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Relations of hydrogeologic factors and temporal variations of nitrate contents in groundwater, Sandıklı basin, Turkey

Fatma Aksever · Aysen Davraz · Remzi Karagüzel

Abstract In recent years, elevated nitrate content of groundwater has become a growing concern in the Sandıklı basin. Groundwater is the major source for using as irrigation and drinking water in the basin. The average nitrate concentration of groundwater is 23.64 mg/l, and 37 % of these water samples exceeded the maximum acceptable level (50 mg/l NO_3) according to WHO regulations. Agricultural practices involving inorganic fertilizer and animal manure applications are the main sources of nitrate contamination in groundwater in the study area. The most important aim of the study is to analyze the temporal and spatial variability of nitrate concentrations in groundwater and to determine the impact of key parameters such as groundwater depth and flow direction, hydraulic conductivity, land use, soil type, vadose zone, topography, and net recharge. *R*-mode factor analysis was used to identify parameters that are more effective for increase of nitrate contents in groundwater. According to factor analysis results, land use and vadose zone are the most effective parameters for increase of nitrate concentrations in dry and wet seasons.

Keywords Nitrate · General hydrogeology · Contamination · Agriculture · Sandıklı

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Introduction

Nitrate (NO_3) is one of the most widespread groundwater contaminants globally (Landon et al. 2011; Babiker et al. 2003; Spalding and Exner 1993). The maximum contaminant level of nitrate is given to be 50 mg/l in World Health Organization (WHO 2008). However, if nitrate concentration is over 10 mg/l, it is indicated that groundwater is affected from anthropogenic factors. NO_3 is regulated as a contaminant in drinking water because it can cause methemoglobinemia in infants (EPA 2012; Spalding and Exner 1993) and may be associated with some types of cancer (Ward et al. 2005).

The main sources of nitrate are either natural or anthropogenic activities (Almasri 2007; Almasri and Kaluarachchi 2007; Khanfar 2008; Ternamche 1991). The anthropogenic sources of groundwater contamination by nitrate can be classified into point and non-point sources. Non-point sources of nitrate are considered as fertilizer, dairy farms, manure application, leguminous crops, irrigation return-flows and dry deposition. Point sources of nitrogen such as septic systems, cesspits and interference of thermal water can be major sources of nitrate pollution (Babiker et al. 2003; Joosten et al. 1998; Mitchell et al. 2003; Rodvang et al. 2002; Stournaras 1998).

Natural nitrate concentration in groundwater under aerobic conditions is a few milligrams per liter and depends strongly on soil type and geological situation (WHO 2007). The largest natural source of nitrogen in groundwater occurs from incomplete utilization of nitrate by sparse vegetation in arid regions. This nitrate accumulates in the unsaturated zone of alluvial aquifers below the root zone. Another natural nitrogen sources are also natural vegetation and nitrogen-bearing rock units. In the absence of anthropogenic contamination, natural nitrate concentration

is less than 1 mg/l in groundwater. Nitrate is very mobile in groundwater because of its solubility and its anionic form (Almasri 2007; Almasri and Kaluarachchi 2007; Fytianos and Christophoridis 2003). NO_3 transport can be attenuated in aquifers with anoxic conditions, primarily due to denitrification (Korom 1992). Other attenuation mechanisms such as dissimilatory nitrate reduction and assimilation of nitrate into microbial biomass are unlikely to be important in most aquifers (Rivett et al. 2008). In regional aquifers heavily utilized for crop irrigation, large withdrawals from wells and recharge from irrigation applications can substantially increase groundwater velocities and vertical flow components (Burow et al. 2007), potentially affecting nitrate transport and degradation rates (Landon et al. 2011).

Many studies showed that agricultural activities are the main sources of elevated nitrate concentrations in groundwater (Almasri 2007; Almasri and Kaluarachchi 2007; Ator and Ferrari 1997; Hallberg and Keeney 1993; Harter et al. 2002; Hudak 2000; Ledoux et al. 2007; Sall and Vanclooster 2009; Spalding and Exner 1993; Wylie et al. 1995). Recent studies revealed that groundwater contamination by nitrate is a globally growing problem due to the high rate of population growth and increasing consumption of food (Jalali 2005; Liu et al. 2005; Thorburn et al. 2002; Wakida and Lerner 2005). To control and manage groundwater quality, the characterization of groundwater contamination and identification of the factors affecting the nitrate concentration of groundwater are significant.

The Sandıklı Basin is selected as the investigation area because it is one of the regions in Turkey which has nitrate contamination problem. This basin is located to the southeast of Afyonkarahisar province in Turkey (Fig. 1) and it is one of the largest agricultural areas in the inner Aegean region of Turkey. Groundwater is widely used for drinking, domestic and irrigation purposes in the basin. The objectives of this paper are to identify and to explore the probable sources of elevated nitrate concentrations in the groundwater of the Sandıklı basin. The assessment is carried out using multi-component statistical analyses.

Materials and methods

A total of 75 water samples were collected periodically for porous aquifer. These water samples were collected from 25 wells in three times for dry (August–October 2009) and wet (April 2010) seasons in 2009/2010 years. All sample locations were situated with GPS equipment. Physical properties of the water samples such as pH, temperature (T; °C) and electrical conductivity (EC; μS/cm) were measured in situ with YSI Professional Plus handheld multiparameter instrument that were calibrated with

standard solutions. Samples were collected in clean polyethylene bottles and dispatched for analysis to the laboratory in an ice-filled box. Determination of nitrate (NO_3-N) was performed on HACH DR/2000 spectrophotometer, with the cadmium reduction method using pads. NitraVer 5th Quantitative determination of ammonia (NH_3-N) was carried out by the method of Nessler. Analyses were performed on the spectrophotometer HACH DR/2000, with maximum absorbance at 425 nm. Accuracy was checked using the standard solution method (0.2 mg/l nitrate nitrogen standard solution and 1 mg/l nitrogen ammonia standard solution). These solutions were read with spectrophotometer after sample analysis. Also, cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}, HCO_3^-) were measured taking into consideration standards of analyses (TS 4530, TS 4474, TS 3790, TS 4164, EN ISO 9297, TS 5095) in the laboratory of the State Hydraulic Works (SHW). An ionic error balance was computed for each chemical sample and used as a basis for checking analytical results. In accordance with international standards, results with ionic balance error greater than 5 % were rejected (Appelo and Postma 1993). Charge balances (CB) were calculated using Eq. (1):

$$CB = [(\Sigma z M_c - \Sigma z M_a) / (\Sigma z M_c + \Sigma z M_a)] \tag{1}$$

where z is the ionic charge of cation (c) or anion (a) and M molar concentration of major solutes. Groundwater levels were regularly measured at wells using groundwater level meter in the basin in 2009 and 2010 years and groundwater level map was prepared. In addition, hydraulic conductivity of aquifers is calculated using AquiferTest 3.5 Pro software with Cooper–Jacob time-drawdown method.

Results and discussion

Geology–hydrogeology

Paleozoic, Mesozoic and Cenozoic aged rocks outcropped in the research area (Fig. 1). Sedimentary and volcanic rocks are located on the metamorphic base. Quaternary units are covered all of the units as discordant. Precambrian aged Kestel formation which is composed of metamorphic rocks is a foundation unit of the study area. The metamorphic foundation is composed of quartz, sericite schist, albite, quartzite, calc-schist, phyllite and metabasalt. Cambrian aged Hüdai quartzite is composed of quartzite and schist, Çaltepe formation is composed of dolomite and limestone, Seydişehir formation is composed of siltstone. Permo–Triassic aged Karatepe formation which is composed of sandstone, conglomerate and siltstone is discordant with the Seydişehir formation. Jurassic aged Derealanı
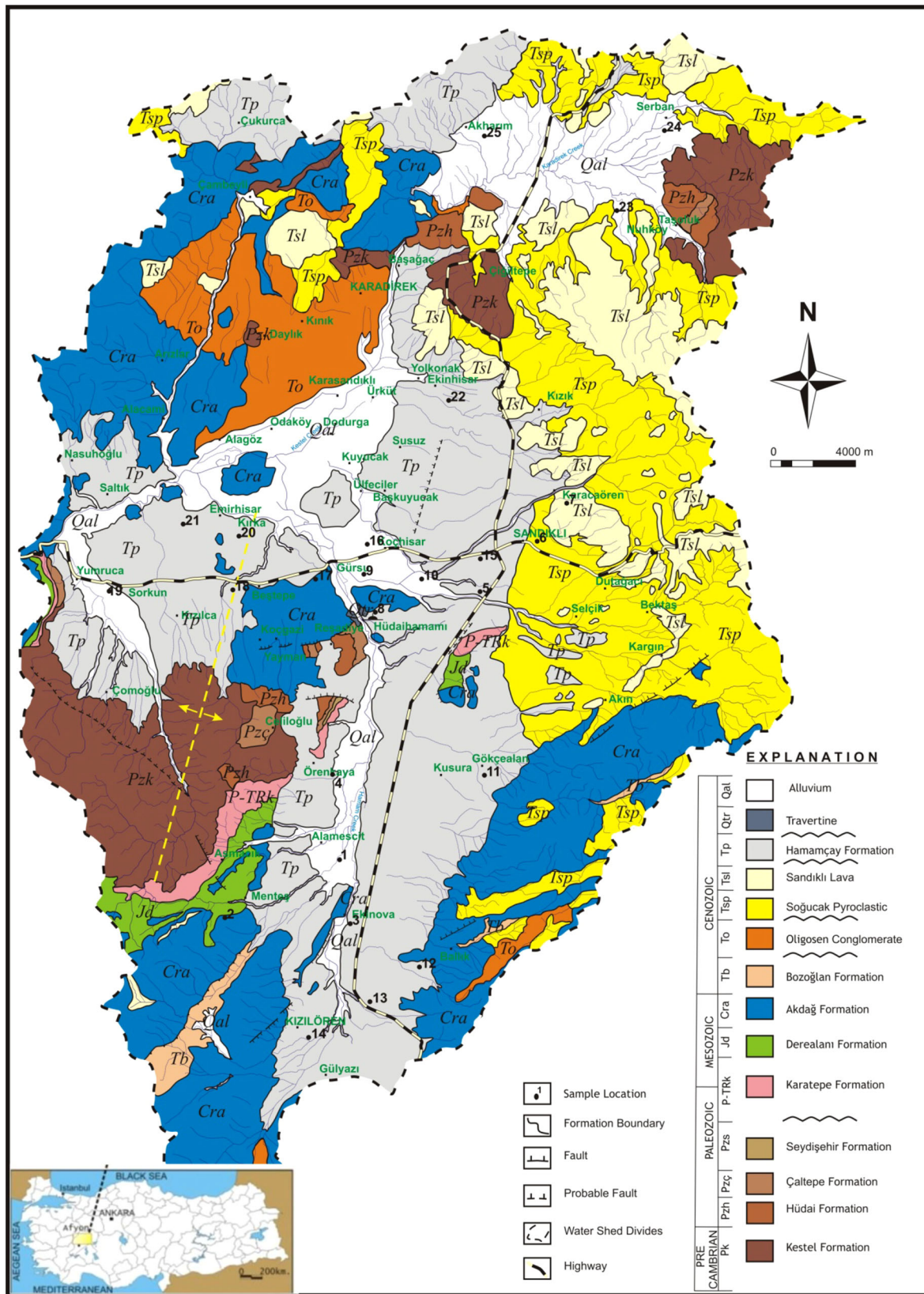
Fig. 1 Geological map

