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ORIGINAL ARTICLE

Seasonal and spatial variations in water quality of deep aquifer in the Harran plain, GAP project, southeastern Anatolia, Turkey

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Abstract

Groundwater is used for both drinking and irrigation purposes. Thus, its monitoring and understanding the processes controlling its quality are crucial in terms of sustainable use. Groundwater samples were collected from 11 deep aquifer wells located in the Harran plain, Southeastern Anatolia during four seasons and analyzed for TDS, EC, pH, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, F^-, SO_4^{2-}, HCO_3^-, NO_3^-. Techniques such as ANOVA, correlation analyses, heat-mapping and Principal Component Analyses (PCA) were used to investigate main factors controlling seasonal and spatial variations in groundwater quality parameters. Grounwater quality parameters were also associated with topographical parameters [elevation, slope, flow direction, flow accumulation, and Topo Wetness Index (TWI)]. According to WHO standards, average values of all parameters investigated were in general within allowable limits for drinking water with a few exceptions for NO_3^-, SO_4^{2-} and F^- that exceeded threshold limits at some locations. Seasonal variations in all water quality parameters except EC, TDS and SO_4^{2-} were statistically significant ($p < 0.05$). Parameters such as EC, TDS, Ca^{2+}, Mg^{2+}, NO_3^-, F^- were the main parameters controlling the qualities of groundwater sampled according to PCA analyses results, which separated the wells into two main groups; the wells located in the lower parts of the plain with higher values of EC, TDS, TWI, Flow Accumulation and the wells located in upper part of the plain with higher EC, TDS, elevation, slope and Flow Direction. Spatial variations in selected groundwater quality variables by topographical parameters ranged from 40.7 to 94.8%. Overall, the results of the study will contribute to good groundwater management efforts on a local and global scale.

Keywords Deep aquifer · Irrigation · GAP project · Turkey

Introduction

Groundwater is the source where the need for clean water is met, thus a separate and special effort is required in order to maintain its quality. For many reasons, especially the growing population, these efforts must be increased. Significant sources that feed groundwater are rain, lakes and rivers. However, water leaking from over-irrigation and channels are also considered as other factors that feed groundwater sources. Therefore, it is possible to say that groundwater consists of surface water resources.

Groundwater with high quality has many uses, especially as drinking water. It has been widely reported that poor quality or contaminated groundwater may cause variety of health disorders when used for drinking purpose (Yeşilnacar et al. 2016; Sahu et al. 2018; Prasad et al. 2018). It may also cause health problems indirectly when transferred from crop to humans after being used as irrigation. In addition to health disorders, pollution of groundwater impact social prosperities, economic growth and sustainable developments of countries as well as the environment (Srivastava et al. 2012). Sources that cause groundwater contamination are listed by EPA (Environmental Protection Agency) as follows: deep wells, pesticides, fertilizers, septic tanks, drinking water wells, wastewater lagoons, treatment plants, irrigation wells, wastes discharged into surface waters feeding groundwater and solid waste storage areas (USEPA 1992a, b).

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Monitoring and understanding mechanism controlling its quality becomes crucial considering the importance of groundwater in terms of health and socio-economic aspects. For this purpose, groundwater is sampled and monitored during regular intervals or in different seasons and periods i.e. pre- and post-monsoon seasons (Sahu et al. 2018) or wet and dry seasons (Yolcubal et al. 2019; Bilgili et al. 2018) and concentrations levels of contaminants within them are compared with threshold values set by international and national organizations. Among them, the World Health Organization is accepted as the main standard in most situations (WHO 2007).

Groundwater quality varies seasonally and spatially. Seasonal and spatial variations in groundwater qualities have been monitored by earlier researches with laboratory and field analyses integrated with different statistical approaches, quality indexes obtained by combination or ratio of different quality parameters for mainly multiple purposes; such as determination of groundwater for suitability for drinking or irrigation; effective utilization of groundwater resources and better managements of them (Liu et al. 2018). Statistical approaches used for identification and investigation of seasonal and spatial distribution of groundwater qualities mostly included univariate and multivariate statistical techniques such as correlation analyses, and multivariate statistical methods such as cluster analysis, PCA analysis, factor analysis and cluster analyses (Sahu et al. 2018; Ganiyu et al. 2018; Maskooni et al. 2017), correlation analyses (Yolcubal et al. 2019), hierarchical cluster analysis (Prusty et al.2018; Yolcubal et al. 2019), geostatistical methods (Srivastava et al. 2012; Zhai et al. 2015; Wang et al. 2019; Prasad et al. 2018). Multivariate statistical methods have been shown to be useful for analyses and interpretation of complex data sets and thus for groundwater quality management. One or more multivariate statistical methods have been used together in characterization of groundwater quality and finding out pollutions origin and sources and their results were compared (Sahu et al. 2018).

Factors impacting seasonal and spatial variations in groundwater qualities are multiple. Earlier studies grouped the factors controlling chemical compositions of groundwater of the wells into natural factors such as drainage, rainfall, mineral dissolution, ion precipitation, microbial activities, groundwater-rock interactions, weathering process, and into anthropogenic factors such as excessive use of fertilizer and pesticides, sewage application, effluents from septic tanks, agricultural wastes and dumping municipal wastes, improper disposal of domestic sewage, disposal of industrial and mining wastes (Maskooni et al. 2017; Sahu et al. 2018; Ganiyu et al. 2018; Prusty et al. 2018; Yolcubal et al. 2019).

In addition, management practices such as irrigation type may impact the concentrations of chemicals within the groundwater. Climate and exploitation of groundwater with increasing urbanization are among other factors impacting groundwater quality (Masoud 2013).

Topography is known as another important factor controlling groundwater movement and its quality and it has impact on spatial distribution of groundwater contamination (Jeelani et al. 2014; Wang et al. 2019). Although it has been emphasized as a significant structural factor explaining variations in spatial distribution of contaminants, there has not been much studies investigating associations between topographical parameters and groundwater quality variables.

Groundwater quality has also been related with land use (Machiwal and Jaa 2015). These authors reported that urbanization, higher population, etc. causes pollution in groundwater. The influence of land use activities on the underlying groundwater quality can be observed also in this study. Urbanization has also recently been a great issue in the Harran plain. Harran Plain, in southern Turkey, is located on the border of Turkey and Syria in upper Mesopotamia. The Harran plain which has 1600 square km plain area has the largest groundwater reserves in the middle east and the biggest irrigation field in Southeastern Anatolia region with 165,000 hectares of irrigation area. Land use has changed in the Harran plain after irrigation started in 1995 as part of the multibillion dollars GAP project (Southeastern Anatolia Project) that was launched with the aim of removal of economic and social imbalances among regions as agricultural. The GAP project is mainly an energy production and irrigation project to foster economic and social development covering 10% of Turkey's population and total area. The project increased the prosperity of the region however, it caused significant environmental problems such as salinization, erosion, contamination of surface and ground water sources with nutrients and urbanization (Bilgili et al. 2018). After the start of irrigation, urbanization rates increased in the plain as a result of increasing population and prosperity. Urbanization combined with excessive irrigation and intensive agricultural activities with high amounts of fertilizer and pesticide applications caused overall deterioration of groundwater sources as well as surface waters such as drainage water in the plain (Bilgili et al. 2018). On the other hand, groundwater is used for drinking purposes in villages located in the plain. Therefore, it is imperative to examine groundwater as an important part of the hydrological system of the region in terms of pollution it is exposed to, for sustainable groundwater management using all technological facilities and methods. There have been studies examining the aquifer water qualities in the plain before (Yeşilnacar and Gulluoglu 2008). This current study was conducted in a deeper aquifer compared to them.

The aim of this study was (i) to characterize deep aquifer groundwater quality of the Harran Plain under irrigation conditions with field, laboratory studies and various statistical approaches (ii) to determine seasonal and spatial variability in quality of groundwater and (iii) to understand the factors impacting seasonal and spatial differences in quality of groundwater especially in relation to topographical parameters.

Materials and methods

Study area and sampling

The study has been performed in the Harran Plain. The Harran Plain lies in the southeast of the province of Şanlıurfa, Southeastern Anatolia Region and (Fig. 1) and is located between 36° 43′ N–37° 10′ N latitudes and 38° 47′ E–39° 10′ E longitudes. Harran Plain has the largest irrigation area in GAP and the largest groundwater reserve in the Middle East. The plain starts around Şanlıurfa-Mardin highway in the north, opens to Syria in the south and continues up to the Syrian territory. It is separated from the Ceylanpınar basin in the east by the Tektek mountains and in the west from the Suruç basin by the Fatik mountains. Its north is quite hilly and there is a distinct boundaryin the east–west direction. Tektek mountains in the east have a height of 600–700 m and Fatik mountains in the west are

