

# Nitrate and heavy metal pollution resulting from agricultural activity: a case study from Eskipazar (Karabük, Turkey)

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**Abstract** In most countries of the world, groundwater and surface water are at a serious risk of pollution due to chemicals used in agricultural activities. The present study examined whether such a risk exists in Eskipazar, Turkey and the surrounding area, which covers a surface area of 696 km<sup>2</sup>. Nitrate pollution (NO<sub>3</sub>) was observed in waters discharging from the Örencik Formation, consisting of loose conglomerate, sandstone, mudstone, siltstone, and claystone levels; from the Yörük member of the Örencik Formation consisting of limestone, from areas where the Örencik Formation and Yörük member are located together, and from alluvium. Agricultural is practiced in these areas, and the waters discharging from these formations are used as drinking water and for domestic purposes. In particular, periodically varying levels of pollutants, such as B, Pb, Hg, Se were detected in wells drilled in Örencik Formation featuring a high NO<sub>3</sub> concentration. The concentrations of S, Cr, Mn, Fe, Cu, Zn, Ga, Br, Sr, Y, I, Ba, and U in these waters are also slightly higher than other cold waters in the study area. In addition to the NO<sub>3</sub> pollution, high levels of Ca and SO<sub>4</sub> pollution was observed at a well drilled in alluvium. In addition, some trace element concentrations identified in the wells drilled in the Örencik Formation were higher than the average values at geothermal and/or mineral springs in the study area. The study area has an adequate sewage system and has no sources of pollution, such as mineralization, industrial center, waste disposal area, etc. Therefore, it is believed that the main causes of NO<sub>3</sub> and trace element pollution are fertilizers and pesticides used in agricultural activities. Water–rock

interaction, usage period of fertilizers and pesticides, amount of precipitation, groundwater level, usage of elements by plants, mobility of elements, pH value of the environment, redox potential, adsorption/desorption, biochemical processes, etc. are thought to be the causes of the periodical variation of some trace element concentrations observed in these waters.

**Keywords** Groundwater pollution · Agricultural activity · Hydrogeology · Eskipazar (Karabük)

## Introduction

The suitability of physical, chemical and biological parameters of groundwater and surface water are highly significant in terms utilization by living organism. However, excess use of fertilizers and pesticides in agricultural activities to enhance productivity due to rapid population increase and development of technology threaten the groundwater and surface water on a large scale. Turkey, and most other countries, have soils and waters which have been polluted by fertilizers and pesticides used during agricultural activities. These waters and soils continue to be polluted, as the necessary precautions have not been taken. In this instance, it shows that there is an obvious risk for human in the future. A direct relationship was found between the levels of agricultural chemical usage and levels of groundwater and surface water pollution (Mikayilov and Acar 1998). Therefore, identifying the optimal levels of agricultural chemicals required by plants and appropriate regulation of substances with potentially harmful effects is of crucial importance.

Nitrate usually exists in surface and groundwaters organically and anthropogenically. Decomposed vegetable

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and animal wastes, leaching of solid wastes, domestic wastes, industrial waste waters (industries such as nitrogenous manure, nitric acid, etc.), fertilizers used in agriculture, irrigation return run-off, washing of atmospheric nitrogen by rainfall and effluent waters of waste water treatment facilities are the major sources of nitrate in surface and groundwaters (McNeely et al. 1979; Lawrance 1983; Ritter and Chirnside 1984; Hem 1985; Kaçaroğlu 1991, 1997).

