ORIGINAL ARTICLE

Assessment of geochemistry and hydrogeochemical processes in groundwater of the Tefenni plain (Burdur/Turkey)

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Abstract The Tefenni (Burdur) plain is located in the southwest of Turkey and is semi-closed basin. Groundwater is densely used as drinking, irrigation and domestic water in the Tefenni plain. Hydrogeochemical processes controlling groundwater chemistry and geochemical assessment of groundwater were investigated in the Tefenni (Burdur/Turkey) plain. The conceptual hydrogeological model of the plain was prepared for qualitative description of the underground geology and interpretation of hydrogeochemical processes of the study area. In this study, groundwater samples for two seasons were analyzed and major ion chemistry of groundwater was researched to understand the groundwater geochemistry. Two major hydrochemical facies $(Ca^{2+}-Mg^{2+}-HCO_3^{-})$ and $Mg^{2+}-HCO_3^{-}$ $Ca^{2+}-HCO_{3}^{-}$) were determined in the area. Mg^{2+} , Na^{+} , SO₄²⁻ and Cl⁻ concentrations of water samples increased seasonally related to ion exchange of minerals in rocks by rainwater in wet season. Various graphical plots and multivariate statistical analysis (Pearson correlation analysis) were used for identifying the occurrence of different geochemical processes. Carbonate weathering in dry season and silicate weathering in wet season were the major hydrogeochemical processes in the study area. In addition, ion exchange and reverse ion exchange were two possible processes of water-rock interaction in the basin. The mechanism controlling groundwater chemistry at the

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Geology Engineering Department, Suleyman Demirel University, Isparta, Turkey e-mail: aysendavraz@sdu.edu.tr Tefenni plain is originally regulated by the geogenic process rather than antropogenic activities.

Keywords Hydrogeochemical process · Major ions · Geochemistry · Tefenni plain · Turkey

Introduction

Hydrogeochemistry of groundwater is important for sustainable development and effective management of groundwater. The hydrogeochemical processes of the groundwater system help to obtain an insight into the contributions of rock/soil-water interaction and anthropogenic influences such as agriculture, sewage disposal, mining and industrial wastes on groundwater (Matthess 1982; Kumar et al. 2006). The chemical composition and quality of the groundwater are controlled by various factors, like evaporation, dissolved ion content, precipitation, climate, oxidation-reduction, sorption and exchange reactions, transformation of organic matter, regional geology, degree of chemical weathering of the various rock types, quality of recharge water and mixing processes (Carrillo-Rivera et al. 2007; Singh et al. 2011; Aghazadeh and Mogaddam 2010; Bozdag and Gocmez 2013; Stamatis et al. 2011).

Water interacts with rocks and minerals during infiltration to underground. It solves rocks and minerals and this process continues until to reach saturation of water. Chemical composition of groundwater is a function of mineralogical and chemical properties of aquifers, flow conditions and flow speed and residence time of water into the aquifer (Freeze and Cherry 1979; Appelo and Postma 1993; Andreo and Carrasco 1999). Hence, to get knowledge about the groundwater chemistry is important to learn

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the geological history of the aquifers and the suitability of groundwater for domestic, industrial and agricultural purposes. To utilize and protect water resources effectively and predict the change in groundwater environments, it is necessary to understand the hydrogeochemical characteristics of the groundwater and its evolution under natural water circulation processes (Guendouz et al. 2003; Wen et al. 2005, 2008; Edmunds et al. 2006; Tizro and Voudouris 2008). In this study, hydrogeological and hydrogeochemical data of Tefenni plain (Burdur) were investigated and used to determine the main factors and mechanisms controlling the chemistry of groundwater in the area.

Materials and methods

Groundwater level map was prepared for the alluvial aquifer with groundwater level measurements taken from 26 wells in May 2010 (in wet season) (Fig. 1). The hydraulic conductivity and transmissibility coefficients of the alluvial aquifer were determined using well pumping test results by State Hydraulic Works (SHW) with AquiferTest 3.5 Pro (Hall and Smol 1996) software program.

In this study, a total of 56 water samples taken from wells, springs and lake waters were analyzed at two hydrological seasons [July 2009 (dry) and May 2010 (wet)] for hydrogeochemical assessment. Samples were stored in two polyethylene bottles. One of the bottles was acidified with suprapure HNO_3^{-} for determination of cations and another was kept unacidified for the anion analyses. The discharge temperature, pH and electrical conductivity (EC) were measured in the field. The major chemical constituents were analyzed by ICP-MS (inductively coupled plasma-mass spectrometer) at the ACME Laboratory (Vancouver, Canada, an ISO 9002 accredited company). HCO_3^{-} , CO_3^{2-} concentrations were determined by titrimetric method; Cl⁻ and SO₄²⁻ were determined using ion chromatography in the laboratory of the SHW (Isparta, Turkey). The charge-balance error of the water samples was less than 5 %, which is within the limits of acceptability. Data were analyzed with the SPSS software version 10.0 for Windows. Continuous variables from the study groups were reported as mean \pm standard deviation. Statistical significance was defined as p < 0.05.

In addition, geology, hydrogeology and hydrogeochemistry maps were prepared using GIS-ArcView computer code. ArcGIS 9.3 software, Spatial Analyst extension and inverse distance weight (IDW) interpolation methods were applied throughout research evaluations and the study area was mapped to a UTM Zone 35, ED50 datum. IDW is referred to as deterministic interpolation methods because they are directly based on the surrounding measured values or on specified mathematical formulas that determine the smoothness of the resulting surface. IDW model is a quick deterministic interpolator that is exact, and can be a good way to take a first look at an interpolated surface. Kriging model is very flexible and allows user to investigate graphs



Fig. 1 Location, geological and groundwater level maps (in wet season) of the study area (Varol 2011)

of spatial autocorrelation. Kriging model uses multiple datasets and is very flexible. IDW model has minimum mean error and root mean squared error eventually. IDW model was regarded as optimal model to create simulation map (Li et al. 2008). Therefore, IDM model was used in this study.

Geology and hydrogeology

The Tefenni (Burdur) plain is located in the southwest of Turkey (Fig. 1) and has a 1,527 km² watershed area (Varol 2011). Generally, climate of the plain and its vicinity is affected from Mediterranean climate zone in the middle Anatolian climate zone. According to data obtained from Turkish State Meteorological Service (TSMS), the mean rainfall is 465.03 mm with minimum values in the August 10.13 mm and maximum values in December 73.31 mm (Varol 2011). The actual evapotranspiration was calculated as 326.74 mm for the study area with Thornthwaite method (Varol 2011). Groundwater is an important resource for drinking, agriculture and livestock uses in the study area.

The groundwater quality of the area studied is related to both the lithology and the residence time of the water in contact with rock material. Therefore, geological and hydrogeological properties of the study area were primarily determined. Autochthonous and allochthonous units are outcropped in the study area (Varol 2011; Fig. 1). Allochthonous units are composed from Marmaris peridotite, Kızılcadag ophiolitic melange, Orhaniye formation, Dutdere limestone, Kayalısırtı flysch unit, Söbüceyayla, Mamatlar, Varsakyayla, Karanasıflar, Karaböğürtlen, Yavuz and Elmalı formations. Cameli formation, alluvium and slope debris are autochthonous units (Table 1). The geological structure of the Tefenni plain developed depending on tectonism. This region is located on the west side of the regional geological structure known as Isparta angle in the SW-Turkey (Kocyigit et al. 2000). Fethiye-Burdur Fault zone is located between the Fethiye gulf and Burdur Lake in the study area. This zone has 300 km length. It is the most active fault system in the southwest Anatolia (Bozcu et al. 2007).