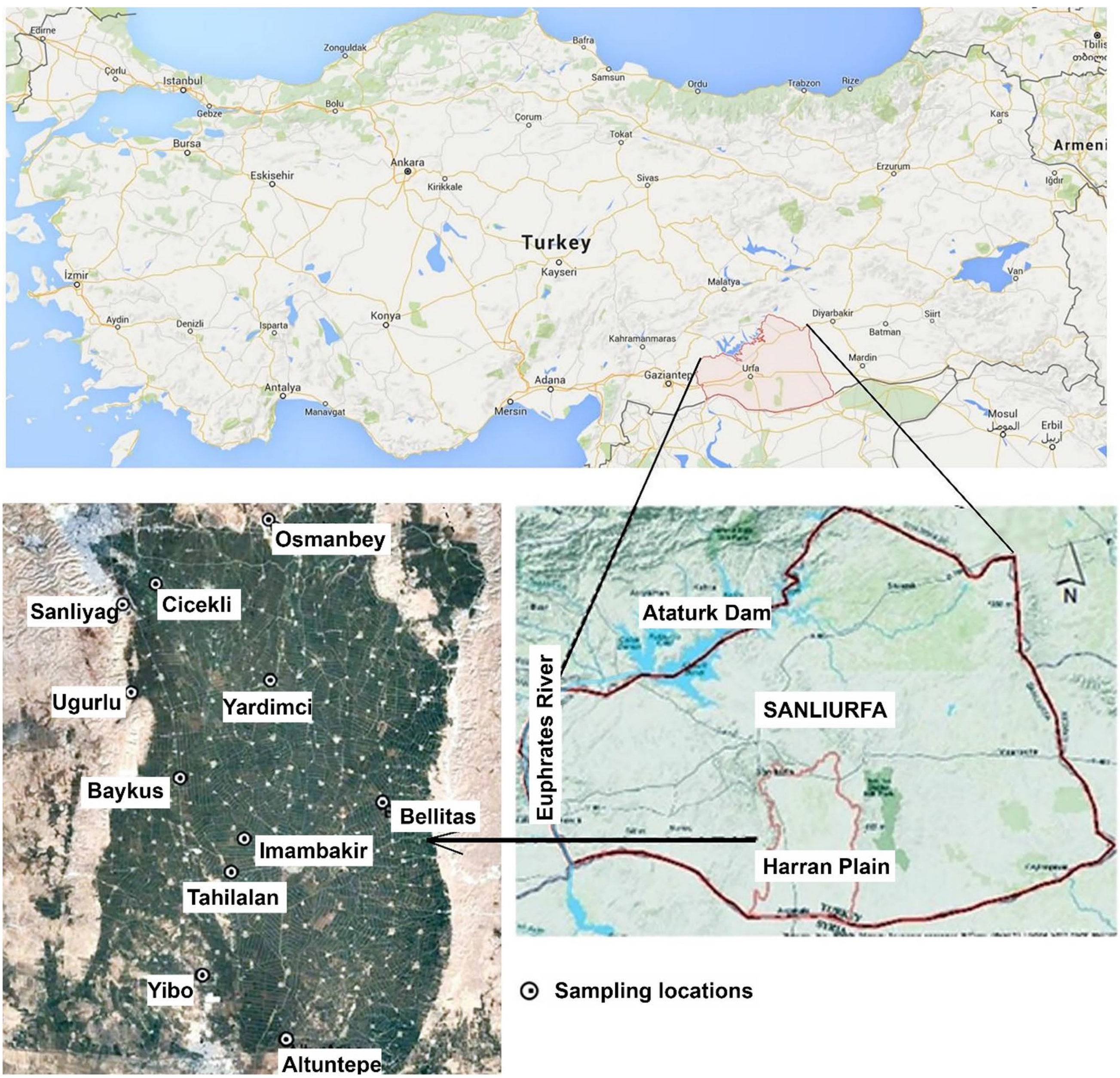

Fig. 1 Maps of the study area and sampling locations

800 m. Hills up to 850 m in the north surround the plain. Altitude of the plains ranges from 500 m in North to 350 m in Turkey-Syria border in the south (Fig. 1). The plain was opened to irrigation since 1995. Main irrigation practice is furrow irrigation and main cropping design is cotton, wheat–corn cultivation, respectively.

Sampling was carried out by including a sufficient number of observation wells in terms of data evaluation, which would represent the plain with a homogeneous feature. A total of 11 deep aquifer groundwater wells with an average depth ranging from 180 to 400 m were sampled during four seasons; winter (in February 2019), spring (in April 2019), summer (in July 2019) and fall (in September 2019). The study area and sampling locations are shown in Fig. 1. Taking samples from sampling points and transferring them into the laboratory have been performed according to general standards of D4448-01 Standard Guide for Sampling Ground-Water Monitoring Wells (ASTM 2001) and D6517-00 Standard Guide for Field Preservation of Ground-Water Samples (ASTM 2005).

Hydrogeology

The study area Harran Plain has a graben type geomorphological structure and has been included in the literature as Akçakale Graben (Tardu et al. 1987). Geological formations in the region consist basically of sedimentary and volcanic rocks. There are only basalts as igneous rocks that are seen locally on some hills surrounding the plain. These basalts are the eruptions of Karacadağ volcanism. Sedimentary units dominating the study area are mostly composed of marl, limestone, clayey limestone and clays that have different gypsum levels locally formed in different lithological time periods such as Paleocene, Eocene, Miocene, Pliocene and Pleistocene, respectively (Fig. 2). Paleocene unit with an 800 m thickness consists of marl and does not have any aquifer. It is covered by an Eocene aged unit that is composed of karstic, fractured limestone and has around 300 m thickness. This unit forms deep and confined aquifers in northern, western and eastern parts of the area. Most of the boreholes whose yields range from 20 to 100 l/s pump water in this unit. It is overlaid by a Miocene aged unit, which is composed of clayey limestones and has a 100 m thickness. This unit pumps water in the southeastern part of the area and the yield of the wells located in this unit range from 10 to 100 l/s. The Miocene unit is overlaid by an Pliocene unit with a thickness of around 200 m. This unit is mostly composed of clay containing gypsum minerals. This unit does not have an aquifer. It is overlaid by Pleistocene aged unit which is composed of clay, sand and gravel. The thickness of Pleistocene unit is around 60 m and it has a shallow unconfined aquifer. The groundwater samples were obtained from boreholes located in the deep aquifer in the Eocene unit. Figure 2 depicts the order of geological formations and their locations in the study area (DSI 2003).

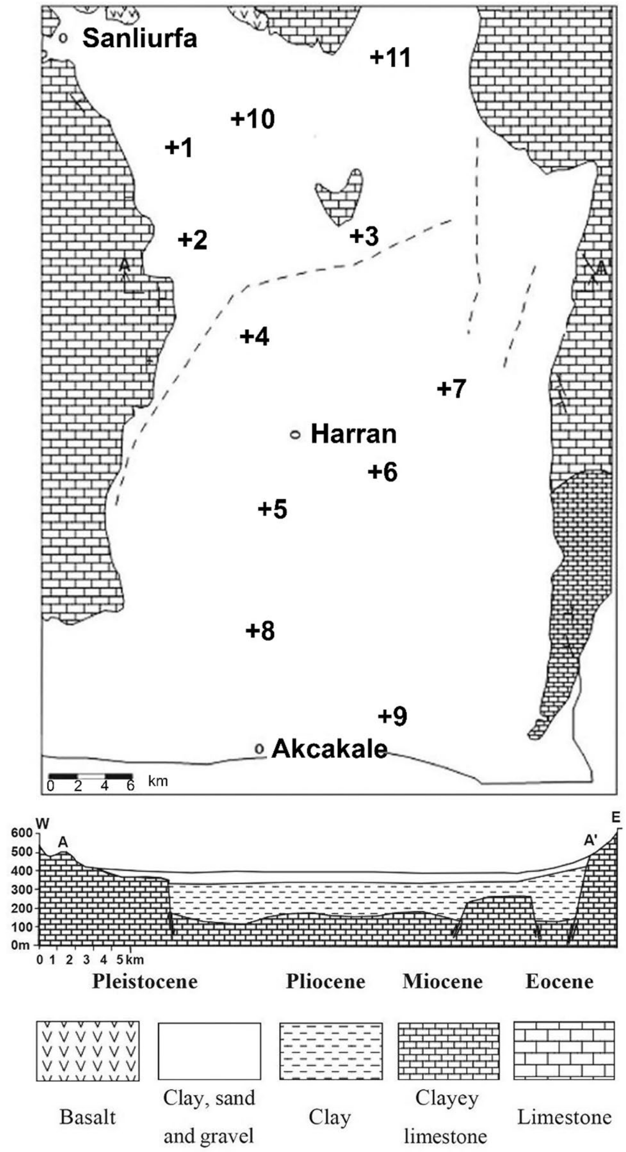

Fig. 2 The sampling points (1: Sanliyag, 2: Ugurlu, 3: Yardimci, 4: Baykus, 5: Tahilalan, 6: Imambakir, 7: Bellitas, 8: Yibo, 9: Altuntepe, 10: Cicekli, 11: Osmanbey) over the geological map and cross section of the study area (adapted from DSI 2003)

Analyses of the water samples

Parameters such as temperature, pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were measured during field sample collection using SevenGo pro—SG7 conductivity meter.

Water samples taken from these sampling points in four different seasons and transferred into the laboratory were analyzed for parameters such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-},

$NO^-{}_3$ and $HCO^-{}_3$ and F^-, $SO_4{}^{2-}$ using standard methods for water analysis (American Public Health Association 1998). Cl^-, $SO_4{}^{2-}$, $HCO^-{}_3$, $NO_3{}^-$ using ion chromatography (Shimadzu HIC2-0A). Ca^{2+}, Mg^{2+}, Na^+ and K^+ with ICP-OES (Perkin Elmer Optima 5300 DV).

Topographical parameters

Topographical maps (1:5000 scale) of the study area were digitized to create a Digital Elevation Map (DEM). From the DEM, topographical parameters such as slope (%), flow accumulation, flow direction and Topo Wetness Index (TWI) were delineated using spatial analysis tools in ArcGIS 10.5 (ESRI Inc. Figure 3). The information of topographical indicators belonging to groundwater sampling locations was extracted by overlapping the sampling locations on the raster maps for each topographical parameter.

The Topo Wetness Index (TWI) was calculated as (Sorensen et al. 2005):

$$TWI = \ln\left({}^{\alpha}/_{\tan\beta}\right)$$

where α is the upslope contributing area obtained from flow accumulation and b is the slope gradient (%). TWI is an indicator that shows potential areas where water can accumulate. The areas with a high TWI values are most likely to be saturated. It is widely used to quantify the control of topography in hydrological processes (Sorensen et al. 2005).

Statistical analysis

In addition to general statistical analyses showing variations in the spatial and seasonal distributions of contents of the water samples collected from observation wells during four seasons Anova statistics and PCA analyses were performed.

