

Assessment of nitrate contamination in a transnational groundwater basin: a case study in the Ceylanpinar Plain, Turkey

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Abstract A study was undertaken to determine seasonal variations in nitrate concentrations in a transnational groundwater resource beneath the Ceylanpinar Plain near the border between Turkey and Syria. Spatial distribution maps of nitrate pollution for groundwater in the study area were created using a geographical information system (GIS), and the potential for contamination in the entire plain was determined. Seasonal variations of nitrate concentrations in groundwater were assessed by sampling during spring, summer, autumn, and winter in the period April 2012 to January 2013. The groundwater samples were analyzed for nitrate (NO₃). The results obtained were evaluated using a number of national and international standards and classifications. Seasonal average concentration distribution maps were established for nitrate to determine the extent and severity of contamination by this parameter in groundwater in the region. The monitoring indicated that nitrate concentrations in only two wells exceeded the recommended drinking water limit and that groundwater beneath the basin is currently suitable for irrigation.

Keywords Groundwater · Water quality · Nitrate pollution · GIS · Ceylanpinar Plain

Introduction

Groundwater is the largest fresh water source in the world by volume and has the potential to be used at low cost because it is generally of good quality in its natural state and not required treatment (Driscoll 1986). For this reason, in recent years, there has been a great increase in the use of groundwater, especially in developing countries as a natural consequence population increases in regions where there is a limited availability of surface water resources.

In addition, groundwater is used as an important source of water for domestic, industrial, and agricultural activities (Delgado et al. 2010). Additionally, groundwater discharge is the main source of stream flows in some regions (Kahraman et al. 2016). Maintaining groundwater discharge is also necessary for sustaining the vitality and biodiversity of many aquatic ecosystems. In many parts of the world, there are transboundary surface waters as well as groundwater bodies that contain potable quality water. These comprise 31% of the total freshwater in the world, compared with 0.3% for rivers and lakes (Shiklomanov 1993).

The natural qualities of groundwater are determined by the quality of the water that falls on the earth as rainfall and by chemical reactions between organic matter and minerals in soil and rocks in the subsurface (Sargin 2010). Settlements, domestic, commercial, industrial, and agricultural activities can affect groundwater quality through the leaching of contaminants from the land surface (Zaporozec and Miller 2000). Therefore, it is important to know the quality characteristics of the aquifer when evaluating whether groundwater resources are suitable for a variety of uses.

Monitoring of many of the world's aquifers has indicated that there has been a substantial degradation in groundwater quality during the twentieth and twenty-first

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centuries from agricultural practices, particularly through increases in the nitrate content of groundwater during this period. The transient agricultural groundwater signal has important implications for long-term trends and spatial heterogeneity in discharge (Böhlke 2002). Nitrate level in groundwater usually increases with higher nitrogen inputs in regions where shallow aquifers are highly vulnerable to contamination (USGS 2017). The increased nitrate concentrations in groundwater are due to the widespread use of human and animal wastes and the increased use of nitrogenous fertilizers in agricultural areas, and as a consequence, many drinking water supplies are threatened because of elevated nitrate concentrations (Durmaz et al. 2007; Kahraman et al. 2016).

Contamination of groundwater can result in poor drinking agricultural water quality, loss of water supply, high clean-up costs, high costs for alternative water supplies, and/or potential health problems.

A study was conducted by Nas and Berktaş (2006) in Konya City, Turkey, to determine and assess the spatial distribution of nitrate concentration and nitrate pollution based on 1998 and 2001 data by using geographic information system (GIS) technology. It was concluded that the distribution of nitrate concentrations is not correlated with well depths within the study area. Another study conducted in Çeltikçi Plain located in the southwest of Turkey by Davraz and Özdemir (2014) concluded that concentrations of Mn, NO₃, and total hardness exceed the prescribed limits of World Health Organization (WHO). Various physical and chemical parameters were measured by Yesilnacar and Gulluoglu (2008), in order to determine the distribution of groundwater quality in the shallow aquifer in the region where irrigated agriculture takes place on the Harran Plain, which is adjacent to the project area. This study was carried out to determine the suitability of groundwater in the area for human consumption and agricultural purposes. This study found that nitrate and EC values in groundwater were significantly higher than the acceptable values of 50 mg/L and 650 µS/cm, respectively. Yesilnacar et al. (2008) estimated pollutants and nitrate concentrations in Harran Plain, which are very common in groundwater in the shallow aquifer, by undertaking modeling using artificial neural networks (ANN). As a result, nitrate levels at all sampling points were found to be higher than the maximum acceptable values.

The Ceylanpinar Plain, in which this study was conducted, is the largest agricultural and animal breeding area of Turkey. The plain has a surface area of roughly 2,000 km², about 1,750 km² of which belongs to the Ceylanpinar Directorate of Agriculture in General Directorate of Agriculture (TİGEM). In this study, seasonal average groundwater distribution maps were prepared for

sensitive and high-risk areas in order to monitor the groundwater quality and to determine the potential risk of nitrate contamination of groundwater occurring. The Ceylanpinar Plain is also located on the border with Syria and has transboundary groundwater that is shared with that nation. For this reason, it is important to determine the groundwater quality in this area.

Consequently, this study was undertaken to determine the extent and severity of nitrate contamination of shallow groundwater on the Ceylanpinar Plain, particularly from discharges from intensive animal feedlots (confined animal feeding operations) in the region (Yetis 2013).