Previous researchers have detected different types of pollution in groundwaters and surface water, which originate from different types of fertilizers and agricultural pesticides. Evaluation of these studies indicated that the range of chemicals in fertilizers and pesticides includes major ions, such as Na, Mg, Ca, K, Cl, SO<sub>4</sub>; nitrogen pollutants, such as NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>; and trace elements, such as As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, U, V, Zn, Fe, Mn, Br, Cs, Co, F, Sn, Sr, Te, Ba, B, S (Chu and Wong 1984; Wong 1990; Chen et al. 1997; Alloway 1990; Fergusson 1990; Herrero and Martin 1993; Mermut et al. 1996; Moon et al. 1999; Kaçaroğlu 1991, 1997; Alloway 1995; Kumbur et al. 2008; Sen 1996; Yüksel et al. 1997; Mikayilov and Acar 1998; Arslan and Akkaya 2001; Baba and Ayyıldız 2006; Eryurt and Sekin 2001; Böhlke 2002; Manta et al. 2002; Elhatip et al. 2003; Kara et al. 2004; Krishna and Govil 2004; McBride 2004; He et al. 2005; Fuge 2004; Atabey 2005a; Daniş 2005; Atabey 2005; Cangir 2005; Mühendis and Birligi 2006; Nouri et al. 2006; Polat et al. 2007; Guo et al. 2007; Kumbur et al. 2008; <http://www.gubretas.com.tr>, <http://www.tarimziraat.com/gubreleme>; <http://www.artesalimited.com>, etc.).

Increased use of fertilizer to improve agricultural productivity has also affected the quality of groundwater, including nitrate pollution in groundwaters (Smith et al. 1971; Schepers et al. 1983; Houzim et al. 1986; Kaçaroğlu 1991, 1997). In a study conducted in Eskişehir Plain, Kaçaroğlu (1991, 1997) stated that some wells in the plain displayed NH<sub>3</sub>, NO<sub>2</sub> and NO<sub>3</sub> pollution parameters as a result of agricultural activities. Sen (1996) suggested that the nitrate pollution in Bursa Nilüfer and Ayvalı Basins probably stemmed from the use of nitrate fertilizers (Baba and Ayyıldız 2006). Chen et al. (1997) found As, Cd, Cu and Zn pollution in agricultural soils in Hong Kong due to application of pesticide, animal manure and chemical fertilizer. Mikayilov and Acar (1998) discussed the amounts of different trace elements which may be present in some fertilizers and stated that the use of fertilizers is generally excessive, leading to the pollution of ground and surface water sources, soil, agricultural products and atmosphere. Furthermore, they indicated that the major source of heavy metal pollution in soil is organic fertilizers. In their studies carried out in the northeast China, Moon et al. (1999) mentioned the

presence of Cd, Pb, Ni and Cr in agricultural soils and adjacent river sediments.

During a study conducted in the Manisa region, Eryurt and Sekin (2001) found that the main source of the nitrate pollution in some wells was fertilizers and agricultural activities. Arslan and Akkaya (2001) reported that the source of high levels of nitrate pollution in groundwater in the vicinity of Urla and Menemen, located in the Aegean region, was fertilizers and pesticides used in agricultural activities (Baba and Ayyıldız 2006). Manta et al. (2002) stated that the use of garden fertilizers had an effect on Hg, Pb, Zn, Cu contents of green field and greenery park zone soils in Palermo, Italy. According to Böhlke (2002), agricultural activities have a direct or indirect effect on inorganic chemical concentrations in groundwaters, including NO<sub>3</sub>, N<sub>2</sub>, Cl, SO<sub>4</sub>, H, P, C, K, Mg, Ca, Sr, Ba, Ra and As. In studies carried out in Kayseri and its vicinity, Elhatip et al. (2003) indicated that agricultural activities are directly or indirectly effective on the concentrations of some elements in groundwater, such as NO<sub>3</sub>, N<sub>2</sub>, Cl, SO<sub>4</sub>, H, K, Mg, Ca, Fe, Cu, B, Pb and Zn. They reported that direct effects include the dissolution and transport of excess quantities of fertilizers with associated materials and hydrological alterations related to irrigation and drainage. Indirect effects may include changes in water–rock reactions in soils and aquifers caused by increased concentrations of dissolved oxidants, protons, and major ions. Krishna and Govil (2004) detected Pb, Cr, Cu, Zn, Sr, V pollution in the soil of the Pali industrial area of India, due to industrialization and intense agricultural activities, and stated that increasing amount of heavy metals in the soil may result in groundwater pollution. In studies performed in the Misli Plain of Niğde, Kara et al. (2004) reported Cd and Cu deposition in the soil as a result of fertilizers and pesticides used for potato farming. In a study carried out in southwest China, Guo et al. (2007) found an increasing amount of SO<sub>4</sub> and NO<sub>3</sub> in groundwater and river due to seasonal use of fertilizer. Kumbur et al. (2008) suggested that Cu, Mn, Cr, Ni and Mo levels detected in stream and irrigation channel samples from agricultural areas of Mersin province originated from agricultural pesticides.

