Groundwater Pollution by Nitrate from Agricultural Fertilizers: The case of Menemen Basin (Aegean Region, Turkey)

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Abstract: Groundwater is an essential drinking water source in Menemen sub-basin of İzmir city, Turkey. The aim of this study was to investigate the groundwater contamination by nitrates of agricultural lands. For this purpose, we evaluated variations of groundwater pH, redox potential, electrical conductivity (EC), major anions (NO_3, Cl, SO_4, HCO_3 and CO_3) and cations (Na, K, Ca and Mg). A statistical correlation procedure and piper diagram for hydrogeochemistry of groundwater were also applied. Nitrate levels were found to be higher around agricultural areas. Also EC values and Cl^- were measured to be higher as proximity to coastal areas increased, indicating seawater intrusion. Agricultural activities and excessive freshwater withdrawal were shown to impair groundwater quality and quantity at Menemen sub-basin.

Keywords: Groundwater, nitrate, Menemen sub-basin, fertilizer.

1. INTRODUCTION

Agriculture is the largest industry in many parts of the world with adverse environmental effects. Groundwater pollution has emerged as a global environmental problem that is frequently encountered at regions of extensive agricultural industry. Excessive use of nitrogenous fertilizer is known to cause nitrate (NO_3^-) contamination in water sources. Although nitrate is a vital nutrient for plants, it causes health problems in humans and animals [1, 2]. Nitrogenous fertilizer is mainly used to increase the crop yields. While crops metabolize the major and minor nutrients that are provided by fertilizers for metabolic activities, excess nutrients reach water sources, causing contamination [3]. Solubility of nitrate in water is relatively high, being easily transferred from the vadose zone to saturated zone by infiltration. Therefore, excessive use of nitrogenous fertilizers results in nitrate accumulation in croplands and negatively effects the quality of soil, air, surface water and groundwater.

Nitrate is toxic to human beings in high concentration and may cause many serious diseases including gastric and renal cancer in adults, leukaemia, possible increased incidence of brain tumors, nasopharyngeal tumors in children and "blue baby syndrome" (methemoglobinemia) in infants [4, 5]. Therefore the World Health Organization and US Environmental Protection Agency recommended maximum contaminant levels (MCLs) of nitrate for drinking water as 11.3 mg/L NO_3-N and 10 mg/L NO_3, respectively [6, 7]. According to Turkish Legislations of 'Regulation Concerning Water Intended for Human Consumption', MCL of nitrate in drinking water is 11.3 mg/L NO_3-N [8].

In recent years, the contamination of groundwater resulting from immoderate use of fertilizers, industrial activities, uncontrolled wastewater discharge, atmospheric precipitation, manures and irrigation with sewage have become a serious worldwide problem [3, 9]. Natural and anthropogenic nitrate contamination has been reported in many parts of the world including, China, Brazil, Italy, USA, Iran, Egypt, India, Korea and Turkey [9, 10, 11, 12].Compositions of human-generated nitrate source to groundwater was determined in California. Human-generated nitrate sources in croplands were classified as; synthetic fertilizer (54%), animal manure (33%), irrigation source water (8%), and municipal effluents (2%) (California nitrate Project) [13].

In a study that was conducted in northeast Spain, researchers have measured nitrate concentrations as high as 590 mg/L [14]. Another study from Shimabara City, Japan studied the use of coprostanol's potential use in nitrate source identification [15]. They collected samples from 33 wells and 13 of the wells had nitrate concentrations that were above the Japanese standard of 10 mg/L. To date, numerous cases of agricultural nitrate pollution in groundwater have been reported in Turkey, namely Konya (0.4 -110 mg/L) [12], Kütahya-Köprüören basin (0.04-23 mg/L) [16], Antalya- Köprüçay irrigation district (0.01-454.08 mg/L) [17], Şanlıurfa- Harran plain (1.3-806 mg/L) [18].