The stratigraphic units within the study area have different hydrogeological characteristics. These units were grouped qualitatively as impermeable (aquifuge), semipermeable (aquitard-1, 2), permeable-1 (granular aquifer) and permeable-2 (karstic aquifer). The units of similar hydrogeological characteristics are summarized in Table 1. Alluvium which is the most important aquifer in the basin has an area of approximately 174 km². The well logs indicated that the thickness of the alluvium ranged from 5 to 130 m in the Tefenni plains. The thickness increased in the middle of the plain. The coefficient of transmissibility of alluvium aquifer was calculated using Jacob method with timedrawdown data between 1.03×10^{-3} and 9.54×10^{-4} m²/s. The hydraulic conductivity of alluvium aquifer was between 1.18×10^{-4} and 8.48×10^{-6} m/s (Varol 2011).

The groundwater in the study area occurs under unconfined conditions. The seasonal variation of groundwater level is controlled with natural factors such as precipitation, evaporation, runoff and artificial factors such as withdrawing groundwater from wells and recharge with irrigation from Lake Karataş. Rainfall is the main recharge source of groundwater in the plain. The maximum and minimum groundwater level indicated fluctuations seasonally in May and September. The depth to groundwater table varied between 3.75 and 50.05 m in May 2009, 5.20 and 49.90 m in October 2009, 3.70 and 49.06 m in May 2010 and between 7.75 and 48.35 m in October 2010, below the ground level. The general groundwater flow direction in the porous aquifer was toward Burdur Lake which is located in the north of the plain in both wet and dry seasons (Fig. 1). Generally, groundwater level curves occurred closer to each other in the north and northeast of the study area. In these regions, hydraulic gradient was determined between 1.11×10^{-3} and 0.010. This situation represents areas having low permeability and the high hydraulic slope. Because, the thicker and more frequent clay levels within the alluvium aquifer were observed in these areas. Otherwise, groundwater level curves were sparse in the west of the plain due to sand, and coarse granular sediment levels are extensive and thick in these regions, and hydraulic gradient was determined to be 3.44×10^{-3} .

Conceptual hydrogeological model of the basin

The conceptual hydrogeological model of the Tefenni plain was prepared for qualitative description of the underground geology and interpretation of hydrogeochemical processes of the study area (Fig. 2). Thus, changes in groundwater chemistry during infiltration were interpreted clearly and simply. The model is pictorial description of the groundwater system, including a delineation of the hydrogeologic units, the system boundaries, inputs/outputs, and a description of the soils and sediments and their properties (Meyer and Gee 1999). The natural system beneath the underground is complex, consisting of fine to coarse sediments deposited in a heterogeneous manner and different rock units are situated. In the study area, limestones, dolomitic limestones, ophiolitic complex and Neogene units were existed as intricate via tectonic activities. Ca^{2+} - $Mg^{2+}-HCO_{3}^{-}$, $Mg^{2+}-Ca^{2+}-HCO_{3}^{-}$, $Na^{+}-CO_{3}^{2-}-Cl^{-}$ and $Na^+-HCO_3^--Cl^-$ water types were observed due to water-rock interaction. According to this model, aquifer chemistry and tectonic structures have dominant effects on the change in the groundwater types in the study area.

Age	Formation	Lithology	Reference	Hydrogeological properties
Quaternary	Alluvium (Qal)	Gravel, sand and mudstone	_	Permeable (Granular Aquifer)
Quaternary	Slope Alluvium (Qym)	Attached to the loose gravel, sand and mudstone	-	Permeable (Granular Aquifer)
Pliocene (Neogene)	Çameli formation (Ply)	Conglomerate, sandstone, claystone, clayey limestone, marl, conglomerate	Erakman et al. (1982)	Semipermeable (Aquitard-1)
L. Lutetian–E. Burdigalian (Eocene-Miocene)	Elmalı formation (Te)	Turbiditic sandstones, shales	Onalan (1979)	Semipermeable (Aquitard-2)
L. Lutetian–Priabonian (Eocene)	Yavuz formation (Tey)	Flysch composed of sandstone, claystone and siltstone	Poisson (1977)	Semipermeable (Aquitard-1)
L. Lutetian–Priabonian (Eocene)	Varsakyayla formation (Tev)	Sandstone, conglomerate, limestone	Poisson (1977)	Semipermeable (Aquitard-1)
Montian–Thanetian (Paleocene)	Mamatlar formation (Tpm)	Conglomerate, claystone, sandstone, conglomerate, nodular limestone, marl and clayey limestone	Poisson (1977)	Semipermeable (Aquitard-2)
Aptian-Albian (Cretaceous)	Marmaris peridotite (Kmo)	Peridotite, serpentinite and serpentinized peridotite	Capan (1980)	İmpermeable (Aquifuge)
L. Cenoniyen (Cretaceous)	Karaböğürtlen formation (Kka)	Sandstone, claystone, cherty limestone, blocky flysch	Poisson (1977)	Semipermeable (Aquitard-2)
L. Cenoniyen (Cretaceous)	Söbüceyayla formation (Ksö)	Orbitoidic sandstone	Poisson (1977)	Semipermeable (Aquitard-2)
L. Cenoniyen (Cretaceous)	Kızılcadağ ophiolites (Kkzm)	Limestone, chert, diabase, and serpentinite blocks within ophiolitic matrix	Poisson (1977)	İmpermeable (Aquifuge)
L. Cenoniyen (Cretaceous)	Karanasıflar formation (Kkn)	Limestone and breccia with chert membered	Senel et al. (1989)	Permeable (Karstic Aquifer)
L. Triassic-Cretaceous	Kayalısırtı units (JKks)	Pelletoidal limestone, red micrite, cherty micrite, radiolarite	Senel et al. (1989)	Permeable (Karstic Aquifer)
ML. Triassic	Dutdere Limestone (TrJd)	Recrystallized limestone	Senel et al. (1989), Bilgin et al. (1990)	Permeable (Karstic Aquifer)
Jurassic-Cretaceous	Orhaniye formation (JKo)	Calciturbidite, cherty limestone	Meshur et al. (1989)	Semipermeable (Aquitard-2)

Table 1 Stratigraphic relations of the geologic units and hydrogeological properties (Varol 2011; Senel et al. 1989)

Results and discussion

Groundwater geochemistry

Hydrogeochemical characteristics of groundwater in the study area were evaluated separately as discharge lithologies and localities (Tables 2, 3). Springs are discharged from Dutdere limestone, Çameli and Orhaniye formations in the area. Wells are situated in alluvium and Çameli formation.

Seasonal evaluation of physical parameters

The pH of spring waters varied for dry and wet season in the range 5.80–9.20 and 7.20–10.40, respectively. The pH of the well water was measured in the range 5.90–8.00 in dry season and 7.40–8.40 in wet season. The increase in pH

was determined in the wet season in comparison to dry season in spring and well waters. This increase is related to high interaction between rock and rainwater, so, it was enhanced due to the dissolution.