From the findings of previous studies, it is clear that excessive use of fertilizers and pesticides during agricultural activities in different countries presents a significant pollution risk to groundwater and surface water. The waters in Eskipazar and the immediate vicinity were examined to determine the existence and scale of this pollution risk. NO<sub>3</sub> and some trace element pollutions identified in the groundwater are believed to originate from agricultural activities. The findings are in accordance with those in the literature. NO<sub>3</sub> pollution was observed in waters discharged from slightly cemented, conglomerate, sandstone, mudstone, siltstone and claystone levels and intensive

cracked, cavernous and fragile limestones on which agricultural activities are conducted. In addition, heavy metal pollution, such as B, Pb, Hg, Se and major ion pollutants, such as Na, Ca,  $\text{SO}_4$  as well as  $\text{NO}_3$  pollution were observed in wells drilled in clastic materials.

## Materials and methods

The present study was conducted between July 2007 and December 2008. Data were collected from 24 springs, 5 drilled wells, 7 geothermal and/or mineral spring and 2 river measurement points within the study area. The survey examined discharge ( $Q$ ), electrical conductivity (EC), pH, total dissolved solid (TDS), temperature ( $T$ ) and dissolved  $\text{CO}_2$  measurements. Chemical analyses of water samples included major anion–cation, F and nitrite ( $\text{NO}_2$ ), nitrate ( $\text{NO}_3$ ), ammonium ( $\text{NH}_4$ ) analysis, carried out using an ion chromatography device at the Water Chemistry Laboratory, Faculty of Engineering, Department of Geological Engineering, Cumhuriyet University (Turkey). Trace element analyses were performed in the Water Chemistry and Environmental Tritium Laboratory, Hacettepe University, Turkey.  $\text{HCO}_3$  and  $\text{CO}_3$  ions were analyzed using a titration method at the Water Chemistry Laboratory, Faculty of Engineering, Department of Geological Engineering, Cumhuriyet University (Turkey). As a result of these measurements, physical property, chemical composition, nitrogen contaminants and trace element concentrations of the samples were identified. Evaluation was carried out in accordance with the Turkish Standards for Water Intended for Human Consumption (TS 266 2005), as revised 29 April 2005, and; the World Health Organization regulations (WHO 2006).

## Geology

Eskipazar is located 35-km southwest of Karabük Province in the Eastern Black Sea Region of Turkey (Fig. 1). Figure 2 shows a geological–hydrogeological map of the study area and its vicinity.

