



Assessment of groundwater quality using multivariate statistical techniques in the Azmak Spring Zone, Mugla, Turkey

Sukran Acikel¹ · Mehmet Ekmekci²

Received: 8 August 2018 / Accepted: 1 November 2018 / Published online: 15 November 2018
© Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract

About 150 coastal spring outlets discharging from a karstified carbonate rock aquifer constitute the Azmak streamflow which is slightly brackish with 3000 mg/l of total dissolved solids. In this study, multivariate statistical methods were applied including the use of factor analysis, correlation analysis and cluster analysis to evaluate groundwater quality of Azmak Spring Zone using eight variables (Ca, Mg, Na, K, Cl, SO₄, EC₂₅ and B) at 19 water points sampled in the dry and wet seasons. Hydrochemical analysis results revealed that for majority of the sampling points, the abundance of cations and anions were ordered as Na + K > Mg > Ca and Cl > SO₄ > HCO₃ + CO₃, respectively. Factor analysis results indicated that three factors explain 98% and 91% of the total variance in the dry and wet seasons, respectively. Factor 1 was found to be associated with the seawater, factor 2 indicated the effect of fresh water and factor 3 was defined to reflect the effect of seasonal fresh surface water contribution. Cluster analysis results indicated that two main groups and four subgroups could be defined with respect to the ratio of the seawater contribution. Cluster A (A1 and A2) represents the waters affected by seawater while waters less affected by the seawater intrusion are grouped in cluster B (B1 and B2).

Keywords Multivariate statistical method · Cluster analysis · Factor analysis · Coastal spring · Seawater intrusion

Introduction

Karstic groundwater systems are among the most important, yet the most vulnerable fresh water resources. The uncontrolled population growth is an issue having serious impact on the availability of fresh water. The major karstic groundwater systems in Turkey mostly exist in the Taurus Mountain range which extends along the Mediterranean Sea. Owing to the well-developed karst, the aquifers discharge through large karstic springs at low altitudes, mostly as coastal and to a lesser extent as submarine springs (Ekmekci 2003). Coastal karstic springs are even more vulnerable to changes in groundwater systems (Arfib et al. 2007; Montety et al. 2008; Najib et al. 2017). Salinization due to sea water intrusion induced by exploitation of the aquifer to meet the

increasing demand for fresh water is the primary threat on these water resources. Prediction of the hydrogeological behavior of karstic springs in response to exploitation is crucial for an effective management of the karst aquifer. This paper presents a complex coastal karstic spring zone where salinity is an issue. The complexity of the system is revealed in the irregular distribution of salinity at the closely located spring outlets. Chemical characterization of these coastal karstic springs was the major objective of this study. This objective was achieved by employing multivariate analysis on large volume of hydrochemical data collected from the field.

Multivariate statistical analysis techniques such as factor analysis (FA) and cluster analysis (CA) are commonly carried out on hydrogeological data sets for the characterization of the groundwater systems (Arslan 2013; Behera and Das 2018; Belkhir et al. 2011; Bilgin and Konanc 2016; Fatoba et al. 2017; Li et al. 2011; Kazakis et al. 2017; Martinez-Tavera et al. 2017; Masoud et al. 2018; Siepak and Sojka 2017; Subbarao et al. 1996; Yidana et al. 2018). The main applications of FA are to reduce the number of variables and to detect structure in the relationships between variables or to classify them (Davis 1973; Liu et al. 2003; Matiatos et al.

✉ Sukran Acikel
sukransahbudak@yahoo.com

¹ Hacettepe University Hydrogeological Engineering Program, Beytepe, 06800 Ankara, Turkey

² International Research and Application Center for Karst Water Resources, Hacettepe University, Beytepe, 06800 Ankara, Turkey

2014; Semar et al. 2013; Simonov et al. 2003; Zhang et al. 2016). In addition to FA, cluster analysis (CA) can be used to classify groups of hydrochemical data according to their similarities to each other and distinguish different groundwater systems (Filho et al. 2017; Suk and Lee 1999). All these studies have proved that multivariate statistical analysis is very efficient in characterizing groundwater systems particularly in terms of water quality.

The study area is located at the coast in the southwestern part of Turkey in a semi-arid region (Fig. 1). The local people suffer from water scarcity especially in summer months because the area is a touristic attraction site. The population is around three thousand in winter, whereas it increases to ten thousand in summer time. The mean annual precipitation and temperature in the region are 1146 mm and 15 °C, respectively. The precipitation is higher than the regional average, however due to the high annual air temperature about 70% of the precipitation is lost by evapotranspiration. This study focuses on the karst spring zone, known

as the “Azmak springs” that discharge through about 150 outlets along 2 km. The spring outlets are aligned along a major fault line. The specific electrical conductivity (EC_{25}) which is an indication of salinity ranges between 1300 and 15,000 $\mu\text{S}/\text{cm}$. The springs flow into a natural channel which also collects groundwater flow from the surrounding karst and alluvial aquifer as well as the seasonal surface runoff. The total streamflow at the channel (named the Azmak Stream) is measured at the automatic Azmak Gauging Station, located close to the sea. The average total flow at the Azmak Gauging Station is calculated as about 11 m^3/s and the average specific electrical conductivity is about 5000 $\mu\text{S}/\text{cm}$. This value represents the complete mixing of all flow components including the karstic coastal springs, the alluvial groundwater and the surface runoff.

The salinity of the karst springs is high and not suitable for drinking. Multivariate analysis techniques were also employed to identify salinity sources and pollution indicators in the region. In addition, analysis of seasonal changes

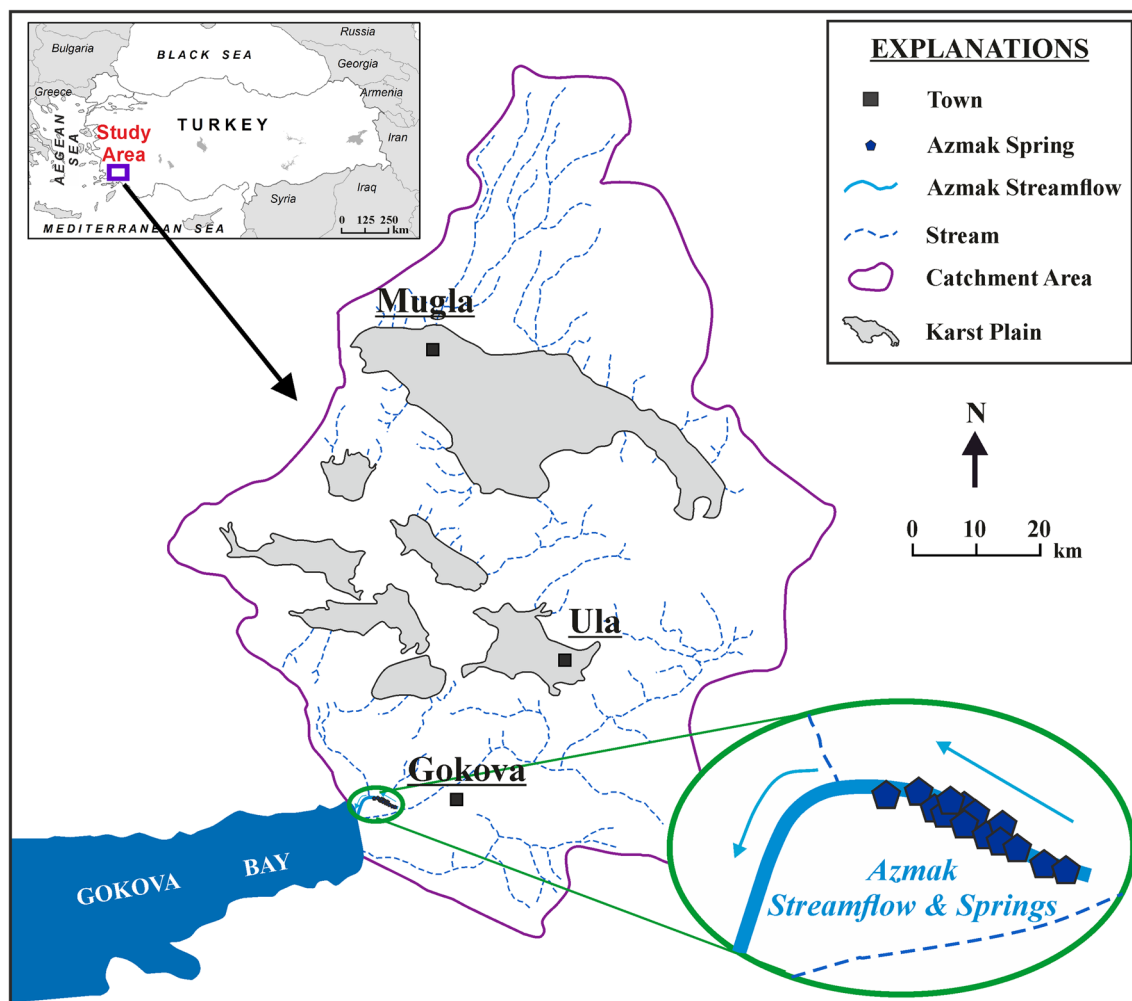


Fig. 1 Location map of the study area

of salinity and hydrochemical properties of springs also provides an important tool for a better understanding of the hydrogeological system. In this study, seasonal changes were also considered to evaluate the hydrochemical characterization of the Azmak streamflow karst system.