The EC values of spring waters were measured in the range $630-1,372 \ \mu$ S/cm in dry season and $520.20-1,521.00 \ \mu$ S/cm in wet season. The EC values of well waters also varied in the range $5.27-3,028.50 \ \mu$ S/cm in dry season and $5.85-2,875.50 \ \mu$ S/cm in wet season. The EC values of groundwaters in the wet season were higher than the dry season in the study area (Fig. 3). Especially, the EC values of well waters, which were taken from Çameli formation, were higher than the EC value of other samples. Clay content of the Çameli formation was high. Salts, which held back in the interstice or pores in clay while groundwater is evaporated or water table falls, get leached



Fig. 2 Conceptual hydrogeological model of the study area (Senel et al. 1989)

back into the groundwater during the wet season (Raju 2007; Singh et al. 2011; Rao et al. 2013). Hence, the wet season waters had higher EC values as compared to the dry season. Very high standard deviation in EC for both dry and wet seasons indicated the spatial variability of leaching and dilution with recharging rainfall water.

Seasonal evaluation of major ions

Generally, sequence of ions was $Ca^{2+} > Mg^{2+} > Na^+ > K$; $\begin{array}{ll} HCO_{3}^{-} > SO_{4}^{2-} > Cl^{-} > CO_{3}^{2-} & \mbox{in dry season and} \\ Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}; & HCO_{3}^{-} > SO_{4}^{2-} > Cl^{-} > \end{array}$ CO_3^{2-} in the wet season (Table 2). According to the analysis results, Mg²⁺ ion of water samples increased seasonally in specific locations. This difference was related to water-rock interactions (Fig. 3). Ca²⁺ and Mg²⁺ originate mainly from carbonate-rich rocks such as limestone, dolomitic limestone, and were the major sources for carbonate weathering. The available carbonates in these rocks might have been dissolved and added to the groundwater system during irrigation, rainfall infiltration and groundwater movement. The increase in Mg^{2+} ion in wet season was observed at both well waters drilling within the alluvium and Cameli formation, and spring waters which discharge from Dutdere limestone and Cameli formation. The major source of Mg²⁺ in the groundwater was ion exchange of minerals in rocks and soils by water. The increase in Na was determined only for wet season at Karacaören spring which discharges at the contact of the Dutdere limestone and Kızılcadağ ophiolites (Fig. 3). This increase is related to ion exchange due to water-rock interaction.

The SO_4^{2-} concentrations of Kayalı and Akpınar spring waters discharging at the contact of the Dutdere limestone and Kızılcadağ ophiolites increased related to ion exchange of minerals in rocks by rainwater in wet season (Fig. 4). In addition, the Cl⁻ content increased at Yuvalak and Kılavuzlar wells drilling in alluvium aquifer (Fig. 4). This increase is probably related to anthropogenic effects such as agricultural

activities. However, the Cl concentration of Barutlusu spring (S6) which has $Na^+-Ca^{2+}-CO_3^{2-}-Cl^-$ facies and mineral water character also increased in wet season due to water-rock interaction between K1z1lcadağ ophiolites and rainwater. In addition, increase in Cl⁻ concentration of the Barutlusu spring can be related to deep groundwater due to discharging from fault zone (Varol and Davraz 2010).

Pearson correlation analysis (PCA) was carried out to evaluate the relationship between various physiochemical parameters. All the processes were performed using SPSS software version 15.0 for Windows. According to PCA results, Mg²⁺ was positively correlated with HCO₃⁻ (r = 0.503, p = 0.006 in dry season and r = 0.520,p = 0.005 in wet season; Tables 3, 4). These results supported that water-rock interaction occurred between carbonate-rich rocks and rainwater in the study area. Additionally, Mg²⁺ was also positively correlated with SO_4^{2-} (r = 0.627, p < 0.001 in dry season and r = 0.641, p < 0.001 in wet season, Tables 3, 4). The increase in Mg^{2+} and SO_4^{2-} concentrations was observed in groundwater which was affected with clayey and marly rocks such as Cameli formations. In addition, Na⁺ was positively correlated with HCO₃⁻ and Cl⁻ (r = 0.859, p < 0.001 and r = 0.930, p < 0.001, respectively, in dry season and r = 0.868, p < 0.001 and r = 0.945, p < 0.001, respectively, in wet season, Tables 3, 4). This relation represented ion exchange reactions in groundwater. Generally, Na⁺ content of groundwater increased due to interaction with clayey rocks. Most of the clay minerals have colloidal structure (Freeze and Cherry 1979). These clay particles due to colloidal structures easily absorbed onto ions such as Cl^{-} and SO_4^{2-} (Freeze and Cherry 1979; Edzwald et al. 1976; Sahinci 1991).

Hydrogeochemical facies

Hydrogeochemical facies reflect the effects of chemical reactions occurring between the minerals within the

Sample Loc.	No.	Sample type	Discharged lithological units	Dry season		Wet season	
				Cation sequence	Anion sequence	Cation sequence	Anion sequence
Çallıca	SI	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Karataş L.	S2	Lake water	I	Mg > Na > Ca > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > CO_3 > SO_4 > CI$
Çallıca	S3	Groundwater	Alluvium	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$	$\mathrm{Ca} > \mathrm{Mg} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$
Karamanlı	$\mathbf{S4}$	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	$\mathrm{Ca} > \mathrm{Mg} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$
Kılcan	S5	Spring	Çameli formation	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Barutlusu	S6	Spring	Dutdere limestone	$\mathrm{Na} > \mathrm{Ca} > \mathrm{Mg} > \mathrm{K}$	$CO_3 > CI > HCO_3 > SO_4$	$\mathrm{Na} > \mathrm{Ca} > \mathrm{Mg} > \mathrm{K}$	$Cl > CO_3 > SO_4 > HCO_3$
Tefenni	S7	Spring	Dutdere limestone	Mg > Ca > Na > K	$HCO_3 > CO_3 > CI > SO_4$	Mg > Ca > Na > K	$HCO_3 > CO_3 > CI > SO_4$
Bedirli	S8	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	$\mathrm{Ca} > \mathrm{Mg} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$
Bedirli	S9	Groundwater	Alluvium	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Çaltepe	S10	Spring	Dutdere limestone	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$	$\mathrm{Mg} > \mathrm{Ca} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$
Bademli	S11	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	$\mathrm{Mg} > \mathrm{Ca} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$
Yuvalak	S12	Groundwater	Alluvium	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	$\mathrm{Mg} > \mathrm{Ca} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > CI > SO_4 > CO_3$
Bayramlar	S13	Spring	Orhaniye formation	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Hüyük	S14	Groundwater	Alluvium	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$	$\mathrm{Mg} > \mathrm{Ca} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$
Manca	S15	Groundwater	Alluvium	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Kayalı	S16	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > CI > SO_4 > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Kılavuzlar	S17	Groundwater	Alluvium	$\mathrm{Mg} > \mathrm{Ca} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > CI > SO_4 > CO_3$
Akpınar	S18	Spring	Dutdere limestone	$\mathrm{Ca} > \mathrm{Mg} > \mathrm{Na} > \mathrm{K}$	$HCO_3 > CI > SO_4 > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Kapaklı	S19	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Bozlar	S20	Groundwater	Alluvium	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Kayıköy	S21	Spring	Çameli formation	Ca > Mg > Na > K	$HCO_3 > CI > SO_4 > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Kozluca 1	S22	Groundwater	Çameli formation	Na > Mg > Ca > K	$HCO_3 > CI > SO_4 > CO_3$	$\mathrm{Na} > \mathrm{Mg} > \mathrm{Ca} > \mathrm{K}$	$HCO_3 > Cl > SO_4 > CO_3$
Kozluca	S23	Groundwater	Çameli formation	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$
İğdeli	S24	Groundwater	Dutdere limestone	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Karacaören	S25	Spring	Dutdere limestone	$\mathrm{Ca} > \mathrm{Na} > \mathrm{Mg} > \mathrm{K}$	$HCO_3 > SO_4 > CI > CO_3$	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Pınarbaşı	S26	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Elmacık	S27	Spring	Dutdere limestone	Ca > Mg > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$
Boğaziçi	S28	Groundwater	Çameli formation	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$	Mg > Ca > Na > K	$HCO_3 > SO_4 > CI > CO_3$