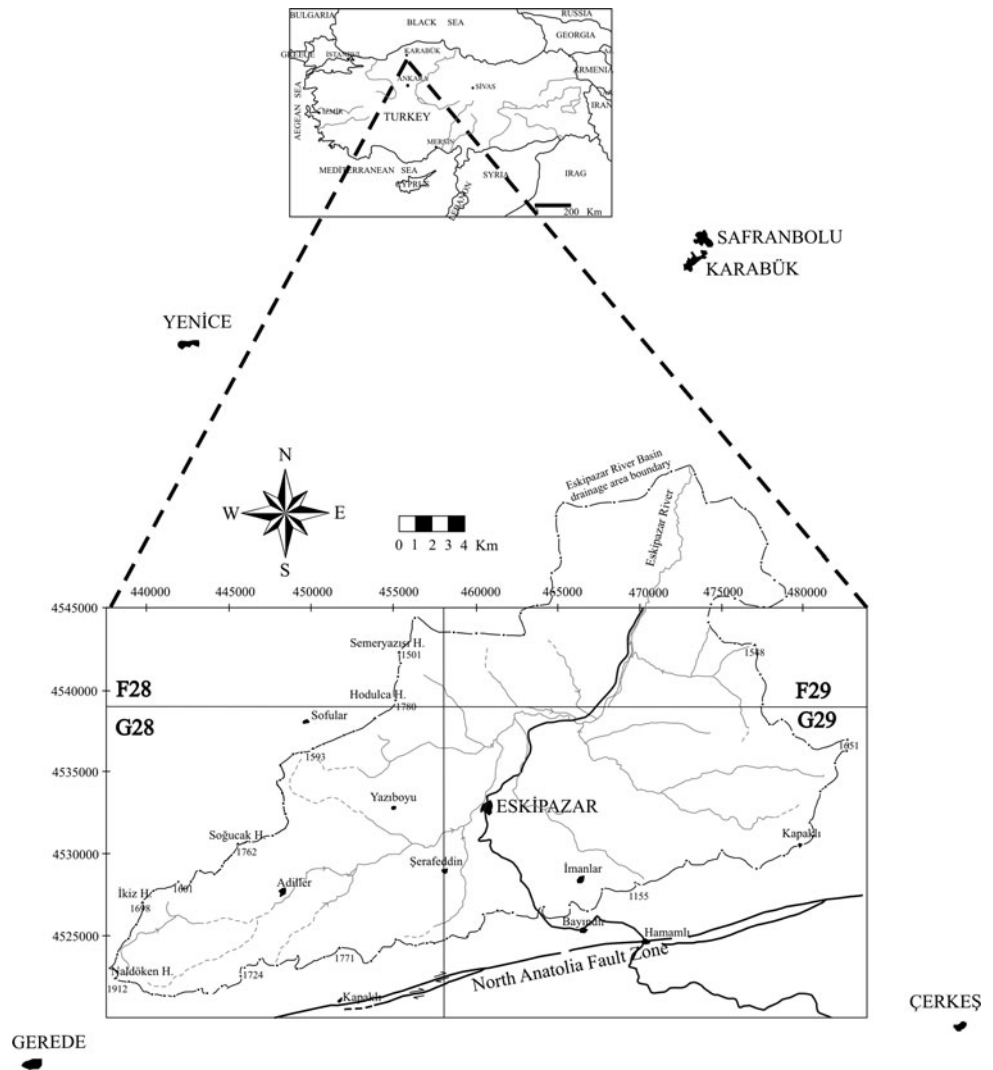
In this study, the geological studies of Şaroğlu et al. (1995), Tokay (1973), Alan and Aksay (2002), Timur and Aksay (2002), Sevin and Aksay (2002) and Bilginer et al. (2002) were used (with revision in some parts) and a geological map of the study area was produced at a scale of 1:100,000. The study area is located in a region where Western Pontides and Central Sakarya come together along the Northern Anatolian Fault Zone (NAFZ). The area covers units of the Western Pontide Zone, Armutlu-Almacık-Arkotdağı Zone and Sakarya Zone. In the northern part of the NAFZ, the base of the Western Pontide is made

up of Precambrian metamorphics (not outcropped in the study area) and crosscutting pre-Ordovician granitoid and volcanites (Bolu Granitoid). This base is overlain unconformably by Ereğli and Yılanlı Formations consisting of Paleozoic clastics and carbonates. On these units, the Ulus Formation composed of turbiditic clastics containing various Early Cretaceous olistoliths of the Western Pontide Zone, is unconformable, whereas the Abant Formation, which consists of Upper Campanian-Maestrichtien olistostrome and turbiditic clastics, is unconformable with the former formation. These units are covered by the Early Eocene Akveren Formation consisting of limestone and clastics; the Early Middle Eocene Kışlaköy Formation, comprising volcanic and, more commonly, clastics; the Safranbolu Formation, composed of Early Middle Eocene limestone constitutes a transitive coverage thereof. A subsection of the Sakarya Zone, in the south of the NAFZ, includes the Soğukçam Formation, consisting of Callovian-Aptian subpelagic cherty limestone and calciturbidites. This unit is conformably overlain by the Yenipazar Formation, featuring Albian-Maestrichtien turbiditic rocks. These units, located in the north and south of the NAFZ, are conformably overlain by Upper Miocene Özlü Basalt, the Pliocene Örencik Formation and Quaternary terrace, travertine and alluvium (Şaroğlu et al. 1995; Tokay 1973; Alan and Aksay 2002; Timur and Aksay 2002; Sevin and Aksay 2002 and Bilginer et al. 2002) (Fig. 2).