Geology and hydrogeology

The watershed of the coastal spring zone which covers an area of 460 km² is located on the western coast of Turkey. The area is located on the thrust zone between the allochthonous Bodrum Nappes and the autochthonous Menderes Massif. The geological formations consist of a sequence of autochthonous and allochthonous rock masses of Paleozoic to Cenozoic age (Fig. 2). The autochthonous Menderes Massif's bedrocks consist of Paleozoic schists which are overlain by pervious, extensively karstified carbonate units of Mesozoic age. The allochthonous Bodrum Nappes consisting of impervious non-carbonate rocks and karstic carbonate rocks overthrust these two autochthonous units. The Plio–Miocene age post-tectonic units composed of

conglomerates, overlies all older units. The major aquifers are the well-karstified autochthonous and allochthonous carbonate rocks in the study area (Acikel 2012). The alluvial deposits in the Gokova plain constitute the third extensive aquifer, which is partly under confined conditions. The karstic aquifers discharge mainly through the coastal and submarine springs, whereas alluvial aquifer discharges through the Azmak streamflow as baseflow.

Based on detailed analyses of hydrogeological, hydrochemical and isotopic data, Acikel (2012) has distinguished three main circulation systems in the study area. The sampled water points have been classified to belong to a shallow circulation system, deep circulation system and those affected by seawater mixing (Fig. 3). Figure 3 is a plot of δ¹⁸O versus specific electrical conductivity (EC₂₅). It depicts 3 clusters of waters, namely low EC₂₅-depleted δ¹⁸O (indication of high altitude of recharge area and deep circulation), low EC₂₅-enriched δ¹⁸O (indication of local recharge and shallow circulation) and increasing δ¹⁸O with increasing EC₂₅ (indication of mixing with seawater). Figure 3 suggests that the wells tap shallow circulated groundwater and the majority of the springs originate from deep circulated groundflow.

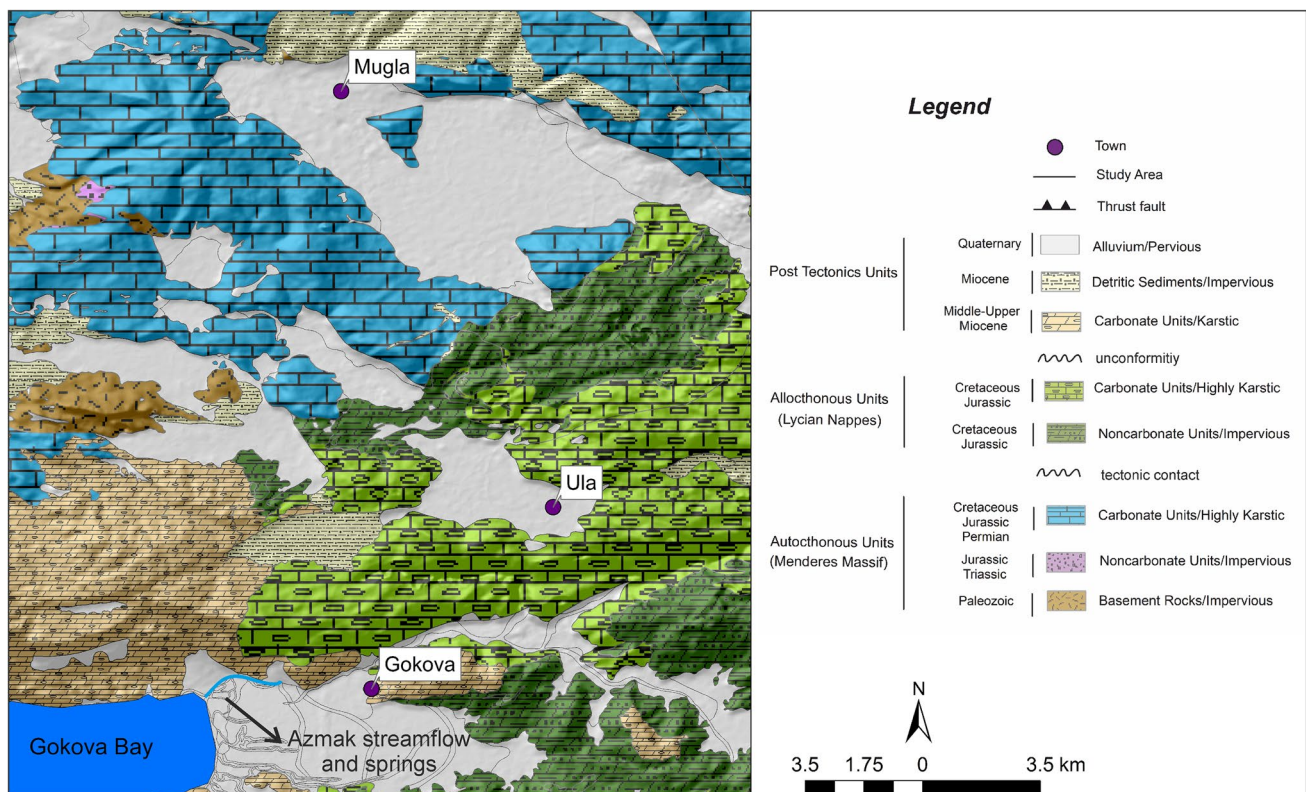


Fig. 2 Geological map and a general cross-section of the study area (Acikel 2012)

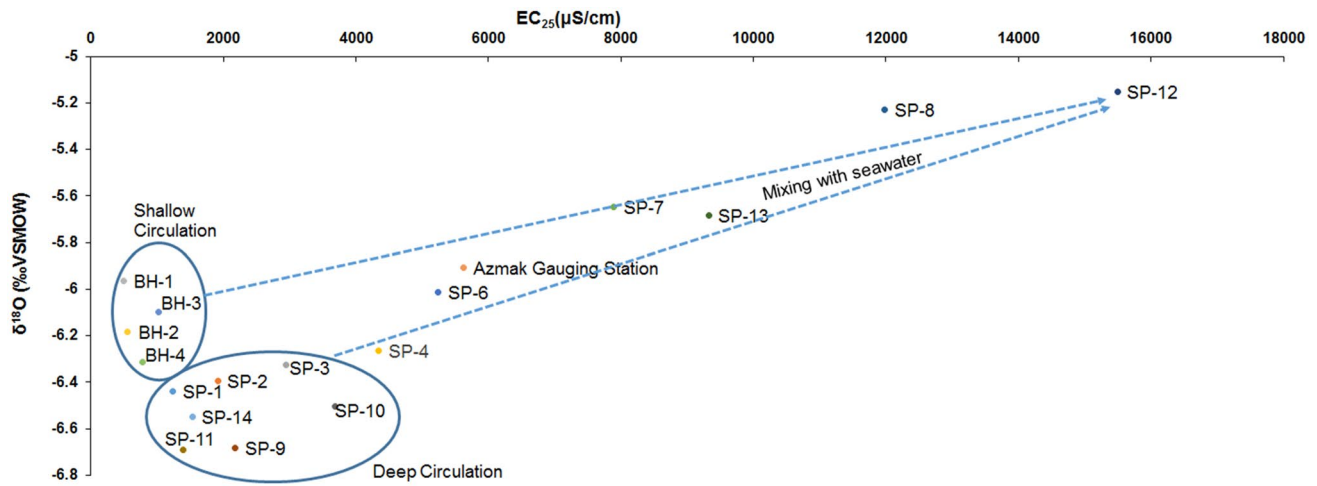


Fig. 3 Plot of EC_{25} and $\delta^{18}O$

Materials and methods

Sampling and analysis

During field studies, a total of 13 springs (SP-1, SP-2, SP-3, SP-4, SP-6, SP-7, SP-8, SP-9, SP-10, SP-11, SP-12, SP-13, SP-14) of 150 coastal springs were selected for sampling and chemical analysis. The springs are numbered according to their distance from the sea (SP-1 is the farthest, SP-14 is the closest to the sea). The Azmak Gauging Station (AGS) was also selected as a sampling point. In addition, four wells which represent the karst groundwater (BH-1 and BH-4), confined plain aquifer (BH-2), unconfined plain aquifer (BH-3) and seawater (SeaW) were sampled. A map showing the sampled points is given in Fig. 4. The basic information on the sampling points is given in Table 1.

