recently, with the increasing number of physical and chemical variables of groundwater, a wide variety of statistical methods are now used for accurate analysis and interpretation of data (Subyani & Al Ahmadi 2010). Multivariate statistical analysis methods have been used frequently in fields such as soil and water resources in the last years (Masoud *et al.* 2018; Chaudhry *et al.* 2019; Dash & Kalamdhad 2021). Cluster analysis (CA), factor analysis (FA), principal components analysis (PCA), discriminant analysis (DA) and several other multivariate statistical analyses are widely used to present spatial variations in groundwater quality and to determine impact factors (Ma *et al.* 2014). Yidana (2010) used multivariate statistical analyses (hierarchical cluster analysis) to assess groundwater quality and obtained four clusters representing three main types of groundwater. It was also determined that groundwater chemistry was designated by three primary factors. Arslan (2013) classified groundwaters in coastal areas of Bafra plain with multivariate statistical techniques. Cluster analysis revealed three clusters for groundwaters of the research site (A, B and C) and factor analysis revealed that 12 variables explained 89.64% of total variation and three factors were identified as the primary ones. Ma *et al.* (2021) used piper diagram and multivariate statistical analysis methods to designate irrigation water quality, hydro-chemical properties, water type and water-rock interactions. Bodrud-Doza *et al.* (2019) investigated the spatial and temporal distribution of groundwater pollution sources in Dhaka province of Bangladesh using GIS and multivariate statistical analysis methods. Silva *et al.* (2021) used multivariate statistical techniques to determine the water quality index and the integration of groundwater quality with geographic information systems in a semi-arid basin and principal component analysis to calibrate the water quality index. They also reported that the physical, chemical and biological involvement affecting the water quality of the principal components analysis play a role in determining the relationships between the variables. Seawater intrusion and anthropogenic activities lead to the danger of salinization in groundwater resources in coastal areas (Jayathunga *et al.* 2020). Kumar *et al.* (2020) revealed that hydro-chemical analysis and multivariate statistical methods can be combined in the determination of seawater intrusion. Prusty & Farooq (2020) applied mathematical and statistical (HCA) methods to classical hydro-chemical data in their study to investigate the suitability of groundwater in coastal areas for irrigation and the status of seawater intrusion. Khan *et al.* (2021) utilized hydro-chemical and statistical techniques to present the relationships between seawater intrusion and groundwater geochemical properties. While principal component analysis was used to determine the hydro-chemical relationships from the obtained data and they benefited from Pearson correlation to explain the factors affecting salinity.

Management of groundwater in coastal areas is very crucial. In case of excessive water withdrawal from this type of water, the water will become salty and unusable. For this reason, the relations between groundwater and seawater should be revealed in coastal areas clearly. Paddy farming is carried out intensively and only groundwater is used as irrigation water in the Alaçam region. There has not been any study on the determination of irrigation groundwater quality so far in the study area. Therefore, whether the groundwater is affected by the salinization process in a paddy-growing area close to the coast and the effects of seasonal changes on the groundwater's hydro-chemical properties were investigated using multivariate statistical techniques in the Alaçam region. Identification of the results of excessive groundwater utilizations in irrigation and passing such results efficiently and instantly to the decision-makers are significant issues to take timely measures and for sustainability of agricultural practices.

MATERIALS AND METHODS

The study area

Present research site (Alaçam) is located in the Middle Black Sea Region of Turkey between 41° 36'–41° 40' North latitudes and 35° 33'–35° 47' East longitudes. Alaçam is located 80 km west of Samsun province. The town has a semi-humid climate,

December is the month with most precipitation (120.6 mm) and July is the driest month (39.0 mm). The long-term annual average total precipitation is 784.7 mm. Kızılırmak river, Alaçam, Yenice and Bedeş creeks constitute the primary water resources. According to 2015 data, there were not any irrigation systems within the boundaries of Alaçam town and existing drainage canals were not efficiently operating. The location of the research site is presented in Figure 1.

Sampling and analysis

In this study, groundwater samples were collected from 35 different bore and hand pumps in April and September 2014. Figure 1 shows the study area and the sampling points. Wells were operated for 10 minutes, then samples were taken into polyethylene bottles. Samples were preserved at +4 °C until the time of analysis. Before the analyses, samples were filtered through 0.45 µm acetate cellulose filter papers. Samples were subjected to EC, pH, TDS (Total Dissolved Solids), Na⁺, K⁺, Ca²⁺, Mg²⁺, CO₃²⁻, HCO₃⁻, SO₄²⁻, NO₃, DO, temperature, Cl⁻ and hardness analyses. Additionally, SAR (Sodium Adsorption Ratio), RSC (Residual Sodium Carbonate) and Na% were calculated. A pH meter (Mettler Toledo S20 Seven Easy) was used to measure pH of groundwater samples. A conductivity meter (Jenway 4510) was used to measure temperature, EC and TDS of the samples. All quality parameters were determined in the laboratory using American Public Health Association standard methods (APHA 1999). The Ca²⁺ and Mg²⁺ concentrations were determined with EDTA titration. Total hardness (TH) was calculated from Mg²⁺ and Ca²⁺ concentrations identified as calcium carbonate. Na⁺ and K⁺ were determined in a flame photometer. Phenolphthalein indicator was used for carbonate (CO₃²⁻) and methyl orange indicator was used for bicarbonate (HCO₃⁻) and sulphuric acid titration method was used to determine CO₃²⁻ and HCO₃⁻ concentrations. Chlorine (Cl⁻) concentration was determined with the use of potassium chromate indicator and silver nitrate titration. Sulfate (SO₄²⁻) and nitrate (NO₃⁻) concentrations were determined with the use of a UV-visible spectrophotometer (APHA 1999). Dissolved oxygen (DO) was determined in accordance TS 5677 EN25814 standards (TSE 1996). Accuracy of the analysis results on