ANOVA statistics

ANOVA test was used to test significance of seasonal distribution in water quality parameters. A one-way ANOVA with Tukey test at 95% significance level ($p = 0.05$) was applied for each different parameter separately by considering them as independent variable. The statistical analyses were applied in the R program (R Core Team 2017). Before the ANOVA test a normality, test was used to see whether water quality variables distribute normally abd to see if the requirement of a normal distribution of parameters for ANOVA was met.

PCA analyses

PCA is a multivariate statistical method and mostly used in variable reduction and pattern recognition. The goal of PCA is to reduce the dimensionality of the data while retaining the variation present in the original data set. The PCA decomposes highly correlated variables in a data set into a smaller data set with uncorrelated variables, which are called principal components. They are weighted linear combinations of the original variables. Generally, the first a couple of principal component accounts for almost all the variability in the data and the remaining variability is explained by succeeding components. The first principal component tends to account for most of the variability in the data. The criteria in selecting variables using PCA analyses is first to select PCAs with eigenvalues higher than 1 showing the PCs that explains the highest variation in the data set. Then, within each PCA the variables with highest weighted loading values or variables within 10% of highest weighted loading value are selected as the as the most significant variables controlling the qualities of water sampled (Brejda et al. 2000). Principal component analysis (PCA) was conducted using the R program.

Results

Groundwater quality parameters

Water quality of deep aquifer wells located in the Harran plain, Southeastern Turkey, used for drinking purpose were monitored with field and laboratory analyses and some selected quality parameters including $NO_3{}^-$ contents were measured in four different seasons (Fall, Winter, Spring and Summer) in 2019. A statistical summary showing seasonal variations in selected quality parameters of collected groundwater samples from the wells located at different locations in the Harran plain along with WHO threshold values for these measured water quality parameters are given in Table 1.

pH values of groundwater samples were neutral to alkali ranging from 7.10 to 7.50, 7.49–7.96, 7.10–8.30 and 7.40–8.30 in fall, winter, spring and summer seasons, respectively. pH values were within WHO permissible levels during all seasons. Electrical conductivity values ranged from 0.25 to 1.20 dS/m, 0.33–1.0 dS/m, 0.33–1.20 dS/m and 0.32–1.14 dS/m in fall, winter, spring and summer seasons, respectively. Accordingly, water samples were non-saline and values in average lied within the permissible limit of 1 dS/m according to WHO standards although values were higher than 1 dS/ m in some wells. Total dissolved solid (TDS) amounts in fall, winter, spring and summer seasons ranged from 120 to 590 mg/l, 166–501 mg/l, 160–600 mg/l and 160–570 mg/l, respectively. In all seasons TDS values lied below WHO specified threshold value of 1000 mg/l (Table 1).

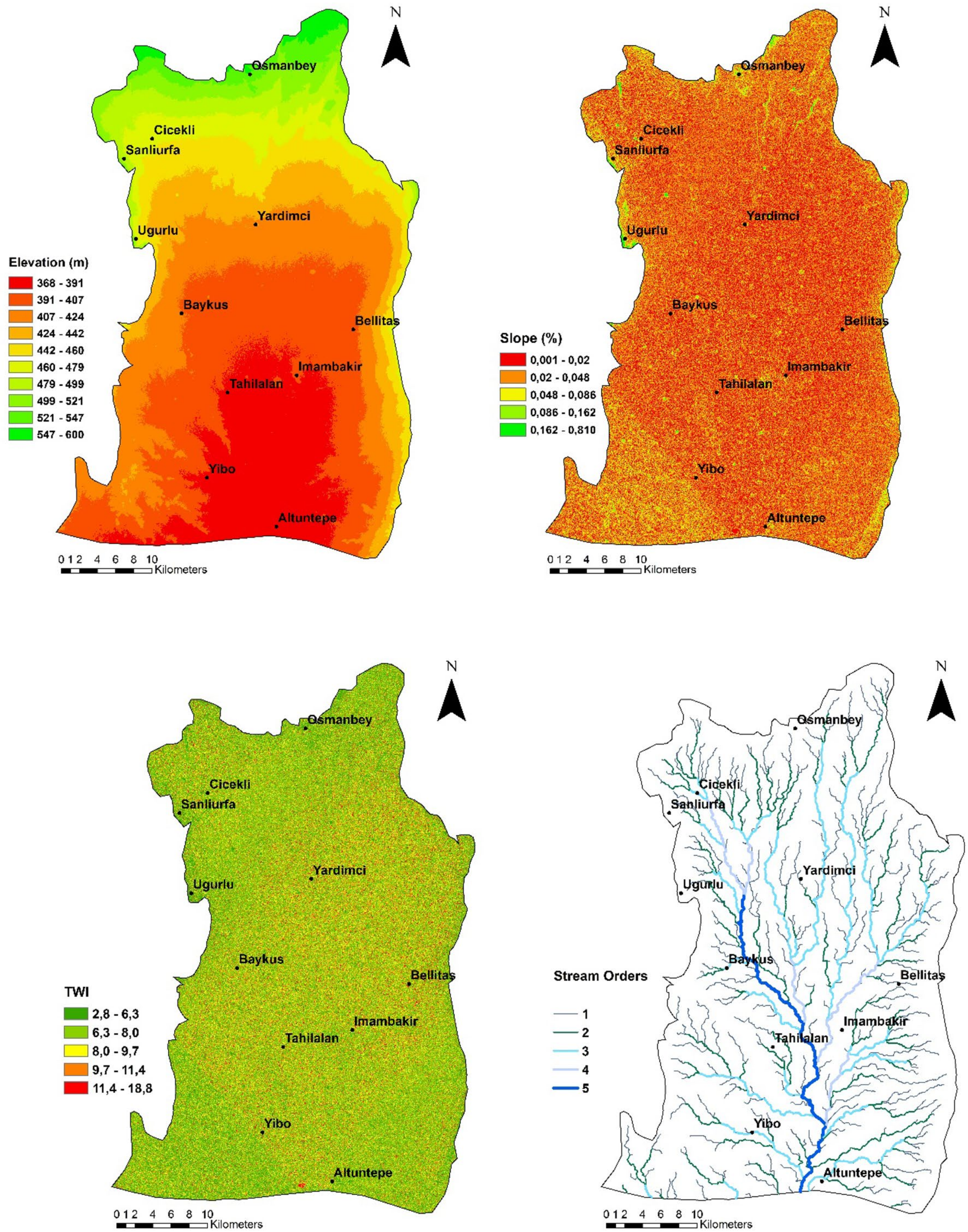

Fig. 3 Maps of elevation, slope, TWI and distribution of stream orders extracted from Digital Elevation Model

Cations were ordered as $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$. For cation Ca^{2+} concentrations of groundwater samples, respectively, ranged from 3.5 to 76.3 mg/l, from 21.9 to 131.8 mg/l, from 16.7 to 186.1 mg/l and from 21.9 to 120.9 mg/l in four different seasons; fall, winter, spring and summer. In these seasons Mg^{2+} concentrations ranged from 0.2 to 35.5 mg/l, from 0.7 to 23.7 mg/l, from 7.3 to 58.5 mg/l and from 6.9 to 48.7 mg/l, respectively. The concentrations for Na^{+} ranged from 5.4 to 34.8 mg/l, 1.4–52.6 mg/l, 3.0–52.6 mg/l and 3.1–50.9 mg/l and correspondingly. K^{+} concentrations in

Table 1 Descriptive statistics belonging to water quality parameters and WHO threshold values

Seasons	pH	Temp (°C)	EC (dS/m)	TDS (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	NO_3 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	F (mg/l)
WHO[a] limits	6.5–9.5			1000 (mg/l)	200 (mg/l)	75–200 (mg/l)	200 (mg/l)		45 (mg/l)	250 (mg/l)	250 (mg/l)		1.5 (mg/l)
Fall													
Mean	7.30	26.82	0.63	312	40.5	12.7	16.9	2.4	22.4	34.9	122.3	25.2	0.5
Min	7.10	25.00	0.25	120	3.5	0.2	5.4	0.0	0.0	3.8	0.0	11.2	0.2
Max	7.50	28.00	1.20	590	76.3	35.5	34.8	7.2	50.7	75.4	573.5	34.6	0.9
Std dev	0.11	0.98	0.25	125	28.0	11.1	9.8	2.2	12.5	19.1	168.2	7.1	0.2
CV	1.50	3.66	39.85	40	69.2	87.4	58.0	90.3	55.8	54.6	137.5	28.4	52.0
Winter													
Mean	7.73	19.12	0.67	337	71.3	5.3	26.3	2.4	12.3	29.9	141.3	30.5	0.9
Min	7.49	13.60	0.33	166	21.9	0.7	1.4	0.7	1.8	3.3	5.9	19.7	0.6
Max	7.96	24.30	1.00	501	131.8	23.7	52.6	4.7	28.2	67.2	639.8	43.3	1.5
Std dev	0.15	2.79	0.23	116	27.0	6.5	13.5	1.4	7.1	18.1	182.4	7.6	0.3
CV	1.94	14.59	34.53	35	37.8	123.3	51.3	58.0	57.9	60.5	129.1	25.0	28.7
Spring													
Mean	7.54	22.91	0.69	343	94.1	26.2	30.9	4.2	24.7	38.0	128.6	26.6	0.9
Min	7.10	18.00	0.33	160	16.7	7.3	3.0	1.7	4.9	6.5	6.9	11.3	0.7
Max	8.30	25.00	1.20	600	186.1	58.5	52.6	8.3	55.3	102.4	506.1	41.7	1.4
Std dev	0.31	2.17	0.25	126	43.6	16.4	14.0	1.9	13.4	25.9	153.4	8.7	0.2
CV	4.17	9.45	36.96	37	46.4	62.6	45.3	44.1	54.3	68.2	119.3	32.5	23.5
Summer													
Mean	7.64	25.36	0.64	318	67.7	21.7	26.8	2.7	22.3	38.6	139.8	25.5	0.5
Min	7.40	21.00	0.32	160	21.9	6.9	3.1	0.8	1.2	4.6	5.4	12.7	0.2
Max	8.40	30.00	1.14	570	120.9	48.7	50.9	5.9	52.3	90.4	582.1	36.6	0.9
Std dev	0.27	2.16	0.25	125	28.1	13.0	13.4	1.6	12.3	22.7	172.5	6.7	0.2
CV	3.58	8.51	38.92	39	41.6	60.0	49.9	61.8	54.8	58.8	123.5	26.4	47.9

[a]WHO (2007)

groundwaters ranged from 0 to 7.2 mg/l, 0.7–4.7 mg/l, 1.7–8.3 mg/l and 0.8–5.9 mg/l, respectively.