These 19 water points were sampled for the dry and wet seasons in 2010 and 2011 to study the seasonal variability of hydrochemical characterization on the sampling points. Thus, a total of 38 samples were collected and analyzed for this study. During sampling, some parameters were also measured in the field. The specific electrical conductivity (EC_{25}), pH and temperature (T) were carried out by a multiprobe (YSI-56 MP5™) with an accuracy of $\pm 0.01 \mu S/cm$, ± 0.01 units and ± 0.01 °C, respectively. Major cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), anions (Cl^- and SO_4^{2-} , HCO_3^-) and trace element (B, Br, Sr and Li) were analyzed at the ALS Laboratories (Sweden).

In situ measurements and hydrochemical analysis

Major ions (Ca, Mg, Na, K, Cl, SO_4 , HCO_3) and trace elements (Br, B, Sr, Li) of the sample points were analyzed and in situ measurements (T , EC_{25} , TDI and pH) carried out at the sampling points during the dry and wet seasons.

The results given in Table 2 were evaluated using a semi-log (Schoeller) diagram, ionic ratios and statistical parameters such as the coefficient of variation.

Multivariate statistical analysis

SPSS 11™ (Statistical Package for Social Science) was used to perform the correlation among variables and multivariate analysis for sampling points in the study area. Multivariate statistical methods are ever-expanding set of techniques for the classification, modeling and interpretation of large datasets from environmental monitoring programs and hydrochemical quality evaluations (Simeonov et al. 2003). Statistical methods such as cluster analysis (CA) and factor analysis (FA) are among the most commonly used multivariate statistical methods. These methods were also employed on 38 samples for 8 variables in this study.

For statistical analysis, the Shapiro–Wilk statistics test was applied to check if the data are normally distributed. Shapiro–Wilk test results were greater than 0.834 and 0.702 for all variables except Ca for dry and wet season, respectively. For dry and wet seasons, Mg, Na, K, Cl, SO_4 , EC_{25} and B were log-transformed to accommodate normally distributed data. Then, all variables were standardized to avoid misclassification because of the differences in dimensionality by calculating their standard scores (z -scores) as follows:

$$Z_i = \frac{X_i - X}{S}, \quad (1)$$

where Z_i is the standard score of the sample i ; X_i is the value of sample i ; X is the mean, and S is the standard deviation (Güler et al. 2002).

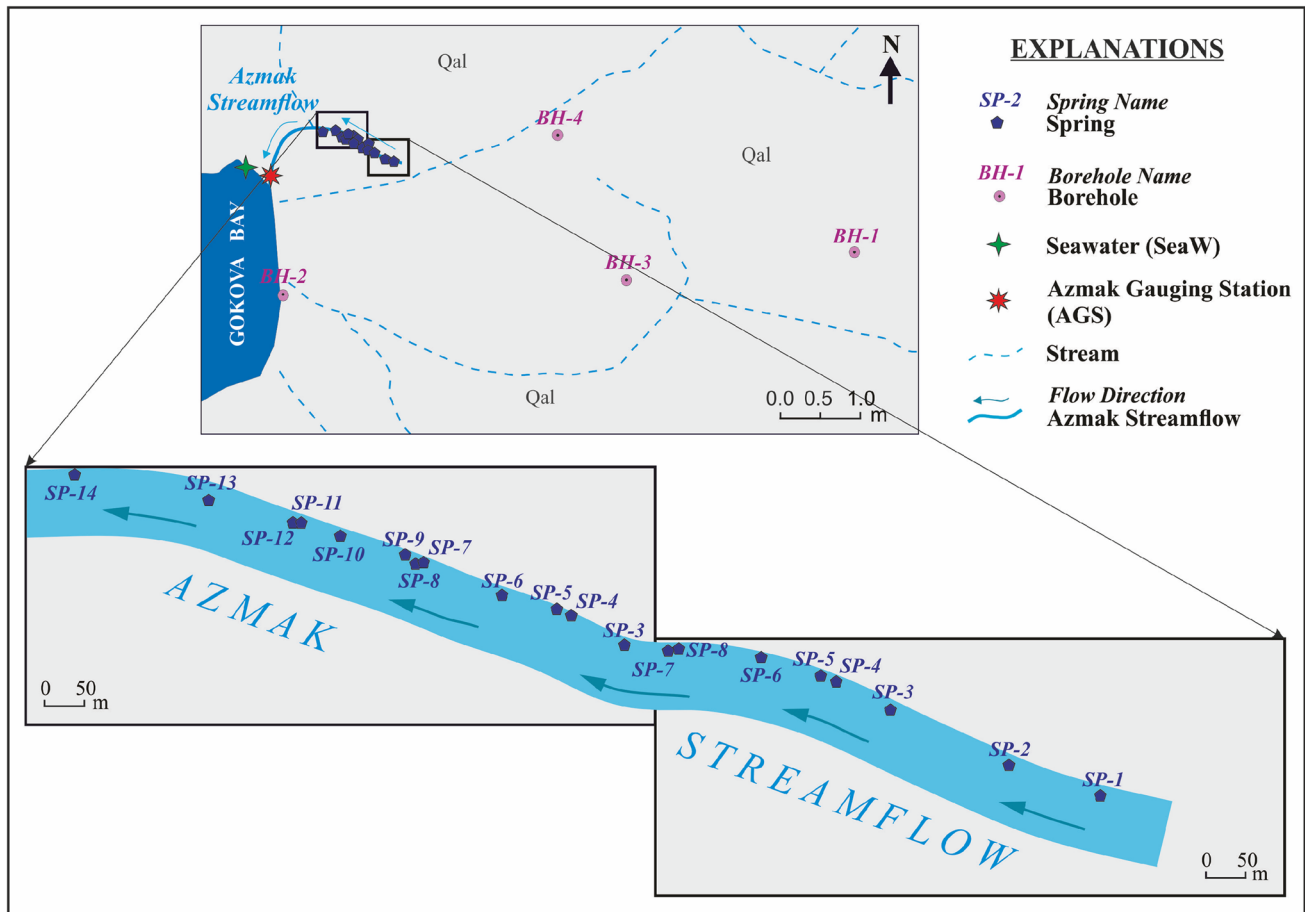


Fig. 4 Sampling map of the study area

Table 1 Basic information on the sampling points

Sample code	Sample type	Distance from sea	TDS (mg/l)
SP-1	Spring	1850 (m)	804
SP-2	Spring	1800 (m)	1222.5
SP-3	Spring	1011 (m)	1920
SP-4	Spring	835 (m)	2870.5
SP-6	Spring	725 (m)	3446
SP-7	Spring	712 (m)	4697
SP-8	Spring	657 (m)	8467
SP-9	Spring	582 (m)	1324.5
SP-10	Spring	566 (m)	2619
SP-11	Spring	563 (m)	910.5
SP-12	Spring	447 (m)	9760
SP-13	Spring	378 (m)	5861
SP-14	Spring	290 (m)	989
AGS	Gauging station	160 (m)	3767.5
SeaW	Sea	0 (m)	36,710
BH-1	Well	7 (km)	281.5
BH-2	Well	2 (m)	368
BH-3	Well	4.5 (km)	651.5
BH-4	Well	3 (km)	500.5

Correlation analysis

Correlation analysis is a common and useful statistical tool indicating the strength of the association between variables. Correlation coefficients (r) of the variables were used to measure relationship between variables in the current study. The correlation coefficients of the all variables were calculated using Pearson’s correlation analysis and are given in Table 3. In Table 3, where + 1 indicates a perfect positive relationship and 0 indicates no relationship between the correlated parameters, all correlation coefficients are positive expressing the similarity in the same direction.