Study area

Physical characteristics

The study area covers the Ceylanpinar Plain which is located in Sanliurfa Province in the southeastern part of Turkey. The study area has about 2,000 km² of surface area (Fig. 1). The length of the Ceylanpinar plain in the east–west direction is 80 km, and the width in the south–north direction is 40 km. It is located between 36° and 37°20' eastern longitudes and 39°30' and 40°10' northern latitudes. The average altitude from sea level is 397 m. Land in the area generally slopes from the northwest to the southeast. The highest elevation ranges from 527 m to the lowest elevation of 370 m.

The study area is bounded by Ceylanpinar and Kiziltepe in the east, Akcakale and Harran districts in the west, the Syrian State in the south, and the Viransehir District in the north. About 88% of the Ceylanpinar plain with a 2000 km² surface area belongs to the General Directorate of Agricultural Enterprises (TIGEM in Turkish acronym) and the Ceylanpinar Agriculture Directorate.

The Ceylanpinar Plain is one of the largest agricultural and animal breeding use areas of Turkey. It has a reservoir of groundwater that is sufficiently large to supply 20% of Turkey's domestic water needs (Yetis 2013). It is also the economic and social hub of the Ceylanpinar District with a population of 60,000. The surface area consists of about 151,514 hectares (ha) of agricultural land and about 24,612 ha of non-agricultural land. In addition, a total of 176,126 ha of agricultural land consists of 60,900 ha of irrigated land and 92,000 ha of irrigable land. There is a transboundary groundwater reserve in the Southeastern Anatolia Region that can be recharged at a total of 2.310 billion m³ per year. The Ceylanpinar Plain contains 1.350 billion m³ per year of this reserve. Within the context of the South Anatolian Project (GAP in Turkish acronym), which is the largest integrated project of Turkey, the Ceylanpinar Plain and the TIGEM lands have been

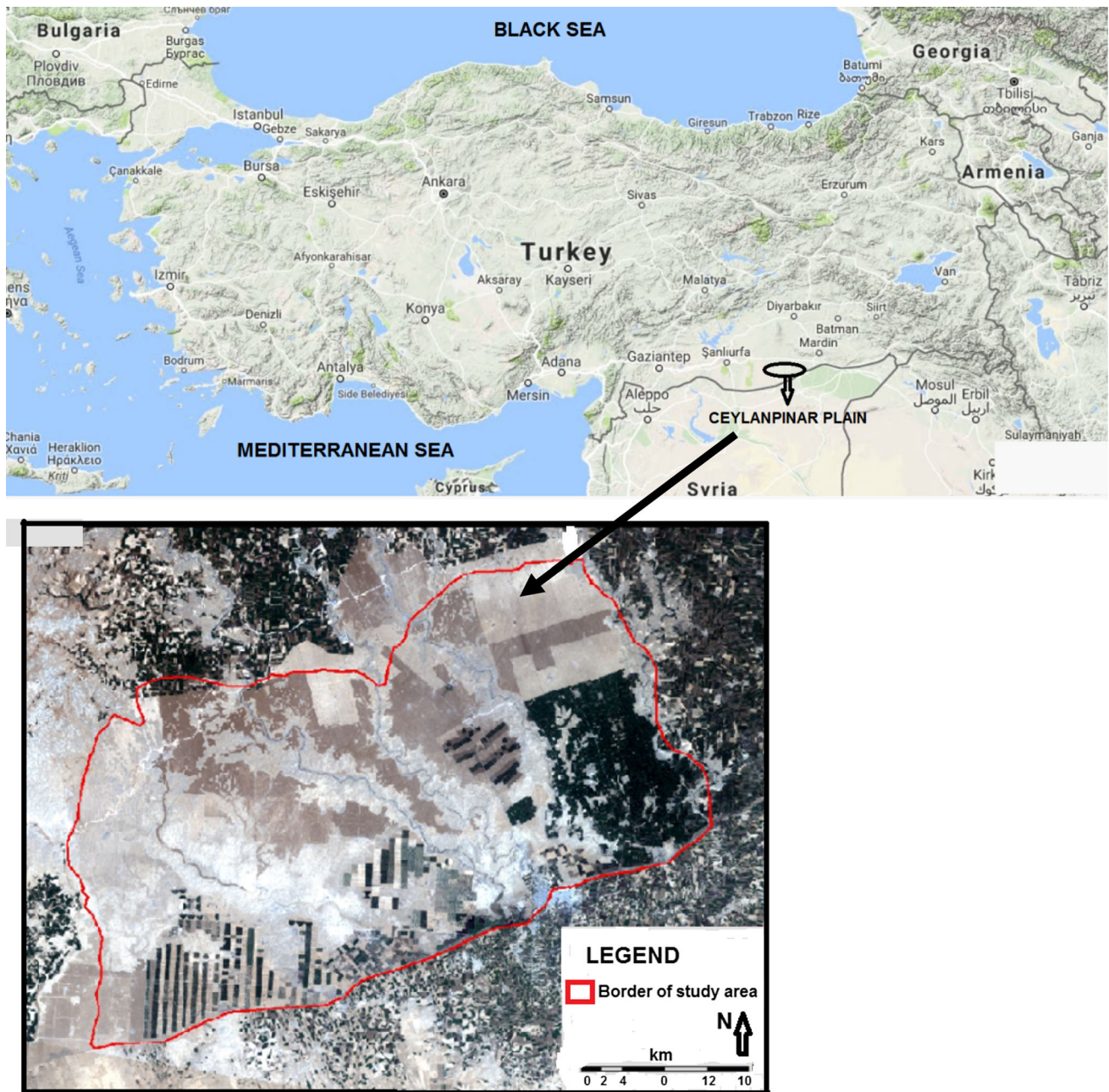


Fig. 1 Location map and satellite image of the Ceylanpinar Plain

subjected to an assessment of the volume of groundwater that is available for irrigation. In this context, 1,300 km² of the land in the Ceylanpinar Plain is planned to be irrigated from groundwater while the remaining area is to be irrigated by water from the Atatürk Dam via the Mardin Ceylanpinar Main Canal (DSI 2011).