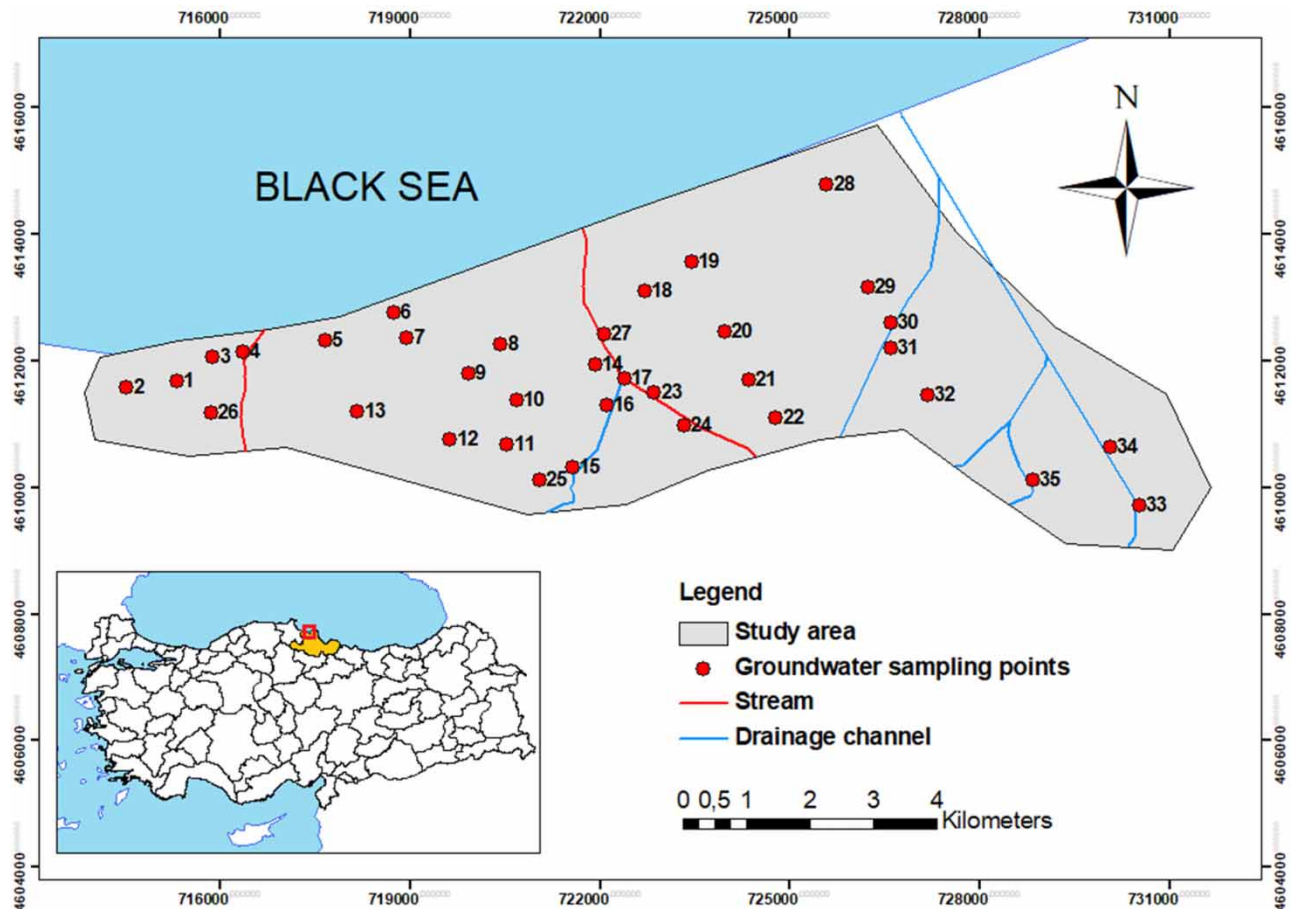


Figure 1 | Research site and sampling points.

physicochemical parameters was checked for Ionic Balance Error (IBE) (Equation (1)). In the following equations, all anions and cations were expressed in meq/L.

$$IBE = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} \times 100 \quad (1)$$

Calculated ionic balance error was within $\pm 10\%$ acceptable limits (Domenico & Schwartz 1990).

SAR (Richards 1954), RSC (Eaton 1950) and %Na (Wilcox 1955) values were calculated with the use of the following equations (respectively with Equations (2)–(4)). In these equations, Na^+ , K^+ , Ca^{2+} and Mg^{2+} concentrations were expressed in meq/L.

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{\frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2}}} \quad (2)$$

$$\text{RSC} = (\text{CO}_3^- + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (3)$$

$$\text{Na}\% = \frac{\text{Na}^+ + \text{K}^+}{\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}} \quad (4)$$

The evaluation criteria and references of the quality of water used for irrigation are shown in Table 1.

The hydro-chemical properties of the groundwater in the study area were classified by a Piper-Trilinear diagram (Piper 1944). Piper trilinear diagram was drawn using Rockware AqQA (version AqQA1.5) software (Rockware AqQA Software 2015).

Multivariate statistical analysis

Multivariate statistical methods are commonly used in hydrological and environmental researches to define and assess soil characteristics, groundwater and surface water quality (Belkhiry & Narany 2015; Singh *et al.* 2017a; Kumar *et al.* 2019). In this study, principal component analysis and cluster analysis were applied on 35 groundwater samples (70 in total) taken in two different periods. Multivariate statistical analyses were performed using Windows SPSS 21.

Table 1 | Water assessment criteria for irrigation

Parameter	Range	Irrigation water quality	Parameter	Range	Irrigation water quality
EC (Ayers & Westcot 1985) (dS/m)	0–0.25	Low	pH (Acatay 1996)	6.6–7.3	Notr
	0.25–0.75	Medium		7.4–7.8	Slightly alkaline
	0.75–2.25	High		7.9–8.4	Alkaline
	>2.25	Very high		8.5–9.1	Strong alkaline
Na (Ayers & Westcot 1985) (mg/L)	<70	Suitable	% Na (Wilcox 1955)	>9.1	Very strong alkaline
	70–200	Permissible		<20	Excellent
	>200	Unsuitable		20–40	Good
NO ₃ (Anonymous 1975)	<5	No problem	Cl (Wilcox & Magistad 1943) (mg/L)	40–60	Permissible
	5–30	Increasing problem		60–80	Doubtful
	>30	Severe problem		>80	Unsuitable
RSC (California Fertilizer Committee 1975)	<1.25	Good	TDS (Heath 1983) (mg/l)	<178	Good
	1.25–2.5	Medium		178–355	Permissible
	>2.5	Unsuitable		>355	Doubtful
SAR (Mandel & Shiftan 1981)	0–10	Excellent		<1,000	Fresh
	10–18	Good		1,000–3,000	Slightly saline
	18–26	Doubtful		3,000–10,000	Moderately saline
	>26	Unsuitable		10,000–30,000	High saline (sea)

Datasets were normalized to eliminate effects from differences in units before analysis (Equation (5)).

$$Z = \frac{(x - \bar{x})}{S} \quad (5)$$

where, Z is standardized value; x , is measurement value, \bar{x} , is mean and S is standard deviation.

The multivariate statistical analysis methods used in the study are summarized below.

Cluster analysis (CA)

Cluster analysis is one of the multivariate techniques that group objects according to their properties. Euclidean distance was used to measure the similarity between water quality variables and Ward's method was used as the joining rule. The resultant clusters of cluster analysis (groups) were used to comprehend hydro-chemical processes encountered in the region.

Factor analysis/principal component analysis

Principal component analysis (PCA) is used to reduce the large data sets with a minimum loss of information (Singh *et al.* 2017b). In present study, principal component analysis and factor analysis were used to get correlations between hydro-chemical components of groundwater samples with the use of factor-score values. The first principal component explains the majority of the total variance in a data set, while the remainder of the variance is then explained by the other components. In PCA, only components with an eigenvalue >1 were selected and then subjected to the varimax rotation before being used for interpretation (Kaiser 1960; Ganiyu *et al.* 2021).

Statistical analysis

The results were processed using the basic descriptive statistics such as minimum, maximum, mean and standard deviation (SD). Spatial distribution maps of different factor scores were generated with the use of ArcGIS 10.0 software. Inverse Distance Weighted (IDW) interpolation method was used while generating these maps.