Principal component analysis (PCA)/factor analysis

PCA is one of the multivariate statistical techniques which explains the variance of a large set of variables and transforming into a smaller set of independent variables (Singh et al. 2004). The Kaiser–Meyer–Olkin (KMO) and Bartlett sphericity tests were applied to the correlation matrix of variables for testing of the PCA compatibility. The KMO indicates the proportion of variance in variables. High

Table 2 Values of the variables during dry and wet seasons

Sample code	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	TDI(mg/l)	EC (µS/cm) ₂₅	T(°C)	pH	Br (ppb)	B (ppb)	Sr (ppb)	Li (ppb)	
Dry season																
SP-1	113	36	105	5	212	180	250	901	1232	16	7	721	56	1329	3	
SP-2	138	53	208	10	374	285	243	1310	1914	16	7	1232	94	1971	4	
SP-3	159	77	381	20	748	443	246	2075	2939	16	7	2401	189	2854	8	
SP-4	187	107	614	36	1320	624	246	3134	4339	16	7	4997	358	4611	18	
SP-6	192	123	764	45	1590	644	246	3605	5245	16	7	6467	464	4613	17	
SP-7	176	161	1250	72	2210	554	245	4668	7886	16	7	9364	597	3587	24	
SP-8	197	254	2160	103	4250	845	243	8052	11,981	16	7	17,396	1121	4600	50	
SP-9	113	52	270	11	484	175	251	1356	2172	15	7	1812	88	1203	4	
SP-10	106	58	394	18	687	169	253	1685	3682	15	7	2702	155	1070	6	
SP-11	88	38	180	9	338	81	256	990	1397	15	7	947	71	432	3	
SP-12	240	331	2830	136	4930	1100	242	9809	15,500	17	6	19,738	1242	5948	61	
SP-13	151	194	1640	93	2870	503	249	5699	9330	15	7	11,121	743	2398	28	
SP-14	87	37	178	9	350	84	261	1005	1536	15	7	1342	92	524	4	
AzmaK Gauging Station (AGS)	170	127	850	50	1750	561	246	3754	5622	16	7	6363	428	3381	17	
Min	87	36	105	5	212	81	242	901	1232	15	6	721	56	432	3	
Max	240	331	2830	136	4930	1100	261	9809	15,500	17	7	19,738	1242	5948	61	
x	151	118	845	44	1580	446	248	3432	5341	16	7	6186	407	2751	18	
SD	46	90	837	42	1508	303	5	2785	4368	1	0	6178	393	1754	18	
cv	30	76	99	95	96	68	2	81	82	4	3	100	97	64	103	
BH-1	84	21	5	1	7	65	237	419	492	16	7	55	13	911	1	
BH-2	57	40	9	1	18	123	201	449	554	16	7	88	20	1214	2	
BH-3	95	55	40	2	101	244	231	768	1021	17	8	20	12	422	1	
BH-4	111	34	15	1	31	199	259	649	781	17	7	313	27	1435	3	
Min	57	21	5	1	7	65	201	419	492	16	7	20	12	422	1	
Max	111	55	40	2	101	244	259	768	1021	17	8	313	27	1435	3	
x	87	37	17	1	39	158	232	571	712	17	7	119	18	995	2	
SD	23	14	16	0	42	80	24	166	241	0	0	132	7	438	1	
cv	26	39	92	36	108	51	10	29	34	2	6	111	39	44	65	
Seawater (SeaW)	189	630	7710	315	14,400	1830	210	25,284	54,575	30	8	47,655	3231	5882	123	
Wet season																
SP-1	106	36	97	5	196	169	257	866	1241	15	7	489	43	1152	2	
SP-2	127	53	177	9	378	380	248	1372	1846	16	7	932	79	1905	4	
SP-3	140	84	466	25	984	492	194	2384	2968	16	7	2022	187	2828	8	
SP-4	180	106	600	33	1140	500	249	2807	4492	16	6	3079	259	3544	15	

Table 2 (continued)

Sample code	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	TDI(mg/l)	EC (µS/cm) ₂₅	T (°C)	pH	Br (ppb)	B (ppb)	Sr (ppb)	Li (ppb)
SP-6	185	121	747	41	1680	640	245	3659	5367	16	7	3710	309	3504	18
SP-7	158	133	990	52	2200	521	237	4290	6564	16	7	4805	407	2494	19
SP-8	199	272	2520	116	4800	880	243	9030	14,075	16	9	11,766	874	3744	41
SP-9	103	48	246	10	542	174	295	1418	1903	15	9	1192	87	956	4
SP-10	110	80	569	29	1280	261	248	2576	4359	15	8	2930	245	1235	13
SP-11	81	32	125	7	278	73	262	858	1399	15	8	642	63	411	3
SP-12	231	334	3200	139	6440	1180	240	11,764	15,200	17	8	13,027	982	4614	45
SP-13	134	166	1540	80	3180	539	251	5890	8716	15	7	7133	560	1850	25
SP-14	82	34	151	8	345	80	262	962	1504	15	8	820	72	430	3
AzmaK Gauging Station (AGS)	162	128	881	47	1910	563	249	3940	5992	16	8	4689	383	2948	19
Min	81	32	97	5	196	73	194	858	1241	15	6	489	43	411	2
Max	231	334	3200	139	6440	1180	295	11,764	15,200	17	9	13,027	982	4614	45
x	143	116	879	43	1811	461	248	3701	5402	16	8	4088	325	2258	16
SD	45	90	940	42	1852	311	21	3242	4516	1	1	4016	298	1325	14
cv	32	78	107	98	102	67	9	88	84	3	10	98	92	59	87
BH-1	40	21	5	2	7	12	205	292	374	15	7	18	16	57	0.4
BH-2	57	42	8	1	20	127	195	451	580	16	8	56	15	917	1
BH-3	89	56	40	2	101	227	229	743	983	16	7	241	25	1355	3
BH-4	110	35	13	1	27	195	257	639	759	16	8	71	18	1270	2
Min	40	21	5	1	7	12	195	292	374	15	7	18	15	57	0.4
Max	110	56	40	2	101	227	257	743	983	16	8	241	25	1355	3
x	74	39	16	1	39	140	222	531	674	16	7	97	19	900	2
SD	31	14	16	1	42	95	28	200	259	1	1	99	5	593	1
cv	42	37	96	46	109	68	13	38	38	6	7	102	24	66	64
Seawater (SeaW)	210	800	8500	370	14,400	2000	210	26,490	58,385	18	8	25,493	2200	4018	92

Table 3 Correlation matrix of variables

Correlations		Ca	Mg	Na	K	Cl	SO ₄	EC ₂₅	B
Dry season									
Ca		1							
Mg		0.857 ^a	1						
Na		0.824 ^a	0.892 ^a	1					
K		0.853 ^a	0.906 ^a	0.985 ^a	1				
Cl		0.824 ^a	0.893 ^a	0.998 ^a	0.976 ^a	1			
SO ₄		0.919 ^a	0.937 ^a	0.815 ^a	0.823 ^a	0.827 ^a	1		
EC ₂₅		0.843 ^a	0.967 ^a	0.958 ^a	0.967 ^a	0.953 ^a	0.885 ^a	1	
B		0.868 ^a	0.928 ^a	0.962 ^a	0.981 ^a	0.955 ^a	0.856 ^a	0.972 ^a	1
Wet season									
Ca		1							
Mg		0.896 ^a	1						
Na		0.870 ^a	0.883 ^a	1					
K		0.855 ^a	0.891 ^a	0.972 ^a	1				
Cl		0.862 ^a	0.874 ^a	0.998 ^a	0.960 ^a	1			
SO ₄		0.907 ^a	0.891 ^a	0.849 ^a	0.773 ^a	0.857 ^a	1		
EC ₂₅		0.893 ^a	0.965 ^a	0.965 ^a	0.964 ^a	0.957 ^a	0.869 ^a	1	
B		0.884 ^a	0.925 ^a	0.925 ^a	0.993 ^a	0.972 ^a	0.828 ^a	0.984 ^a	1

^aCorrelation is significant at the 0.01 level (2-tailed)

values (close to 1.0) generally indicate that a factor analysis may be useful with these data. The Bartlett sphericity tests hypothesize that the correlation matrix is an identity matrix, which would indicate that variables are unrelated and therefore unsuitable for structure detection. Small values (less than 0.05) of the significance level indicate that a factor analysis may be useful (IBM SPSS eleven). In order to distinguish the variations of variables, dry and wet seasons data were performed in the current study. During the factor analysis, variances and eigenvalues were calculated and varimax rotation was used to obtain interpretable factors (Kalayci 2016).