formation which is composed of sandstone, siltstone, claystone and clayey limestone is harmonic on the Karatepe formation. Akdağ formation which consists of limestone, reef limestone and sandy limestone is also harmonic the Derealanı formation. Paleocene aged Bozoğlan formation which consists of marly limestone, conglomerate, sandstone, siltstone and shale is crop out on the Akdağ formation. Oligocene conglomerate is situated on the Bozoğlan formation. The Sandıklı Lava is composed of andesite, trachyandesite and basalt. The Soğucak pyroclastic is also composed of tuff, tuffite and agglomerate. Miocene aged the Sandıklı Lava is crop out as discordant on the Oligocene conglomerate formation. Pliocene aged Hamamcay formation is harmony on the Sandıklı Lava. The Hamamçay formation is intercalated gravel, clay, sand, silt, sandstone, claystone and loosely attached conglomerate. The youngest units are Quaternary aged travertine and alluvium. Alluvium which is composed of uncemented clay, sand, silt and gravel levels overlie above another units (Afşin 1991; Aksever 2011; Çakmakoğlu 1986; Öngür 1973).

Quaternary alluvium and Pliocene aged the Hamamçay units are porous aquifers. The alluvium which consists of sand, gravel, clay and silt levels and the Hamamçay unit which is composed of conglomerate having loose tissue and sand levels have a good aquifer character. Groundwater conditions are unconfined. The alluvium is covered an area of 174 km^2 and the Hamamçay formation is also covered 366 km^2. The Hamamçay formation is locally transitive and below of the alluvium. The well logs indicate that the thickness of the Quaternary and Pliocene units is between 200 and 300 m. The thickness of these units is lower in the Nuh, Serban and Akharım villages which are located northeast of the basin. The average annual yield of wells which are drilled on the alluvium units, for approximately 43 wells, is between 4.78 and 51.1 l/s. 52 wells located on the Hamamçay formation and average annual yield of these wells is between 7.44 and 50.46 l/s (Aksever 2011). Primary sources of recharge are precipitation, percolation of irrigation return and seepage from rivers.

Hydrogeochemistry

The major chemical constituents were analyzed at three terms (August 2009, October 2009 and April 2010). So, nitrate (NO_3), nitrite (NO_2) and ammonia (NH_3) were analyzed. A statistical summary of chemical parameters is given in Table 1. In NO_3, concentrations were divided into four categories (0–15, 16–30, 31–50, >50 mg/l) to see the statistical evaluation related to the increase of nitrate. According to chemical analyses results of groundwater in the research area, the relative abundance of cations in groundwater within the study area is in the order: Ca > Mg > Na > K, while, that of anions is in the order: HCO_3 > SO_4 > Cl. Calcium, magnesium and sodium concentrations in groundwater vary from 16.03 to 144.49, from 2.92 to 34.90 and from 3.0 to 248.0 mg/l, respectively. The increase of Na concentration is related to interference of a deep thermal system of Hüdai geothermal field with a shallow cold aquifer in the area (Afşin 1991; Afşin et al. 2013). Hüdai geothermal field is located in the middle of the Sandıklı basin. Bicarbonate and sulfate contents in groundwater samples were also determined between 9.15 and 535.76 mg/l, 2.0 and 451.48 mg/l, respectively (Table 1). The increase of sulfate concentrations in groundwater demonstrated to effects of mixing thermal water (Afşin 1991; Afşin et al. 2013). Electrical conductivity (EC) of water is directly related to the concentration of dissolved solids in water, and is important parameter for usability classifications of waters. The EC values of groundwater vary within a range 124–801 μS/cm (Table 1). The pH of groundwater varies from 6.18 to 8.68, indicating alkaline nature of groundwater.

Factor analysis as applied to widely differing sets of groundwater hydrogeochemical data appears to be moderately successful as a statistical tool for revealing hydrochemical and hydrogeological features (Mahlknecht et al. 2004). Weathering processes and anthropogenic inputs are the two main contributors for changing the geochemical composition of the groundwater (Chan 2001). R-mode factor analysis was carried on a subset of 10 selected variables (pH, EC, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-), which represent the overall geochemical framework.

Cold groundwater dry season

Factor 1 of the principal component factor matrix of cold water in the Sandıklı plain is characterized by the strong loading of pH, EC, Ca^{2+}, Mg^{2+} and Cl^- in dry season (48.74 % of the variance, Table 2). Strong loads Ca^{2+}, Mg^{2+} and Cl^-s that Factor 1 represents the natural hydrogeochemical evolution of groundwater by groundwater–rock interaction which can be explained by the dissolution of rocks and minerals in sediments by chemical weathering. The increase of these ions is associated with recharge area and rocks in the groundwater system during circulation. pH has moderate loading for hydrogeochemical evolution of groundwaters in this season. Factor 2 explains 16.50 % of the total variance in the season. The loading of Na^+, K^+ and SO_4^{2-} indicates natural weathering of rock minerals and various ion-exchange processes in the groundwater system in the research area. The increase of these ions could be related to interaction of thermal water. Factor 3 indicates that groundwater chemistry is controlled by the temperature variation in the aquifer system.

Table 1 A statistical summary of chemical parameters

Parameter	Mean	Median	Standard deviation	Minimum	Maximum	Coefficient of variation (%)
EC (µS/cm)	348.88	323.00	168.76	124.00	801	48.37
pH	7.79	7.93	0.69	6.18	8.68	8.89
T (°C)	18.05	16.13	7.60	10.71	48.61	42.10
Na^+ (mg/l)	24.56	10.24	49.58	3.00	248.00	201.87
Ca^{2+} (mg/l)	60.04	59.32	30.64	16.03	144.49	51.04
K^+ (mg/l)	6.64	4.25	8.22	0.39	42.23	123.79
Mg^{2+} (mg/l)	14.73	15.08	6.76	2.92	34.90	45.85
Cl^- (mg/l)	16.82	10.82	19.29	3.55	100.71	114.69
HCO_3^- (mg/l)	197.53	200.50	111.18	9.15	535.76	56.28
SO_4^{2-} (mg/l)	59.81	24.27	90.57	2.00	451.48	151.44
NO_2^- (mg/l)	0.11	0.01	0.35	0.00	1.56	323.88
NH_3^- (mg/l)	0.03	0.00	0.08	0.00	0.49	289.59
NO_3^- 0–15 (mg/l)	7.42	9.19	5.10	0.00	13.96	69
NO_3^- 16–30 (mg/l)	22.09	20.30	4.15	16.70	30.10	19
NO_3^- 31–50 (mg/l)	38.26	36.53	6.02	31.52	19.70	16
NO_3^- >50 (mg/l)	78.51	78.51	11.61	66.90	90.12	15