Menemen sub-basin is located in west part of Gediz basin, which is located at West Anatolia, near the Aegean Sea. Menemen sub-basin has an irrigation area of 22.865 ha, with cotton and grapes being the major products [19]. Table 1 summarizes the variation of produced crops and the amount of nitrogen required for the growth of crops in Menemen sub-basin [20]. The croplands were classified in three groups; (i) cereals and other herbals, (ii) vegetables and fruit and, (iii) beverage and spice. The amount of crop production increased with the increasing population. Also, consumption of nitrogenous fertilizers has increased from 2.686 to 3.243 thousands tones, from 2011 to 2015 (Table 1).

Table 1. Total population, croplands and nitrogen consumption in Menemen sub- basin

Years	Total population	Cereals and other crops (decare)	Vegetable product (decare)	Furit, beverage and spice products (decare)	Consumption of N fertilizer (kilogram)
2011	134.889	109.602	38.930	38.374	2686800
2012	138.143	110.728	38.930	38.412	2704260
2013	142.836	118.290	38.930	61.695	3166935
2014	148.662	119.520	38.930	65.060	3235860
2015	156.974	117.806	41.679	65.060	3243138

It should also be noted that Menemen sub-basin, being a part of the Gediz basin, is water stressed and use of fertilizers is not accounted for. Population growth in Menemen has consequential effect on groundwater resource. An excessive growth of population can increase the crop demand, fertilizer use and as well as the demand for safe drinking water. Since Menemen sub-basin was limited in terms of high quality surface water resources, consumption of groundwater resources has increased with the increasing population. Increase of population, agricultural activities and depletion of groundwater may increase the significance level of groundwater pollution. Groundwater contamination is often concentrated in densely polluted areas. The accelerated use of agricultural fertilizers and other chemicals have affirmatively increased the crop yields. However, these modern agricultural practices had a negative impact on the quality of groundwater. The objectives of this paper are to determine and define the seasonal trends of nitrate concentration in the groundwater of the Menemen basin.

2. MATERIALS AND METHODS

2.1. Study area

The study site (Figure 1) was located in the Menemen plain (latitudes 38°34′48.22″–38°34′49.24″ N; longitudes 27°1′23.05″–27°1′24.14″ E), in the lower Gediz river basin in İzmir province. On the west side of the study area lies the Aegean Sea and on the west there is city of Manisa. Menemen sub-basin constitutes a large part of the Gediz basin. Total drinking water supply of Menemen and Foça regions and approximately 9% of the drinking water of İzmir city are provided from this sub-basin. Menemen plain is one of the most famous agricultural areas of Turkey. The total area of the plain is 69.449 ha of which 20.237 ha is currently used for agriculture.

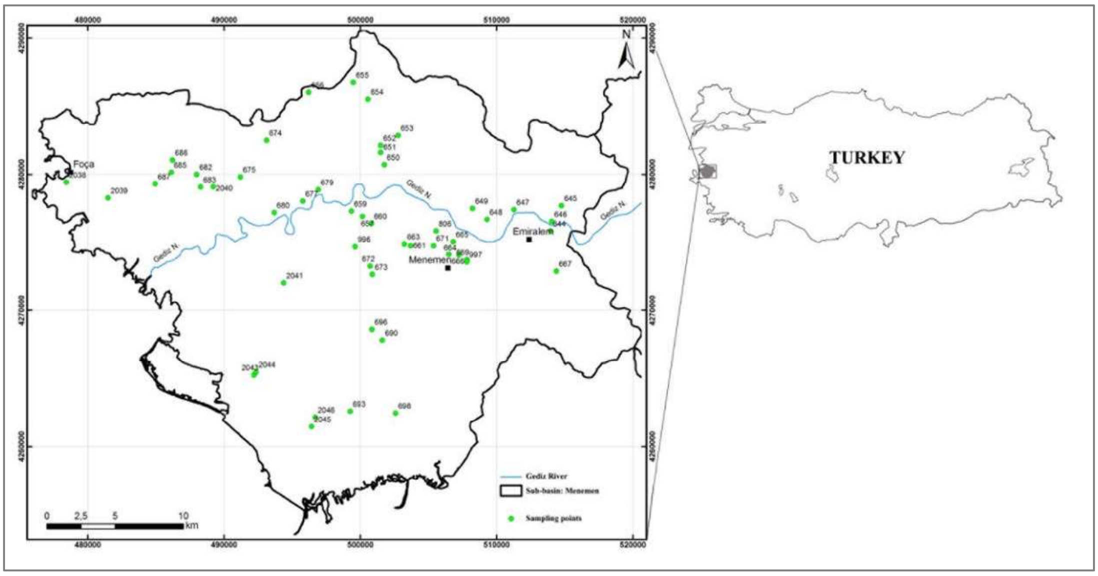

Figure 1. Sampling points in Menemen sub-basin.