Cluster analysis

CA is a well-known classification tool which endeavour detecting either the distance or the similarity between the objects to be clustered which used to group of samples according to their similarities and typically illustrated by a dendrogram which provides a visual summary of the clustering processes (Michalic 2008). The analysis was carried out with the “Z-score” correction. The classification is termed Q-mode classification which is commonly applied to water-chemistry investigations in order to define groups of samples that have similar chemical and physical characteristics (Güler et al. 2002). CA was applied on 19 sampling points using normalized Ca, Mg, Na, K, Cl, SO₄, EC₂₅ and B values using Euclidean distance with Ward’s method in the study.

Results and discussion

Evaluation of in situ measurements and hydrochemical analysis results

The hydrochemical analyses results including the major ion (Ca, Mg, Na, K, Cl, SO₄, HCO₃), in situ measurement (T, EC₂₅, TDI and pH) and trace element (Br, B, Sr, Li) are summarized in Table 2 for dry and wet seasons. Based on the field measurements, the temperature of Azmak springs and groundwater in boreholes show very little variation (Cv = 4 for springs, Cv = 2 for boreholes) and is generally about 16 °C. The average EC₂₅ value of springs is 5341 μS/cm (Cv = 0.82) for dry and 5402 μS/cm (Cv = 0.84) for wet season. For groundwater in boreholes it is 712 μS/cm (Cv = 0.34) and 674 μS/cm (Cv = 0.38) for the dry and wet seasons, respectively. Regarding all major ions and trace elements for the springs, the coefficients of spatial variations of Na, K, Cl, Br, B and Li are higher than 90%. The high variation implies the seawater mixing ratio on spring discharges. For the boreholes, the spatial variations of Na, Cl and Br are high (around 90%) during the two seasons because one of the boreholes (BH-3) is apparently affected by seawater intrusion.

The major ion content of the springs was evaluated using Schoeller diagrams. The dominant cation content is ordered as Na + K > Mg > Ca and anions as Cl > SO₄ > HCO₃ + CO₃ for the majority of the springs for both the dry and wet seasons (Fig. 5). Spring waters, thus are classified in two

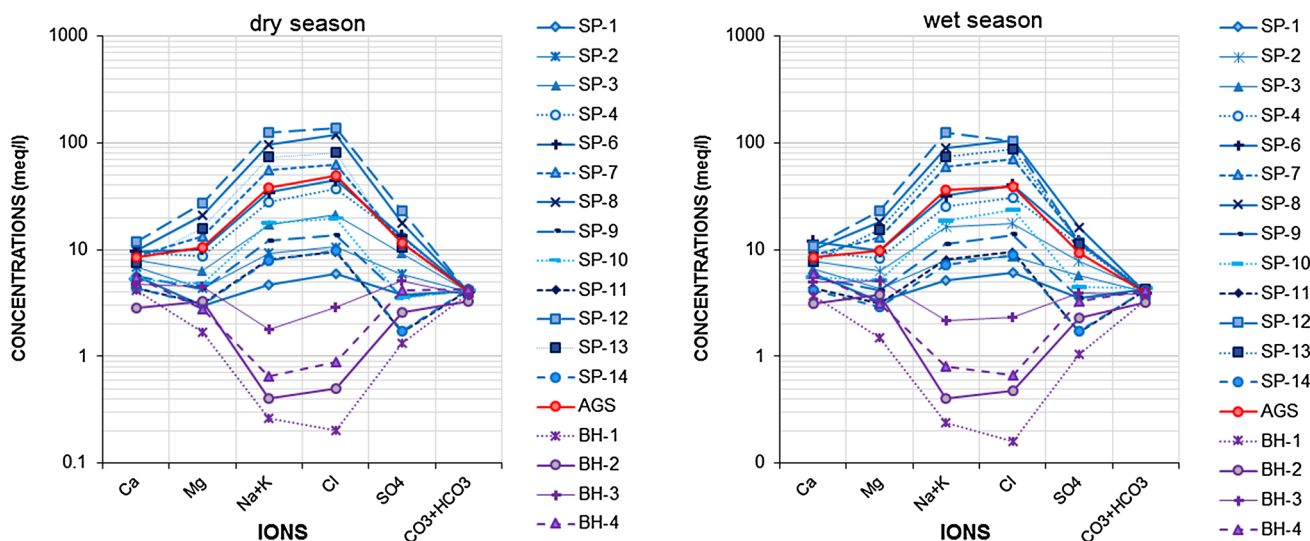


Fig. 5 The Schoeller (1977) diagrams of sampling points for dry and wet seasons in the study area

groups; as very saline springs and moderately saline springs. The groundwater in boreholes is classified as fresh water. The diagrams also imply that the majority of the springs have originated from the same lithological units. Furthermore, seawater intrusion is a major impact on the chemistry of sampling points and all springs have different ratios of seawater mixing. On the other hand, the seawater mixing ratio is not associated with distance from the sea.

Ionic ratios were used to determine the key factors that have influenced the composition of groundwaters. In the current study, the plot of Mg/Ca versus SO₄/Cl was used to assess the effects of seawater intrusion on groundwater quality (Fig. 6). The plot showed that most samples have high Mg/Ca and low SO₄/Cl ratios, indicating the influence of seawater on water composition. The Mg/Ca ratio increases, but SO₄/Cl ratio decreases with the proportion of seawater in the mixture. Figure 6 indicates that three main groups of samples can be distinguished on the basis of the mixing ratio namely: seawater (sea); mixed water (springs) and freshwater (groundwater from boreholes). A closer look at the spring data in the plot of Fig. 6 reveals that three different groups can also be distinguished as more saline springs (9023 μS/cm < EC₂₅ < 54,575 μS/cm), saline springs (4415 μS/cm < EC₂₅ < 7225 μS/cm) and brackish springs (1236 μS/cm < EC₂₅ < 4020 μS/cm). The pattern of the plots does not change significantly between dry and wet seasons (Fig. 6).

Evaluation of multivariate statistical analysis results

As the first step of statistical analysis, values of all variables were presented in box and whisker plots based on minimum, maximum and quartile values for the dry and wet seasons (Fig. 7). The box and whisker plots primarily indicate that

groundwater is saline based on measurements of Na, Cl, Br, B, Sr, EC₂₅, TDI and values of variables do not have major seasonal changes. Ca, Mg, K and Li have the lowest values in the dry and wet seasons.

Correlation analysis

The correlation matrix among all variables is given in Table 3 for both the dry and wet seasons. According to this table, most of the correlation coefficients are higher than 0.90 in the dry and wet seasons. There are significant and positive correlations which may suggest that the specific electrical conductivity is function of Mg, Na, K, Cl, and B. This high correlation implies that the salinity is mainly controlled by these ions. In the dry season, high positive correlations of Na with K (0.985) and Cl (0.998), Ca with SO₄ (0.919), Mg with B (0.928), K with B (0.981), Cl with Na (0.998) and B (0.955), B with K (0.981) and Na (0.962) suggest that seawater intrusion might be playing a major role in the hydrochemistry of the sampling points. In the wet season correlations between Mg and Na (0.883), K (0.891), Cl (0.874), SO₄ (0.891), B (0.925); between K and Cl (0.960), SO₄ (0.773); between SO₄ and Ca (0.907), Mg (0.891), K (0.773), B (0.828) still high and indicative of seawater intrusion. By comparison, the correlation coefficients obtained for dry and wet seasons differ showing a decrease for some of the ions in dry season. Significance tests showed that these differences are not statistically meaningful.