 Table 3
 Statistical summary of hydrogeochemical parameters of spring waters in the study area

Spring	Dry season Mean ± SD (minmax.)	Wet season Mean ± SD (min.–max.)
Dutdere limesto	ne $(n = 12)$	
pH	7.28 ± 0.81 (5.80–9.20)	$8.01 \pm 0.83 \; (7.20 10.40)$
EC	$1,066.70 \pm 214.59$ (630–1,372)	$1,029.78 \pm 302.14 \; (520.20 - 1,521.00)$
Т	$15.99 \pm 4.31 \ (9.10-27.00)$	$14.36 \pm 4.77 \ (8.20 - 28.00)$
Hard.	$26.80 \pm 12.70 \; (4.69 – 50.01)$	$23.51 \pm 9.51 \; (6.95 37.75)$
Na	$11.3 \pm 12.21 \ (1.09-35.79)$	$10.55 \pm 11.24 \ (1.14-40.00)$
К	$1.65 \pm 2.05 \ (0.33 - 7.94)$	0.81 ± 0.71 (0.39–2.34)
Ca	$69.37 \pm 54.44 \; (7.35 - 185.25)$	52.33 ± 35.21 (7.01–112.42)
Mg	$22.97 \pm 29.60 \; (1.25 - 89.99)$	$25.41 \pm 25.42 \ (3.76 - 82.08)$
Cl	11.45 ± 11.61 (4.61–46.44)	$13.45 \pm 18.91 \ (3.90-72.76)$
HCO ₃	223.04 ± 101.79 (39.50–391)	266.25 ± 120.78 (3.05-431.27)
CO ₃	$7.17 \pm 17.09 \ (0.00-51)$	$5.25 \pm 12.26 \ (0.00 - 32.40)$
SO_4	15.33 ± 11.95 (1.00–39)	$13.68 \pm 8.75 \ (5.76 - 32.66)$
Çameli formatio	$\operatorname{bn}(n=3)$	
pH	6.40 ± 0.34 (6–6.60)	8.16 ± 0.40 (7.70–8.40)
EC	$1,129.50 \pm 137.30 \ (976.50 - 1,242)$	$1,287.60 \pm 69.80 \ (1,242.45 - 1,368.00)$
Т	$16.16 \pm 3.17 \ (12.60 - 18.70)$	$16.10 \pm 3.46 \ (12.10 - 18.20)$
Hard.	$36.61 \pm 3.85 (32.97 - 40.65)$	$28.81 \pm 6.57 \; (23.45 36.15)$
Na	$11.54 \pm 6.83 \ (3.69 - 16.13)$	9.18 ± 4.53 (4.12–12.87)
К	$4.77 \pm 6.71 \ (0.41 - 12.50)$	$1.08 \pm 0.65 \ (0.39 - 1.70)$
Ca	$74.79 \pm 31.04 \ (46.84 - 108.21)$	$48.36 \pm 2.05 \; (46.09 - 50.10)$
Mg	$43.60 \pm 14.09 \; (33.13 - 59.63)$	40.73 ± 14.89 (29.06–57.51)
Cl	14.18 ± 5.83 (7.45–17.73)	$11.47 \pm 3.83 \ (7.09-14.19)$
HCO ₃	$343.66 \pm 24.70 \ (321 - 370)$	323.50 ± 90.49 (259.25–427.00)
CO ₃	0.00 ± 0.00	$3.20 \pm 5.54 \ (0.00 - 9.60)$
SO_4	$17.66 \pm 7.76 \ (9-24)$	$19.20 \pm 7.10 \ (11.04 - 24.01)$
Orhaniye forma	tion $(n = 1)$	
pH	7.30	8.00
EC	639	606.60
Т	11	11.3
Hard.	13.9	15.65
Na	1.78	2.52
К	0.45	0.39
Ca	43.39	45.09
Mg	7.48	10.70
Cl	4.25	3.90
HCO ₃	143	182.39
CO ₃	0	0.0
SO_4	10	7.68

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All values are in mg/l except pH, EC (µmhos/cm), T

lithologic framework and groundwater. Hydrogeochemical diagrams are aimed at facilitating interpretation of evolutionary trends, particularly in groundwater systems, when they are interpreted in conjunction with distribution maps and hydrogeochemical facies. An overall characterization of hydrogeochemical data may be possible by knowing the hydrogeochemical facies of water, generally known as water type, using various plots such as Durov (1948), trilinear (Piper 1944), Schoeller (1965) and Chadha (1999) diagrams. The Chadha diagram proposed as a newer

diagram in different researches for geochemical classification of natural waters and interpretation of chemical data.

In this diagram (Fig. 5), the difference in mill equivalent percentage between alkaline earths $(Ca^{2+} + Mg^{2+})$ and alkali metals $(Na^+ + K^+)$, expressed as percentage reacting values, was plotted on the *x*-axis, and the difference in mill equivalent percentage between weak acidic anions $(CO_3^{2-} + HCO_3^-)$ and strong acidic anions $(Cl^- + SO_4^{2-})$ was plotted on the *y*-axis. The mill equivalent percentage differences between alkaline earths and alkali



Fig. 3 The spatial distribution maps of EC, Ca^{2+} , Mg^{2+} , Na^+ in dry and wet seasons (Varol 2011)

metals and between weak acidic anions and strong acidic anions would plot in one of the four possible sub-fields of the rectangle diagram. The rectangular field describes the overall character of the water. To define the primary character of water, the rectangular field is divided into eight subfields, each of which represents a water type (Chadha 1999).



Fig. 4 The spatial distribution maps of CO_3^{2-} , HCO_3^{-} , CI^- , SO_4^{2-} in dry and wet seasons (Varol 2011)

Table 4 Statistical summary of hydrogeochemical parameters of well water in the study area