RESULTS AND DISCUSSION

Groundwater chemistry

Descriptive statistics for pre and post-irrigation groundwater samples are presented in Table 2. Except for EC, TDS and Cl, the other parameters were not significantly different during the pre- and post-irrigation periods. The EC values were ranged from 0.60 to 5.45 dS/m with an average 1.21 dS/m in the pre-irrigation period and from 0.49 to 6.13 dS/m with an average 1.30 dS/m in the post-irrigation period. The EC value was lower than 0.75 dS/m in 14% of the water samples analyzed in both periods and it was found to be moderately saline according to Ayers & Westcot (1985). EC values were between 0.75 and 2.25 dS/m (high level) in 83 and 80% of the water samples, and 3 and 6% were greater than 2.25 dS/m (very high) in the pre-and post-irrigation periods, respectively. The increase in the EC values of groundwater in the post-irrigation period can be attributed to seawater intrusion in coastal areas. Callender *et al.* (2011) indicated that seawater had quite greater chemical components than freshwater; thus, seawater intrusion should continuously be monitored as a reliable indicator of changes in groundwater chemistry. While low-salinity waters could be used for almost all plants and soils, highly saline waters could only be used for salt-tolerant plants.

TDS values were ranged from 381.54 to 3,489.29 mg/L with an average of 773.461 mg/L in the pre-irrigation period and from 310.28 to 3,922.03 mg/L with an average of 830.838 mg/L in the post-irrigation period (Table 2). In both periods, the TDS value was found to be greater than 3,000 mg/L in 3% of the sampled points in the study area. These waters are not recommended for irrigation (Freeze & Cherry 1979). The average TDS value increased by approximately 8% in the post-irrigation period compared to the pre-irrigation period. The reason for this is the influence of seawater on the groundwater wells. As a result of excessive groundwater use in the post-irrigation period, TDS values exceeding 1,000 mg/L were obtained in some wells located approximately 4 km inland from the coast, and the effects of seawater were observed in these wells.

In addition, the level of Cl^- ions in all groundwater samples were measured and found to have an average of 120.02 mg/L in the pre-irrigation period and 170.80 mg/L in the post-irrigation period (Table 2). The average Cl ion concentrations increased by 42% in the post-irrigation period. High Cl⁻ ion concentration is used as a pollution index and is commonly used in groundwater quality monitoring (Loizidou & Kapetanios 1993). Total hardness is one of the important influencing parameters on the suitability of groundwater for drinking (Ghaffari *et al.* 2021). Total hardness (TH) values ranged from

Table 2 | Descriptive statistics of groundwater samples

Parameters	Unit	Pre-irrigation				Post-irrigation			
		Minimum	Maximum	Mean	Std. Dev.	Minimum	Maximum	Mean	Std. Dev.
pH	/	7.09	7.97	7.58	0.24	7.16	7.66	7.37	0.13
EC	dS/m	0.60	5.45	1.21	0.80	0.48	6.13	1.30	0.96
TDS	mg/L	381.54	3,489.29	773.46	513.65	310.28	3,922.03	830.84	612.84
Na ⁺	mg/L	14.10	759.00	90.34	130.14	14.40	740.00	91.42	126.60
K ⁺	mg/L	0.70	29.10	5.80	6.15	1.10	36.60	6.41	6.91
Ca ²⁺	mg/L	59.69	281.84	135.25	43.46	34.96	359.44	137.98	51.87
Mg ²⁺	mg/L	11.63	130.29	38.78	21.34	23.27	167.26	50.84	26.36
TH	mg/L	297.02	1,235.97	495.78	175.84	336.36	1,580.76	552.02	211.48
CO ₃ ²⁻	mg/L	0.00	79.20	48.31	21.59	8.40	124.80	54.77	38.79
HCO ₃ ⁻	mg/L	274.59	661.46	439.17	76.71	152.55	805.46	440.42	132.11
Cl ⁻	mg/L	14.41	1,347.39	120.02	222.48	18.01	1,567.15	170.79	277.70
SO ₄ ²⁻	mg/L	1.71	593.81	87.62	111.19	2.66	233.81	64.67	54.25
NO ₃ ⁻	mg/L	4.00	40.00	12.97	11.61	0.00	42.00	9.93	9.30
Temperature	°C	18.50	24.50	20.97	1.74	17.00	24.00	20.45	1.73
DO	mg/L	2.23	9.90	6.10	1.74	2.23	15.20	7.12	3.41
%Na	%	9.27	66.83	24.03	13.67	7.14	51.09	22.65	10.57
SAR	-	0.34	9.37	1.66	1.85	0.30	8.08	1.53	1.47
RSC	meq/L	0.00	3.16	0.36	0.77	0.00	2.38	0.16	0.49

297.02 to 1,235.97 mg/L in the pre-irrigation period and from 336.36 to 1,580.76 mg/L in the post-irrigation period. According to the classification made by [Sawyer & McCarty \(1967\)](#), almost all of the groundwater in the study area is classified as 'very hard' because it is greater than TH > 300 mg/L. Although the acceptable limit of hardness is 300 mg/L, the value may be extended up to 600 mg/L if there is no alternative source of water ([WHO 1990](#)). [Dewandel et al. \(2006\)](#) reported that mainly the hardness of the water is due to the contact of groundwater with rock formations.

pH values of the groundwater were ranged from 7.09 to 7.97 in the pre-irrigation period and from 7.16 to 7.66 in the post-irrigation period, thus showing that these groundwaters are slightly alkaline ([Acatay 1996](#)).

Among the cations examined, the concentrations of Na, K, Ca, and Mg ions showed a wide variation from 14.10 to 759.00 mg/L, from 0.70 to 29.10 mg/L, from 59.69 to 281.84 mg/L and from 11.63 to 130.29 mg/L in the pre-irrigation period, and from 14.40 to 740.00 mg/L, from 1.10 to 36.60 mg/L, from 34.96 to 359.44 mg/L and from 23.27 to 167.26 mg/L in the post-irrigation period, respectively ([Table 2](#)). The permissible limit for sodium concentration is 200 mg/L for irrigation waters ([Ayers & Westcot 1985](#)) and a quite low number of samples (6%) passed this limiting value. Since groundwaters with high sodium concentrations tend to spoil soil structure, they should be used for agricultural purposes. In natural waters, potassium concentrations are generally below 10 mg/L ([WHO 1990](#)). The K values of 97% of the samples in the pre-irrigation period and 86% of the samples in the post-irrigation period was below 10 mg/L. High potassium concentrations of groundwaters are attributed to anthropogenic sources and saline water intrusion ([Ghalib 2017](#)). [Akshitha et al. \(2021\)](#) reported that seawater intrusion may cause high concentrations of potassium and magnesium values in groundwater in coastal areas. Hence, the water of well number 28 in the study area has the highest K and Mg values. Calcium and magnesium are the most abundant elements in surface and groundwaters and these elements exist primarily in bicarbonate form and slightly in sulfate and chlorine forms ([Sarath Prasanth et al. 2012](#)). Among the cations, Ca²⁺ contents may exhibit seasonal variations; long-term agricultural practices may directly or indirectly influence mineral dissolution in groundwaters ([Böhlke 2002](#); [Satish Kumar et al. 2016](#)).

The concentrations of anions such as CO₃, HCO₃ and SO₄ were ranged between 0 and 79.2 mg/L, 274.59 and 661.46 mg/L and 1.71 and 593.81 mg/L in the pre-irrigation period, and between 8.40 and 124.80 mg/L, 152.55 and 805.46 mg/L and 2.66 to 233.81 mg/L in the post-irrigation period, respectively ([Table 2](#)). Nitrate (NO₃) concentrations were ranged from 4 to

40 mg/L in the pre-irrigation period and from 0 to 42 mg/L in the post-irrigation period (Table 2). In some parts of the study area (7 wells pre-irrigation and two wells post-irrigation), the NO_3^- value was determined to be above 30 mg/L. Ayers & Westcott (1985) reported that these wells may cause problems if they are used for irrigation purposes. Since there were not any lithological NO_3^- sources in the present research site, such high NO_3^- concentrations were mostly attributed to applied nitrogenous fertilizers, seepage from domestic wastewaters and septic tanks (Cushing *et al.* 1973; Todd 1980).