Geological and hydrogeological setting

A limestone of Eocene age underlies the Ceylanpinar Plain. This limestone is in turn overlain by a Miocene limestone,

and by beds of gypsiferous gravelly clays and clayey sands. In the northern part of the area, basalt flows overlie these sediments. The Miocene formation is generally composed of clay, limestone, marl, gravel and sand levels, and mixtures of these sediments. The thickness of Miocene sediments decreases from south to north and from west to east. The basalts are spread from north to south and partly over the Miocene series and partly over the Eocene limestone. The most important formation carrying groundwater in plain is the Eocene limestone and, to a lesser extent, basalt. Only limited supplies of poor-quality groundwater are

available from the Miocene sediments. Basalts spread to the north of the study area.

The Eocene limestones, which are the most sources of groundwater in the area, are located under basalts in the northern part of the area and beneath Miocene sediments in the southern and eastern parts of the area. The geological map of Ceylanpinar Plain and the map showing the distribution of the old and new wells in TIGEM, which was opened by the DSI for the purpose of irrigation before the study, is given in Fig. 2.

Climate

The Ceylanpinar Plain has a continental semiarid climate (Csa in the Köppen classification system) (Rubel and Kottek 2010). The average annual precipitation of the Southeastern Anatolian Region is 532.6 mm (MGM 2017). The study area is dry and hot in summers, and cold and rainy in winters. The precipitation is low but the evaporation rate is high during the summer months. According to the meteorological records for the period 1970–2012, the highest temperatures occur in July (up to a maximum of 48.2 °C), and the lowest temperatures occur in January (down to a minimum of −2.3 °C). The average annual average precipitation on the Ceylanpinar Plain varies from

about 295 to 458 mm, and typically no precipitation occurs in June, July, and August each year. The observed values of average monthly temperature, relative humidity, and precipitation of the study area for 2012 are shown in Fig. 3.

Soils

Much of the study area is underlain by heavy clayey soils. Some loamy and sandy soils occur in the vicinity of ephemeral streams and on hillslopes, but these soil types are found in very small amounts in the study area. Typically, the upper horizons of soil horizons in the area are blocky or granular, whereas the lower part of soil horizons are blocky. Soils in the area typically have brown to reddish brown color. In the areas where the leprosy is widespread, white, dirty white, and grayish brown soils are encountered (DSI 1986).

Sampling, chemical analysis, and data assessment methods

Sampling of wells to be used for water supply in the study area were sampled in spring, summer, autumn, and winter to assess seasonal changes in groundwater quality. A total