G. water	Dry season	Wet season
	Mean \pm SD (min.–max.)	Mean \pm SD (min.–max.)
Alluvium (n =	= 7)	
pН	$7.10 \pm 0.56 \; (5.907.50)$	$7.88 \pm 0.28 \; (7.50 - 8.40)$
EC	$1,049.78 \pm 164.90 \; (841.50 - 1,372.50)$	$1,240.26 \pm 223.06 \ (821.70 - 1,498.50)$
Т	$15.75 \pm 1.94 \ (13.0 - 18.10)$	$14.58 \pm 1.38 \; (12.40 16.40)$
Hard.	$29.53 \pm 10.91 \; (16.11 - 51.07)$	$28.93 \pm 6.77 \; (16.65 – 37.40)$
Na	$16.18 \pm 3.80 \ (8.99-19.74)$	$19.11 \pm 6.59 \; (10.34 27.12)$
Κ	$1.35 \pm 0.60 \; (043 - 2.26)$	$0.89 \pm 0.62 \; (0.39 1.95)$
Ca	$64.79 \pm 43.12 \; (17.97 - 156.08)$	$53.67 \pm 23.56 \; (16.03 - 92.38)$
Mg	$32.21 \pm 5.32 \ (27.76 - 42.78)$	$35.62 \pm 8.50 \ (24.44 - 48.27)$
Cl	$12.91 \pm 3.36 \ (7.80 - 18.79)$	$12.72 \pm 3.50 \ (10.29 - 20.23)$
HCO ₃	$255.07 \pm 48.06 \; (184.50 - 318)$	$325.91 \pm 66.70 \; (208.62 427.00)$
CO ₃	0.00 ± 0.00	0.00 ± 0.00
SO_4	44.14 ± 17.68 (23–73)	$32.65 \pm 25.57 \ (9.12-84.05)$
Cameli forma	tion $(n = 4)$	
pН	7.37 ± 0.43 (7.00–8.00)	$7.62 \pm 0.33 \; (7.40 - 8.10)$
EC	$1,\!434.56 \pm 1,\!242.61 \; (5.27 \!-\! 3,\! 028.50)$	$1,782.33 \pm 1,255.16 \; (5.85 - 2,875.50)$
Т	$16.02 \pm 1.09 \ (14.80 - 17.30)$	$14.50 \pm 0.43 \; (14.10 15.10)$
Hard.	$46.39 \pm 22.34 \ (23.78 - 72)$	$46.41 \pm 17.03 \; (26.7 65.7)$
Na	$167.09 \pm 237.33 \ (36.80-522.80)$	$186.33 \pm 248.23 \ \textbf{(60.00-558.68)}$
Κ	$3.02 \pm 1.30 \ (1.31 - 4.37)$	$2.63 \pm 0.66 \; (1.95 3.51)$
Ca	$65.92 \pm 48.29 \; (10.18 120.44)$	$67.53 \pm 42.90 \; (16.03 - 118.23$
Mg	$72.75 \pm 25.67 \; (50.71 - 101.90)$	$71.88 \pm 15.97 \; (55.20 - 88.03)$
Cl	$116.86 \pm 100.75 \ (30.13 - 259.40)$	109.23 ± 98.49 (35.49–250.96)
HCO ₃	$547.50 \pm 354.21 \; (301.50 1,073.50)$	$692.64 \pm 409.36 \; (391.01 1, 295.60)$
CO ₃	0.00 ± 0.00	0.00 ± 0.00
SO_4	$126.50 \pm 84.53 \ (36-230)$	$145.64 \pm 49.88 \; (76.36 - 191.15)$

All values are in mg/l except pH, EC (µmhos/cm), T

Analysis results of groundwaters were plotted on the Chadha diagram for geochemical classification and studied hydrochemical processes of dry and wet seasons (Fig. 5). According to the diagram, the majority of groundwater samples in the study area located in the 5th region. Namely, alkaline earths and weak acidic anions exceeded both alkali metals and strong acidic anions, respectively. Such water has temporary hardness. The positions of data points in this domain represent $Ca^{2+}-Mg^{2+}-HCO_{3}^{-}$ water type (Chadha 1999; Varol and Davraz 2010). According to the results of chemical analysis, Barutlusu mineral water with Kozluca wells showed the different properties in Chadha diagram. Barutlusu spring water (S6) was in the 7th region of the Chadha diagram in which Na⁺ and Cl⁻ ions were dominant ions in both periods. Barutlusu spring (S6) had Na⁺-Ca²⁺- CO_3^{2-} -Cl⁻ facies (Varol and Davraz 2010). This water type was related to the interaction with Marmaris peridotite, Kızılcadag ophiolitic mélange, Dutdere limestone and deep circulation. Kozluca 1 (S22) well water samples were located on the 8th region of the Chadha diagram within the both periods. This groundwater had Na⁺-HCO₃⁻-Cl⁻

facies. The increases in Na^+ and Cl^- contents were originated from clay and claystone which belongs to Çameli formation.

Hydrogeochemical process

The geological formations, water–rock interaction and relative mobility of ions are prime factors influencing the geochemistry of groundwater (Yousef et al. 2009). Major ions are a significant part of the total dissolved solids in groundwater. The concentrations of these ions in groundwater depend on the hydrogeochemical processes that take place in the aquifer system. Generally, different chemical processes occur during rock–water interaction, which include dissolution/precipitation, ion exchange processes, oxidation and reduction (Dehnavi et al. 2011). Water–rock interaction reflects the differences in mineral composition of the aquifer, existence of fissures, faults and cracks which affect groundwater movement in the subsurface medium (Kumar et al. 2012). The use of scattered plots for TDS vs. $Na^+/(Na^+ + Ca^{2+})$ and TDS vs. $Cl^-/(Cl^- + HCO_3^-)$

Fig. 5 Chadha diagrams belongs to dry and wet seasons



(Gibbs 1970) can be used to identify of rock-water interaction processes. Gibbs's diagrams are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation-dominance (Gibbs 1970). The chemical data of groundwater sample points of the area were plotted in Gibbs's diagrams (Fig. 6). Samples from both seasons fell in rock-dominance zone suggesting precipitationinduced chemical weathering along with dissolution of rock forming minerals.

In addition, some possible hydrogeochemical processes, which are observed in the study area, were explained below.

Ion exchange

Knowledge of the changes brought about in the chemical composition of the groundwater during its travel underground is essential (Sastri 1994; Singh et al. 2011). The geochemical variations in the ionic concentrations in the groundwater can easily be understood when they are plotted along an *X*–*Y* coordinate (Aghazadeh and Mogaddam 2011). Results from the chemical analyses were used to identify the geochemical processes and mechanisms in the groundwater aquifer system. The chemical data of the water samples were plotted for $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + CO_3^{2-})$ diagram (Fig. 7a). The water samples in



Fig. 6 Gibbs diagrams, illustrating the mechanisms controlling the chemistry of groundwater samples

wet season fell below the equiline (1:1), which suggests that an excess of alkalinity in the water has been balanced by alkalis (Na⁺ + K⁺). In addition, the water samples in dry season fell above the equiline (1:1). This suggests that a large fraction of calcium and magnesium was derived from non-carbonate sources and was balanced by some other anions like SO_4^{2-} and Cl^- (Fig. 7a). The plot of TC (total cation) versus (Ca²⁺ + Mg²⁺) showed few of the samples far below the theoretical line (1:1) (Fig. 7b), indicating an increasing contribution of alkalis to the major ions in these samples, which shows anthropogenic input in the groundwater (Subba Rao and Devadas 2003; Fig. 7b).

In a plot of $(Na^+ + K^+)$ versus TC (total cation), the chemical data of the samples fell below the equiline line (Fig. 7c). This leads to infer that the supply of cations via silicate weathering and/or soil salts is more significant (Stallard and Edmond 1983), whereas the increase in alkalis with a simultaneous increase in $(Cl^- + SO_4^{2-})$ (Fig. 7d) reflects a common source for these ions from the dissolution of soil salts (Sarin et al. 1989; Datta and Tyagi 1996). Most of the samples had a Na⁺/Cl⁻ ratio around or above 1, indicating that ion exchange process is prevalent in the study area (Kumar et al. 2006) (Fig. 7e). As pointed out, the higher concentration of Na⁺ is an index of ion exchange.