Dissolved oxygen (DO) values of the groundwater samples ranging from 2.23 to 9.90 mg/L in the pre-irrigation period and from 2.23 to 15.20 mg/L in the post-irrigation period. Groundwater temperatures were measured showing the values ranging from 18.5–24.5 °C in the pre-irrigation period and from 17 to 24 °C in the post-irrigation period.

Groundwater suitability for irrigation was assessed through %Na, SAR and RSC of the samples. The %Na values ranging from 9.27 to 66.83% (average 24.03%) in the pre-irrigation period and from 7.14 to 51.09% (average 22.65%) in the post-irrigation period (Table 2). The %Na values of the majority of the underground wells were found in the ‘good’ class in both periods (Wilcox 1955). The only one well located in the middle of the study area and close to the sea had a % Na value above 60% in the pre-irrigation period. High %Na levels result in soil deflocculating and spoil soil permeability. The SAR values of the samples varied between 0.34 and 9.37 (average 1.66) in the pre-irrigation period and between 0.30 and 8.08 (average 1.53) in the post-irrigation period (Table 2). SAR is commonly used to assess the availability of water resources for irrigation (Singh *et al.* 2012) and indicates the absorbed Na level of the soil. Present samples were all classified as ‘very good’ (Mandel & Shiftan 1981). Residual sodium carbonate (RSC) designates hazardous effects of carbonate and bicarbonate on water quality for agricultural purposes (Saha *et al.* 2019). RSC values varied between 0–3.16 meq/L (mean 0.36 meq/L) in the pre-irrigation period and between 0–2.38 meq/L (mean 0.16 meq/L) in the post-irrigation period (Table 2). Two water wells in the study area are not suitable for irrigation in terms of RSC in the pre-irrigation period ($\text{RSC} > 2.5$, California Fertilizer Committee 1975). It has been determined that the waters of the other wells have RSC values suitable for irrigation except for these two wells.

Piper trilinear diagram

A Piper trilinear diagram was drawn to determine the hydro-chemical composition of the water samples in the study area and to understand the different processes affecting the groundwater (Piper 1944). Figure 2 shows the hydro-chemical components of water samples pre- and post-irrigation period in 2014. According to this diagram, there were 3 different types of water in the pre-irrigation period and 2 different types of water in the post-irrigation period (Figure 2). The diagram showed that calcium was the predominant cation and bicarbonate was the predominant anion. Majority of water samples are composed of bicarbonate-type freshwaters. In both pre and post-irrigation periods, the majority of the samples were placed into section 1 of the diamond-shaped area and this section indicated CaHCO_3^- type water. Calcium bicarbonate water is mainly due to the

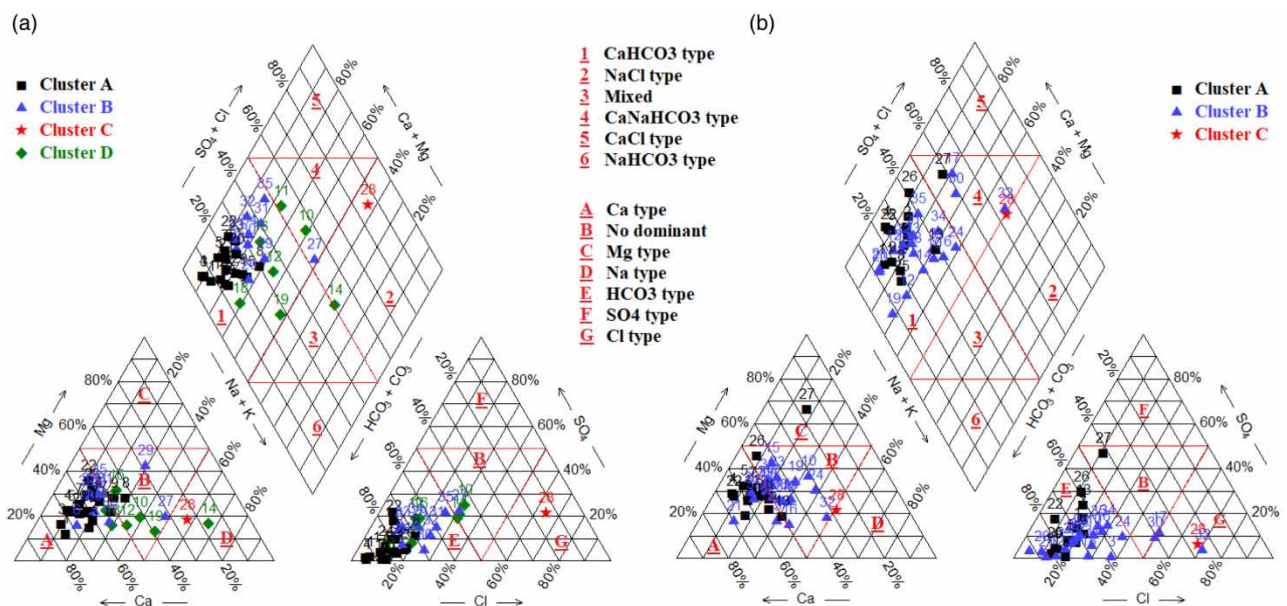


Figure 2 | Piper diagram of groundwater samples; (a) Pre-irrigation, (b) Post-irrigation.

dissolution of limestone (Frisbee *et al.* 2016). In the pre-irrigation period, 9% of the samples were placed into section 4 indicating CaMgCl^- type mixture waters. The groundwater samples of wells 14 and 28 had NaCl^- type water. In the post-irrigation period, 14% of the samples were placed into section 4 of the diagram. Piper diagrams are able to assess water quality only in terms of small and large ions. They may be insufficient in the assessment of potential impacts of agricultural practices and seawater intrusion. Güler *et al.* (2002) reported that the combined use of graphical and statistical techniques allowed the better presentation of classical graphics and offered a reliable and objective tool for the classification of a large number of samples. In this study, use of multivariate statistical techniques (cluster analysis and factor analysis) for hydro-chemical data eliminated the limitations of Piper diagrams.

Multivariate statistical analysis

Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) was performed with Square Euclidean distance and Ward method to classify wells with similar chemical properties in the study area. The resulting dendrograms of the cluster analysis (CA) grouped the studied samples into four main clusters (Cluster A, Cluster B, Cluster C and Cluster D) in the pre-irrigation period and in three main clusters (Cluster A, Cluster B and Cluster C) in the post-irrigation period (Figure 3). In pre-irrigation period, Cluster A was composed of 17 sampling points, Cluster B was composed of 10, Cluster C was composed of 1 and Cluster D was composed of 7 sampling points. In post-irrigation period, Cluster A was composed of 14, Cluster B was composed of 20 and Cluster C was composed of 1 sampling point. In addition, it was determined that the clusters were influenced by seawater intrusion, ion exchange, mineral dissolution and anthropogenic activity, as explained below.