Climate of the study area shows Mediterranean characteristics, with average annual rainfall being 540 mm. On the Menemen plain, climate can be characterized as semi-dry and hot during the summer season and rainy in the winter. The average maximum temperature is 33°C in August, and the average minimum temperature is 5°C in January. The Menemen plain consists of sand, gravel, and silt materials. These alluvium units have high porosity and permeability.

2.2. Sampling and analyses

Groundwater samples were collected from the wells mainly in agricultural areas of Menemen sub-basin, which were mainly used for drinking. Boundaries of study area and location of monitoring wells were shown in Fig.1. Groundwater quality parameters were measured by State Hydraulic Works (DSI) in 50 wells during April 2013 (P1), October 2013 (P2) and April 2014 (P3).

Temperature (T), redox potential, pH, electrical conductivity (EC), salinity and dissolved oxygen (DO) of samples were measured in situ with a portable Hach-Lange HQ40D multimeter, which was previously calibrated. Water samples were filtered through cellulose acetate fiber filters (Milipore, 45 μm fiber) and were collected in 50 mL labeled plastic bottles before anion and cation analysis. Concentrations of main cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (NO_3^-, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) were analyzed by ion chromatography (IC). All samples were analyzed in General Directorate of State Hydraulic Works Laboratories.

3. RESULTS and DISCUSSION

3.1. Hydrogeochemistry of Groundwater in Menemen Sub-basin

Physicochemical charactestics of groundwater in Menemen sub-basin were demonstrated in Figure 2. Atmospheric oxygen is the main source of DO in groundwater. DO concentration of groundwater is generally lower than the surface waters due to the limited oxygen source, decomposition of organic matter and microbial respiration. Conversely; in this study, measured values of DO were high in groundwater of Menemen basin. Determined DO concentrations of groundwater of Menemen basin at period 1, 2 and 3 were 4.76±2.21, 11.64±5.24, and 10.54±5.32, respectively. These results indicated that the microbial reduction of oxygen was ineffective and/or atmospheric oxygen was effectively transferred to groundwater. Synthetic fertilizers and animal manure are the main nitrate sources in croplands. Nitrate drains to the groundwater by precipitation and irrigation. Therefore, nitrate contamination is the main problem in croplands. Average concentrations of NO_3 at period 1, 2 and 3 were determined as 17.67±22.33, 15.72±18.47, and 14.56±16.86 ppm, respectively. However, NO_3 concentrations were higher than MCL in some wells. Drinking of high nitrate content drinking water without denitrification may occurs some health problems like methemoglobinemia. Nitrogenous compounds oxidized by nitrification bacteria with oxygen. In Menemen basin un-oxidized nitrogenous compounds, like NH_4^+ and NO_2^-, were determined above the MCL (both 0,5 mg/L). Inefficient microbial oxidation of these compounds or continuous sources of these might be the reason of this situation. Average concentration of sulfate at period 1, 2 and 3 were estimated as 89.47±99.34, 74.00±76.21, and 70.63±70.39 ppm, respectively. Sulfate concentrations of some wells were higher than the MCL of 250 mg/L.