Reverse ion exchange process

To compare the importance of ion exchange and reverse ion exchange processes, samples were plotted on the $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-} + HCO_3^{-})$ diagram (Fig. 7f). All of the points in dry season fell in the $(Ca^{2+} + Mg^{2+})$ side, suggesting that carbonate weathering is the major hydrogeochemical process in the Tefenni plain. Also, it indicates that excess of calcium and magnesium might be derived from other processes such as reverse ion exchange reactions. In wet season, the sampling points fell below the equiline (1:1) in this diagram. This is due to an excess of HCO₃⁻, which, further, confirms the role of silicate weathering as a major mechanism for the occurrence of dissolved salts in the groundwater (Rao and Rao 2010; Fisher and Mullican 1997). This may imply that Na concentration is reduced from the groundwater because of the ion exchange process, and HCO₃⁻ increases. Moreover, weathering of soda feldspar (albite) and potash feldspars (orthoclase and microcline) is greatly responsible for the contribution of Na⁺ and K⁺ ions to groundwater. Feldspars are more susceptible for weathering and alteration than quartz in silicate rocks.

Chloroalkaline indices

The chloroalkaline indices (CAI) 1, 2 are suggested by Schoeller (1965, 1977), which indicate the ion exchange between the groundwater and its host environment. The ion exchange between the groundwater and its host environment during residence or travel can be understood by studying the chloroalkaline indices (Eqs. 1, 2 Schoeller 1965, 1977):



Fig. 7 Ions scatter diagram of groundwater in the study area (solid line denotes 1:1)

 $CAI-1 = [Cl^{-} - (Na^{+} + K^{+})]/Cl^{-}$ (1)

$$CAI-2 = [CI^{-} - (Na^{+} + K^{+})] / (SO_{4}^{2-} + HCO_{3}^{-} + CO_{3}^{2-} + NO_{3})$$
(2)

(All values are expressed in milliequivalent per liter)

CAI is negative when there is exchange between sodium and potassium $(Na^+ + K^+)$ in water with calcium and magnesium $(Ca^{2+} + Mg^{2+})$ in rocks. If the ratio is positive, then there is no base exchange (Aghazadeh and Mogaddam 2011). During this process, the host rocks are the primary sources for dissolved solids in the water (Nagarajan et al. 2010).

CAI (Table 5) indicates that 7 (25 %) and 10 (32 %) of water samples showed positive ratios in dry and wet seasons, respectively, while 21 (75 %) and 19 (68 %) of water samples showed negative ratios in dry and wet seasons, respectively, depicting the type of base exchange. The positive values indicate absence of ion exchange and the reaction as a cation–anion exchange reaction.

Most groundwater samples in Fig. 8 showed negative CAI-1 and CAI-2 within the study area in dry and wet

Table 5 Chloroalkaline indices (CAI) in dry and wet season

Sample loc.	Sample no.	Dry season		Wet season			
		NO ₃ (mg/l)	CAI-1	CAI-2	NO ₃ (mg/l)	CAI-1	CAI-2
Çallıca	S1	11.12	0.45	0.02	2.62	0.28	0.11
Karataş L.	S2	0	-3.45	-0.23	0.30	-2.43	-0.11
Çallıca	S 3	43.75	-0.69	-0.05	10.44	-1.07	0.05
Karamanlı	S4	19.35	0.20	0.01	6.07	0	0
Kılcan	S5	1.55	0.15	0.004	0.93	0.05	0.001
Barutlusu	S6	0	-0.17	-0.05	0.37	0.15	0.13
Tefenni	S7	0.73	0.40	0.01	0.41	0.26	0.006
Bedirli	S8	27.63	-0.33	-0.02	3.25	-2	-0.08
Bedirli	S9	28.96	-0.51	-6.44	6.68	-2.41	-0.11
Çaltepe	S10	3.011	0.21	0.004	0.25	0.29	0.006
Bademli	S11	17.05	-2.6	-0.09	4.25	-1.44	-0.08
Yuvalak	S12	29.63	-0.66	-0.04	3.75	-0.96	-0.04
Bayramlar	S13	3.72	0.27	0.01	1.20	-0.1	-0.003
Hüyük	S14	10.89	-1.26	-0.05	3.83	-7.28	-0.27
Manca	S15	14.75	-1.78	-0.08	3.74	-1.29	-0.10
Kayalı	S16	7.62	-0.42	-0.03	2.32	-0.78	-0.004
Kılavuzlar	S17	9.83	-2.19	-0.11	1.22	-1	-0.07
Akpınar	S18	2.3	-0.57	-0.05	1.39	0.5	-0.01
Kapaklı	S19	6.33	-0.07	-0.01	0.77	-0.05	-0.001
Bozlar	S20	12.93	-0.07	-0.004	3.51	-0.65	-0.02
Kayıköy	S21	0	-0.39	-0.03	0.84	-0.56	-0.03
Kozluca 1	S22	6.91	-2.11	-0.80	0.81	-2.44	-0.70
Kozluca	S23	165.63	0.46	0.07	35.60	0.01	0.002
İğdeli	S24	29.49	-1.51	-0.14	9.34	-1.66	-0.13
Karacaören	S25	6.2	-7.72	-0.31	1.50	-0.18	-0.005
Pınarbaşı	S26	6.73	-1.65	-0.09	1.62	-1.81	-0.10
Elmacık	S27	3.41	-1.08	-0.07	0.52	-0.25	-0.01
Boğaziçi	S28	15.28	-0.48	-0.06	6.18	-1	-0.08

seasons, confirming cation–anion exchange reaction, in which exchange takes place between Ca^{2+} or Mg^{2+} in the groundwater and Na^+ in the aquifer material. The negative values of the ratio indicate base exchange between sodium and potassium in water with calcium and magnesium in the rocks. This, further, confirms that the host rocks are the primary sources of dissolved ions in the groundwater, in which the ion exchange is one of the major contributors for higher concentration of Na^+ in the groundwater.

Carbonate weathering and dissolution

In the study area, calcium and magnesium were dominant cations and bicarbonate was dominant anion in ground-water. The points plotted on the line $Ca^{2+}/Mg^{2+} = 1$ indicate waters controlled by dolomite dissolution, while

the Ca^{2+}/Mg^{2+} ratio ranging from 1 to 2 characterizes the dissolution of calcite (Maya and Louks 1995). In natural waters, Ca^{2+}/Mg^{2+} ratio up to 2 is mainly due to the dissolution of silicate minerals (Katz et al. 1998; Nayak and Sahood 2011; Elango et al. 2003).