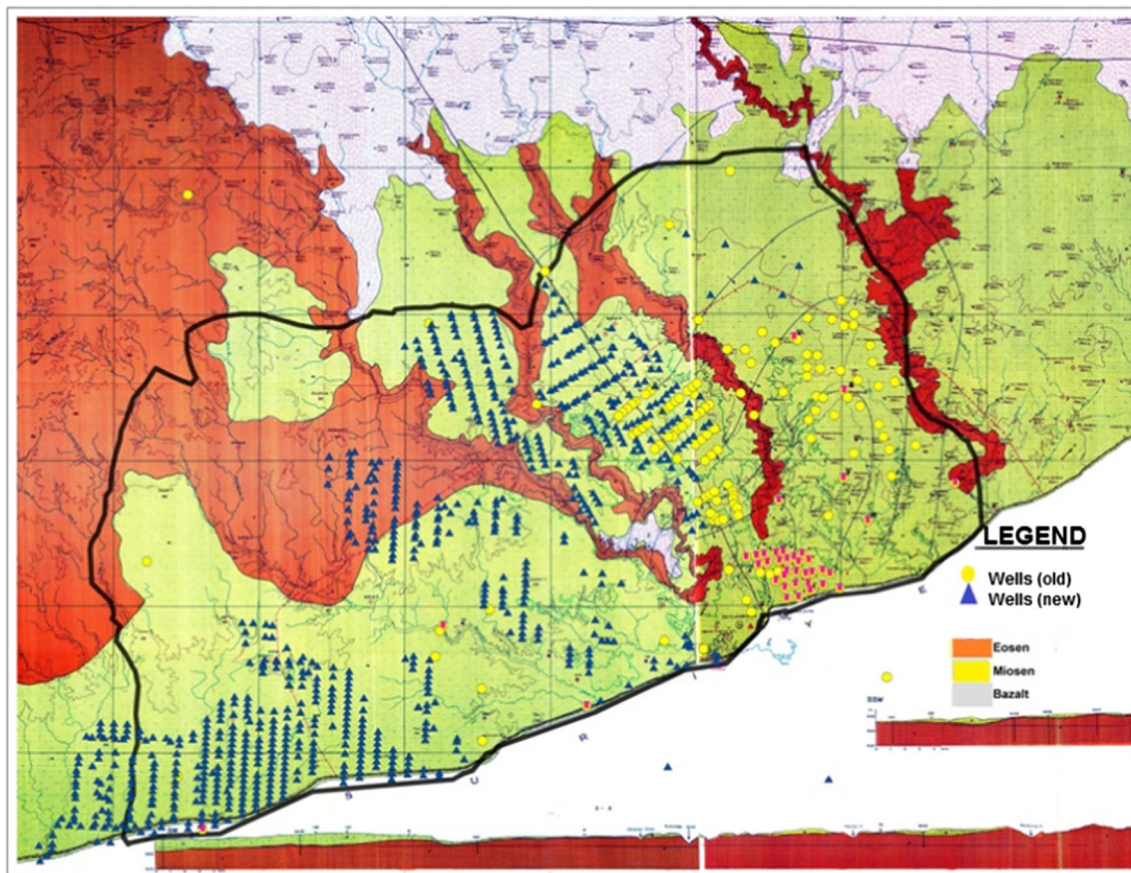
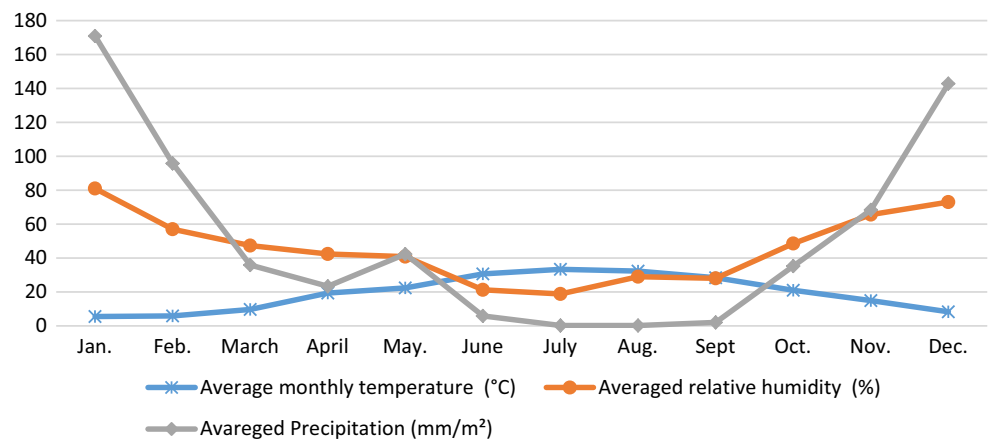


Fig. 2 Ceylanpinar Plain geological map and locations of wells in TIGEM

Fig. 3 Average monthly temperature, relative humidity, and precipitation of the study area for 2012 year



of 46 wells were sampled in the area (2012 March–2013 January) (Fig. 4). Coordinates of groundwater samples were measured with a Magellan Meridian Platinum handheld global positioning system (GPS) receiver. Groundwater samples were taken from a single depth. Sampling from different depths was not possible due to restrictions such as the depth of some wells, the lack of necessary equipment, and inconvenience of wells. The information (their depth, static water level, dynamic water level, elevation, and coordinates) of each well is given in Table 1. Plastic sample bottles were used for collecting groundwater samples, and samples were kept in the laboratory at the end of the day for analysis according to the APHA (1998), 1060 C sample storage, and preservation method. In our country, importance is given in determining the places sensitive to nitrate pollution caused by agriculture in underground waters, in line with regulations and directives. Therefore, this study is based on the nitrate parameter (MFA & FWA 2016). Nitrate measurements in groundwater samples were carried out using a Shimadzu ion chromatography (IC) instrument.

After the field studies and measurements were completed, groundwater nitrate pollution maps of the study area were created using Surfer Version 12.00 Golden Software, and the potential for contamination and areas vulnerable to contamination in the entire plain were determined. Topographic and geological maps of the study area were created by using ArcGIS ArcMap 10.1 software (ESRI 2016). A satellite image that was transferred to this software was digitized, and nitrate distribution maps were created by using observed nitrate values. By overlaying these maps with the location maps, it is possible to query the distribution of nitrate pollution and groundwater levels (in both two and three dimensions) at every sampling location. Since the sampling points were evenly distributed throughout the study area, the spatial variation of the values obtained from the point measurement results was mapped using a kriging interpolation technique. The

kriging interpolation technique was used to estimate nitrate concentrations at unmeasured points from the measured values. Kriging models are used in statistics to estimate the values of a given time and location or a number of mutual variables (Karatas et al. 2008; Yaprak and Arslan 2008).

Results and discussions

A groundwater static level map was obtained from static water level in the TIGEM archives (TIGEM 2012) and is shown in Fig. 5.

The depth of the groundwater in the plain is more than 50 m. In the year of 2010, approximately 1,000 new wells were opened for irrigation and intensive irrigation started in the plain. As in the Harran Plain adjacent to the Ceylanpinar Plain, there will be problems with salinization and drainage as well as agricultural problems due to excessive fertilizer usage. In addition, it is possible that nitrate contamination can be caused by excess nitrate levels, as can be seen from the groundwater level measurements that have been carried out for many years on both plains (Yeşilnacar et al. 2007, Yesilnacar et al.2008; Atasoy and Yesilnacar 2010; Yesilnacar and Yenigun 2011). Apart from agricultural activities, if we consider the vadose zone and there is an increase in the nitrate values here, it is up to a regular monitoring schedule that it can be detected in the groundwater. Our aim in this study is to determine how the irrigation and livestock activities cause changes in nitrate levels between seasons depending on precipitation and the distribution of nitrate in the area. As the study area is very large (2000 km²), you appreciate, this study takes a very long time to carry out with these frequent sampling points. According to the World Health Organization (WHO) guideline, leaching of nitrate from soils can cause significant increases in nitrogen concentrations in groundwater from predominantly anthropogenic rather than geogenic sources. Fertilizers, animal wastes, and urban and industrial