The most abundant anion was SO_4^{2-} and the order of anions changed as $SO_4^{2-} > Cl^- > HCO_3^- > NO_3^-$. NO_3^- levels of analyzed groundwater samples ranged from 0 to 50.7 mg/l, from 1.8 to 28.2 mg/l, from 4.9 to 55.3 mg/l and from 1.2 to 52.3 mg/l in fall, winter, spring and summer seasons, respectively. NO_3^- concentrations at some points were found to be higher than threshold values specified by WHO which is 50 mg/l in fall, spring and summer seasons (Fig. 4). Cl^- concentrations in groundwaters were under permissible limits of 250 mg/l in all four seasons ranging from 3.8 to 75.4 mg/l, 3.3–67.2 mg/l, from 6.5 to 102.4 mg/l and from 4.6 to 90.4 mg/l. In contrast, SO_4^{2-} concentrations exceeded permissible level of 250 mg/l at some points (Fig. 4) in all seasons and ranged from 0 to 573.5 mg/l, from 5.9 to 639. 8 mg/l, from 6.9 to 506.1 mg/l and from 5.4 to 582.1 mg/l, respectively. HCO_3^- values ranged from 11.2 to 34.6 mg/l, from 19.7 to 43.3 mg/l, from 11.3 to 41.7 mg/l and from 12.7 to 36.6 mg/l in fall, winter, spring and summer seasons respectively. F^- concentration in groundwater sampled during fall, winter, spring and summer seasons ranged from 0.2 to 0.9 mg/l, 0.6–1.5 mg/l, from 0.7 to 1.4 mg/l and from 0.2 to 0.9 mg/l, respectively.

Seasonal variations and ANOVA statistics

Concentrations of water quality parameters showed both locational and seasonal differences (Table 1). Seasonal differences among water quality variables were investigated

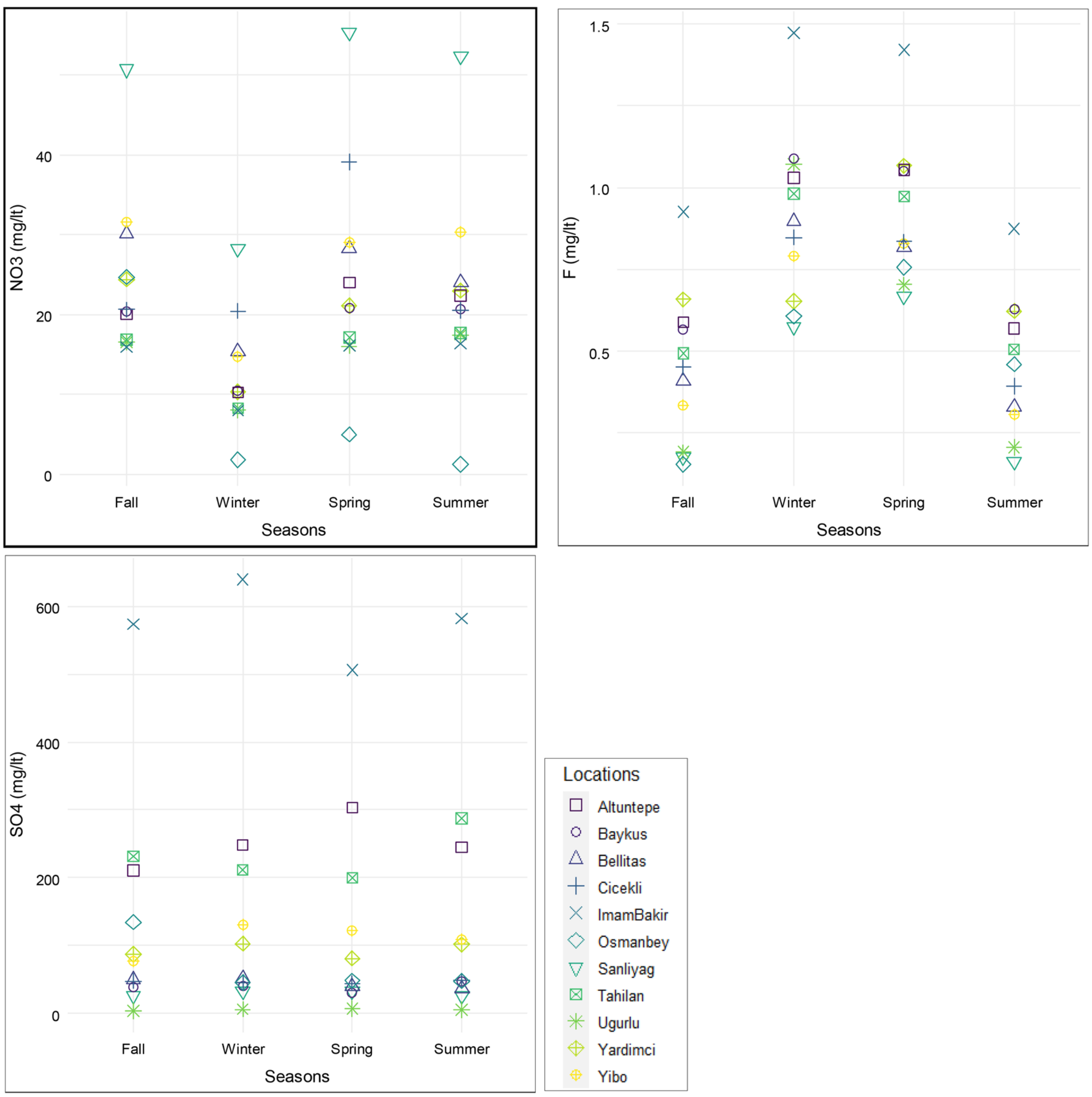

Fig. 4 Seasonal and locational distribution of groundwater quality parameters; NO_3; SO_4 and F

Table 2 ANOVA statistical results showing seasonal differences in water quality parameters

Parameters	Season	Mean	Standard Error of Sum	Letter	*p*	Parameters	Season	Mean	Standard Error of Sum	Letter	*p*
pH	Wn	7.73	0.50	a	0.000***	K	Wn	2.43	4.68	b	0.000***
	Sp	7.54	1.04	a			Sp	4.21	6.16	a	
	Sm	7.64	0.91	a			Sm	2.65	5.44	b	
	Fl	7.30	0.36	b			Fl	2.42	7.24	b	
EC	Wn	673.7	771.5	a	0.0831	NO_3	Wn	12.3	23.7	b	0.000***
	Sp	686.4	841.4	a			Sp	24.7	44.5	a	
	Sm	643.6	830.9	a			Sm	22.3	40.6	a	
	Fl	631.8	835.1	a			Fl	24.3	33.6	a	
Ca	Wn	71.3	89.4	a	0.000***	Cl	Wn	29.9	60.0	b	0.007**
	Sp	94.1	144.6	a			Sp	38.0	86.1	a	
	Sm	67.7	93.4	ab			Sm	38.6	75.3	a	
	Fl	40.5	93.0	b			Fl	34.9	63.2	ab	
Mg	Wn	5.3	21.7	c	0.000***	SO_4	Wn	605.1	141.3	a	0.729
	Sp	26.2	54.5	a			Sp	508.6	128.6	a	
	Sm	21.7	43.2	ab			Sm	572.3	139.8	a	
	Fl	12.7	36.8	bc			Fl	541.2	134.7	a	
Na	Wn	26.3	44.8	ab	0.007**	HCO_3	Wn	30.5	25.3	a	0.004**
	Sp	30.9	46.4	a			Sp	26.6	28.7	ab	
	Sm	26.8	44.3	ab			Sm	25.5	22.4	b	
	Fl	16.9	32.4	b			Fl	25.2	23.7	b	
TDS	Wn	505.3	578.6	a	0.083	F	Wn	0.91	0.87	a	0.000***
	Sp	514.8	631.1	a			Sp	0.93	0.72	a	
	Sm	482.7	623.2	a			Sm	0.48	0.73	b	
	Fl	473.9	626.3	a			Fl	0.45	0.78	b	

Wn winter, *Sp* spring, *Sm* summer, *Fl* fall

*$p < 0.05$; **$p < 0.01$; ***$p < 0.001$ at significance level

using ANOVA test statistics and Table 2 summarizes the results of ANOVA statistics, which compares seasonal differences in water quality variables. Accordingly, all parameters except EC, SO_4^{2-} and TDS showed statistically significant differences ($p < 0.05$) among different seasons having a statistically different result at least for one season.

Correlations among groundwater quality parameters and topographical parameters

Correlation graphs (correlograms) show correlations between groundwater quality parameters and topographical parameters as well as the correlations among different water quality parameters (Fig. 5). In order to understand the cause of the spatial variations, concentrations of water quality parameters at sampled wells were related with corresponding topographical parameters at the same locations.

Among some water quality parameters statistically positive and negative correlations were found. There were statistically significant negative correlations between NO_3^- and pH in all seasons except the fall season. NO_3^- had a statistically significantly positive correlation with K^+ and HCO_3^- in winter and spring seasons. In the same seasons there were significant negative correlations between pH and HCO_3^- (Fig. 5). Between EC and anions and cations such as Ca^{2+}, Na^+, Cl^- and SO_4^{2-} there was a significant positive correlation in winter, spring and summer seasons. It has the only significant positive correlation with Cl^- and SO_4^{2-} anions in the fall season. SO_4^{2-} had statistically significant positive correlations with salinity parameters such as TDS, EC and F^- in all four seasons. SO_4^{2-} had also significant positive correlations with cations of Mg^{2+}, Ca^{2+} except in the fall season and with Na^+ in winter and summer seasons. SO_4^{2-} had also significant positive correlations with Cl^- and pH in the fall season.