Within the study area, the Örencik Formation, comprises terrestrial conglomerate, sandstone, mudstone, siltstone and claystone alternations and lacustrine limestone. This formation mainly outcrops in the vicinity of Eskipazar county seat and ensures the recharge and discharge of the waters that  $\text{NO}_3$ , Na and some trace element pollutants were observed. Lacustrine limestone that is intricate with the formation in some sections was differentiated as the Yörük member. There are mudstones on the formation base. The existence of mudstone levels in the unit precipitated in a fluvial environment indicates a connection with the lake (Şaroğlu et al. 1995; Sevin and Aksay 2002). The formation is slightly cemented; in general, it is horizontal or close to horizontal. The formation obtained its gravels from the Abant Formation. The formation features type section of the well field with a thickness of 250–300 m (Şaroğlu et al. 1995) and the thickness of the Yörük member, which is primarily related with the formation, is 100–150 m. The limestone is highly jointed, brittle, decomposed and some sections are travertine-like and have karstic openings.

The Abant Formation (KTab), which is the source rock of the clastic levels of Örencik Formation, has a wide distribution in the study area and ensures the recharge and/or discharge of springs with various flow rates. The formation consists of marl, siltstone, sandstone, blocky

**Fig. 1** Location map of the study area and its vicinity



conglomerate and pelagic limestone of different ages (Şaroğlu et al. 1995; Tokay 1973; Alan and Aksay 2002; Timur and Aksay 2002; Sevin and Aksay 2002 and Bilginer et al. 2002). Limestones feature intensive cracks and karstic openings in places. No significant  $\text{NO}_3$  or trace element pollution was observed in waters discharged from this formation.