Table 2 Factor loadings from R-mode factor analysis for groundwaters

Parameter	Dry period			Wet period		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
pH	**0.689**	0.654	0.313	**0.930**	0.365	−0.033
EC	**−0.724**	0.630	0.280	−0.311	**0.834**	0.456
T	0.014	0.419	**−0.908**	0.194	−0.414	**0.889**
Na	0.159	**0.911**	0.198	**0.734**	0.406	−0.232
K	0.154	**0.937**	0.799	**0.867**	0.131	−0.338
Ca	**0.898**	0.291	0.140	0.307	**0.759**	0.198
Mg	**0.843**	0.255	0.334	**0.877**	0.296	0.205
HCO3	0.540	0.374	−0.242	0.519	0.689	**0.930**
Cl	**0.820**	0.431	0.280	**0.915**	−0.234	0.821
SO4	0.415	**0.710**	0.233	**0.827**	0.154	−0.137
% Total var.	48.742	16.498	11.317	53.797	15.944	10.557

Factor loadings of the rotated solution of principal component analysis (R-mode factor analysis). Variables displaying significant weights on the extracted factors are in bold

Cold groundwater wet season

Factor 1 is characterized by strong loading of pH, Na^+, K^+, Mg^{2+}, Cl^- and SO_4^{2-} which accounts for 53.79 % of the variance in wet season (Table 2). In this season, hydrogeochemical characteristics of groundwater are different according to dry period and natural weathering is dominant. Factor 2 explains 15.94 % of the total variance in this season. The loading of Ca^{2+} and EC indicates various ion-exchange processes in the groundwater system in the research area. Factor 3 includes temperature, HCO_3^- and Cl^- which accounts for 10.55 % of total variance. The strong loading of HCO_3^- ions with alkali and alkaline earth metals supports the view of natural weathering sources. The HCO_3^- can come from the dissolution of carbonate minerals, from soil CO_2 or from the bacterial degradation

of organic contamination. The increase of Cl^- ion is also associated with water–rock interaction.

In the study area, young cold waters have fast circulation and $Ca–Mg–HCO_3$ hydrochemical facies. Mixing waters have relatively longer circulation and $Ca–Mg–HCO_3–SO_4$ and $Ca–Mg–SO_4–HCO_3$ hydrochemical facies (Afşin et al. 2012; 2013; Fig. 2). According to major ion concentrations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) and physical parameters (EC, pH, temperature) of groundwater, all of the water samples are within the recommended limits of WHO (2008) and groundwater can be used for drinking purposes. In other words, there is no problem for usage as drinking water in terms of major ions concentrations and physical parameters of groundwater.

The most problem is nitrate contamination of groundwater in the basin. Nitrate contents of groundwater

Fig. 2 Piper diagram
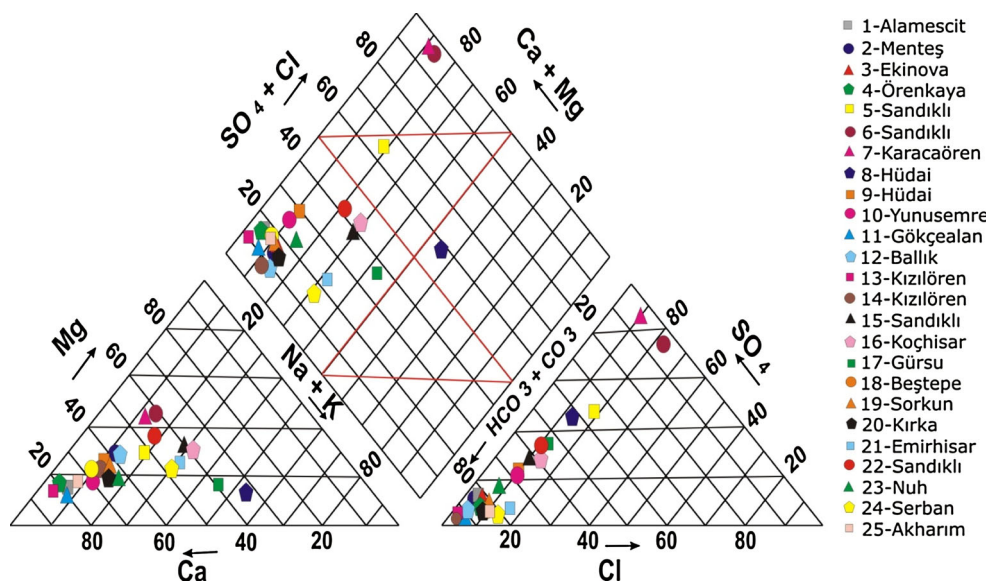
**Table 3** The results of NO$_3$ analyses in groundwater

Sample no.	Area	Sample type	NO$_3$ (mg/l) August 2009	NO$_3$ (mg/l) October 2009	NO$_3$ (mg/l) April 2010
1	Alamescit	Well	9.4	17.48	3.55
2	Menteş	Well	0.15	8.23	0
3	Ekinova	Well	**88.2**	**65.62**	**66.9**
4	Örenkaya	Spring	38.4	43.4	33.85
5	Sandıklı	Well	30.45	**55**	33.76
6	Sandıklı	Spring	28.85	39.2	27.52
7	Karacaören	Spring	1.1	9.08	0.67
8	Hüdaihamamı	Spring	2.75	10.83	0
9	Hüdaihamamı	Well	16.3	20.3	26.9
10	Yunusemre	Well	33.7	41.78	31.52
11	Gökçealan	Well	16.85	32.9	20.79
12	Ballık	Well	11.25	19.33	20.74
13	Kızılören	Well	13.5	21.58	13.92
14	Kızılören	Well	10.55	18.63	10.78
15	Sandıklı	Well	10.55	17.98	10.33
16	Koçhisar	Well	19.2	27.28	46.97
17	Gürsu	Well	25.7	39.77	20.29
18	Beştepe	Well	19.85	29.4	22.14
19	Sorkun	Well	0.3	8.38	0.03
20	Kırka	Well	19.65	30.1	28.92
21	Emirhisar	Spring	**82.8**	**90.12**	13.96
22	Sandıklı	Well	16.7	19.6	33.14
23	Nuh	Spring	34.4	49.7	9.29
24	Serban	Spring	9.85	17.93	0
25	Akharım	Spring	0.55	8.63	13.96

collecting from wells were analyzed in August 2009, October 2009 and April 2010. Nitrate concentrations of groundwater in August 2009, October 2009 and April 2010 vary from 0.15 to 88.2, from 8.23 to 90.12 and from 0 to 66.9 mg/l, respectively (Table 3). Groundwater samples were collected again in October 2009 to observe nitrate variations in groundwaters at the end of the irrigation season due to the determination of high nitrate concentration in August 2009. The distribution map of nitrate was prepared for porous aquifers. The highest nitrate concentrations are observed in the Ekinova and Emirhisar regions as 88.20 and 90.12 mg/l, respectively (Fig. 3). The average nitrate concentration in the groundwater is 23.64 mg/l. About 37 % of the samples exceeded the recommended maximum allowable value for nitrate in potable water according to the WHO (50 mg/l NO$_3$). The nitrate concentrations of groundwater compared to some local hydrogeologic and land use properties (Table 4). The nitrate concentration and electrical conductivity values which are measured in August 2009, October 2009 and April 2010 (Table 3) were plotted in same diagram. There is a strong relationship between the nitrate concentration and electrical conductivity of groundwater in the study area (Fig. 4). The highest EC values were measured in the Ekinova and Emirhisar regions as parallel to nitrate contents.

Key parameters

Inherent in each hydrogeologic setting is the physical characteristic which affects the groundwater pollution