There were statistically significant positive and negative correlations between groundwater quality parameters analyzed at different seasons and significant topographical parameters such as elevation, slope, Topo Wetness Index (TWI), flow direction and flow accumulation (Fig. 5). Although relations between two was partly depended upon seasons; i.e. significant correlations existed in some seasons

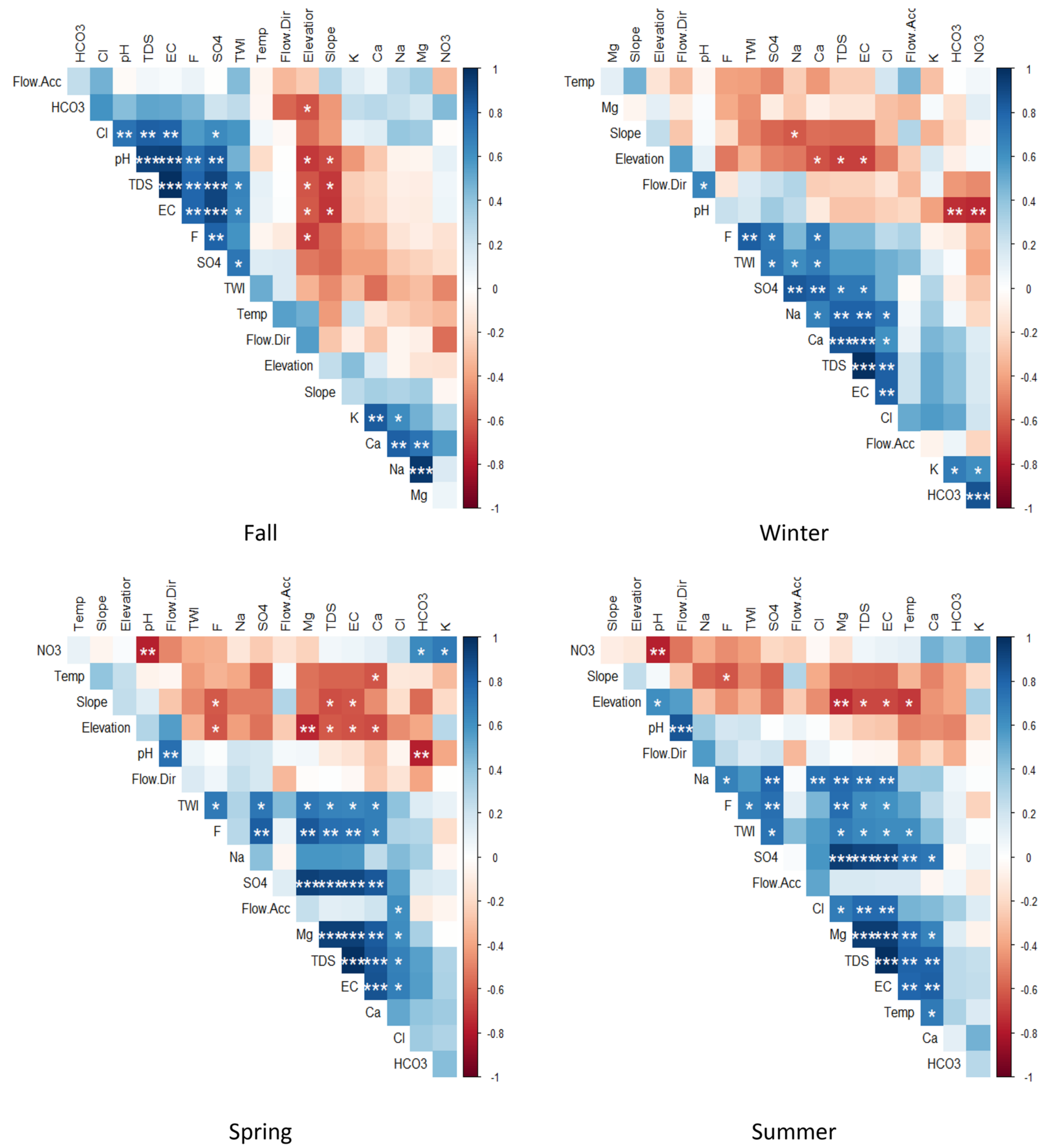

Fig. 5 Correlations among grounwater parameters and topographycal parameters

but, could not be found in other seasons, overall, there was a trend. Elevation had a statistically significant negative correlation with parameters such as TDS and EC in all seasons and with pH, F^-, Ca^{2+}, Mg^{2+}, HCO_3^- and temperature in other seasons. Similarly, slope had a significant negative correlation with EC, TDS, F^- and pH. In contrast to elevation and slope, TWI was positively correlated with groundwater quality parameters. TWI had a significant positive correlation with SO_4^{2-} anions in all seasons and with TDS and EC in all seasons except in the winter season. There were other significant positive correlations between TWI and Ca^{2+}, Mg^{2+}, Na^+ and F^-. Flow direction had only a significant correlation with pH and similarly, flow accumulation had a significant positive correlation only with Cl^- (Fig. 5). On the other hand, there were no significant correlations between NO_3^- and K^+ and with none of the topographical parameters.

Heat-maps

Heat-maps are useful for revealing patterns the data sets. Colormaps show which wells are critical in terms of salinity and pollution for different seasons. In all four seasons; the wells showed a trend i.e. the wells such as Sanliyag and Çiçekli had higher amount of NO_3^-, HCO_3^- and K^+ when grouped together; while the wells of Altuntepe, Tahılalan and Imambakır were higher in salinity parameters of Ca^{2+}, TDS, EC, Mg^{2+} when grouped together (Fig. 6).

PCA analysis

PCA analyses was conducted for standardized concentrations of all water quality parameters. PCA analyses were performed for each season separately. The analyses results, including eigenvalues, total variance, percentage and cumulative percentage of variances are shown in Table 3 and PCA Biplots showing the grouping of wells together with quality parameters for different seasons are shown in Fig. 7.

In all seasons, the first four PCs were found to have significant eigenvalues larger than 1. Total cumulative variance in the data sets explained by these first four PCs were 91.53, 88.9, 90.24 and 91.86%, respectively, in fall, winter, spring and summer seasons (Table 3). Overall parameters such as EC, TDS, SO_4^{2-} and cations such as Ca^{2+} and Mg^{2+} were having yhe highest loading in PC1; while parameters such as NO_3^- and pH had the highest loadings in PC2 (Table 3).

Biplot helps to interpret relations between variables and PCs and patterns in the data sets after the data was projected onto new PCs. When we look at the biplots at different seasons there was a pattern in all seasons except the fall season. Two most distinguishing groupings between wells and water quality parameters can be observed. The first grouping was formed by wells such as Altuntepe, Imambakır, Yibo and Tahilalan that are located in the southern part of the study area (Fig. 1) and have a larger value in PC1 axis and the parameters such as TDS, EC, Cl^-, SO_4^{2-}, Ca^{2+} and Na^+, which had also high positive values in PC1. Similarly, wells such as Osmanbey, Yardımcı, Bellitas, Baykus and

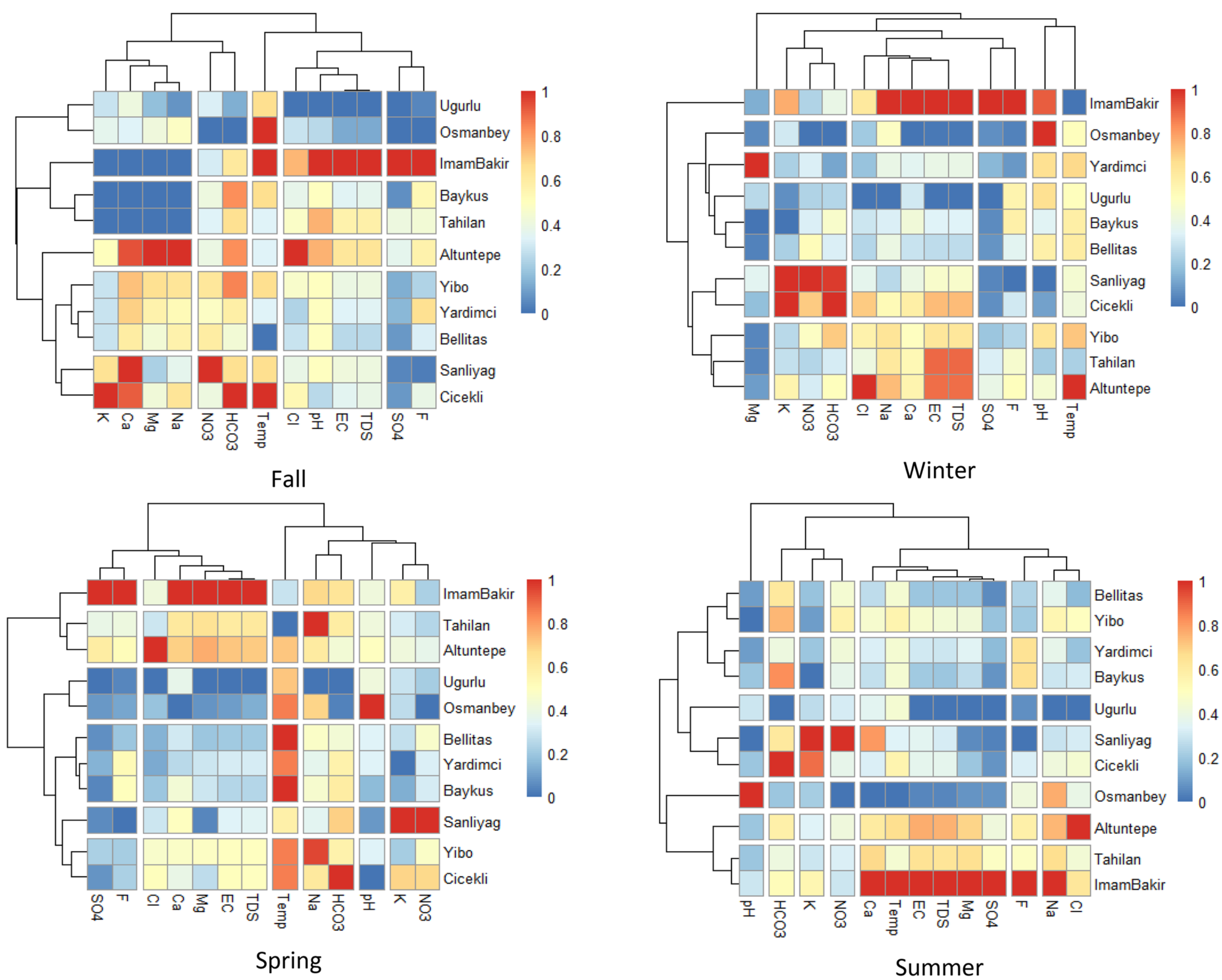

Fig. 6 Heat Maps showing magnitudes of relations among wells and water quality parameters