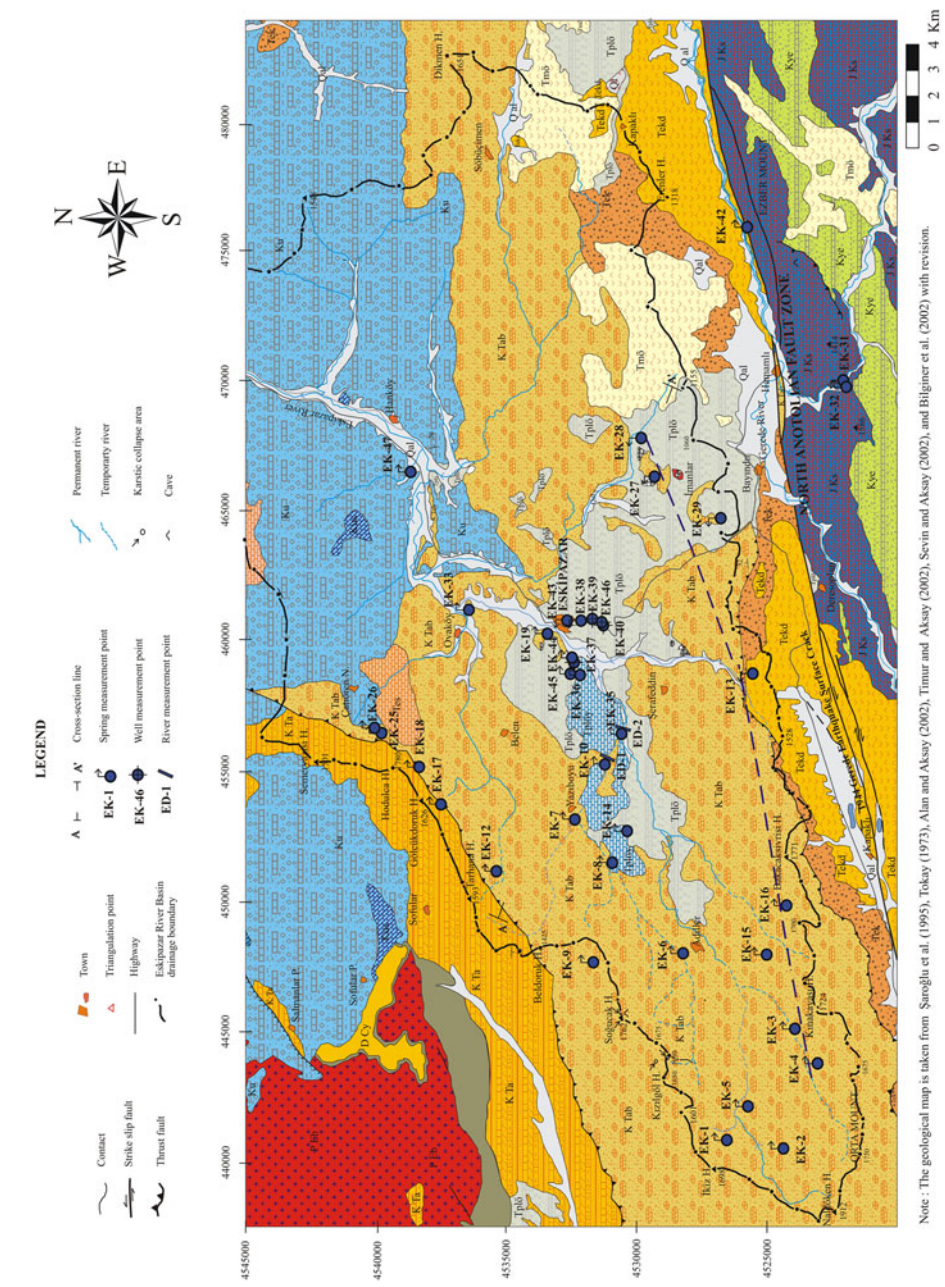
### Hydrogeology

The units indicating primary aquifer characteristics in the study area are the Abant Formation, Soğukçam Formation, Örencik Formation and alluviums. The Abant Formation consists of levels, indicating limestone and flysch characteristics; Soğukçam Formation consists of intensive fractured crystallized limestones; Örencik Formation consists of limestone and slightly cemented conglomerate, sandstone, mudstone, siltstone and claystone. The limestones of

Örencik Formation are lacustrine. Limestones are transitive from place to place with clastic level and the source rock of clastic levels is Abant Formation.

Fifteen springs with flow rates between 0.5 and 305 l/s and 5 geothermal and/or mineral springs with flow rates between 0.3 and 2.5 l/s are recharged and/or discharged from Abant Formation. Two springs with flow rates between 15 and 30 l/s and 1 geothermal spring with a flow rate of 0.3 l/s are recharged and/or discharged from Soğukçam Formation. Nine springs with flow rates between 0.15 and 3 l/s and four drilled wells with approximate flow rates between 0.1 and 1.5 l/s are recharged and/or discharged from the Örencik Formation. There is one drilled well with a flow of 1.2 l/s in the alluvium. As can be seen on the map in Fig. 2, the main flow direction of the Eskipazar River draining the waters in the study area is from SW to NE, and the flow direction of its tributaries are from NW to SE in the north section and from SE to NW in the south section. River gauging was