Fig. 3 Distribution map of median nitrate concentration
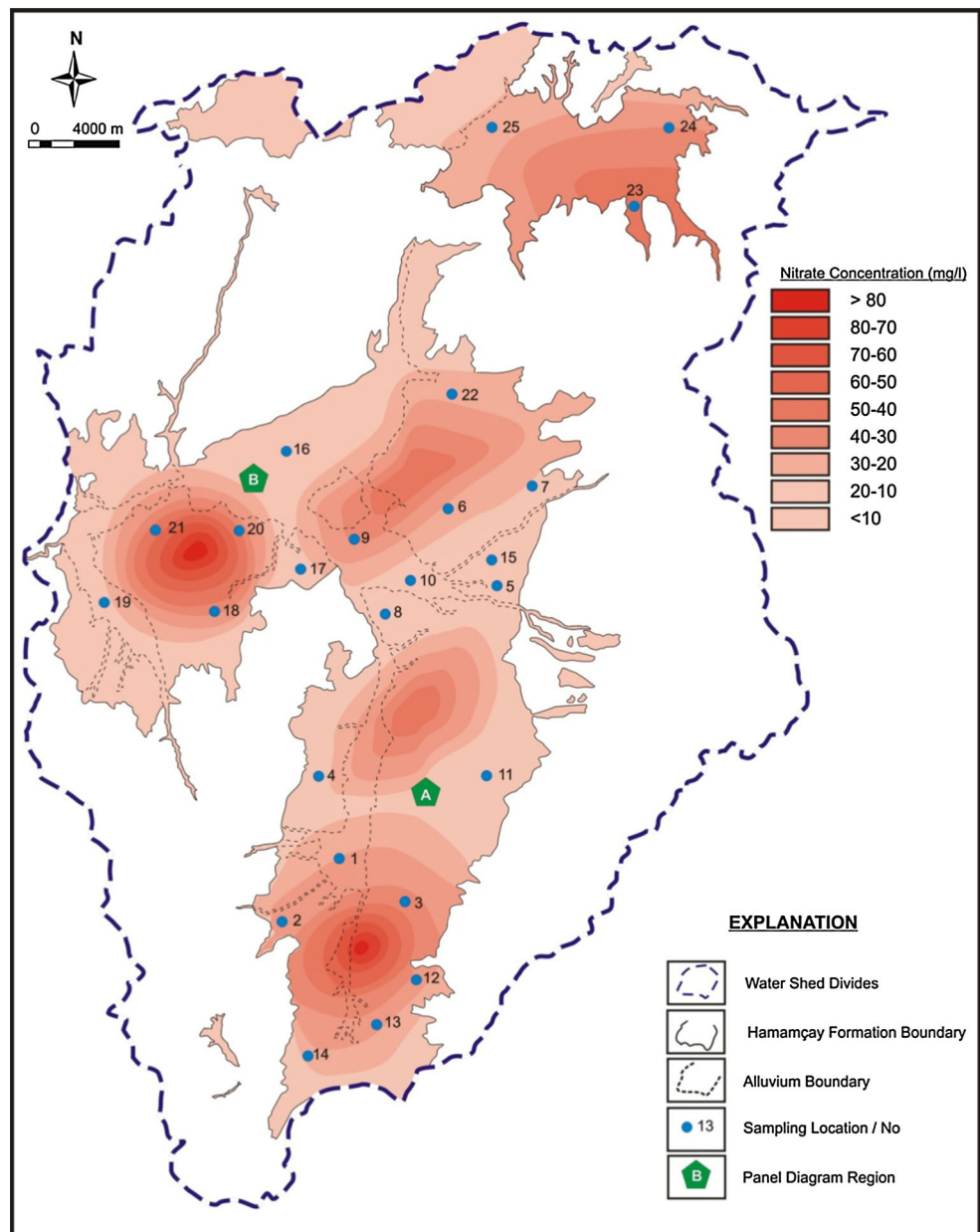
potential (Aller et al. 1987). In this study, parameters which are controlled to temporal variations at the nitrate contents of groundwater in porous aquifer were investigated. The most important factors that control the groundwater pollution potential were determined benefiting from the DRASTIC model of Aller et al. (1987). These key parameters such as groundwater depth and flow direction, hydraulic conductivity, land use, soil type, vadose zone, topography and net recharge were determined with geological, hydrogeological and hydrological investigation of the study area. Each parameter is assigned different ratings in a scale of 1 (least significant for increase of nitrate) to 5 (most significant for increase of nitrate) depending on the effect to increase of nitrate contents in groundwater

(Table 5). The rating ranges were determined according to the hydrogeological properties of the study area. This rating range may change from one study area to another. To determine rating ranges of the parameters, geological, hydrological, hydrogeological and environmental properties of the study area must be well known.

Groundwater depth and flow direction

For this study, groundwater head measurements were made in 22 piezometers (Aksever 2011). The groundwater depth was measured between 2.65 and 83.65 m in the wells during the field work in 2009 and 2010 years. Groundwater level decreased between 3 and 30 m in the basin for these

Table 4 The comparison of nitrate concentration, EC, groundwater depth, hydraulic conductivity, agricultural activity and aquifer type

Sample no.	Area	NO_3^- (mg/l)	Electrical conductivity (EC-µs/cm)	Groundwater depth (m)	Hydraulic cond. (m/day)	Land use	Aquifer
1	Alamescit	3.55–17.48	324–337	52.24	1.02×10^{-1}–1.64×10^{-1}	Wet agr. land	Alluvium
2	Menteş	0–8.23	311–344	42.04	1.24×10^{-2}–6.54×10^{-2}	Pasture–forest lands	Hamamçay formation
3	Ekinova	65.62–88.20	547–674	3.90	1.15×10^{-2}–7.79×10^{-2}	Wet agr.–pasture lands	Alluvium–Hamamçay F.
4	Örenkaya	33.85–45.40	278–458	23.82	1.60×10^{-1}–4.84×10^{-1}	Wet agr.–pasture lands	Alluvium
5–6–15–22	Sandıklı	30.45–55.00	299–586	7.88	3.51×10^{-1}–4.89×10^{-1}	Wet agr.–pasture–forest land	Alluvium-Hamamçay F.
7	Karacaören	0.67–9.08	152–191	17.88	3.38×10^{-1}–4.62×10^{-1}	pasture land	Hamamçay formation
8–9	Hüdaiham.	16.3–26.9	291–379	58.75	3.72×10^{-1}–7.29×10^{-1}	Wet agr. land	Alluvium
10	Yunusemre	31.52–45.78	350–438	15.96	3.67×10^{-1}–8.84×10^{-2}	Wet agr. land	Hamamçay formation
11	Gökçealan	16.85–32.90	195–227	83.65	2.46×10^{-1}–3.61×10^{-2}	Wet agr. land	Alluvium-Hamamçay F.
12	Ballık	11.25–20.74	313–322	47.91	1.34×10^{-2}–6.26×10^{-2}	Wet agr. land–Marsh. mass etc.	Hamamçay formation
13–14	Kızılören	10.55–21.58	265–347	30.65	1.24×10^{-2}–7.85×10^{-2}	Wet agr. land-Marsh. mass etc.	Hamamçay formation
16–17	Koçhisar	19.20–56.97	429–624	17.0	3.08×10^{-1}–8.80×10^{-1}	Wet agricultural land	Alluvium
18	Beştepe	19.85–29.40	311–392	15.94	2.56×10^{-1}–8.37×10^{-2}	Wet agricultural land	Hamamçay formation
19	Sorkun	0.03–8.38	135–237	18.04	1.31×10^{-1}–9.60×10^{-2}	Wet agr. –Forest lands	Hamamçay formation
20	Kırka	19.65–30.1	316–395	28.54	3.99×10^{-1}–4.83×10^{-2}	Wet agricultural land	Alluvium-Hamamçay F.
21	Emirhisar	13.96–90.12	313–669	10.02	4.28×10^{-2}–4.89×10^{-2}	Wet agr.–Pasture -forest land	Alluvium
23	Nuh	9.29–19.7	166–377	2.65	1.26×10^{-1}–1.38×10^{-1}	Wet agr.–Forest lands	Alluvium
24	Serban	0–17.93	124–134	4.85	1.09×10^{-1}–2.81×10^{-1}	Wet agr.–Forest lands	Alluvium
25	Akharım	0.55–13.96	184–247	5.98	1.65×10^{-1}–2.67×10^{-1}	Wet agr.–Pasture lands	Alluvium

periods. This decrease in groundwater level is originated excessive withdrawals from wells for especially irrigation. The highest nitrate concentrations have been detected in the Ekinova and Emirhisar regions which groundwater depth is less than 10 m (Table 4). The nitrate concentration of groundwater is inversely proportional with groundwater depth in the study area. Shallow aquifers can be easily contaminated by nitrate comparing to deep aquifers. The groundwater level map of the study area was prepared (Fig. 5a). The rating for depth to water table varies from 5 (for 0–20 m) to 1 (for >80 m, Table 5). The general flow direction of groundwater is W–E and NW–SE in the east of the basin, S–N and SE–SW in the west of the basin. In the saturated zone of aquifer, concentration of nitrate at any location is governed by the nitrate content of the water recharging from the unsaturated zone above and by the

additions from groundwater flowing from the surroundings (Peña-Haro et al. 2011). The nitrate content of groundwater is increased as directly proportional with groundwater flow direction in the basin. Therefore, the rating for groundwater level assigned from 5 to 1 and the rating values are increased according to groundwater flow direction.

Hydraulic conductivity

Hydraulic conductivity is an important hydrogeological property of soil and is spatially variable in heterogenous aquifers (Almasri 2007). Hydraulic conductivity is maximal when all the pores are filled with water; this is referred to as the saturated hydraulic conductivity. For a given porosity, pore size is the principal factor controlling hydraulic conductivity. Thus, a massive rock containing
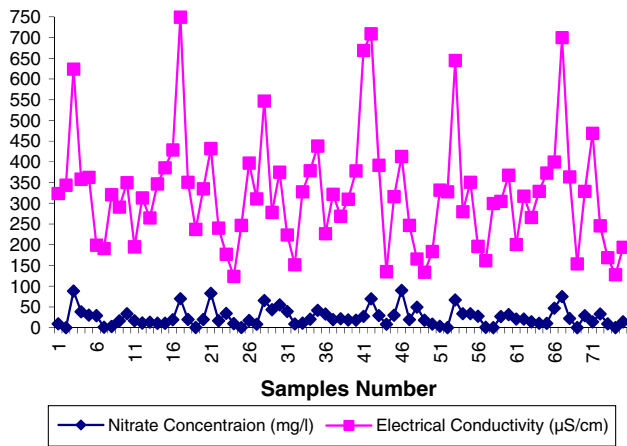
Fig. 4 The relationship between the EC and nitrate concentration of groundwater

only a few large fractures may have a much higher hydraulic conductivity than a porous but fine-grained rock whose pores are all of very small radius. For fractured rocks, it is likely that as the volume increases beyond that which is a representative of the macroscopic properties of rock matrix, the flow parameters will start to vary again before becoming constant once more for large volumes of rocks (Domenico and Schwartz 1990). In the zone of saturation, flow is likely to remain Darcian, even in a well-fissured rock, since the hydraulic gradient is usually low, though clearly the highest individual pore velocities are associated with the largest fractures (Burt and Trudgill 1993). The hydraulic conductivity of the aquifer controls to the amount of water percolating throughout the aquifer (Tilahun and Merkel 2009). Thus, contaminant migration is limited as related to hydraulic conductivity of the aquifer. The hydraulic conductivity of the aquifer was calculated from data obtained from field pumping tests which are made by SHW during drilling of wells using AquiferTest 3.5 Pro software with the Cooper–Jacob time-drown method for unconfined and porous aquifers. Hydraulic conductivity values of alluvium aquifer and Hamamçay formation varied between 1.03×10^{0} and 9.25×10^{-2}, 1.02×10^{0} and 9.60×10^{-2} m/day, respectively (Aksever 2011). Hydraulic conductivities of alluvium and Hamamçay formation are similar values (Fig. 5b). The range and rating distribution of hydraulic conductivity are shown in Table 5 and Fig. 5b.