Table 3 PCA analyses results

	Fall				Winter			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
pH	**0.395**	0.072	– 0.176	– 0.092	– 0.083	**0.458**	0.067	– 0.193
Temp	0.02	– 0.108	**0.692**	**0.432**	– 0.148	– 0.139	**0.726**	– 0.169
EC	**0.41**	0.089	0.035	0.091	**0.396**	– 0.02	0.091	– 0.101
Ca	– 0.173	**0.456**	– 0.016	0.12	**0.381**	0.062	– 0.184	– 0.014
Mg	– 0.086	**0.427**	0.098	**– 0.437**	– 0.101	– 0.073	– 0.245	**– 0.826**
Na	– 0.097	**0.463**	0.12	– 0.312	**0.342**	0.198	0.209	– 0.148
K	– 0.186	**0.358**	0.297	0.312	**0.255**	– 0.288	– 0.197	– 0.175
NO_3	– 0.027	0.241	– 0.55	**0.486**	0.078	**– 0.499**	– 0.168	0.003
Cl	0.31	**0.289**	0.206	– 0.084	0.338	– 0.099	**0.46**	– 0.041
SO_4	**0.395**	– 0.05	0.117	– 0.054	**0.328**	0.294	– 0.121	– 0.148
HCO_3	0.193	0.299	– 0.124	**0.357**	0.194	**– 0.447**	– 0.022	0.19
F	**0.368**	0.011	– 0.014	– 0.121	0.233	0.307	– 0.142	**0.346**
TDS	**0.41**	0.096	0.044	0.09	**0.396**	– 0.02	0.091	– 0.101
Eigen value	**5.59**	**3.68**	**1.39**	**1.24**	**5.83**	**3.35**	**1.28**	**1.11**
% variance	**43**	**28.29**	**10.68**	**9.57**	**44.82**	**25.76**	**9.84**	**8.57**
Cumulative	**43**	**71.29**	**81.96**	**91.53**	**44.82**	**70.58**	**80.42**	**88.99**
	Spring				Summer			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
pH	– 0.049	**– 0.496**	– 0.25	**0.342**	– 0.076	**– 0.491**	**0.436**	0.067
Temp	– 0.243	0.061	**0.577**	0.049	**0.312**	0.142	– 0.293	– 0.143
EC	**0.386**	0.026	0.029	0.03	**0.378**	0.057	0.046	– 0.011
Ca	**0.347**	0.061	– 0.167	– 0.284	**0.295**	0.261	0.175	– 0.369
Mg	**0.37**	– 0.151	0.116	– 0.024	**0.368**	– 0.095	– 0.156	– 0.068
Na	0.221	– 0.105	0.2	**0.621**	**0.296**	– 0.267	0.251	0.204
K	0.109	**0.405**	**– 0.539**	0.144	0.068	0.33	**0.672**	0.042
NO_3	0.009	**0.558**	– 0.04	0.092	– 0.001	**0.543**	0.067	– 0.043
Cl	0.258	0.085	0.139	**0.445**	0.292	– 0.048	0.197	**0.417**
SO_4	**0.356**	– 0.173	– 0.127	– 0.108	**0.358**	– 0.123	0.025	– 0.236
HCO_3	0.199	**0.405**	0.357	– 0.004	0.098	0.292	– 0.204	**0.745**
F	**0.299**	– 0.191	0.258	– 0.415	**0.268**	– 0.28	– 0.255	0.068
TDS	**0.386**	0.014	0.022	0.048	**0.379**	0.043	0.039	– 0.01
Eigen value	**6.62**	**3.01**	**1.07**	**1.03**	**6.84**	**2.97**	**1.09**	**1.03**
% variance	**50.95**	**23.15**	**8.21**	**7.93**	**52.65**	**22.86**	**8.41**	**7.94**
Cumulative	**50.95**	**74.1**	**82.31**	**90.24**	**52.65**	**75.51**	**83.92**	**91.86**

Bold numbers shows the parameters with the highest weighted loadings values and variables within the 10% of the highest weighted loading values in each PC

Ugurluare located in the upper part of the plain and have lower PC1 values (Fig. 7). The second grouping was formed by the wells of Cicekli and Sanliyag that had higher values in PC2 axis and parameters such as NO_3^- and HCO_3^-.

Modeling

In addition to correlation analyses between groundwater quality variables and topographical parameters, the relations between two were modeled with classical multiple regression models in order to see how well topography explains the variations in different water quality parameters. The models result show the explanatory power of the models that were presented with R^2 values as well as impacts of each parameters involved in the models with significance levels of each individual topographical variables. R^2 values ranged from 0.78 to 94.28% depending upon the groundwater quality parameters and sampling season (Table 4). The highest R^2 value was obtained for F.

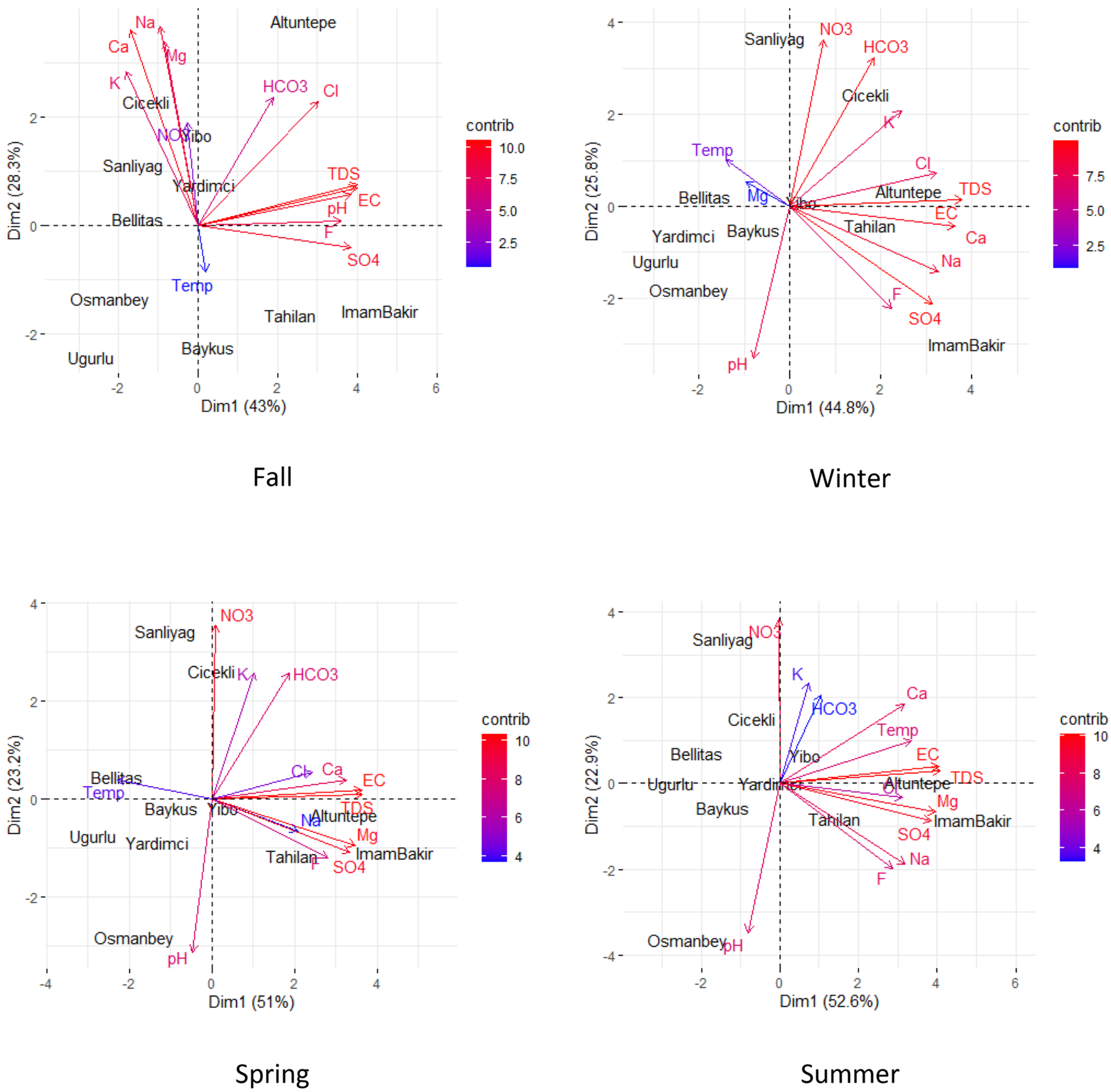

Fig. 7 PCA analyses Biplots obtained data set including groundwater quality and topographical parameters; well numbers 1: Sanliyag; 2: Ugurlu; 3: Yardimci; 4: Baykus; 5: Tahilalan; 6: Imambakir; 7: Bellitas 8:Yibo; 9: Altuntepe; 10: Cicekli; 11: Osmanbey

Discussion

Groundwater quality parameters

The chemical characterization of groundwater can provide useful information in water sources management and reveal its suitability for irrigation and drinking (Zhai et al. 2015). The chemical composition of groundwater is affected mostly by the host-rock and water interactions, the total time of residence of water within the host rock, geochemistry of rocks and soil and external factors such as anthropogenic ones and dissolution of groundwater with irrigation, precipitation or exploitation of groundwater that may change concentrations of chemicals within groundwater (Prasad and Rao 2018).