Factor analysis

Ca, Mg, Na, K, Cl, SO₄, and EC₂₅, B were used for factor analysis as variables in a factor analysis of the water quality

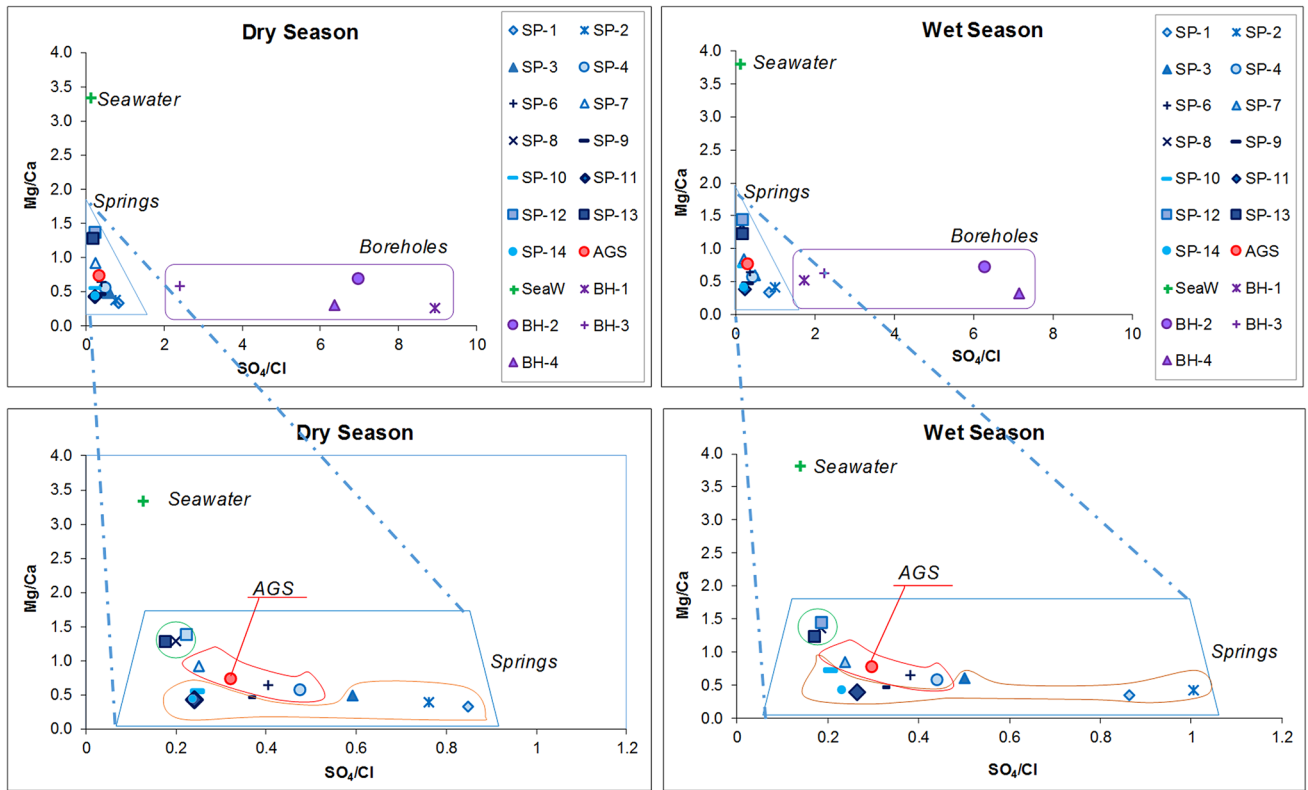


Fig. 6 The graph of Mg/Ca versus SO_4/Cl values of the sampling points

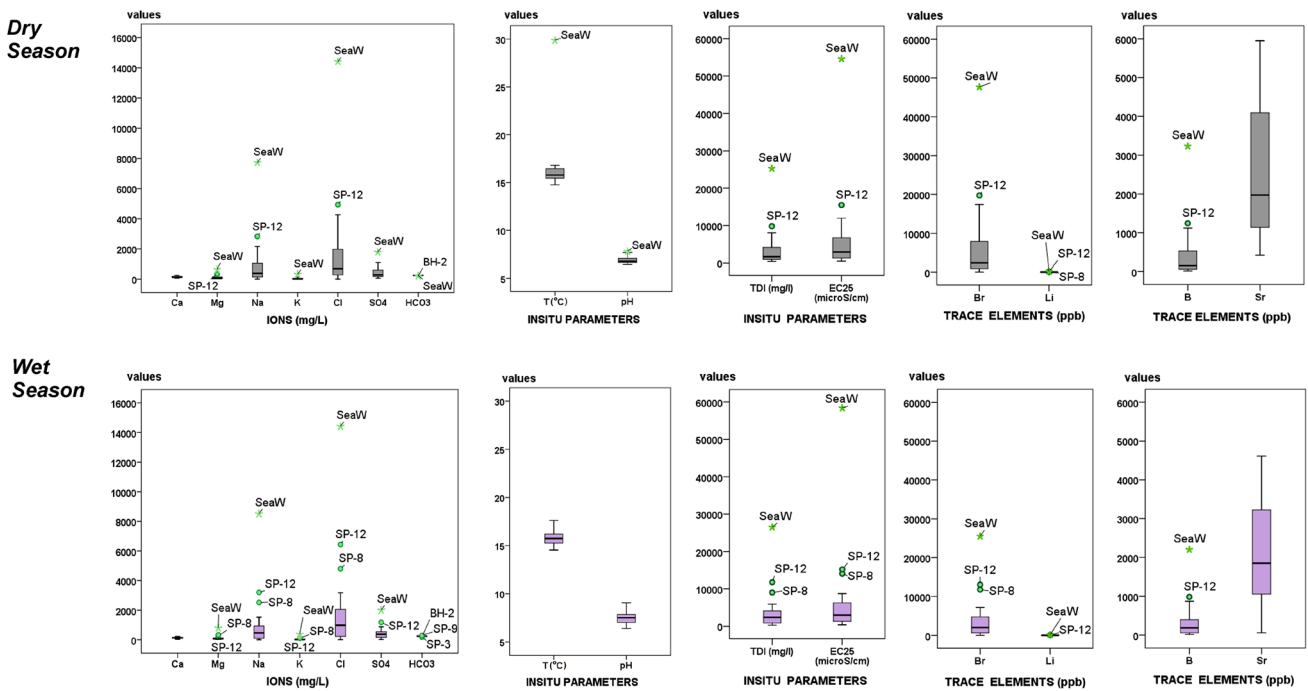


Fig. 7 Box and whisker plots for Ca, Mg, Na, K, Cl, SO_4 , HCO_3^- , TDI, T, pH, EC_{25} , Br, B, Li and Sr of water sampling points

data. The factor analysis was undertaken using the varimax rotation procedure to maximize the sum of the variance of factor coefficients and a three-factor model was determined (Table 4). According to Table 4, three factors explain 98% and 91% of the total variance in the dry and wet seasons, respectively, and scree plots for sampling points showed a distinct change of slope after the three factors (Fig. 8).

The terms ‘strong’, ‘moderate’, and ‘weak’ as applied to factor loadings, refer to the absolute loading values of 0.75, 0.75–0.5 and 0.5–0.3, respectively, in the analysis (Liu et al. 2003). In the dry and wet seasons factor 1 accounts for 50 and 48%, respectively, of the total variance and has strong positive loadings of Na, Cl, K, B, EC₂₅. This factor regarded as an indication of seawater intrusion into the aquifer implies

the general trend of hydrochemical characteristics of the study area. Factor 2 accounts for 26% and 27% of the total variance in the dry and wet seasons and strong loadings on Ca suggest that factor is related to mixing with freshwater. Factor 3 accounts for 23% of the total variance revealed moderate loadings for Mg, SO₄ and EC₂₅ in the dry season. By contrast, 15% of the total variance has moderate loadings for Mg in the wet season which suggests that freshwater inputs influence water quality at this time of the year.