According to cluster analysis results, mean concentrations of analyzed water quality parameters were categorized under 4 main groups in the pre-irrigation period and 3 main groups in the post-irrigation period (Table 3).

In the pre-irrigation period, Cluster A had the least concentrations of EC, TDS, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , TH, HCO_3^- , Cl^- , %Na and SAR parameters. Mean EC of this cluster was 0.89 dS/m. Water type of Cluster A is CaHCO_3 (Table 3). CaHCO_3 fields in

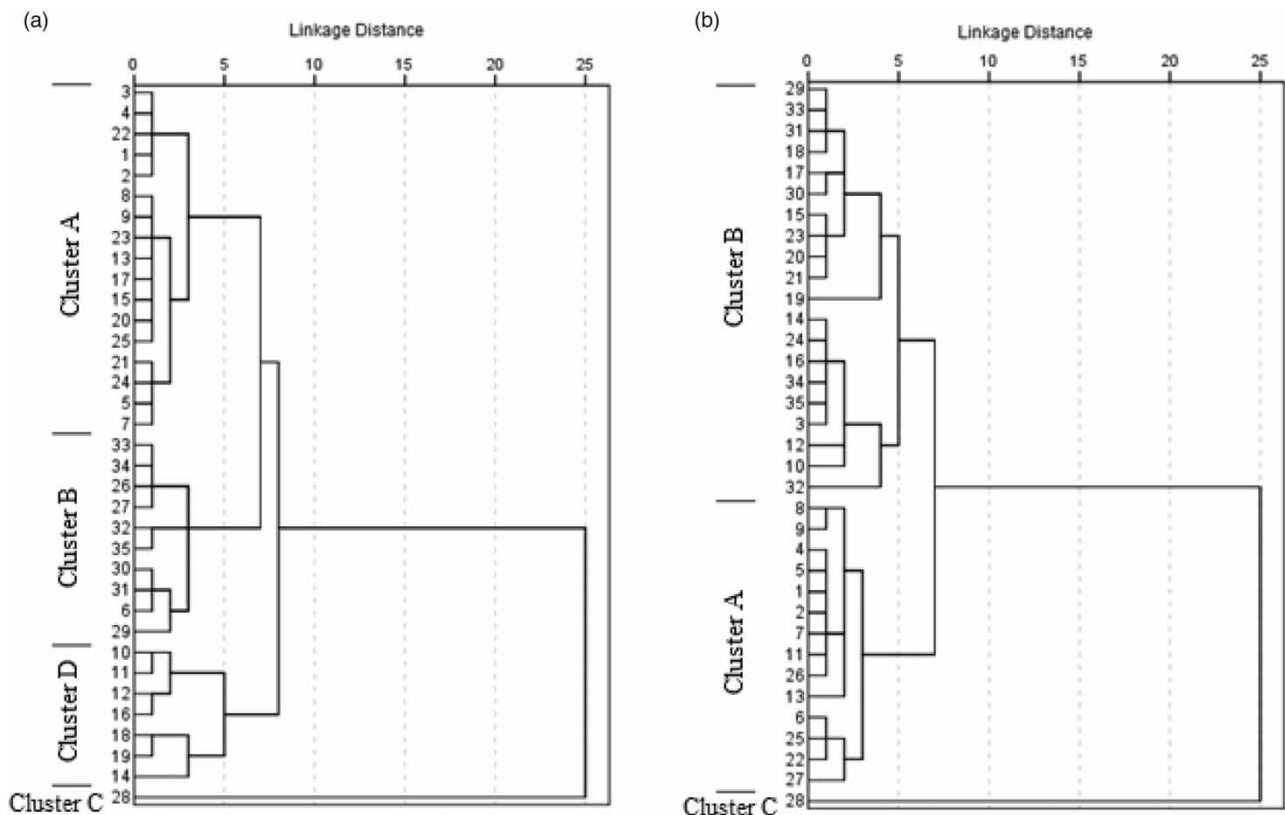


Figure 3 | Dendrogram of Q-mode hierarchical cluster analysis, (a) Pre-irrigation, (b) Post-irrigation.

Table 3 | Average values of physicochemical properties of each cluster in pre and post irrigation seasons

Parameters	Pre-irrigation				Post-irrigation		
	Cluster A (n=17)	Cluster B (n=10)	Cluster C (n=1)	Cluster D (n=7)	Cluster A (n=20)	Cluster B (n=14)	Cluster C (n=1)
pH	7.68	7.33	7.27	7.72	7.34	7.40	7.27
EC	0.89	1.13	5.45	1.49	0.83	1.38	6.13
TDS	570.81	721.34	3,489.29	952.10	533.2	884.62	3,922.03
Na ⁺	40.19	65.49	759	152.13	38.25	96.21	740.0
K ⁺	3.59	6.08	29.1	7.43	4.01	6.58	36.60
Ca ²⁺	122.87	131.28	281.84	150.03	114.33	143.45	359.44
Mg ²⁺	29.50	43.27	130.29	41.84	39.72	52.81	167.26
TH	426.91	504.32	1,235.97	545.12	447.53	573.73	1,580.76
CO ₃ ²⁻	55.34	22.32	21.60	72.17	37.46	64.35	105.60
HCO ₃ ⁻	403.95	463.14	453.99	488.33	384.34	461.43	805.46
Cl ⁻	45.56	101.23	1,347.39	152.34	61.24	177.66	1,567.15
SO ₄ ²⁻	31.16	92.50	593.81	145.46	70.37	54.59	186.59
%Na	17.18	22.41	57.65	38.16	16.20	25.74	51.09
SAR	0.84	1.31	9.37	3.03	0.79	1.71	8.08
NO ₃ ⁻	6.65	22.60	40.0	10.71	14.25	6.95	9.0
Temperature	20.88	20.18	19.50	22.51	18.94	21.54	20.0
DO	6.36	5.46	6.23	6.34	6.81	7.38	6.33
RSC	0.22	0.04	0.0	1.18	0.06	0.23	0.0
Water type	CaHCO ₃	CaHCO ₃	NaCl	CaHCO ₃ CaNaHCO ₃	CaHCO ₃	CaHCO ₃ CaNaHCO ₃	NaCl

the piper diagram are indicative of anthropogenic influences and irrigation return flow (Jeevanandam *et al.* 2007). This group is the freshest group of the study. Wells of this group were not influenced by seawater intrusion.

Cluster B had medium concentrations of EC, TDS, Na⁺, Cl⁻ and SO₄²⁻ parameters. Mean EC of this group was 1.13 dS/m which was greater than Cluster A and less than Cluster C (Table 3). Majority of wells of Cluster B had water type of CaHCO₃ without any dominant ions. In this period, only well 27 with a high Na content had CaNaHCO₃ water type. The wells 6, 29, 30, 31, 32 and 35 of this cluster had greater NO₃⁻ contents than the other wells. These wells are mostly located on the east side of the study area around the drainage canals. Excessive nitrogenous fertilizer treatments are the primary reason for nitrate pollution in groundwaters (Zhou *et al.* 2015). Wells of this Cluster was mostly influenced by excessive nitrogenous fertilizers used in paddy farming.