Vadose zone

The vadose zone is defined as the zone above the water table and generally it is unsaturated or discontinuously saturated zone. The vadose zone has an important role in the percolation of rainfall and surface flow (Sener et al. 2009). The thickness and matrix of the vadose zone

Table 5 Rating values of key parameters

Key parameters	Parameter types	Weight factor
Groundwater depth (m)	>80	1
	60 to 80	2
	40 to <60	3
	20 to <40	4
	0 to <20	5
Groundwater flow direction	Northern part of the plain	1
	Westhern part of the plain	2
	Southern part of the plain	3
	Southwestern part of the plain	4
	Eastern part of the plain	5
Hydraulic conductivity (m/day)	$>1.00 \times 10^{-3}$	1
	4.50×10^{-2} to $<1.00 \times 10^{-3}$	2
	1.01×10^{-2} to $<4.50 \times 10^{-2}$	3
	4.50×10^{-1} to $<1.00 \times 10^{-2}$	4
	1.00×10^{-1} to $<4.50 \times 10^{-1}$	5
Vadose zone	Clay	1
	Gravelly clay	2
	Clayey gravel	3
	Sandy gravel	4
	Gravel	5
Soil type	Absent	1
	Silty clay	2
	Clay loam	3
	Loam–sandy clay loam	4
	Loamy sand–sandy loam	5
Topography (slope %)	>20	1
	15 to <20	2
	10 to <15	3
	5 to <10	4
	0 to <5	5
Net recharge (mm)	410 to <430	1
	430 to <450	2
	450 to <470	3
	470 to <490	4
	490 to 510	5
Land use	Range land + marsh. moras etc.	1
	Forest land	2
	Dry agricultural land	3
	Wet agricultural land	4
	Wet agricultural land + potato	5

determine the travel time and attenuation of a contaminant (Tilahun and Merkel 2009). Many processes that influence the pollution potential of the aquifer system take place in the vadose zone. The character of this zone determines attenuation characteristics of the media above the water table. Moreover, this zone controls the path of contaminant particles to the aquifer system (Baalousha 2006; Babiker
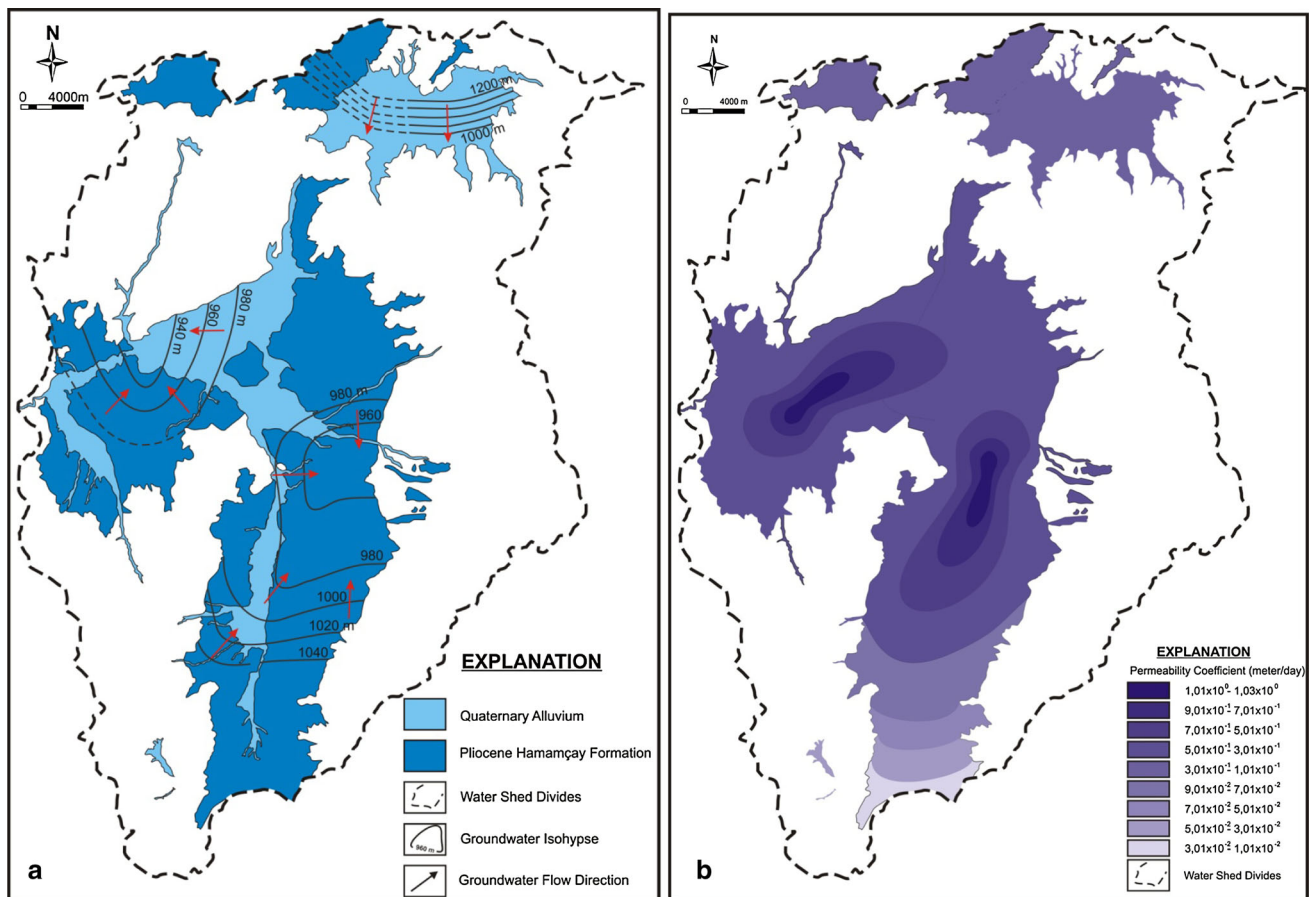
Fig. 5 **a** Groundwater level map, **b** hydraulic conductivity map

et al. 2003; Hitt and Nolan 2005; Hajhamad 2007; Kraft and Stites 2003). Vertical mixing in the saturated zone is likely to be slow and inputs of differing nitrate concentration along a flow path may remain distinct, because the high nitrate water masses migrate through aquifers as plume with little dilution relatively (Datta et al. 1997). After reaching the groundwater, nitrate migrates in the aquifer via advection and dispersion (Rina et al. 2014). Clay, gravelly clay, clayey gravel, sandy gravel and gravel are the main components observed in the study area according to well logs which were obtained from the SHW (Fig. 6). They were assigned with a rating in the range from 1 to 5 according to vulnerability properties (Table 5). Soil levels were extracted from well logs according to the thickness of levels for each well. The rating values of each level were determined as separately using Table 5. The final rating values of each well were calculated by taking average of these ratings.

Soil type

Soil has a significant impact on the amount of recharge that can infiltrate into the ground, and hence on the ability of a

contaminant to move vertically into the vadose zone (Lee 2003). The presence of fine-textured materials, such as silts and clays, can decrease relative soil permeability and restrict contaminant migration. Coarse-textured sands and loams allow contaminants to pass more quickly through open spaces than fine-textured silts and clays. Soil media can be described in terms of its textural classification and ranked in order of pollution potential. The soil map (S) of the basin which was taken from the Management of Agriculture and Village Works was used for the study area (Fig. 7a). The ratings were determined depending on soil classification and field investigations (Table 5).