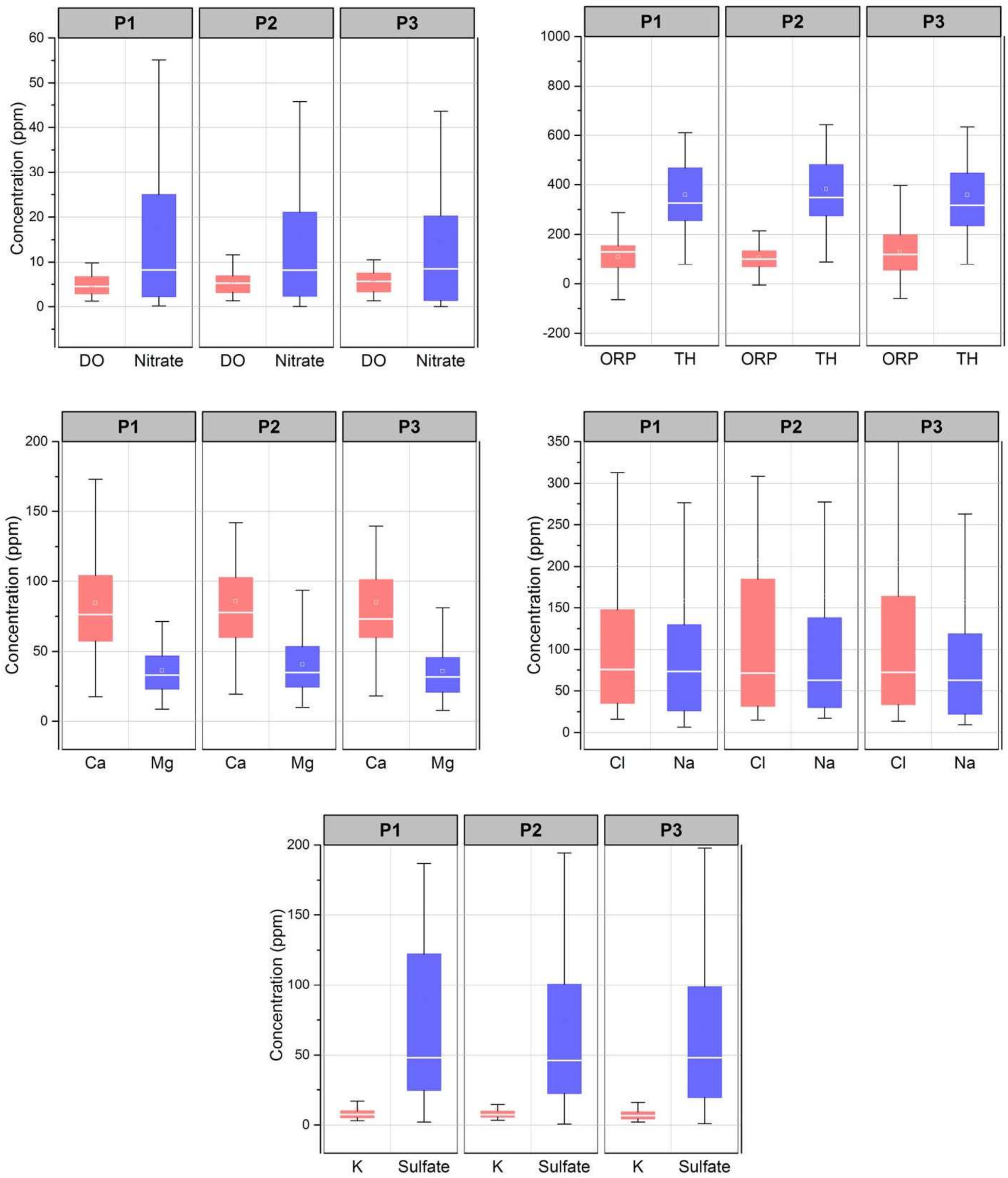

Figure 2. Physicochemical characteristics of groundwater in Menemen sub-basin.

The distribution of nitrate and EC values in groundwater of Menemen sub-basin was shown in Figure 3. Nitrate concentrations were measured to be higher in croplands, whereas nitrate concentrations in other regions were lower. These results indicated that the source of nitrate pollution of the groundwater was in fact the excessive use of nitrogenous fertilizer. On the contrary; EC values in groundwater of Menemen sub-basin were higher in coastal areas. Also EC values in the coastal area of Menemen sub-basin were increased from P1 to P3.

Seawater intrusion due to the excessive use of groundwater sources might be the explanation to elevated EC measurements.