There was only one well (well 28) in Cluster C. The EC, Na⁺, Cl⁻, SO₄²⁻ and SAR values of this group were greater than the values of the other Clusters. Mean EC was 5.45 dS/m, Na⁺ was 759 mg/L, Cl⁻ was 1,347.39 mg/L, SO₄²⁻ was 593.81 mg/L and SAR was 9.37. The NO₃⁻ value of this cluster was 40 mg/L (Table 3). According to Piper diagram, this Cluster had NaCl water type. This group was dominant in sodium and chlorine ions. This well is located northeast of the study area close to the sea and largely influenced by seawater intrusion.

The wells of Cluster D had greater EC, Na⁺, Ca²⁺, Cl⁻, HCO₃⁻, TH and SO₄²⁻ values than the Cluster A and B and lower than the value of Cluster C (Table 3). The majority of the wells of this cluster had CaHCO₃ type of water. The wells 10 and 11 had CaNaHCO₃ type of water and well 14 had mixed type of water. The wells of this cluster were slightly influenced by seawater intrusion.

In the post-irrigation period, Q-mode cluster analysis revealed three main clusters (Figure 3(b)). Clusters A, B and C included 57.14, 40 and 2.86% of total sampling points, respectively. Wells of Cluster A are located in inner and western sections of the study area, wells of Cluster B are located in middle and eastern sections of the study area and the single well of Cluster C is located on north-eastern sections of the study area (Figure 3(b)).

Mean EC value of the wells of Cluster A was 0.83 dS/m, which was lower than the other two clusters. Majority of the samples in Cluster A had CaHCO₃ type of water and HCO₃⁻ was the dominant component. As can be seen in Figure 2, the majority of the samples were bicarbonate-type freshwaters. The wells of this cluster had the freshest waters and were not influenced by seawater intrusion. The wells of 6, 22, 25 and 27 in this cluster had greater NO₃⁻ contents than the other clusters.

The EC, Na⁺, TDS and the other parameters of Cluster B were greater than Cluster A and lower than Cluster C (Table 3). According to the Piper diagram, the majority of wells in Cluster B had CaHCO₃ type of water. Wells 17, 30 and 32 had CaNaHCO₃ type of water. The Cl⁻ contents of wells 16, 17, 24, 30, 32 and 34, located in the middle and eastern sections of the study area, had greater Cl⁻ contents than the Cl⁻ contents of the other wells of the same cluster. The wells of this cluster were slightly influenced by seawater intrusion.

Similar to the pre-irrigation period, only well 28 was placed into Cluster C. The EC, Na⁺, Cl⁻ and SAR values of this well were greater than the other Clusters. Mean EC value of the well was 6.13 dS/m, Na⁺ was 740 mg/L, Cl⁻ was 1,567.15 mg/L and SAR was 8.08 (Table 3). According to Piper diagram, this cluster was placed into section 2 and had NaCl type of water with dominant Cl⁻ ions. The well 28 was moderately influenced by seawater intrusion.

Factor analysis/principal component analysis

Factor analysis and principal component analysis were conducted to obtain correlations between the hydro-chemical components of the groundwater samples (Mondal *et al.* 2010; Arslan 2013). In both pre and post-irrigation periods, the first four factors with an eigenvalue of greater than 1 were selected to represent groundwater hydro-chemical processes without a significant loss of information. The results of factor analysis and principal component analysis performed with 18 parameters for 35 groundwater wells in the study area are given in Table 4.

Table 4 | Varimax-rotated factor loadings of groundwater quality parameters

Variables	Varimax-rotated components (pre-irrigation)				Varimax-rotated components (post-irrigation)			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
TDS	0.980	-0.018	-0.043	0.135	0.976	0.108	0.068	-0.100
EC	0.980	-0.018	-0.043	0.135	0.976	0.108	0.068	-0.100
Cl ⁻	0.969	-0.014	-0.101	0.013	0.961	0.079	-0.017	-0.153
Na ⁺	0.959	0.227	-0.031	-0.033	0.980	0.037	-0.001	-0.030
SO ₄ ²⁻	0.944	-0.019	-0.109	0.022	0.432	-0.206	-0.546	-0.394
SAR	0.857	0.472	-0.004	-0.083	0.946	0.065	0.055	0.021
Mg ²⁺	0.854	-0.157	-0.236	0.169	0.853	0.057	-0.208	-0.166
TH	0.838	-0.349	-0.042	0.400	0.930	0.116	0.059	-0.259
K ⁺	0.721	0.247	-0.111	0.026	0.810	-0.086	-0.020	0.276
Ca ²⁺	0.672	-0.441	0.124	0.514	0.809	0.143	0.271	-0.285
NO ₃ ⁻	0.527	-0.276	-0.345	0.096	-0.130	-0.366	-0.559	0.303
RSC	-0.034	0.869	0.187	0.110	-0.027	0.146	-0.002	0.885
%Na	0.638	0.709	0.016	-0.057	0.760	0.092	0.186	0.219
Temperature	-0.027	0.571	0.363	0.173	0.145	0.554	0.212	0.009
CO ₃ ²⁻	-0.085	0.198	0.950	0.121	0.223	0.828	-0.176	0.077
pH	-0.154	0.132	0.874	-0.295	-0.159	0.568	-0.217	0.396
HCO ₃ ⁻	0.228	0.063	-0.107	0.802	0.543	-0.358	0.563	0.151
DO	-0.057	0.115	-0.007	0.657	0.019	-0.128	0.681	-0.020
Eigen values	8.580	2.412	2.075	1.730	8.760	1.745	1.682	1.562
Variance (%)	47.668	13.402	11.526	9.612	48.665	9.695	9.343	8.676
Cumulative (%)	47.668	61.070	72.596	82.207	48.665	58.360	67.703	76.378

Bold values indicate strong (>0.75) and moderate (0.75–0.50) loading.

In the pre-irrigation period, four factors with an eigenvalue of greater than 1 explained 82.207% of the total variance. In the pre-irrigation period, 47.668% of the total variance was constituted by Factor 1. The EC, TDS, Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , Na^+ , TH and SAR had high positive factor loadings (Table 4). This situation is an indication of the mixing of salty seawater and fresh groundwater (Akshitha *et al.* 2021). The SO_4^{2-} sources in water resources may include atmospheric storage (Wayland *et al.* 2003) and oxidation of SO_4^{2-} containing fertilizer and sulfur compounds (Sidle *et al.* 2000). Medium levels of positive loading of Ca^{2+} , K^+ and NO_3^- may be related to domestic (sewage) effects and fertilizer uses (Aravinthasamy *et al.* 2019). This factor is defined as the salinity factor because it includes parameters that could create salinity in the water, and Cl^- is known as a sign of seawater intrusion into groundwater (Huang *et al.* 2010). The waters in this factor are salty water and the investigation shows that groundwater could have seawater intrusion.

Factor scores were used to assess which parameters were more effective in which wells (Arslan 2013). Spatial distribution of factor scores was interpolated with the use of Inverse Distance Weighted (IDW) geostatistical method (Figure 4). In the pre-irrigation periods, the sections indicated with darker colors had greater scores and these areas represented high salinity areas (Figure 4(a)). The sections with lighter colors had low factor scores and represented low-salinity areas. The greatest PC1 values were marked on northern sites of the study area close to the sea and especially around well 28. This well represents Cluster C in the pre-irrigation period and this well is not recommended to be used in irrigation. There might be medium loadings around wells 29, 30, 31, 32 and 27 of Cluster B with high NO_3^- content located on the east and middle sections of the study area and wells 8, 9, 11, 12, 14 and 15 of Cluster D with high Na contents (Figure 4). In brief, some members of Cluster B and D and the single member of Cluster C might be influenced by Factor 1 in the pre-irrigation period.