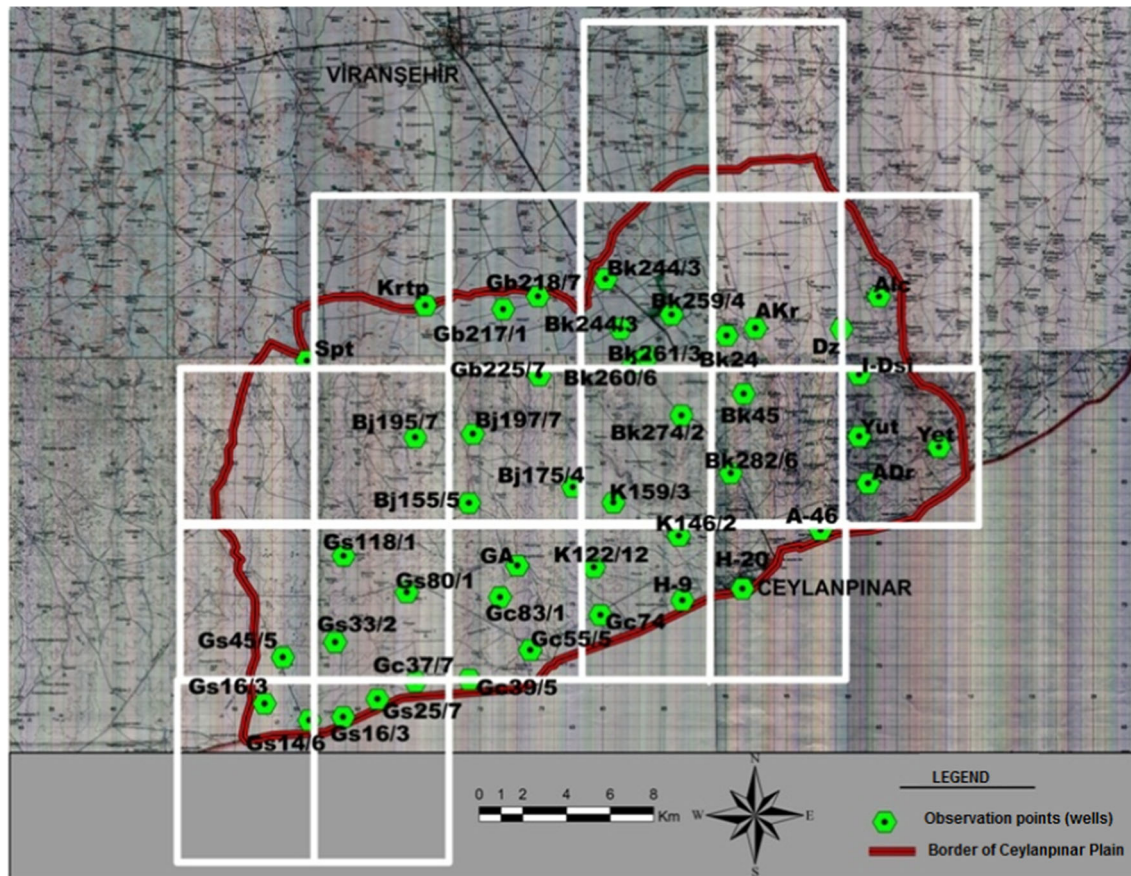


Fig. 4 Location and name of sampling points (wells) in the Ceylanpinar Plain

wastes are considered to be important sources of nitrate pollution in groundwater. Nitrate is often found in moderate concentrations in many natural aquatic environments. However, depending on regions where there is intense agricultural land use or where large amounts of wastewaters are discharged to ground, nitrate concentrations can increase to levels of environmental or public health concern in groundwater.

In this study, seasonal fluctuations in nitrate concentration also observed in groundwater samples from the wells. In general, low concentrations were measured in the wet seasons and high concentrations during the dry seasons as presented in the similar study (Kacaroglu 1997). Seasonal variations depend on the recharge conditions of the groundwater, time of agricultural activities, the changes in the concentration of the pollution sources, changes in meteorological conditions as precipitation and evaporation, groundwater level fluctuation, and changes in the amount of the groundwater abstracted from wells.

The highest nitrate concentration measured in this study was 60 mg/L in summer from the sampling point Gb218/7 located in the basin recharge area in the summer. Conversely, the lowest nitrate concentration measured in this

study was 0.2 mg/L in autumn from the sampling point of Gs45/5 located in basin discharge area in the fall season (Fig. 6).

In some previous studies, nitrate concentrations of up to 200 mg/L were measured in some wells (DSI 1970, 2011). Therefore, it can be said that the results obtained in this study have low values when compared with the highest nitrate concentrations measured in this study on the Viranşehir region in the northern part of the plain and in the southwestern part of the plain where intensive agriculture is carried out (Fig. 7).

Spatial distribution maps have been prepared to see the distribution of nitrate values at depths taken only once in a single study of groundwater samples within the study area boundary.