Topography

This factor affects the flow rate at the surface, and consequently affects biodegradation and attenuation. Areas with low slope tend to retain water longer. This allows a greater infiltration of recharge water and a greater potential for contaminant migration (Baalousha 2006; Sener et al. 2009). Topography refers to slope of an area. Slope affects the flow rate of water at the land surface. Hence, infiltration and contaminant migration increase in the lower sloping
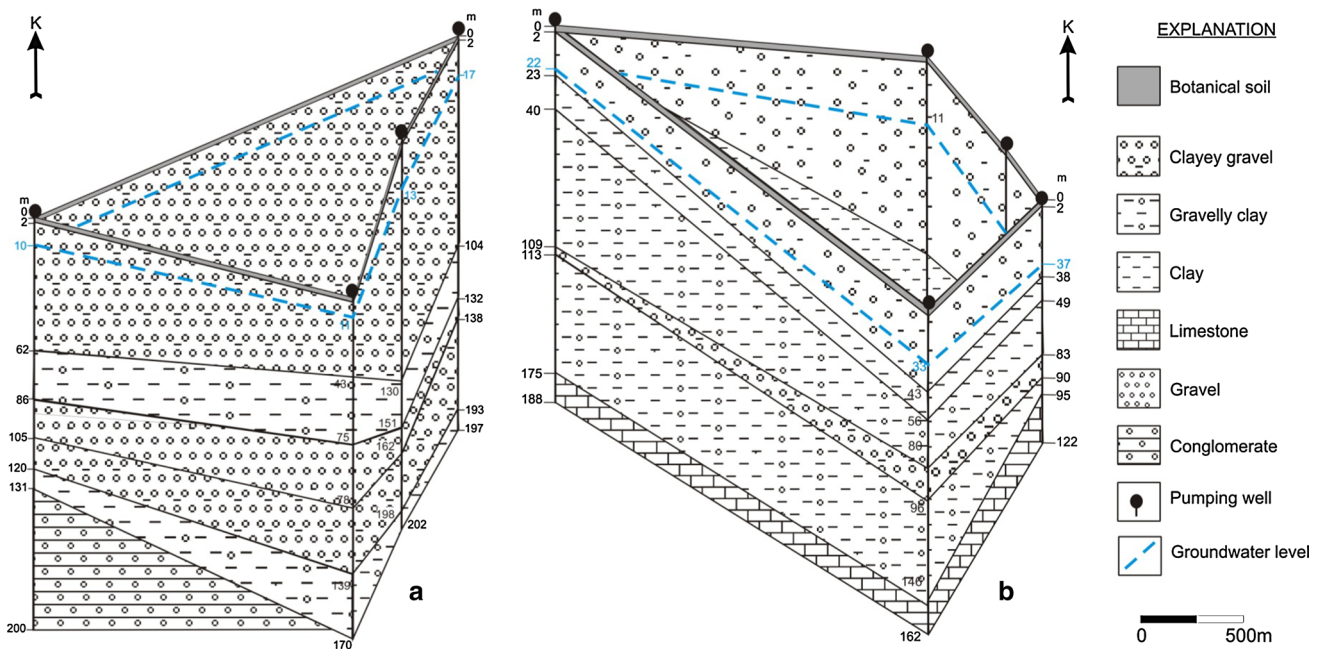
Fig. 6 Panel diagrams. **a** Pliocene Hamamçay formation, **b** quaternary alluvium)
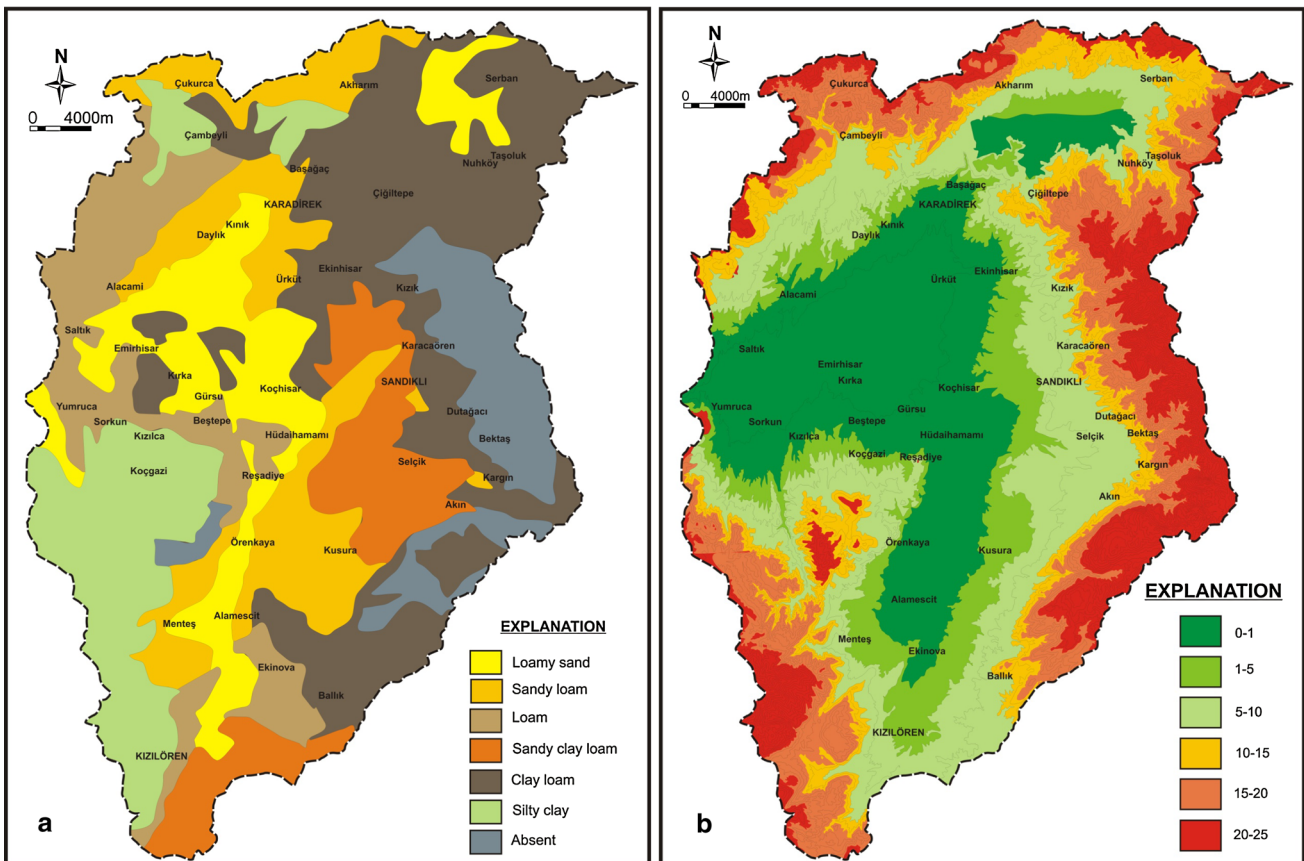

Fig. 7 a Soil type map, **b** slope map

areas (Sener et al. 2009). In the Sandıklı basin, there is relatively little variation in slope. The slope map of the basin was prepared using the topography contour map with 1:25,000 scale and slope ranges were assigned with a rating from 5 to 1 (Fig. 7b; Table 5).

Net recharge

The study area has a semi-arid climate, with hot and dry summers, and winters that are cool and moist. Average annual rainfall is about 453.86 mm (Aksever 2011) with approximately 85 % of precipitation occurring during November through May. Net recharge includes the average annual amount of infiltration and does not take into consideration the distribution, intensity or duration of recharge events (Al-Zabet 2002). The amount of precipitation that percolates through the aquifer varies from 30 to 40 % of the annual rainfall (Baalousha 2006). Precipitation is the primary source of groundwater recharge in the study area. Contaminants can move with groundwater easily depending on water quantity. According to several studies, low nitrate concentrations were measured in the wet seasons and high nitrate concentrations during the dry seasons (Babiker et al. 2005; Lee 2003; Liu et al. 2005; Pionke et al. 1999). Rainfall during dry season is less than in wet season, but, irrigation water requirement is also increased in dry season. The mixture ratio of nitrate to groundwater increased due to the increase of irrigation and usage of nitrogen fertilizer during dry season. In wet period, the amount of percolating water to groundwater with precipitation increases, and; however, the usage of nitrogen fertilizer decreases. Therefore, nitrate concentration of groundwater during the wet season is generally low compared to dry season except for specific locations (9, 12, 16, 22 and 25 samples) in the area (Table 3). In wet season, increase of nitrate contents at 16, 22 and 25 locations is related to dairy farms. Animal wastes dumped irregularly in these locations. Nitrate which is originated from wastes percolates to shallow aquifer in these locations. The increase at 1, 9 and 12 locations can be related to potato culture. Potato is a common crop type in these regions. Nutrient requirement of potato crop is quite high and the application of fertilizers and organic manures is considered essential to obtain economic and high yields. Ammonium sulfate and ammonium nitrate are usually the best fertilizers for potato (http://nhb.gov.in/vegetable/potato/pot007.pdf). Potato cultivation required more irrigation (Kraft and Stites 2003; Pereira and Shock 2006; Shrestha et al. 2010). Potato is a *N*-intensive crop, with high potential for nitrate leaching, which can contribute to groundwater contamination (Venterea et al. 2011). In addition, sample 9 is situated near the Hüdaihamamı spa. Hüdai geothermal field is located in middle of the Sandıklı basin (Afşin 1991;

Aksever 2011). The hydrothermal contribution is determined in the Koçhisar and Gürsu regions which are located in the surrounding of Hüdaihamamı spa (Aksever 2011; Afşin et al. 2013). The nitrate increase in sample 9 can be also related to interference of deep thermal water with shallow cold water.