Factor 2, constituting 13.402% of the total variance, is primarily related to %Na, RSC and temperature. The %Na and RSC are commonly used to assess the suitability of waters for irrigation (Wilcox 1955; Raju 2007). Na^+ reduces soil permeability and is largely used for the classification of irrigation waters. Total carbonate and bicarbonate concentrations greater than total calcium and sodium contents influence the potential use of groundwaters in irrigation. When the total HCO_3^- and CO_3^{2-} exceeded total Ca^{2+} and Mg^{2+} , Ca^{2+} and Mg^{2+} precipitate. Therefore, greater sodium adsorption is encountered and such a case then increases sodium damage (Saha & Paul 2019). This factor is also called the 'sodium hazard' factor. Spatial distribution of scores of Factor 2 is presented in Figure 4(a). The sections with greater %Na and RSC values had greater scores and these sections were indicated with dark colors. Lower scores were indicated with lighter colors. The greatest PC2 values were observed in northern sections of the study area starting from the seashores and extending toward the inner sections. Well 14 of Cluster D had %Na and RSC values quite greater than the allowable limits. This well should not be used in irrigation. Also, wells 14, 18 and 19 of Cluster D had RSC values greater than the suitable value of 1.25 meq/L. The %Na value of well 27 of Cluster B was within the allowable limits.

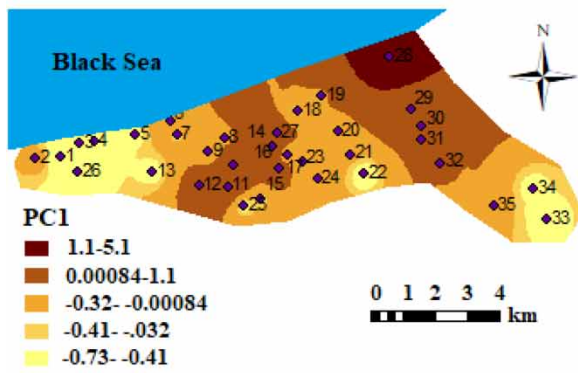
Factor 3 constituted 11.526% of total variation and had strong positive correlations with CO_3^{2-} and pH (Figure 4(a)). The pH of groundwater in the study area was found to be greater than 7. According to Sharma *et al.* (2015), water may be alkaline due to carbonates and bicarbonates added to water while passing through soil or rock. This factor (Factor 3) could be defined as the alkalinity factor. Spatial distribution of factor scores is presented in Figure 4(a). Dark color sections were more influenced by alkalinity and light-color sections were less influenced by alkalinity. Members of Cluster D and A were influenced by Factor 3 (Figure 4(a)). Except for well 14, groundwater wells of this group could be used in irrigation.

Factor 4, constituting 9.612% of total variation, had strong positive factor scores for HCO_3^- and DO. Spatial distribution of factor scores is presented in Figure 4(a). Greater scores were distributed in wells 7, 10, 11, 18, 19, 21, 32 and 35. HCO_3^- may come from carbonate degradation and bacterial destruction of organic pollutants (Selvam *et al.* 2016). Water dissolved oxygen levels partially depend on chemical, physical and biochemical activities. Oxygen is directly related to atmospheric pressure, inversely proportional to water temperature and salinity and has limited solubility in water (Trick *et al.* 2008). This factor (Factor 4) could be defined as the 'ionic exchange' factor. Groundwater chemistry of the study area was controlled by silicate degradation, ion exchange, sea water intrusion, mineral decomposition and anthropogenic factors (fertilizer and pesticide use in agriculture, sewage and etc.).

In the post-irrigation period, there were four factors with eigenvalues greater than 1. These four factors explained 76.378% of the total variation. Eigenvalue of the first factor, constituting 48.665% of total variation, was 8.760. Eigenvalues of the second, third and fourth factors were respectively calculated as 1.745, 1.682 and 1.562 and these factors respectively explained 9.695%, 9.343% and 8.676% of total variation (Table 3).

Factor 1 explained 48.665% of the total variance and was loaded strongly by EC, TDS, TH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , %Na, and SAR (Table 3). This factor is the so-called salinity factor. Dark-color sections of Figure 4(b) had greater scores and

(a) Pre-irrigation



(b) Post-irrigation

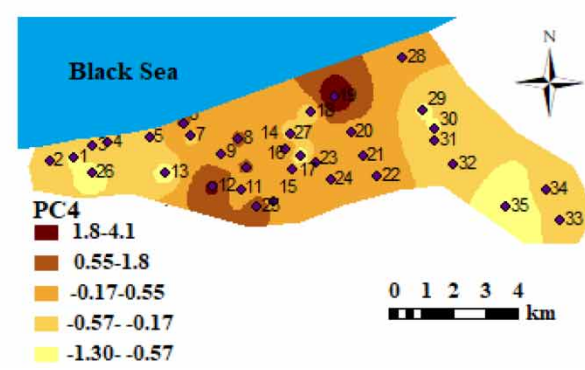
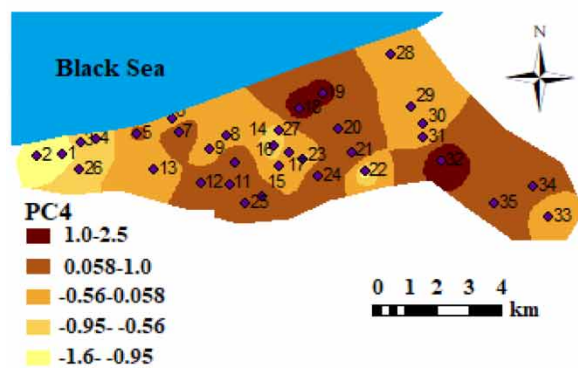
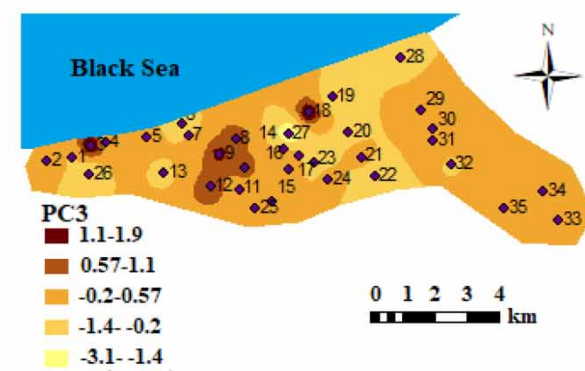
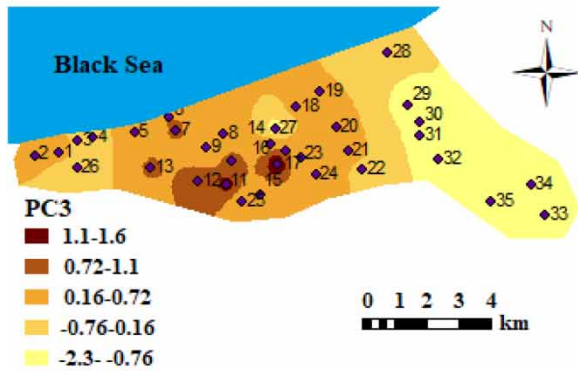
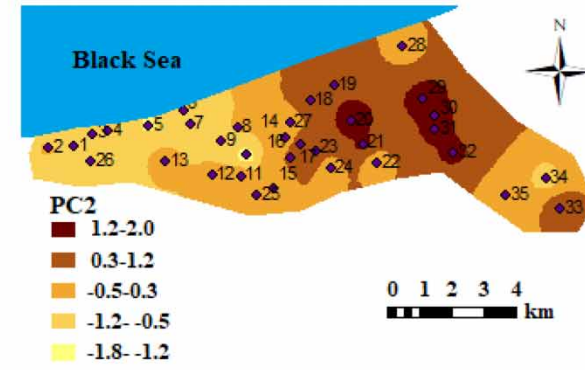
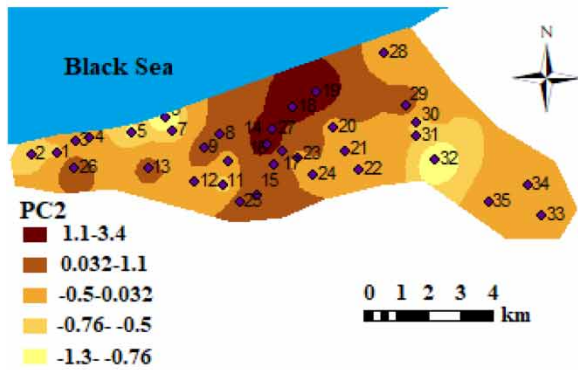
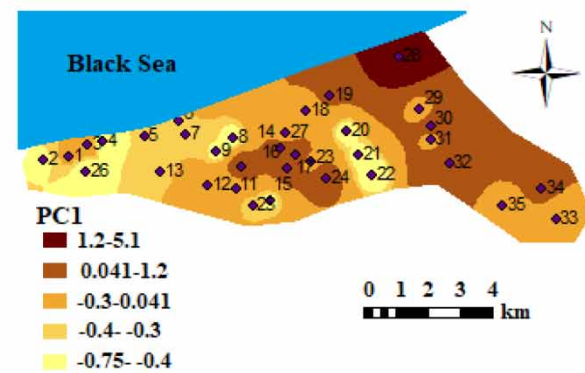