For the reasons stated above, the nitrate parameter was first taken into account, and the study was started. Later on, it was planned to evaluate and carry out the measurement of other water quality parameters with a larger study. Because of the huge study area and economic constraints, it was impossible to make measurements of other parameters related to water quality. However, the nitrate data obtained is important for the planned and future studies.

Table 1 Information about the groundwater sampling points (TIGEM 2012)

Name of wells	Depths (m)	Static levels (m)	Dynamic levels (m)	Elevations (m)	Universal Transverse Mercator (UTM) coordinates	
					X	Y
Gc74	175	47.00	–	391	579,801	4,074,127
Gc55/5	200	99.53	109.43	414	574,073	4,071,260
Gc39/5	175	105.00	106.58	432	569,081	4,068,878
Gc37/7	200	111.14	130.20	442	564,704	4,068,709
Gc83/1	175	97.00	99.15	421	571,611	4,075,571
Gc80/1	200	128.18	128.45	408	563,997	4,075,973
Gs45/5	225	101.90	104.00	437	553,882	4,070,676
Gs33/2	200	92.00	97.00	422	558,150	4,071,893
Gs13/9	254	92.60	94.90	423	552,398	4,066,888
Gs14/6	210	82.00	101.00	422	556,052	4,065,543
Gs16/3	200	82.00	86.82	417	558,802	4,065,801
Gs25/7	200	98.75	104.15	424	561,615	4,067,270
Gs118/1	200	132.50	133.30	459	558,833	4,078,946
Bj195/3	295	159.60	166.80	490	564,681	4,088,557
Bj155/5	295	150.30	169.90	488	569,079	4,083,231
Bj197/7	280	156.78	166.95	481	569,393	4,088,841
Bj175/4	270	129.80	153.00	446	577,554	4,084,541
H-9	110	40.50	40.60	356	586,476	4,075,319
H-20	110	29.95	34.80	352	591,384	4,076,264
A-46	120	27.10	27.47	371	597,755	4,081,049
Bk251/4	350	126.90	141.10	455	581,433	4,097,422
Bk244/3	350	111.80	197.40	460	580,209	4,101,470
Bk260/6	270	124.15	139.95	450	582,503	4,094,580
Bk261/3	225	121.70	141.50	452	583,620	4,095,199
Bk274/2	225	118.50	130.30	450	586,403	4,090,358
Bk282/6	215	83.50	83.80	412	590,440	4,085,675
Bk45	200	105.59	96.59	444	591,476	4,092,105
Bk24	200	122.49	117.73	459	590,101	4,096,856
Bk259/4	348	120.00	142.90	454	585,607	4,098,558
Gb218/7	350	129.20	146.20	432	574,702	4,100,047
Gb217/1	350	140.80	150.20	472	571,865	4,098,995
Gb225/7	355	138.70	145.00	466	574,819	4,093,598
K122/12	173	67.80	74.50	401	579,262	4,078,001
K146/2	120	48.00	49.70	391	586,190	4,080,582
K159/3	192	79.32	82.00	418	580,852	4,083,268
GA	–	–	–	402	573,025	4,078,139
AKr	–	–	–	450	582,407	4,095,822
Dz	–	–	–	449	599,476	4,097,398
Alc	270	–	–	450	602,505	4,100,033
Yut	200	–	–	411	600,909	4,088,634
I-Dsi	100	–	–	415	600,901	4,093,681
Yet	–	–	–	398	607,414	4,087,777
Adr	115	–	–	381	601,633	4,084,852
Krtp	–	–	–	385	565,511	4,099,296
Spt	230	–	–	513	555,854	4,094,812

Fig. 5 Groundwater flow contours for the Ceylanpınar Plain showing the sampling points