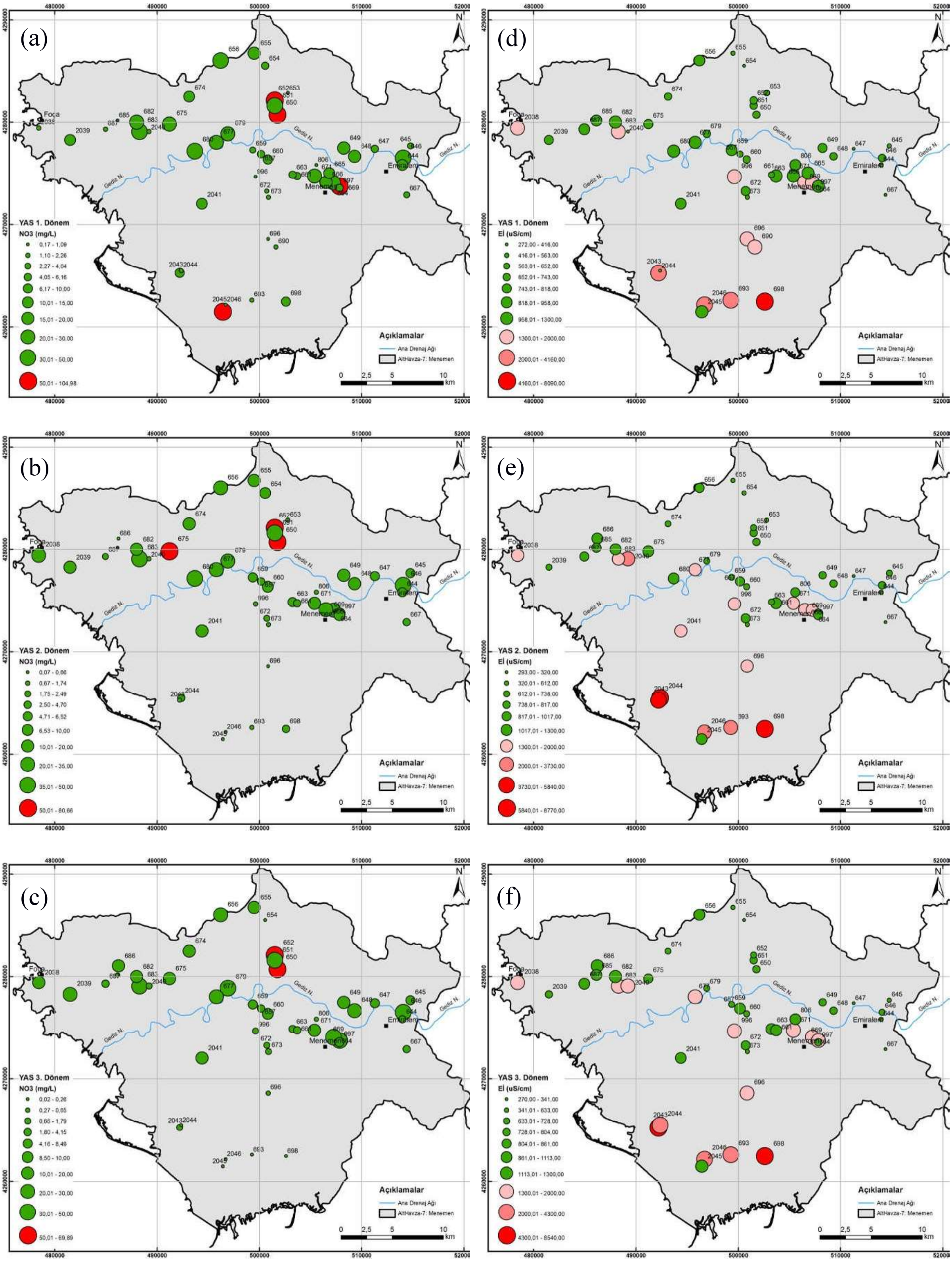

Figure 3. Distribution of NO_3 (a) at P1, (b) at P2, and (c) at P3 and EC values (d) at P1, (e) at P2, and (f) at P3 in Menemen sub-basin [21].