Figure 4 | Spatial distribution of factor scores for the factor analysis (a) PC1 (salinization), PC2 (sodium hazard), PC3 (alkalinity) and PC4 (ionic exchange), (b) PC1 (salinization), PC2 (alkalinity), PC3 (anthropogenic) and PC4 (sodium hazard).

represented highly saline areas. Light-color sections had smaller scores, representing low-salinity areas. Factor 1 was marked mainly around well 28, located in the north-eastern section of the study area. Similar to the pre-irrigation period, this well represented Cluster C in the post-irrigation period and is not recommended to be used in irrigation. If the Cl^- content of shore waters increases, the Na/Cl ratio decreases and the aquifer is then subjected to salinity increase through seawater intrusion (Tasan 2017). Huang *et al.* (2010) indicated that over-pumping spoiled groundwater quality via seawater intrusion. It is recommended that wells of this group (Cluster B) should be used for irrigation in a controlled fashion.

Factor 2 explained 9.695% of the variance and was the best represented by pH, CO_3^{2-} and temperature. In the post-irrigation period, the pH value of groundwater was found to be greater than 7. This factor could be defined as the alkalinity factor. Spatial distribution of scores of Factor 2 is presented in Figure 4(b). Dark-color sections indicate highly alkaline areas and the light-color sections indicate low-alkalinity areas. Members of Cluster B were influenced by Factor 2 (Figure 4(b)). Groundwaters of this group can be used for irrigation.

Factor 3 is responsible for 9.343% of the total variance and is represented by NO_3^- , SO_4^{2-} , HCO_3^- and DO. Spatial distribution of the scores of Factor 3 is presented in Figure 4(b). Wells 3 and 18 had quite high SO_4^{2-} contents as indicated by dark color. The sources of dissolved SO_4^{2-} in natural waters may include dissolution of sedimentary sulfates, oxidation of both sulfide minerals and organic materials, and anthropogenic inputs (Nagaraju *et al.* 2017). Zghibi *et al.* (2013) reported that sulfate-containing fertilizers and livestock manure significantly increased NO_3^- concentrations. This factor is also called the 'anthropogenic' factor. Members of Cluster A were influenced by Factor 3. Groundwaters of Factor 3 could be used for irrigation purposes.

Factor 4 constituted 8.676% of total variation and was largely represented by RSC. This factor could be defined as the 'sodium hazard' factor. Spatial distribution of factor scores is illustrated in Figure 4(b). Dark-color sections had high RSC scores and light-color sections had low RSC scores. Well 19 of Cluster B had an RSC value greater than the suitable value of 1.25 meq/L, but was still at a level that could be used for irrigation (<2.5 meq/L).

CONCLUSIONS

In this study, multivariate statistical analyses (cluster analysis, principal component/factor analysis) were used to determine the factors controlling quality and sustainability of groundwaters in Alaçam town of Samsun province located in the Black Sea region of Turkey. In addition, the suitability of using groundwater for irrigation was evaluated by using EC, SAR, Na % and RSC parameters. It has been identified that most of the groundwater in the study area is in the appropriate range for use for irrigation purposes. The results showed that the groundwater quality in the area close to the sea and the east of the study area was poorer compared with the other areas. The effect of seasonal change was found to be significant in terms of some quality parameters (such as EC, TDS, Cl). EC, K and Mg concentrations of groundwater increased in the post-irrigation period based on seawater intrusion. The Piper diagram showed that most of the water samples consisted of Ca- HCO_3 type freshwaters. While well no 14 showed NaCl-type water characteristic pre-irrigation, well no 28 showed this characteristic both pre and post irrigation periods. According to the cluster analysis results, in both the pre-irrigation and post-irrigation periods, the member of cluster C (well no. 28) was significantly affected by the seawater intrusion. It was suggested that this well should not be used for irrigation purposes. Group D members in the pre-irrigation period and group B members in the post-irrigation period were slightly affected by seawater intrusion. Wells in other clusters provided marginal quality groundwater for irrigation. High nitrate concentrations were determined in 6 (Cluster B) wells pre-irrigation and 4 (Cluster A) wells post-irrigation. These wells were located in the east of the study area and around the surface drainage channels. The use of chemical fertilizers should be reduced for sustainable groundwater quality management. When the principal component analysis results are considered, the first factor (PC1) is strongly associated with the increase in salinity caused by seawater intrusion in both periods. Anthropogenic activities that affected some wells in the study area have been determined (wells no. 8, 9 and 18). Factor scores were illustrated in spatial distribution maps. The spatial distribution maps make an important contribution in determining the areas most affected by water quality parameters. Also, these maps have shown that seawater intrusion and anthropogenic effects are locally present in the study area.

It was concluded based on present findings that multivariate statistical techniques could reliably be used in the assessment of groundwater quality, identification of important factors designating water quality and analysis and interpretation of complex datasets. The lack of irrigation facilities has forced the farmers to use groundwaters for irrigation. Excessive use of groundwaters in areas close to the sea accelerated seawater intrusion and ended up with spoilage of groundwater quality. Therefore, groundwaters of such areas should be used in a controlled fashion.

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CONFLICT OF INTERESTS

The authors of this article declare that they have no conflict of interests.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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