The ratio of Ca^{2+}/Mg^{2+} of studied groundwater ranged between 0.05 and 33.65 in dry season and 0.05–9.41 in wet season (Table 6; Fig. 9). 14 samples in dry season and 23 samples in wet season had a ratio <2 indicating the dissolution of calcite. In addition, 10 samples in dry season and 6 samples in wet season had a ratio >2 which indicates the effect of silicate minerals (Nayak and Sahood 2011; Elango et al. 2003). Mostly, the chemical composition of the groundwater in the study area has resulted from the dolomite weathering by carbonic acid. Carbonate weathering can be caused by rainwater impregnated with CO₂





Table 6 Ca^{2+}/Mg^{2+} (mmol) ratio of the groundwater

Dry sease	on			Wet sease	on		
Sample no.	Ca ²⁺ /Mg ²⁺ (mmol)	Sample no.	Ca ²⁺ /Mg ²⁺ (mmol)	Sample no.	Ca ²⁺ /Mg ²⁺ (mmol)	Sample no.	Ca ²⁺ /Mg ²⁺ (mmol)
S1	11.20	S15	1.07	S 1	9.41	S15	1.02
S2	0.29	S16	2.13	S2	0.57	S16	1.91
S3	0.85	S17	0.38	S 3	1.53	S17	0.31
S4	4.68	S18	33.65	S4	2.66	S18	6
S5	0.51	S19	14.21	S5	0.52	S19	6.92
S6	8.35	S20	3.22	S 6	1.35	S20	1.60
S7	0.05	S21	1.10	S 7	0.05	S21	0.83
S8	4.99	S22	0.11	S 8	1.81	S22	0.17
S9	1.15	S23	0.71	S9	0.91	S23	0.81
S10	0.10	S24	0.53	S10	0.08	S24	0.54
S11	1.23	S25	5.55	S11	0.76	S25	3.98
S12	1.14	S26	1.01	S12	0.48	S26	0.93
S13	3.52	S27	1.98	S13	2.55	S27	0.96
S14	0.89	S28	0.61	S14	0.82	S28	0.58

and become rich in carbonic acid (Nayak and Sahood 2011). The acidic water influences the dissolution of carbonate minerals (calcite and dolomite) in the aquifer system (Nur and Ayuni 2011). This process is responsible for increase in the concentrations of Ca^{2+} , Mg^{2+} and HCO_3^{-} content in groundwater. So, the availability of carbonate minerals in the recharge areas and silicate weathering are the main factors, which led to the increase in carbonates and bicarbonate concentration in the groundwater (Elango et al. 2003). In wet season that silicate weathering was dominant process, and CO_3^{2-} increase in groundwater was determined throughout the groundwater flow path in the study area (Fig. 4).



Fig. 9 Plot of Ca^{2+}/Mg^{2+} (mmol) ratio

Conclusion

Groundwaters have different hydrogeochemical characteristics in the study area. Ca²⁺-Mg²⁺-HCO₃⁻, Mg²⁺-Ca²⁺- HCO_3^- , $Na^+-CO_3^{2-}-Cl^-$ and $Na^+-HCO_3^--Cl^-$ water types are observed. Generally, the groundwater of the study area is dominated by calcium and bicarbonate ions. The chemical composition of groundwater of the study area is strongly influenced by water-rock interaction. Ion exchange and reverse ion exchange are two possible processes of water-rock interaction in the plain. In addition, the carbonate weathering and silicate weathering processes are also contributors for increasing calcium ions in the groundwater. Carbonate weathering is the dominant process in dry season and silicate weathering is the dominant process in wet season. Mg²⁺, Na⁺, SO₄²⁻ concentrations of water samples increase seasonally in specific locations related to ion exchange of minerals in rocks by rainwater. In specific locations, the Mg^{2+} concentration of groundwater is relatively high in wet season when compared to Ca²⁺ concentration. It is mostly due to weathering of magnesium minerals and leaching of dolomites related to Dutdere limestone and Cameli formations consisting of conglomerate, sandstone, claystone, clayey limestone, marl and conglomerate. Na and SO_4^{2-} increases are related to interaction with Kızılcadağ ophiolite and groundwater. The Cl⁻ increase is probably related to anthropogenic effects such as agricultural activities and water-rock interaction as locally.

In addition, the results from the water analysis were used as a tool to identify the process and mechanism affecting the chemistry of groundwater from the study area. The plot was used to determine the mechanism controlling the water chemistry. Samples from both seasons fall in rock dominance zone suggesting precipitation induced chemical weathering along with dissolution of rock forming minerals. Namely, the mechanism, controlling groundwater chemistry at the Tefenni plain is originally regulated by the geogenic process (rock weathering and ion exchange) rather than antropogenic activities in the study area.

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Aghazadeh N, Mogaddam AA (2010) Assessment of groundwater

quality and its suitability for drinking and agricultural uses in the

Oshnavieh Area, Northwest of Iran. J Environ Protect 1:30-40

References

- Aghazadeh N, Mogaddam AA (2011) Investigation of hydrochemical characteristics of groundwater in the Harzandat aquifer, Northwest of Iran. Environ Monit Assess 176:183–195
- Andreo B, Carrasco F (1999) Application of geochemistry and radioactivity in the hydrogeological investigation of carbonate aquifers (Sierras Blanca and Mijas, southern Spain). Appl Geochem 14:283–299
- Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. A. A. Balkema, Rotterdam
- Bilgin ZR, Karaman T, Oztürk Z, Sen MA, Senel M (1990) Geological report of the around Yesilova-Acigol. Mineral Research & Exploration General Directorate Rep: 9071, Ankara, Turkey
- Bozcu M, Yağmurlu F, Şentürk M (2007) Some neotectonics and paleoseismological properties of Fethiye–Burdur fault zone, SW-Turkey. Geol Eng J 31(1):25–48
- Bozdag A, Gocmez G (2013) Evaluation of groundwater quality in the Cihanbeyli basin, Konya, Central Anatolia, Turkey. Environ Earth Sci 69(3):921–937
- Capan U (1980) Approaches petrology, petrochemical characteristics and Internal Structure of the Taurus Belt ophiolite massifs. Hacettepe University Institute of Science. PhD thesis, Ankara, Turkey
- Carrillo-Rivera JJ, Varsányi I, Kovács LO, Cardona A (2007) Tracing groundwater flow systems with hydrogeochemistry in contrasting geological environments. Water Air Soil Pollut 184:77–103
- Chadha DK (1999) A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. Hydrogeol J 7:431–439
- Datta PS, Tyagi SK (1996) Major ion chemistry of groundwater in Delhi area: chemical weathering processes and groundwater regime. Geol Soc India 47:179–188
- Dehnavi AG, Sarikhani R, Nagaraju D (2011) Hydro geochemical and rock water interaction studies in East of Kurdistan, N–W of Iran. Int J Environ Sci Res 1(1):16–22
- Durov SA (1948) Natural waters and graphic representation of their compositions. Dokl Akad Nauk SSSR 59:87–90
- Edmunds WM, Ma J, Aeschbach-Hertig W, Kipfer R, Darbyshire F (2006) Groundwater recharge history and hydrogeochemical evolution in the Minqin Basin, north west China. Appl Geochem 21(12):2148–2170
- Edzwald JK, Toensing DC, Chi-Yew Leung M (1976) Phosphate adsorption reactions with clay minerals. Environ Sci Technol 10(5):485–490
- Elango L, Kannan R, Senthil Kumar M (2003) Major ion chemistry and identification of hydrogeochemical processes of groundwater in a part of Kancheepuram District, Tamil Nadu, India. J Environ Geosci 10(4):157–166
- Erakman B, Meshur M, Gul MA, Alkan H, Oztas Y, Akpinar M (1982) Report of the geology and hydrocarbon potential of the Kalkan-Köyceğiz-Çameli-Tefenni area Depending on the Taurus Project. Turkey Petroleum Corporation (TPC) Report
- Fisher SR, Mullican WF (1997) Hydrogeochemical evolution of sodium-sulfate and sodium-chloride groundwater beneath the northern Chihuahua desert, Trans-Pecos, Texas, USA. Hydrogeol J 5(2):4–16
- Freeze AR, Cherry AJ (1979) Groundwater. Prentice-Hall, Englewood
- Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 170:1088–1090
- Guendouz A, Moulla AS, Edmunds WM, K Zouari, Shand P, Mamou A (2003) Hydrogeochemical and isotopic evolution of water in the Complexe Terminal aquifer in the Algerian Sahara. Hydrogeol J 11:483–495
- Hall RI, Smol JP (1996) Paleolimnological assessment of longterm water-quality changes in south-central Ontario lakes affected by