Annual rainfall has been measured at the nine stations (Şuhut, Dinar, Afyon, Sincanlı, Hocalar, Gümüşsu, Haydarlı, Kızılören, Sandıklı) of the State Meteorology Works. The rainfall map of the basin was prepared using measured annual rainfall data and isohyets method (Fig. 8a). The rating varies from 5 (for 490 to less than 510 mm) to 1 (for 410 to less than 430) in the study area (Table 5). Isohyetal lines (isohyets) joining equal precipitation heights are interpolated from precipitation of neighboring stations in proportion to their distances. This method has an advantage in that it enables reflection of known factors affecting the spatial distribution of precipitation, e.g., orographic factors or terrain-related factors, in the isohyetal line design. The isohyets method is superior to the other two methods especially when the stations are large in number. Areal precipitation is determined by the following equation;

$$\bar{P} = \frac{a_1\left(\frac{P_1+P_2}{2}\right) + a_2\left(\frac{P_2+P_3}{2}\right) + \cdots + a_{n-1}\left(\frac{P_{n-1}+P_n}{2}\right)}{A} \quad (2)$$

$\bar{P}$ where: P_1, P_2, P_3, …, P_n are the values of the isohytes; a_1, a_2, a_3, …, a_4 are the inter isohytes area, respectively; A is the total catchment area—the mean precipitation over the catchment.

Land use-agricultural activity

Agriculture is considered as the main source of nitrate contamination of groundwater (Sacco et al. 2007). The nitrate concentration of groundwater can easily reach several hundred milligrams per liter due to agricultural activities (WHO 1985). Intensive agricultural activities are present on the porous aquifer of the Sandıklı basin. Seventy percent of agricultural lands in the basin have used as wet agricultural land (Fig. 8b). Twenty percent of this area is forest land and the remaining the other agricultural activity lands. Major crops include potato, barley, wheat, corn, chickpea and sugar beet grown in the basin. Especially, potato has commonly cultivated in the Emirhisar and Ekinova vicinities. The nitrate contents of groundwater are highest in these regions. Groundwater contamination by nitrates associated with intensive potato culture had been investigated in several research, and the researches confirm that intensive potato culture on sandy soil could have serious impacts on the quality of groundwater (Olson et al. 1970; Saffigna and Keeney 1977; Tanner et al. 1982; Milburn et al. 1990; Levalloisa et al. 1998; Kraft and Stites 2003; Perez et al. 2003; Pereira and Shock 2006; Jégo et al.
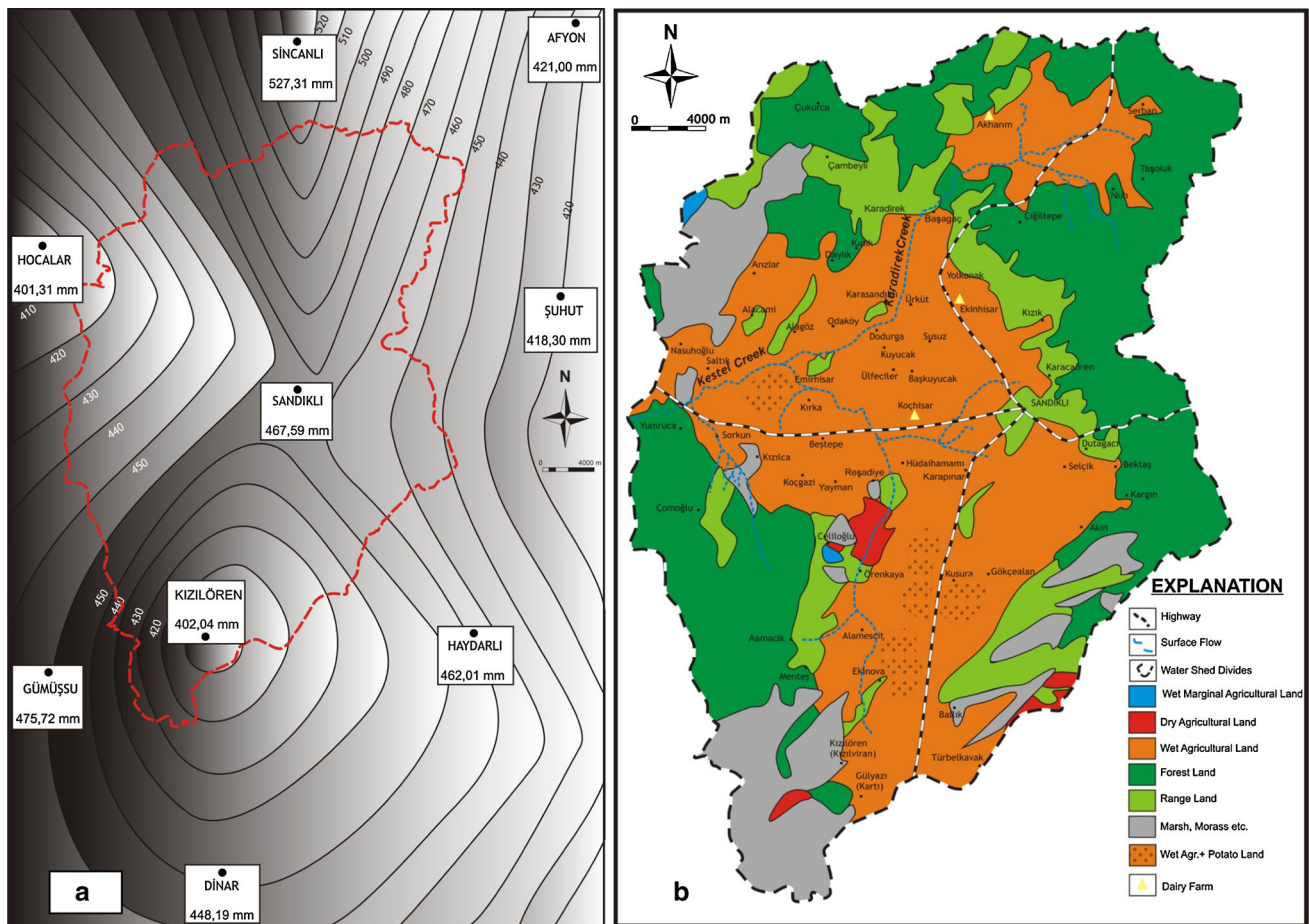
Fig. 8 a Rainfall map, **b** agriculture map

2008; Shrestha et al. 2010). High-value irrigated crops such as potato favor rapid NO₃ leaching to groundwater (Kraft and Stites 2003; Shrestha et al. 2010). Cultivating of potato is requires additional irrigation and usage of nitrogenous fertilizer and animal manure. Fertilizer applications to agricultural crops are the largest sources of nitrogen (N) to the study area. Different nitrate levels in different locations may be due to different fertilizer application rate and crop species (Gunatilake and Iwao 2010). The nitrate input into groundwater is a function of management practice and fertilizing practice related to crop species (Gunatilake and Iwao 2010; Perez et al. 2003; Quevauviller 2008; Wick et al. 2010). Furthermore, usage of animal manure is widely common in the Sandıklı basin. Animal manure is very effective for nitrate contamination in the shallow groundwater (Rosen 2009). They were assigned with a rating in the range from 1 to 5 according to land use (Table 5).

Factor analyses of key parameters

One of the aims of the paper is to present a simple method based on multi-component statistical analysis, which could be useful in examining the origin and transport of nitrate ions through the non-saturated and saturated zones of an aquifer. In other words using statistical analysis, we can draw easier conclusions about the factors affecting nitrate transport (Lambrakis et al. 2004). Factor analysis (R-mode) is the most important multi-component statistical analyses. Factor analysis is useful for interpreting of relationship between groundwater quality data and specific hydrogeologic processes (Lawrence and Upchurch 2006). R-mode factor analysis has proven highly effective in studies of groundwater quality. Factor analyses allow to the determination of basic independent dimensions of variables (Sivasankar et al. 2013). The application of the analysis has proved useful in the interpretation of hydrogeological data (Bakalowicz 1994; Aruga et al. 1995; Elueze et al. 2001; Lambrakis et al. 2004). Factor analysis is an effective means of manipulating, interpreting and representing of data concerning groundwater pollutants (Liu et al. 2003).

R-mode factor analysis (Varimax Rotation with Kaiser Normalization) was carried out with the help of SPSS-15 software to extract the factors. In general, the factor will be related to the largest eigenvalue and will explain the

Table 6 Results of the *R*-mode factor analysis (dry and wet seasons)

Key parameters	Dry season			Wet season		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Hydraulic conductivity	0.218	0.853	0.169	0.359	0.804	−0.014
Groundwater depth	−0.295	0.512	−0.176	−0.281	0.656	−0.103
Groundwater flow direction	0.273	−0.650	0.342	0.212	−0.547	0.474
Vadose zone	0.814	−0.169	0.130	0.798	−0.242	0.116
Topography	0.059	−0.042	0.862	0.084	0.066	0.865
Land use	0.817	0.001	0.027	0.782	0.039	0.225
Soil type	0.290	−0.220	0.882	0.297	−0.111	0.911
Net recharge	−0.181	0.462	0.522	0.234	0.497	0.308
% of Variance	32.060	20.513	14.288	33.189	19.468	13.848
Cumulative %	32.060	55.572	66.860	33.189	52.658	66.505

greatest amount of variance in the data set. The variance attached to a factor is described by the factor's eigenvalue. An eigenvalue gives a measure of the significance of the factor. The factors with the highest eigenvalues are the most significant. Eigenvalues of 1.0 or greater are considered significant (Kim and Mueller 1987; Love et al. 2004).