Cluster analysis

Cluster analysis was used for grouping water samples based on their chemical and physical characteristics at each of the

Table 4 Varimax-rotated factor matrix of the all sampling points during the dry and wet seasons

	Dry season			Wet season			
	Rotated component matrix ^a			Rotated component matrix ^b			
	Component			Component			
	1	2	3		1	2	3
Na	0.86	0.38	0.34	K	0.83	0.31	0.36
Cl	0.85	0.38	0.36	Na	0.82	0.45	0.26
K	0.83	0.42	0.35	Cl	0.82	0.48	0.23
B	0.76	0.44	0.41	B	0.79	0.39	0.39
EC ₂₅	0.73	0.38	0.55	EC ₂₅	0.71	0.45	0.48
Mg	0.58	0.43	0.69	Mg	0.52	0.52	0.62
Ca	0.47	0.82	0.33	Ca	0.48	0.59	0.31
SO ₄	0.41	0.64	0.64	SO ₄	0.42	0.83	0.40
% of variance	49.68	25.88	22.84	% of variance	47.87	27.45	15.19
Cumulative %	49.68	75.57	98.40	Cumulative %	47.87	75.32	90.51

Extraction method: principal component analysis
 Rotation method: varimax with Kaiser normalization
^aRotation converged in 8 iterations
^bRotation converged in 6 iterations

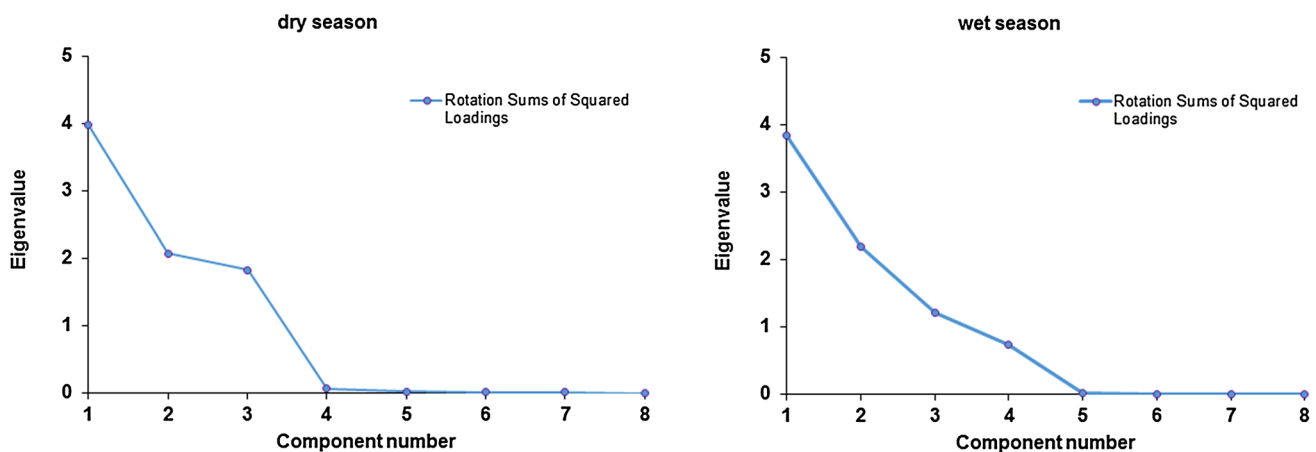


Fig. 8 Scree plots of the eigenvalues for dry season and wet season

sampling points (Shrestha and Kazama 2007). For the hierarchical cluster analysis (HCA), all variables were standardized and Ward's method with Euclidean distances was used to produce dendrograms. HCA was applied for the 19 sampling points using 8 variables (Ca, Mg, Na, K, Cl, SO_4 , EC_{25} and B) for the dry and wet seasons. The results of the analysis are presented as dendrograms in Fig. 9. According to the dendrograms, the study area was classified into two main groups as seawater dominated (A) and fresh water dominated (B). These two main groups (A and B) were further divided into two subgroups as A1, A2 and B1, B2.

Clusters A1 and A2 which have the highest values of Na, K, Cl, B and EC_{25} are the most saline water points in the study area. Cluster A1 (SP4, SP6, SP7, AGS, SP13) contains the sampling points defined as seawater-dominated mixed water where the EC_{25} ranged from 4339 to 9330 $\mu\text{S}/\text{cm}$. Cluster A2 (SP8, SP12 and SeaW) contains the most saline sampling points including the seawater sampling point (11,981 $\mu\text{S}/\text{cm}$ $\text{EC}_{25} < 54,575$ $\mu\text{S}/\text{cm}$). Cluster A2 is extremely affected by seawater intrusion. Clusters A1 and A2 represent springs affected by seawater intrusion. The springs included in these clusters are not necessarily close to the sea. Some of the springs included, for instance in cluster A2 are located closer to the sea, while others in the same cluster are located much farther. This is because the salinity of springs does not follow a pattern designated by the distance to the sea.

Four wells with specific electrical conductivity ranging from 492 to 1021 $\mu\text{S}/\text{cm}$ fall within cluster B1 which implies that they are relatively unaffected by seawater intrusion. The majority of springs from the deep circulation are clustered

in subgroup Cluster B2 (SP1, SP2, SP3, SP9, SP10, SP11, SP14) which contains brackish water with seawater characteristics ($1232 \mu\text{S}/\text{cm} < \text{EC}_{25} < 3682 \mu\text{S}/\text{cm}$). SP1, SP2 and SP3 are located the farthest from the sea are located on the upstream of the Azmak stream. Cluster B2 is moderately affected by seawater intrusion.

All sample points were grouped in same clusters for the dry and wet seasons except for SP3, SP10 and BH-3. These three sampling points were affected by the seasonal effect. After rainy season these sampling points showed different behavior and were grouped into different clusters.

Conclusions

In situ measurements, hydrochemical analysis and multivariate statistical methods (correlation analysis, factor analysis and cluster analysis) were carried out for data from 19 sampling points during the dry and wet seasons in the Azmak spring zone, Mugla-Turkey. The assessment was carried out for Ca, Mg, Na, K, Cl, SO_4 , EC_{25} , TDI, Br, B, Li and Sr for all of the sampling sites. According to the results of the hydrochemical analysis, the majority of the coastal springs are brackish due to elevated concentrations of major ions (Na, K, Cl) and trace elements (Br, B, Li) caused by seawater intrusion. Correlation analysis within the study area shows that there are significant and positive correlations between variables which suggest seawater intrusion in the springs.

Three factors were determined in factor analysis that was carried out on the water quality dataset produced in this study. The first factor is interpreted as being associated

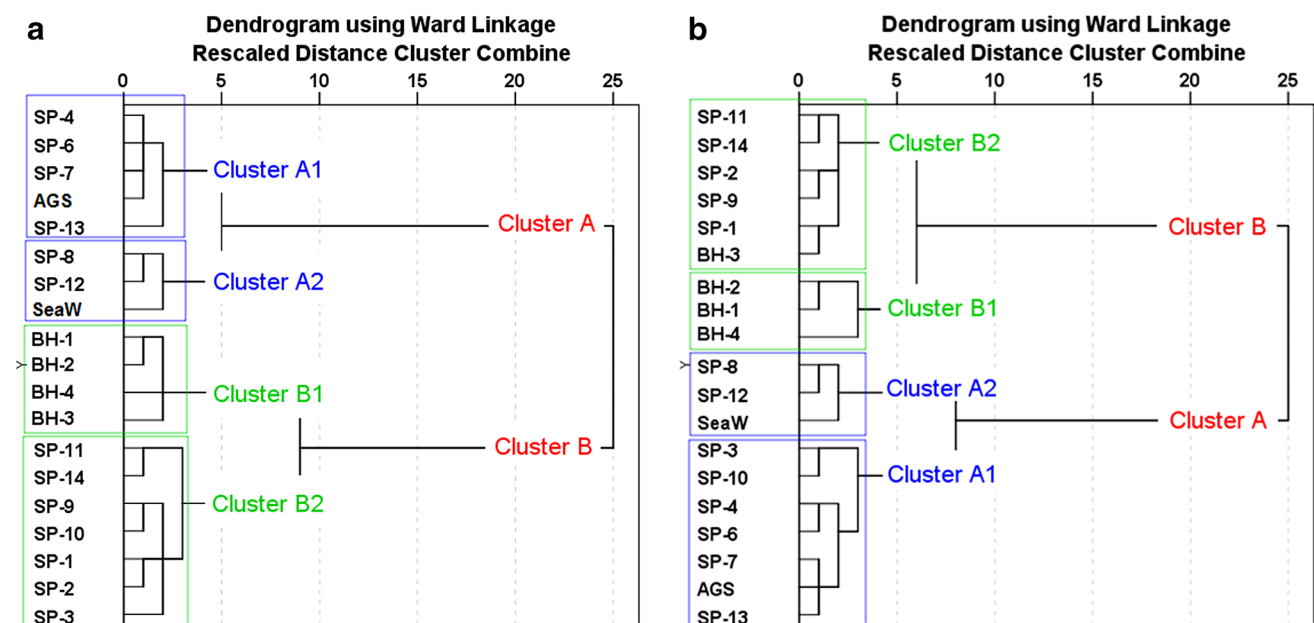


Fig. 9 Dendrograms of the hierarchical cluster analysis of sampling points during **a** dry and **b** wet seasons

with the effects of seawater intrusion, the second factor appears to be associated with the effects of mixing with freshwater and the third factor appears to be associated with variations fresh water circulation patterns on a seasonal basis.