The quality of 11 deep aquifer groundwater wells has been evaluated in terms of various quality parameters, cation and anion concentrations, salinity parameters during four different seasons within one year and compared with the World Health Organization (WHO) permissible limits for drinking water. Most of earlier studies monitoring

Table 4 The results of modeling between groundwater and topographycal parameters

Factor	Season	Model	R^2 (%)
NO_3	F	49.9 + 0.0398 E – 1.69 S – 0.24800 FD – 0.291 Fa – 3.62 TWI	69.28
	W	1.00 + 0.0738 E – 1.136 S – 0.1707 FD – 0.082 Fa – 1.28 TWI	61.67
	Sp	9.70 + 0.1350 E – 2.410 S – 0.3090 FD + 0.031 Fa – 3.05 TWI	60.18
	Sm	38.6 + 0.0675 E – 2.160 S – 0.2560 FD – 0.074 Fa – 3.58 TWI	64.43
SO_4	F	237 – 1.619 E + 4.5 S + 0.96 FD – 8.12 Fa + 81.0 TWI	79.86
	W	348 – 1.888 E + 4.8 S + 1.57 FD – 8.12 Fa + 82.0 TWI	80.31
	Sp	504 – 1.827 E + 1.8 S + 1.70 FD – 2.20 Fa + 51.3 TWI	76.18
	Sm	394 – 1.820 E + 1.8 S + 1.46 FD – 6.13 Fa + 72.2 TWI	80.39
HCO_3	F	48.5 – 0.0136 E – 1.678 S* – 0.1084 FD + 0.303 Fa – 1.05 TWI	78.28
	W	4.00 + 0.0836 E – 1.360 S – 0.17780 FD + 0.086 Fa + 0.19 TWI	46.44
	Sp	32.9 + 0.0289 E – 2.150 S – 0.16080 FD – 0.017 Fa – 0.38 TWI	66.94
	Sm	40.3 + 0.0016 E – 1.370 S – 0.07970 FD + 0.169 Fa – 0.97 TWI	40.78
EC	F	1398 – 2.28 E – 29.4 S + 0.68 FD – 2.35 Fa + 52.1 TWI	78.47
	W	1467 – 1.86 E – 31.6 S – 0.53 FD + 3.80 Fa + 23.3 TWI	69.03
	Sp	1443 – 2.38 E – 24.3 S + 0.71 FD – 0.00 Fa + 52.7 TWI	72.84
	Sm	1604 – 2.70 E – 22.3 S + 1.02 FD + 1.20 Fa + 40.2 TWI	71.48
pH	F	8.089*** – 0.001649 E – 0.0126 S + 0.001011 FD* + 0.00026 Fa – 0.0040 TWI	79.80
	W	8.025*** – 0.001741 E + 0.0328 S + 0.00401 FD* – 0.006760 Fa + 0.0309 TWI	77.19
	Sp	8.666*** – 0.003080 E + 0.0399 S + 0.01058 FD* + 0.011340 Fa – 0.0487 TWI	88.77
	Sm	6.778** + 0.000893 E + 0.0178 S + 0.00633 FD* + 0.009490 Fa + 0.0192 TWI	93.07
TDS	F	691 – 1.124 E – 14.9 S + 0.32 FD – 0.79 Fa + 25.6 TWI	79.13
	W	1100 – 1.40 E – 23.7 S – 0.39 FD + 2.83 Fa + 17.5 TWI	69.03
	Sp	730 – 1.182 E – 12.8 S + 0.49 FD + 0.18 Fa + 24.6 TWI	73.63
	Sm	782 – 1.373 E – 9.7 S + 0.57 FD + 0.310 Fa + 22.8 TWI	72.18
F	F	1.228 – 0.00260 E – 0.0108 S* + 0.0003800 FD – 0.00480 Fa* + 0.0590 TWI**	71.20
	W	– 0.316 – 0.001222 E + 0.0469 S* – 0.00141 FD – 0.01700 Fa* + 0.2230 TWI***	94.28
	Sp	1.552 – 0.00242 E – 0.0100 S + 0.00137 FD – 0.00350 Fa + 0.0632 TWI	78.51
	Sm	1.111 – 0.00209 E – 0.0163 S + 0.00255 FD + 0.00215 Fa + 0.0357 TWI	71.80
Cl	F	130.0 – 0.189 E – 2.58 S + 0.186 FD + 1.469 Fa – 1.990 TWI	69.55
	W	104.9 – 0.134 E – 2.41 S + 0.095 FD + 1.448 Fa – 2.280 TWI	56.50
	Sp	172.0 – 0.215 E – 3.27 S + 0.224 FD + 2.720 Fa – 6.600 TWI	62.33
	Sm	167.4 – 0.234 E – 3.25 S + 0.344 FD + 2.274 Fa* – 4.77 TWI	75.98

E elevation, *FD* Flow direction, *Fa* Flow accumulation, *TWI* Topo Wetness Index

*$p < 0.05$

**$p < 0.01$

***$p < 0.001$ at significance level

groundwater and analyses reports results were obtained in two seasons per year; post- or pre-monsoons (Sahu et al. 2018) or dry and wet seasons, which makes the finding of this study more comparable.

In earlier studies high concentration of most common individual quality parameters of groundwater or their rations of each other has been interpreted in order to better understand the origin of chemical factors controlling quality of waters. High pH shows the alkaline nature of water and the presence of carbonates, which may also be an indication of high HCO_3^- presence in groundwater. HCO_3^- originates from carbonate weathering and carbonic acid dissolution in aquifer systems (Gnanachandrasamy et al. 2020). High TDS values are due to dissolved minerals and it can be used to determine the use of groundwater for agricultural purposes. High TDS values are due to the input of fertilizer industries, wastewater and dissolved minerals. High Cl^- are mostly due to chloride containing minerals while low Cl^- contents are an indication of low surface contamination. High K^+ contents originate from weathering of silicate minerals. A high Ca^{2+} to Mg^{2+} ratio is an indicator of dissolution of salts from the host rock and high Ca^{2+} contents originate from crystalline limestone (Prasad and Rao 2018).

In the present study, average values of different quality parameters are in general under threshold limits set by the WHO (WHO 2017), however for some wells parameters such as SO_4^{2-} and NO_3^- exceeded the threshold limits by the WHO, which were 250 and 50 ppm, respectively. In addition, parameters such as F^- and Ca^{2+} showed concentration values closer to threshold limits according to maximum values observed in some wells for each parameters showing a potential hazard for the usage of drinking water. Other variables were always under the permissible limits for drinking water quality during sampling seasons (Table 1).

The Sanliyag well located at the northern site of the plain had the highest amount of NO_3^- values exceeding threshold values in all but winter season. The high NO_3^- content at this location could be due to the mostly high rate of urbanization and industrialization. Wang et al. (2019) also relates NO_3^- and Cl^- concentrations with the amount of fertilizer and pesticides applied per area.

The causes of high nitrate concentrations have been summarized as application of nitrogenous fertilizers, waste of animals, agrochemicals usage, seepage and industrial effluents (Prasad and Rao 2018). Urbanization is a major factor in the high amount of nitrate concentrations to be found in groundwater (Liu et al. 2018). This nitrate contamination in the deep aquifer can be explained by several reasons in this study. Contaminants are transported from the free aquifer to the deep aquifer, making the well casing suffer from corrosion and thus the passage of pollutants is facilitated (Yeşilnacar and Yenigun 2011). The high sulfate concentrations in the groundwater in the plain cause corrosivity for metallic materials such as well casing (Atasoy and Yesilnacar 2010). In addition heavy irrigation period, long-term fertilizer application in the plain where typical smectite and iron oxide rich Vertisol soils with deep cracks exist may have increased the probability of nitrate movement into wells (Atasoy 2008).

The concentration levels of SO_4^{2-} were always higher than the threshold value for the well of Imambakir in all seasons sampled. Imambakir was the only well exceeding SO_4^{2-} threshold values (Fig. 4).

The increase of SO_4^{2-} concentration in groundwater has been attributed to the dissolution of gypsum mineral, atmospherical deposition and agricultural waste, fertilizers and bacterial oxidation (Ganiyu et al. 2018). High SO_4^{2-} rates mostly originate from host – rock underlying the study area which is high in gypsum content (Aydemir and Sonmez 2009).