cottage development and acidification. Can J Fish Aquat Sci 53:1-17

http://www.groundwateruk.org. Accessed 16 Nov 2012

- Katz VA, Thulke OU, Conrath U (1998) A benzothiadiazole primes parsley cells for augmented elicitation of defence responses. Plant Physiol 117:1333–1339
- Kocyigit A, Unay E, Sarac G (2000) Episodic graben formation and extensional neotectonic regime in west Central Anatolia and the Isparta Angle: a case study in the Akşehir-Afyon Graben, Turkey. Geol Soc Lond Spec Publ 173:405–421
- Kumar M, Ramanathan ALR, Kumar MSB (2006) Identification and evaluation of hydrogeochemical processes in the groundwater environment of Delhi, India. Environ Geol 50(7):1025–1039
- Kumar SK, Chandrasekar N, Seralathan P, Godson PS, Magesh NS (2012) Hydrogeochemical study of shallow carbonate aquifers, Rameswaram Island, India. Environ Monit Assess 184:4127–4138
- Li G, Zhang J, Wang N (2008) Construction and implementation of spatial analysis model based on geographic information system (GIS)—a case study of simulation for urban thermal field. In: 2008 international conference on computational intelligence for modelling control & automation, 10–12 December 2008, Vienna, pp 1095–1098
- Matthess G (1982) Properties of groundwater. Wiley, New York. Translated by John C. Harvey
- Maya AL, Louks MD (1995) Solute and isotopic geochemistry and groundwater flow in the Central Wasatch Range, Utah. J Hydrol 172:31–59
- Meshur M, Yoldemir O, Akpinar M, Oztas I, Alkan H (1989) Report of geology and oil possibilities of the western Taurus. Turkey Petroleum Corporation (TPAO) Rep. (unpublished), Ankara, Turkey
- Meyer PD, Gee GW (1999) Information on hydrologic conceptual models, parameters, uncertainty analysis, and data sources for dose assessments at decommissioning sites. Report Pacific Northwest National Laboratory
- Nagarajan R, Rajmohan N, Mahendran U, Senthamilkumar S (2010) Evaluation of groundwater quality and its suitability for drinking and agricultural use in Thanjavur city, Tamil Nadu, India. Environ Monit Assess 171:289–308
- Nayak KM, Sahood HK (2011) Assessment of groundwater quality in Tangi-Choudwar and Cuttack B- locks of Cuttack District, Orissa, India. Int J Earth Sci Eng 4(6):973–985
- Nur A, Ayuni KN (2011) Hydrogeo-physical study of Michika and environs, northeast Nigeria. Int J Phys Sci 6(34):7816–7827
- Onalan M (1979) The geology of the area between Elmalı and Kas (Antalya), vol 29. İstanbul University Science Monographs of Faculty, PhD thesis, Istanbul, Turkey
- Piper AM (1944) A graphical interpretation of water—analysis. Trans Am Geophys Union 25:914–928
- Poisson A (1977) Recherces geologiques dans les Taurides occidentales (Turquie). These Univ. Paris-Sud, Orsay
- Raju NJ (2007) Hydrogeochemical parameters for assessment of groundwater quality in the upper Gunjanaeru River basin, Cuddapah District, Andhra Pradesh, South India. Environ Geol 52:1067–1074
- Rao NS, Devadas DJ (2003) Fluoride incidence in groundwater in an area of Peninsular India. Environ Geol 45(2):243–251

- Rao NS, Rao PS (2010) Major ion chemistry of groundwater in a river basin: a study from India. Environ Earth Sci 61(4):757–775
- Rao GT, Rao VVSG, Rao YS, Ramesh G (2013) Study of hydrogeochemical processes of the groundwaters in Ghatprabha river sub-basin, Bagalkot District, Karnataka, India. Arab J Geosci 6(7):2447–2459
- Sahinci A (1991). Geochemistry of natural waters. Reform Publications, İzmir, Section 2
- Sarin MM, Krishnaswamy S, Dilli K, Somayajulu BLK, Moore WS (1989) Major ion chemistry of the Ganga–Brahmaputra river system: weathering processes and fluxes to the Bay of Bengal. Geochim Cosmochim Acta 53:997–1009
- Sastri JCV (1994) Groundwater chemical quality in river basins, hydrogeochemical modeling. Lecture notes-Refresher course, School of Earth Sciences, Bharathidasan Univ., Tiruchirapalli, Tamil Nadu, India
- Schoeller H (1965) Qualitative evaluation of groundwater resources. In: Methods and techniques of groundwater investigations and development. UNESCO Water Resources Series, vol 33, pp 44–52
- Schoeller H (1977) Geochemistry of groundwater. In: Groundwater studies—an international guide for research and practice. UNESCO, Paris, Chap. 15, pp 1–18
- Senel M, Selçuk H, Bilgin ZR, Sen AM, Karaman T, Dinçer MA, Durukan E, Arbas A, Orçen S, Bilgi C (1989) Geology of the Çameli (Denizli)–Yesilova (Burdur)–Elmalı (Antalya) and the northern part. Mineral Research & Exploration General Directorate Report: 9429 (unpublished), Ankara, Turkey
- Singh K, Hundal HS, Singh D (2011) Geochemistry and assessment of hydrogeochemical processes in groundwater in the southern part of Bathinda district of Punjab, northwest India. Environ Earth Sci 64:1823–1833
- Stallard RF, Edmond JM (1983) Geochemistry of Amazon, the influence of geology and weathering environment on the dissolved load. J Geophys Res 88:9671–9688
- Stamatis G, Alexakis D, Gamvroula D, Migiros G (2011) Groundwater quality assessment in Oropos–Kalamos basin, Attica, Greece. Environ Earth Sci 64(4):973–988. doi:10.1007/s12665-011-0914-2
- Tizro AT, Voudouris KS (2008) Groundwater quality in the semi-arid region of the Chahardouly basin, West Iran. Hydrol Process 22(6):3066–3078
- Varol S (2011) Hyrogeochemical and hydrogeological properties of Tefenni (Burdur) plain and evaluation for medical geology. Suleyman Demirel University, Institute of Science, PhD thesis, Isparta, Turkey
- Varol S, Davraz A (2010) Hydrogeochemical investigations of Barutlusu ve Pinarbaşı spring water (Tefenni/Burdur). Süleyman Demirel University. J Nat Appl Sci 14(2):156–167
- Wen X, Wu Y, Su J, Zhang Y, Liu F (2005) Hydrochemical characteristics and salinity of groundwater in the Ejina Basin, Northwestern China. Environ Geol 48(6):665–675
- Wen XH, Wu YQ, Wu J (2008) Hydrochemical characteristics of groundwater in the Zhangye Basin, Northwestern China 55(8):1713–1724
- Yousef AF, Saleem AA, Baraka AM, Aglan OSh (2009) The impact of geological setting on the groundwater occurrences in some Wadis in Shalatein–Abu-Ramad area, SE desert, Egypt. Eur Water 25(26):53–68