The *R*-mode factor analysis was carried out using the statistical package for Social Sciences Software (SPSS). It is applied to 25 groundwater samples which are collected from wells and springs in the Sandıklı basin. The correlations between key parameters (hydraulic conductivity, vadose zone, topography, land use, soil type, groundwater depth, groundwater flow direction and net recharge) and the increase of nitrate contents in groundwater are statistically examined with factor analyses. Factor loadings are classified by Liu et al. (2003) as "strong", "moderate" and "weak" corresponding to absolute loading values of >0.75, 0.75–0.50 and 0.50–0.30, respectively. In this study, this classification was used to evaluation of data (Table 6).

In the dry season; Factor 1, explains 32 % of the total variance, has strong positive loading on land use (0.817) and vadose zone (0.814). Factor 2, explains 20.5 % of the total variance (Table 6), with strong absolute loadings of hydraulic conductivity (0.853) and moderate loadings on groundwater depth (0.512). Factor 3 has strong positive loadings on topography (0.862) and soil type (0.882) and moderate loadings on net recharge (0.522).

In the wet season; Factor 1, explains 33 % of the total variance, has strong positive loadings on vadose zone (0.798) and land use (0.782). Factor 2, explains 19 % of the total variance (Table 6), with strong absolute loadings of hydraulic conductivity (0.804), moderate loadings on groundwater depth (0.656) weak loadings on net recharge (0.497). Factor 3 has strong positive loadings on topography (0.865) and soil type (0.911) and weak loadings on groundwater flow (0.474).

According to factor analyses results, land use and vadose zone are the most effective key parameters for

increase of nitrate concentrations in dry and wet seasons. All over the world, wherever nitrogenous fertilizers have been used extensively to increase the agricultural productivity, high-nitrate level in groundwater is evident. The nitrogenous fertilizers are rapidly converted in arable soils to NO_3 form, which are readily available to plants, but are highly soluble and hence easily leachable. When quantity of nitrogen added to the soil exceeds the amount that the plants can use, the excess NO_3 does not get much adsorbed by soil particles, leaches out from the root zone by water percolating through the vadose zone profile and ultimately accumulates into the groundwater (Kundu et al. 2008). Extent of its contamination is associated with transport and fate of nitrate in the vadose zone located between the ground surface and the water table, including denitrification (Zhang et al. 2013). Taking into consideration nitrate contents of groundwater in the study area, elevated nitrate concentrations were determined in the Emirhisar and Ekinova vicinities where potato is densely cultivated. Nitrate leaching is substantial, especially for potato. Potato needs a sustained high soil nitrate level for yield and quality (Sattelmacher and Marschner 1979) and it has a shallow root system (Kraft and Stites 2003). Water requirements are often met through sprinkler irrigation in the basin. These practices, in combination with the shallow root system of potatoes, have led to significant amounts of nitrate (NO_3) leaching to shallow groundwaters in the area. The secondary parameter controlling to increase of nitrate in groundwater is hydraulic conductivity in dry and wet seasons. The rate of dissolution will depend on the solubility of the particular compound in water, the rate of groundwater flow and the degree of mixing that is permitted by the distribution of the solvent in relation to the local hydraulic structure and flow pathways (Burt and Trudgill 1993; Peña-Haro et al. 2011). Groundwater depth has moderate significant. Results thus indicated that the concentration of NO_3 decreased with increasing depth of the wells from which sampling was done. The NO_3

contents of groundwater in wells which have depths between 2 and 20, 20 and 40 and 40 and 60 m were determined as averages 34.2, 26.8 and 14.9 mg/l, respectively. In other words, NO_3 content of groundwater and depth of groundwater in sampling aquifers are inversely proportional. This is a typical feature in nitrate contamination of groundwater observed worldwide (Power and Saikh 1995; Nolan 2001; Kundu et al. 2008). Topography, soil type, groundwater flow and net recharge are the least important key parameters which are controlled to increase of nitrate concentrations in groundwater.

Summary and conclusions

Paleozoic, Mesozoic and Cenozoic aged rocks outcropped in the research area. Kestel formation, Hüdai quartzite, Çaltepe and Seydişehir formations are Paleozoic aged. Precambrian aged Kestel formation which is composed of metamorphic rocks is foundation unit of the study area. The metamorphic foundation is composed of quartz, sericite schist, albite, quartzite, calc-schist, phyllite and metabasalt. Karatepe, Derealanı and Akdağ formations are Mesozoic aged rock units. In addition, Bozoğlan formation, Oligocene conglomerate, Soğucak pyroclastic, Sandıklı Lava, Hamamcay formation and Quaternary units are Cenozoic aged rocks in the area. Quaternary aged travertine and alluvium units are covered all of the units as discordant. Quaternary alluvium and Pliocene aged the Hamamçay units are porous aquifers. The Hamamçay formation is locally transitive and below of the alluvium.

Groundwater contamination by nitrate in the study area was serious because of intensive agricultural activities. In general, nitrate concentration increased with direction of groundwater flows, i.e., relatively high concentrations was observed in the wells of downstream area. In addition, the extent of nitrate leaching from wet agricultural land is influenced strongly by factors inherent in nature such as soil type and climatic conditions. Agricultural practices involving inorganic fertilizer and animal manure applications have been identified as the main sources of nitrate contamination of groundwater in the study area. Quaternary alluvium and Pliocene aged the Hamamçay units which are almost equal to hydraulic conductivities are porous aquifers in the basin. A total of 75 water samples were collected periodically for porous aquifer. These water samples were collected from 25 wells in three times for dry (August–October 2009) and wet (April-2010) seasons in 2009/2010 years. Nitrate contents of groundwater in the alluvium aquifer are determined between 0 and 90.12 mg/l similarly, nitrate contents of groundwater in the Hamamçay formation are also determined 0–88.2 mg/l. The average nitrate concentration in the groundwater is 23.64 mg/l,

37 % of these water samples are above 50 mg/l which is the upper limit in drinking water standards. There is a strong relationship between the nitrate concentration and electrical conductivity of groundwater in the study area. The highest EC values were measured in the Ekinova and Emirhisar regions as parallel to nitrate contents. EC parameter is an indicator representing to elevated nitrate content related to agricultural activities. Seventy percent of agricultural lands in the basin have used as wet agricultural lands. The most common crop type is potato in the regions where the highest nitrate concentration is measured. The nitrate concentration of groundwater exceeds to 10 mg/l in other regions of the basin cultivating potato.

Some hydrogeologic parameters are more important than others in determining aquifer vulnerability. In this study, R-mode factor analysis was used to identify parameters that are more effective for increase of nitrate contents in groundwater. Key parameters are hydrogeological and hydrologic data groups such as groundwater depth, groundwater flow direction, hydraulic conductivity, land use, soil type, vadose zone, topography and net recharge. Groundwater levels were regularly measured at wells using groundwater level meter in the basin in 2009 and 2010 years and groundwater level map was prepared. The groundwater depth was measured between 2.65 and 83.65 m in the wells. The hydraulic conductivity of the aquifer was calculated from data obtained from field pumping tests which are made by SHW during drilling of wells using AquiferTest 3.5 Pro software with the Cooper–Jacob time-drown method for unconfined and porous aquifers. Hydraulic conductivity values of alluvium aquifer and Hamamçay formation varied between 1.03×10^0 and 9.25×10^{-2}, 1.02×10^0 and 9.60×10^{-2} m/day, respectively. The vadose zone character was determined according to well logs which were obtained from the SHW. Clay, gravelly clay, clayey gravel, sandy gravel and gravel are the main components observed in this zone. Soil type was described using the soil map of the basin which was taken from the Management of Agriculture and Village Works. The slope map of the basin was prepared using the topography contour map with 1:25,000 scale. Net recharge was determined using the rainfall map of the basin which is prepared using measured annual rainfall data at the nine stations (Şuhut, Dinar, Afyon, Sincanlı, Hocalar, Gümüşsu, Haydarlı, Kızılören, Sandıklı) of the State Meteorology Works and isohyets method.

The R-mode factor analysis was carried out using the statistical package for Social Sciences Software (SPSS). It is applied to 25 groundwater samples which are collected from wells and springs in the Sandıklı basin. The correlations between key parameters and the increase of nitrate contents in groundwater are statistically examined with factor analyses. According to factor analysis, the first

factors are land use and vadose zone parameters. Hydraulic conductivity and groundwater depth are secondary parameters controlling to increase of nitrate in groundwater for dry and wet seasons. Groundwater flow direction, net recharge, topography and soil type are moderate important key parameters.

For reduction of nitrate leaching in cropland in the study area, vulnerability maps can be prepared identifying risks of nitrate leaching associated with specific crops and irrigation system types. Agricultural management practices should be selected according to field-specific variables (crop and soil characteristics, as well as underlying hydrology). For the study area, firstly, growing of potato can be limited in regions where groundwater depth is less than 20 m. The crop rotations should be modified in these areas. The timing and rates of applied fertilizer N, animal manures and irrigation water should be controlled related to crop needs. Most importantly, farmers must be trained.

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