Florine is considered as a highly toxic element in drinking water. Its threshold value was stated as 1.5 mg l^{-1} (WHO 2007). This value was not exceeded in most of the cases however in the Imambakir well its concentrations were closer to the threshold value in all four seasons as in the case of the SO_4^{2-} parameter (Fig. 4). Higher concentrations of fluorine in groundwater have been associated with a few factors such as improper use of pesticides and fertilizer and industrial wastes, the desorption of fluoride from minerals under alkaline conditions and a high HCO_3^- content in groundwater. In the areas under saline and alkaline conditions similar to the environment where corresponding wells are located, the enrichments of fluorine concentrations in groundwater have been reported due to Ca^{2+} precipitation with evaporation resulting in a reduction of Ca^{2+}–F^- activity by the release of fluorine (Luo et al. 2018). Prusty et al. (2018) stated that fluoride generally occurs in groundwater mainly due to the interaction between groundwater and fluoride bearing minerals or it can also be due to chemicals used in agricultural activities. The dissolution of fluorite, apatite and topaz from local bedrocks leads to high Fluoride concentration in groundwater (Suthar et al. 2008). The dissolving of F^- containing minerals to release fluoride ions into the water environment takes place when they interact with water. Alkaline saline environments or high Na^+ concentrations favor dissolution of fluorine bearing minerals causing increases in fluorine concentration in groundwater and in alkaline groundwater in semi-arid environments and release of fluorine from apatite types minerals in granite rocks in to groundwater (Karanth 1987). Sahu et al (2018) reported a correlation between F^- and SO_4^{2-} similar to the Imambakir well that has the highest concentration of both SO_4^{2-} and F^-. In addition, they found that fluorine correlated with other parameters such as EC, Na^+, EC and TDS in our case, Mg^{2+} was the correlated cation with fluorine, which may be due to interactions of different minerals.

Other significant correlations observed between NO_3^- and pH in the present study could be explained by nitrification and denitrification processes occurring in the environment. While nitrification favoring higher NO_3^- concentrations in water causes decreases in pH since it releases H^+ protons into the environment, denitrification leads to increases in pH by causing the release of OH^- ions as a result of the combination of CO_2 and HCO_3^- (Kim et al. 2019; Kim and Park 2016).

Seasonal and spatial variations in groundwater quality parameters

Factors such as land use, aquifer characteristics and water infiltration may cause spatial and temporal differences in groundwater quality thus over different periods, monitoring of ground water quality may be needed for a better management of it.

Seasonal differences in deep groundwater quality parameters were investigated by ANOVA statistics. According to ANOVA statistical results NO_3^- and F^- showed statistically significant differences among seasons while SO_4^{2-} did not change across seasons (Table 2). Average fluorine concentrations were higher in winter and spring seasons, average NO_3^- concentrations were higher in spring and summer seasons showing an increasing trend as temperature increased from fall to summer. Increases in NO_3^- concentrations in summer and spring seasons can be due to beginning of intensive agricultural activities in the plain along with a high amount of fertilizer applications (Bilgili et al. 2018). Reasons for variations in quality parameters between seasons are discussed by Sahu et al. (2018) where they attribute it to leaching of minerals causing increases in concentration of parameters in groundwater such as Na^+, Cl^- and secondly to the use of agriculture fertilizer as cause of increases in NO_3^- and SO_4^{2-} concentrations in groundwater. There have been studies reporting insignificant differences among seasons in terms of groundwater quality parameters. Zhai et al. (2015) did not obtain a seasonal difference between quality parameters, which can be due to their sampling period that was only two whereas in our case groundwater were sampled during four different seasons.

Causes of locational differences occurred in the wells in terms of contaminants and their controlling factors were investigated by methods such as correlation analyses, PCA analyses and heat map graphs with clustering for all four seasons (Figs. 5, 6, and 7). Heat maps can serve similar purposes as cluster graphs often used in groundwater studies. Relations between wells observed and parameters can be better shown in heat maps, which are quite useful in investigating existing patterns in the data set. Close observation of heat-maps in all seasons showed that there are some wells with distinguishing relations for some parameters. For example, the Imambakir well was highly correlated with parameters such as SO_4^{2-} and cations indicating an $CaMgSO_4$ (Jips) formation in wells combined with higher amount of fluorine.

PCA reduces the number of constituents revealing the most important parameters controlling pollution, save costs and provide opportunity for the identification of pollutant sources (Masoud 2013). Among various multivariate statistical methods, PCA was reported to be superior to other multivariate statistical approaches because of its mathematical processing (Sahu et al. 2018).

PCs with eigenvalues higher than 1 are accepted as significant and those with eigenvalues less than 1 as insignificant (Sahu et al. 2018). Accordingly, the first four PCs with eigenvalues were found as significant (Table 3). High loadings of the parameters such as EC, TDS, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and F^- in PC1s explaining the highest variabilities in groundwater qualities from different wells in all seasons showed that they had a high impact on the water qualities (Sahu et al. 2018). In addition, the strong positive loadings for the parameters such as EC, TDS and SO_4^{2-} and cations in PC1 also caused PC1 to be interpreted as a salinity factor. High loadings of parameters such as EC, TDS, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and F^- in PC1 suggest that salinity due to dissolution of salt minerals is the dominant process controlling groundwater quality in the study area. High loadings for parameters such as Ca^{2+}, Mg^{2+} have been interpreted as calcite and dolomite dissolution weathering process (Ganiyu et al. 2018). On the other hand, high loadings for NO_3^- and pH in PC2 may be interpreted as an anthropogenic pollution factor.

The results of heat mapping with cluster analyses were in very good agreement with PCA analyses results. Like heat maps clustering and grouping were formed as a result of PCA analyses. PC1 sharply separated the wells into two groups; the wells such as at Altuntepe, Imambakir, Tahilalan, Yibo which are located in the lower part of the plain, which were highly correlated with PC1, and the other wells that are located in the upper part of the plain, which have a lower correlation with PC1. The main difference in the two groups is their topography. The wells located at the upper side of the plain are characterized by higher elevation, larger slope, low TWI and flow accumulation values and the wells located at the lower side of the plain are characterized by the opposite; lower elevation, smaller slope and higher TWI and flow accumulation. This has been confirmed also by the correlations between topographical parameters and different groundwater quality parameters (Fig. 5). High correlation between topographical parameters and PC1 also shows that the poor quality due to salinization is mostly controlled by the topographical structure overall indicating that dissolved minerals move toward the flow direction and accumulate in wells located in low lying areas. In addition, atlower locations fields are irrigated with disposal water due to a deficit of water for fields in low lying areas. Thus there should be payed attention to that.

Overall, the results indicated significance of the impact of topography on the quality of the groundwater. There have been groundwater studies focusing on topography (Srivistava et al. 2012); Liu et al. 2018; Masoud 2013; Prasad and Rao 2018). Prasad and Rao (2018) reported increases in TDS (Total Dissolved Salt Contents) with a decrease in elevation and in places where no groundwater movement are seen, high conductivity zones.

The types of salts are also impacted by topography. Most wells located in the upper parts are better in quality than wells located in the lower parts.

Topography was evaluated as a structural factor in groundwater studies (Jeelani et al. 2014; Wang et al. 2019). The researchers stated that mass concentration of ions decreases from north to south and the overall quality of water in the southern region is higher than in the northern one depending upon topography. In the present study, the southern parts are mostly polluted with dissolved solids, cations, EC and TDS, while the northern part is high in NO_3^- levels, which indicates anthropogenic activities (Jeelani et al. 2014; Zhai et al. 2015). Relatively higher NO_3^- concentrations were observed in the western residential and industrial areas of the plain.

Modeling of factors affecting groundwater quality

Depending on groundwater quality parameters and the seasons when the sampling was performed the level of R^2 values changed the interactions between seasonal and spatial factors explained the variations in groundwater quality parameters and the insufficiency of one alone to contribute to this variability. R^2 values can evaluated as 0.75 = substantial, 0.50 = moderate and 0.25 = weak (Hair et al. 2011). Accordingly, the majority of the R^2 values belonging to the models can be classified within substantial groups indicating the power of topographical parameters in explaining the spatial variations in groundwater quality parameters (Table 4). In parallel to correlation analyses results, the impact of each individual parameter on groundwater quality parameters was found significant. Flow direction was found significant in modeling of pH and slope, flow accumulation and Topo Wetness Index were found highly significant in modeling of fluorine indicating the control of topography on spatial distribution of it within the study area. In the aforementioned studies variations in fluorine have been explained as interactions between rock and groundwater or dissolution of minerals containing fluorite under alkaline conditions.

The control and impact of surface topography on groundwater table, groundwater flow patterns and salinity are well known (Nosetto et al. 2013; Mulyadi et al. 2020). Topographycal parameters such as TWI and slope helps in explanation of wash out of the contaminants. Groundwater flow occurring due to gradient difference may help dissolution of minerals (Khan et al. 2017). In deeper aquifer there are also studies reporting relation between topography and groundwater contamination. In a recent study, samples with high As concentrations have been found in areas with low topography depressions (Bindal et al. 2020). As in the present study, the effect of topography on deep aquifer quality can be explained by the interaction of topography and geological structure. It is considered that high flows in the areas where the wells are especially close to recharge areas can help carry pollutant parameters down to lower depths, especially in areas with a limestone dominant geological structure allowing leakage (Fig. 2). Some of the wells investigated are located on or near places near the third degree and above stream orders (Fig. 3). Carbonate rocks with high porosity and fractures can store large amount water and also allows enhanced flow causing sensitivity of aquifers to pollution (Stephen et al. 2017).

Conclusions

Parameters of analyzed groundwater samples were found to lie within standard limits with exception in a few locations. Seasonal variations in groundwater quality parameters were mostly found statistically significant. Statistical techniques used for the spatial and seasonal characterization of groundwater quality parameters revealed two distinguishing groupings among the wells. Overall, spatial distribution of groundwater quality parameter across the study area were highly impacted by topographical parameters and the concentrations of salts and minerals occurred as a results of dissolution of minerals such as carbonate, gypsum increased toward the flow direction becoming higher in low elevation spots. Furthermore, special care is needed for NO_3^- and F^- contamination as well as for salinity parameters, which mostly controlled the quality of groundwater. Overall, the results showed that dissolution of salt minerals and their accumulation toward flow direction was the main mechanism controlling the quality of groundwater. Spatial and temporal assessment of groundwater is very important for sustainable water resources management, especially in arid and semi-arid lands because of global warming and rising temperature that causes a decrease in surface water resources increasing dependence on groundwater resources.

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Availability of data and material Any data and material used in this study can be provided upon request.

Code availability Codes running statistical analysis performed in the study can be provided upon request.

Declarations

Conflict of interest Not applicable.

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