Piper three line diagrams were drawn by using OriginPro trial version software, in order to describe the groundwater geochemical characteristics in the Menemen basin (Figure 4). The piper diagram showed that the charactestics of groundwater were varible. Groundwater samples coming from the alluvial zone were rich in Ca^{2+}-Mg^{2+}-Na^{+}-HCO_3^- and Ca^{2+}-Na^{+}-Mg^{2+}-HCO_3—Cl^--SO_4^{2-} ions. It has been observed that the concentration of Cl^- increased in areas near the sea. Therefore, it was once again demoonstrated that the seawater intrusion has been actively occurring at coastal area. Similar results were obtained during all sampling periods. Overall the seawater intrusion threatens fresh water resources at Menemen sub-basin. The reason for this situation is; (i) over-irrigation of croplands and, (ii) high water consumption as an attempt to meet a portion of the increasing drinking water requirements of Izmir.

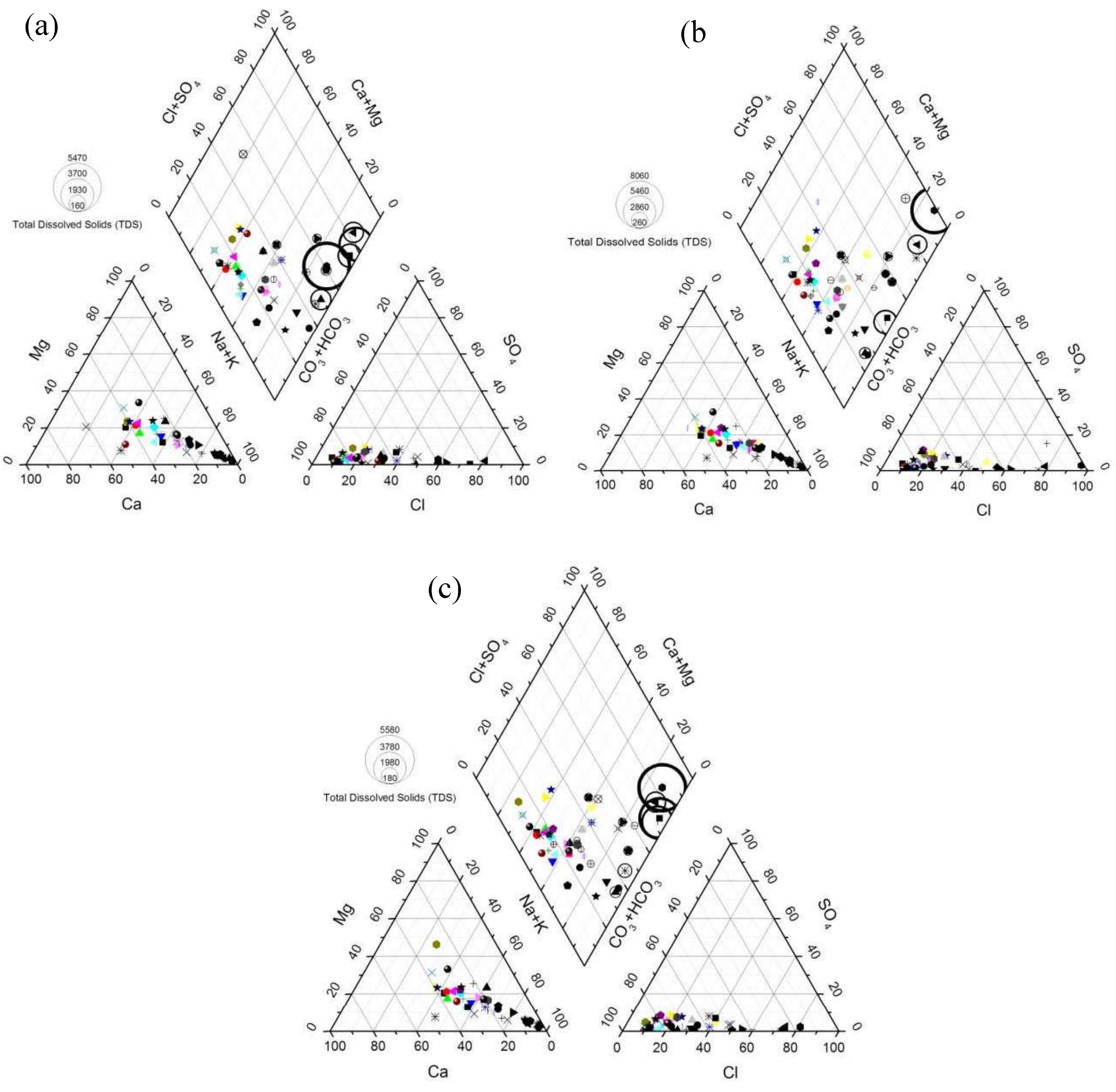

Figure 4. Piper diagrams of groundwater (a) April 2013, (b) October 2013, and (c) April 2014.