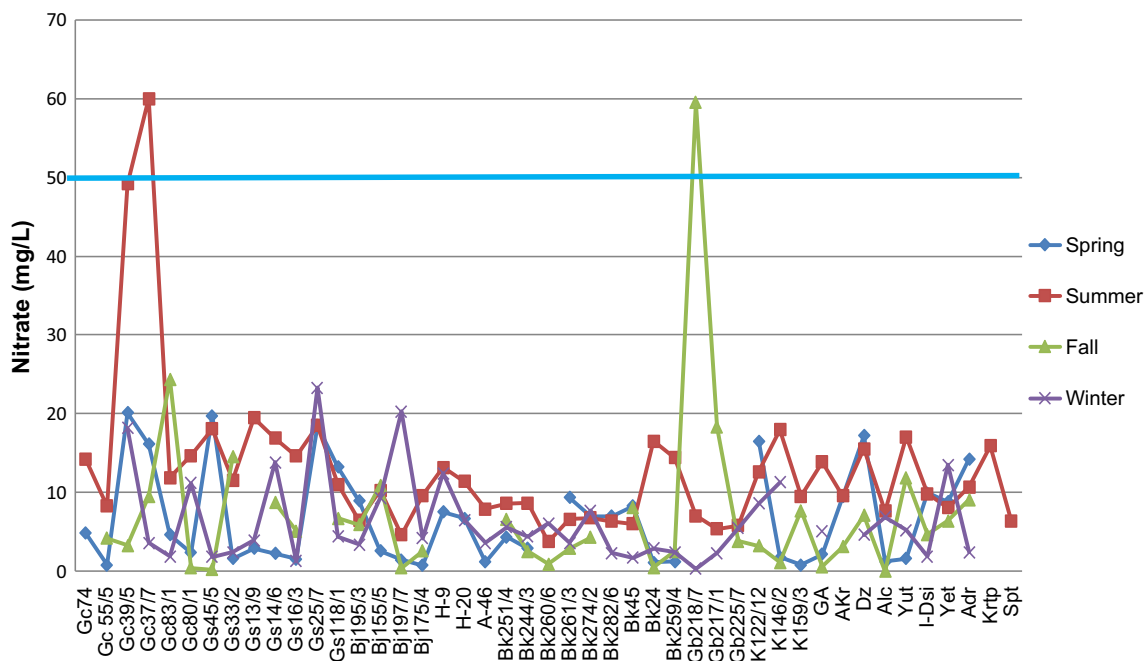
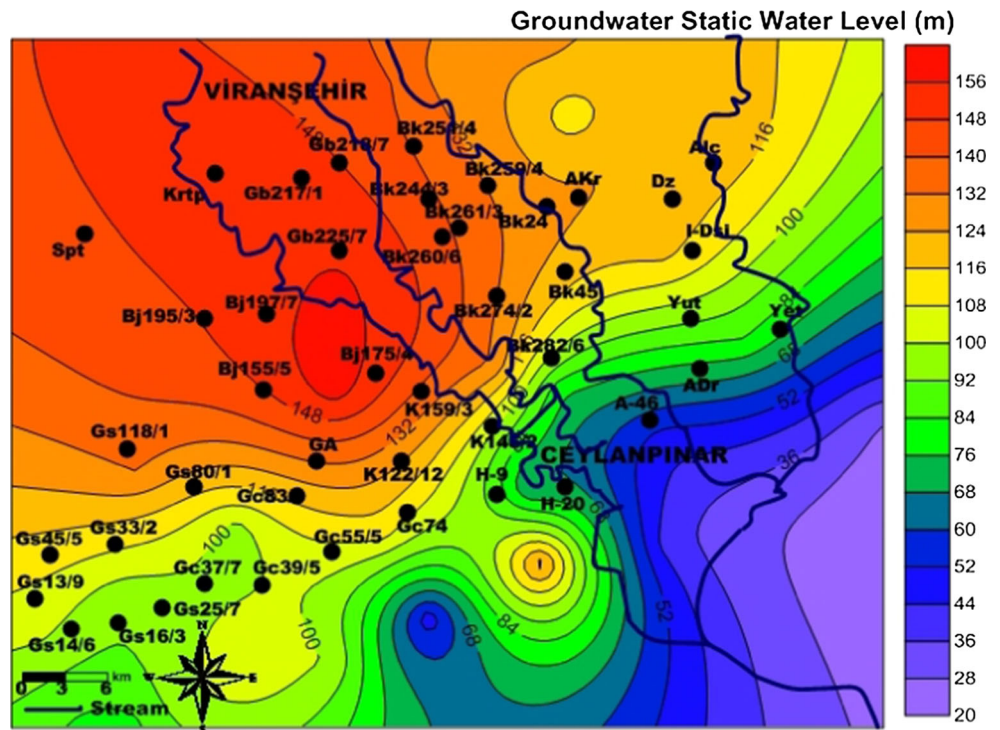


Fig. 6 Seasonal change of nitrate value according to groundwater sampling points

The distribution characteristics of observed nitrate values are presented in Fig. 8 as box plot form. The box plot is a standardized way of displaying the distribution of data sets on the basis of five key numbers: minimum, first quartile, median, third quartile, and maximum (CSBSJU 2017). In the box plot, the center of the distribution, the

spreading width and the extreme values of the data for observed seasonal nitrate values can be seen easily.

The water quality classification for irrigation purposes is given in Table 2, and the limit values for nitrate in national and international standards are given all together in Table 3.