Cluster analysis using in situ field measurements and data from chemical analyses identified two main groups and four subgroups. Cluster A (A1 and A2) appears to be associated with samples that have a chemical composition similar to seawater and cluster B (B1 and B2) is associated with samples that are moderately affected by seawater intrusion. The cluster analysis has confirmed the classifications by conventional diagrams and plots given in Figs. 3 and 6. On the other hand, these conventional diagrams failed to show the effects of seasonal changes, whereas cluster analysis clearly indicated that some of the sample points changed their position on the dendrograms.

This study has indicated that multivariate statistical analysis techniques are useful methods for the description of groundwater flow mechanisms in the study area. The study has shown that seawater intrusion is a problem for the drinking water sources because almost all karst springs in the area are influenced by seawater. The salinity of the springs is not directly related to their distance from the sea which indicates that recharge and salinization mechanisms in the area are complicated.

Acknowledgements This paper which was financially supported by the the Scientific and Technical Research Council of Turkey (TUBITAK, Project No: 109Y302) was produced using the data collected within the framework of the first author's PhD thesis study. The authors are thankful to Dr. Levent TEZCAN, co-adviser of the thesis, for his valuable comments and also to Mr. Bulent Topuz, Ms. Otgonbayar Namkhai, Mr. Deniz Ozbek for their assistance during the field studies, analyses and drawings. The authors are also thankful to Ms. Gulbanu Tekbulut, the English Editor of the International Journals of Science Faculty at Hacettepe University, for revising and improving the English version of the manuscript.

References

- Acikel S (2012) Conceptual modelling of hydrodynamics of discharge and salt water mixing in Gokova-Azmaç (Muğla) karst springs, Dissertation, Hacettepe University
- Arfib B, Marsily GD, Ganoulis J (2007) Locating the zone of saline intrusion in a coastal karst aquifer using springflow data. *Ground Water* 45(1):28–35. <https://doi.org/10.1111/j.1745-6584.2006.00252.x>
- Arslan H (2013) Application of multivariate statistical techniques in the assessment of groundwater quality in seawater intrusion area in Bafra Plain, Turkey. *Environ Monit Assess* 185:2439–2452. <https://doi.org/10.1007/s10661-012-2722-x>
- Behera B, Das M (2018) Application of multivariate statistical techniques for the characterization of groundwater quality of Bacheli and Kirandul Area, Dantewada District, Chattisgarh. *J Geol Soc India* 91:76–80
- Belkhir L, Boudoukha A, Mouni L (2011) A multivariate statistical analysis of groundwater chemistry data. *Int J Environ Res* 5(2):537–544
- Bilgin A, Konanc MU (2016) Evaluation of surface water quality and heavy metal pollution of Coruh River Basin (Turkey) by multivariate statistical methods. *Environ Earth Sci* 75:1029. <https://doi.org/10.1007/s12665-016-5821-0>
- Davis JC (1973) *Statistics and data analysis in geology*. Wiley, New York
- Ekmekci M (2003) Review of Turkish karst with emphasis on tectonic and paleogeographic controls. *Acta Carsol* 32:205–218
- Fatoba JO, Sanuade OA, Hammed OS, Igboama WW (2017) The use of multivariate statistical analysis in the assessment of groundwater hydrochemistry in some parts of southwestern Nigeria. *Arab J Geosci* 10: 328. <https://doi.org/10.1007/s12517-017-3125-7>
- Filho CAD, Moreira RB, Branco OEA, Dutra PH, Dos Santos EA, Moura IFS, Fleming PM, Palmieri HEL (2017) Combined hydrochemical, isotopic, and multivariate statistics techniques to assess the effects of discharges from a uranium mine on water quality in neighboring streams. *Environ Earth Sci* 76:830. <https://doi.org/10.1007/s12665-017-7165-9>
- Güler C, Thyne GD, McCray JE, Turner AK (2002) Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeol J* 10:455–474
- Kalaycı S (2016) SPSS Uygulamalı çok degişkenli istatistik teknikleri. Asil Yayın Dagitım, Ankara (**in Turkish**)
- Kazakis N, Mattas C, Pavlou A, Patrikaki O, Voudouris K (2017) Multivariate statistical analysis for the assessment of groundwater quality under different hydrogeological regimes. *Environ Earth Sci* 76:349. <https://doi.org/10.1007/s12665-017-6665-y>
- Li S, Li J, Zhang Q (2011) Water quality assessment in the rivers along the water conveyance system of the Middle Route of the South to North Water Transfer Project (China) using multivariate statistical techniques and receptor modeling. *J Hazard Mater* 195:306–317
- Liu CW, Lin KH, Kuo YM (2003) Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. *Sci Total Environ* 313:77–89
- Martinez-Tavera E, Rodriguez-Espinosa PF, Shruti VC, Sujitha SB, Morales-Garcia SS, Munoz-Sevilla NP (2017) Monitoring the seasonal dynamics of physicochemical parameters from Atoyac River basin (Puebla), Central Mexico: multivariate approach. *Environ Earth Sci* 76:95. <https://doi.org/10.1007/s12665-017-6406-2>
- Masoud AA, El-Horiny MM, Atwia MG, Gemal KS, Koike K (2018) Assessment of groundwater and soil quality degradation using multivariate and geostatistical analyses, Dakhla Oasis, Egypt. *J Afr Earth Sci* 142:64–81
- Matiatos I, Alexopoulos A, Godelitsas A (2014) Multivariate statistical analysis of the hydrogeochemical and isotopic composition of the groundwater resources in northeastern Peloponnesus (Greece). *Sci Total Environ* 476–477:577–590
- Michalik A (2008) The use of chemical and cluster analysis for studying spring water quality in Świętokrzyski National Park. *Pol J Environ Stud* 17(3):357–362
- Montety V, Radakovitch O, Vallet-Coulomb C, Blavoux B, Hermitte D, Valles V (2008) Origin of groundwater salinity and hydrogeochemical processes in a confined coastal aquifer: case of the Rhône delta (Southern France). *Appl Geochem* 23: 2337–2349. <https://doi.org/10.1016/j.apgeochem.2008.03.011>
- Najib S, Fadili A, Mehdi K, Riss J, Makan A (2017) Contribution of hydrochemical and geoelectrical approaches to investigate salinization process and seawater intrusion in the coastal aquifers of Chaouia, Morocco. *J Contam Hydrol* 198:24–36
- Schoeller H (1977) *Geochemistry of groundwaters in groundwater studies and international research and practice*, vol 15. UNESCO, Paris, pp 1–18

- Semar A, Saibi H, Medjerab A (2013) Contribution of multivariate statistical techniques in the hydrochemical evaluation of groundwater from the Ouargla phreatic aquifer in Algeria. *Arab J Geosci* 6:3427–3436. <https://doi.org/10.1007/s12517-012-0616-4>
- Shrestha S, Kazama F (2007) Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan. *Environ Model Softw* 22:464–475
- Siepak M, Sojka M (2017) Application of multivariate statistical approach to identify trace elements sources in surface waters: a case study of Kowalskie and Stare Miasto reservoirs, Poland. *Environ Monit Assess* 189:364. <https://doi.org/10.1007/s10661-017-6089-x>
- Simeonov V, Stratis JA, Samara C, Zachariadis G, Voutsas D, Anthemidis A, Sofoniou M, Kouimtzi T (2003) Assessment of the surface water quality in Northern Greece. *Water Res* 37:4119–4124
- Singh KP, Malik A, Mohan D, Sinha S (2004) Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India)-a case study. *Water Res* 38:3980–3992
- SPSS (IBM Corp. Released 2010.) IBM SPSS Statistics for Windows, Version 11.0. IBM Corp, Armonk
- Subbarao C, Subbarao NV, Chandu SN (1996) Characterization of groundwater contamination using factor analysis. *Environ Geol* 28(4):175–180
- Suk H, Lee K (1999) Characterization of a groundwater hydrochemical system through multivariate analysis: clustering into groundwater zones. *Groundwater* 37:358–366
- Yidana SM, Bawoyobie P, Sakyi P, Fynn OF (2018) Evolutionary analysis of groundwater flow: application of multivariate statistical analysis to hydrochemical data in the Densu Basin, Ghana. *J Afr Earth Sci* 138:167–176
- Zhang X, Qian H, Wu H, Chen J, Qiao L (2016) Multivariate analysis of confined groundwater hydrochemistry of a long-exploited sedimentary basin in Northwest China. Hindawi Publishing Corporation. *J Chem*. <https://doi.org/10.1155/2016/3812125> (**Article ID 3812125**)