The coefficient of variation (CV) value expressing the relation between the mean and the distribution is very important. CV values of anions and cations were relatively high among sampling points. This phenomenon indicated that the physicochemical characteristics of groundwater in Menemen sub-basin and geological characteristics of Menemen sub-basin were variable (Table 2). Also, results from Piper diagram supported this observation.

Table 2. Coefficient of variation (CV) value of groundwater in Menemen sub-basin.

	T	pH	ORP	DO	EC	TH	SAR	Ca	Na	Cl	SO_4	NH_4	NO_3	NO_2	PO_4
P1	0.12	0.06	0.86	0.46	1.02	0.55	1.45	0.55	1.61	2.12	1.11	5.22	1.26	2.92	4.25
P2	0.11	0.04	1.09	0.45	1.13	0.54	1.42	0.57	1.65	1.97	1.03	5.22	1.17	4.24	6.93
P3	0.10	0.05	0.73	0.45	1.07	0.57	1.48	0.59	1.68	1.80	1.00	4.85	1.16	5.09	4.84

Linear correlation between parameters of groundwater was shown in Table 3. There were a strong positive relationship between EC values, cations and anions. Pearson correlation coefficient (r) values between EC and Na, TH, Ca, Mg, Cl, SO_4 were higher than 0.65. Also, r value between EC and SAR was estimated as 0.534. Since ions were electron carriers, the EC values increased with increasing the concentrations of ions. The r values of Mg^{2+} and Ca^{2+} in terms of total hardness (TH) were high than 0.9 due to the dominancy of Mg and Ca hardness. Beside it has been found that SO_4^{2-} and Cl^- were also highly correlated with TH.

Table 3. Pearson correlation coefficients (r) of groundwater parameters in Menemen basin

Parameter	pH	EC (µs/cm)	DO (mg/L)	Na (ppm)	K (ppm)	TH (mgCaCO₃/L)	Ca (ppm)	Mg (ppm)	SAR	HCO₃ (ppm)	Cl (ppm)	SO₄ (ppm)	NO₃ (ppm)
pH	1												
EC (µs/cm)	-0.054	1											
DO (mg/L)	-0.150	-0.282	1										
Na (ppm)	0.228	0.755	-0.317	1									
K (ppm)	0.284	0.398	-0.184	0.831	1								
TH (mgCaCO₃/L)	-0.353	0.756	-0.106	0.522	0.315	1							
Ca (ppm)	-0.443	0.675	-0.069	0.346	0.128	0.956	1						
Mg (ppm)	-0.187	0.761	-0.141	0.683	0.519	0.923	0.771	1					
SAR	0.404	0.534	-0.376	0.910	0.789	0.186	0.007	0.397	1				
HCO₃ (ppm)	0.306	0.096	-0.260	0.511	0.492	-0.072	-0.229	0.143	0.721	1			
Cl (ppm)	0.029	0.834	-0.196	0.879	0.694	0.763	0.640	0.823	0.620	0.085	1		
SO₄ (ppm)	-0.162	0.776	-0.377	0.535	0.253	0.650	0.613	0.610	0.399	0.130	0.534	1	
NO₃ (ppm)	-0.132	-0.077	0.129	-0.176	-0.247	0.037	0.115	-0.072	-0.088	-0.058	-0.180	0.023	1

4. CONCLUSION

In this study, the groundwater of the Menemen sub-basin has been investigated in terms of major anions and cation concentrations. The Menemen sub-basin is a region of intense agricultural activity despite its stressed water resources. Groundwater resources are used extensively for drinking purposes as well as for agricultural activities. However, excessive fertilizer use in agricultural activities and seawater intrusion caused by excessive water withdrawal results in deterioration of quality and quantity of groundwater resources. In this context, best water management policies and practices should be implemented in Menemen sub-basin.

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