Fig. 7 Averaged seasonal spatial distribution of nitrate values

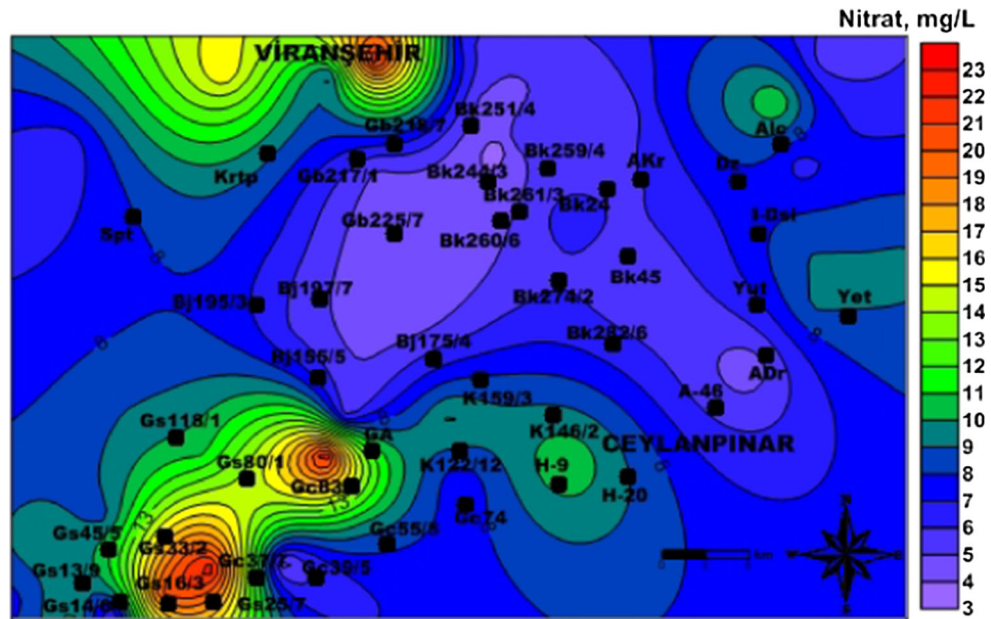
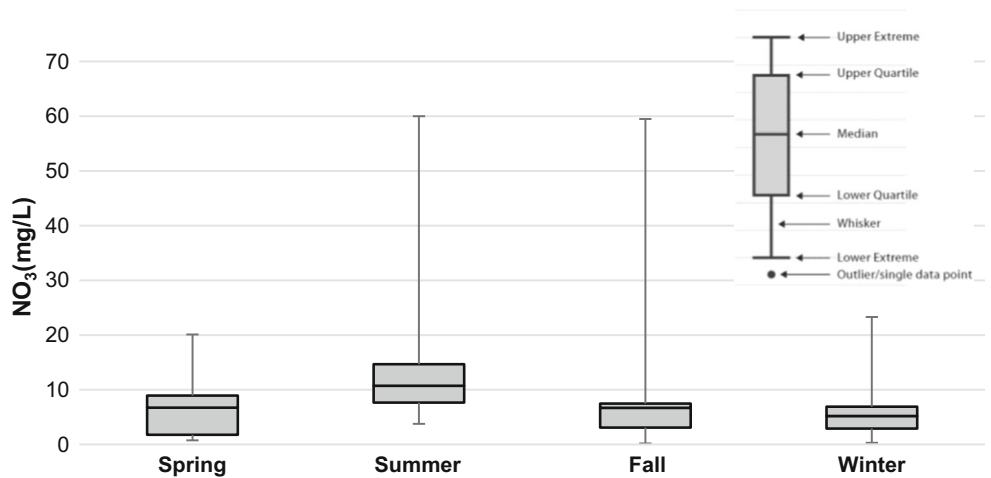


Fig. 8 Box plot of observed seasonal nitrate values



When the seasonal variations of NO_3 values are considered according to the standards and classifications in Table 3, sampling points except Gb218/7, Gc37/7, and Gc39/5 were given as the maximum permissible limit value. According to the criteria in Table 2, in the case of water quality classification for irrigation purpose according to seasonal variation and seasonal averages, it can be said that the above-mentioned three sampling points are in the

Table 2 Water quality classification for irrigation purposes (US EPA 2012)

	Classification		
	Low	Medium	High
NO_3 (mg/L)	< 20	20–130	> 130

“medium” class and that the remaining sites are in the “low” class. So it is very rare that the nitrate is contaminated at a depth of about 10–100 m from the surface.

However, where downstream flow components are important, NO_3 contamination can extend deeper into an aquifer over time. For example, in the deep wells in California, the NO_3 concentration at depth intervals of 240–400 m from the surface increased from 1 to 10–17 mg/L after a period of den 12 years. The fact that nitrate is high in groundwater can also be achieved with natural processes. In other words, it is stated that nitrate may be derived not from fertilizer but also from the oxidation and leaching of natural organic nitrogen from the soil. In addition, the contamination of shallow wells by nitrates and other chemical constituents may also be caused by faulty well construction. In cases where the filtrated upper portions of the wells are not properly insulated with

Table 3 Limit values for NO₃ in national and international standards

	Water Pollution Control Regulation (SKKY 2014)				Ministry of Health (2005)	Turkish Standardization Institute (TSE 2005)		WHO (2011)
	I	II	III	IV		Class 1 and 2, Type 1	Class 2 and Type 2	
NO ₃ (mg/L)	20	45	80	> 80	50	25	50	50

cement and clay, the contaminated water can easily infiltrate down the annular space of a poorly constructed well into an aquifer without attenuation within the soil profile (Freeze and Cherry 2003).

Conclusions

The Ceylanpınar Plain is underlain by a groundwater resource that is sufficiently large to provide 20% of Turkey's drinking water needs. In this study, seasonal measurements were made from 45 sampling points located in the deep aquifer with regular and periodic groundwater sampling for the first time in the plain. All data obtained were classified and evaluated according to standard values in terms of drinking water quality and irrigation water quality according to various national and international standards and classifications. In addition, seasonal average distribution maps were established to determine the extent and severity of nitrate contamination in groundwater beneath the Ceylanpınar Plain. According to the results obtained in this study, concentrations in two wells (Gc37/7 and Gb218/7) exceeded the recommended maximum limit value for drinking water (highest value is 60 mg/L). However, nitrate concentrations in groundwater elsewhere on the plain generally met the drinking water guideline value and are considered to be suitable for irrigation. In order to protect, the limited groundwater should be monitored frequently and suitable protection plans put in place to minimize the risk of nitrate leaching. There is pollution in the study area which is mainly caused by agricultural activities. Impact of agricultural activities on pollution can be achieved by minimizing the use of fertilizers and pesticides. For this reason, fertilizer application and proper irrigation should be done according to plant needs. Additionally, poorly constructed wells should be sealed by cementing to reduce the risk of nitrate leaching. In order to determine groundwater pollution sources and flow directions, dye tracer and isotope tests should be carried out and finally the long-term and more detailed monitoring of groundwater in this region, which is important in the context of transboundary groundwater.

It is also believed that for the first time in this study, the results obtained for this field will strengthen the

interpretations and benchmarks that will be the basis for the other studies in the literature.

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