GEOLOGICAL LEGEND	
Qal	Alluvium
T	Terracine
Q <sub>1</sub>	Terrace filling
Tp1b	Ovech Formation: Loosely cemented conglomerate, sandstone, claystone
Tp1a	Ovech Formation-Yivik member: Limestone
Tim	Otda Basalt: Basalt, tuff
Tis	Safarabola Formation: Nummulitic limestone, marl
K1a	Kishakiy Formation: Conglomerate, sandstone, mudstone, limestone
K1b	Kishakiy Formation: Dolomitic volcanic member: Andesite, dacite, agglomerate
K1c	Alkaven Formation: Semi pelagic limestone, shale, chert, sandstone, conglomerate
K1d	Abant Formation: Block flysch
K1e	Yenipazar Formation: Sandstone, shale, limestone, tuff
K1f	Ulu Formation: sandstone, shale, conglomerate, limestone
K1g	Ulu Formation-Sunduk member: Limestone
J1a	Sohakcam Formation: Semi pelagic chert limestone, calcarenite
D1a	Yakali Formation: Limestone, dolomitic limestone, dolomite
O1a	Ergli Formation: Shale, sandstone, limestone
G1a	Bolu Granitoid: Granodiorite, tonalite, granite, gabbro, lamprophyre, aplite



Note : The geological map is taken from Şarıoğlu et al. (1995), Tokay (1973), Alan and Aksay (2002), Timur and Aksay (2002), Sevin and Aksay (2002), and Bilginer et al. (2002) with revision.

**Fig. 2** Geological map of the study area and its vicinity

performed at two points on the Eskipazar River during the field survey and the flows were gauged to be between 247 and 2,046 l/s.

Measurements and analyses were carried out during various periods, in such a way as to cover rainy and dry periods between July 2007 and December 2008. Spring, well and river measurement points are given in the geological–hydrogeological map in Fig. 2. In the study area, Örencik Formation and the alluvium are usually observed in slightly sloping regions. Agricultural activities are carried out in the large part of these areas. The areas are approximately 90 km<sup>2</sup> in size.

### NO<sub>3</sub> pollution

The presence of even 5–10 mg/l of nitrate in waters is an indicator that the waters are at a risk of pollution (McNeely et al. 1979; Şahinci 1991; Atabay 2005a, b). The level of nitrate in waters is of particular importance for use as drinking water. The usage of waters with a high nitrate level for drinking purpose reduces the oxygen carrying capacity of the blood and can lead to “blue disease” (methemoglobinaemia) in babies. Because babies younger than 6 months have relatively low levels of gastric acid, nitrate is reduced to nitrite, which reacts with hemoglobin in blood, forming methemoglobin. The blood loses its ability to carry oxygen and as a result breathing difficulties may be observed in babies (Lahl et al. 1983; WHO 1984b; Uslu and Türkman 1987; Kaçaroğlu 1991, 1997). Furthermore, nitrate intake may be readily converted into nitrite in the mouth or another body part where acidity is relatively low. Nitrite reacts with secondary and tertiary amines, alcohol ammonium bases and amides in an acidic environment and forms nitrosamines and nitrosamides. Recent studies have indicated that these compounds (especially dimethylnitrosamine and diethylnitrosamine) may have strong carcinogenic effects (WHO 1984b; Uslu and Türkman 1987). In addition, there are numerous findings that these compounds increase the risk of cancer in the digestive system and led to urinary tract diseases (Pontius 1993; Wasik et al. 2001; Polat et al. 2007). In addition, nitrate concentration in water above 500 mg/l causes inflammation of the bowel, digestive and urinary systems (Uslu and Türkman 1987).

In the study area, nitrate pollution is observed in the water discharging from the Örencik Formation, consisting of unconsolidated conglomerate, sandstone, mudstone, siltstone and claystone alternations; and areas where the Örencik Formation and Yörük member are tangled; where the Yörük member, comprises fractured-fissured and partly karstic limestone; and alluvium, where agricultural activities are carried out. Field measurement values and

chemical analysis of geothermal and/or mineral springs, springs discharging from the Abant Formation and rivers in the study area are given in Tables 1 and 2, respectively. Field measurement values and chemical analysis of waters that NO<sub>3</sub> pollution is observed are given in Tables 3 and 4, respectively.

As shown in Table 3, discharge of the springs and wells where nitrate pollution is observed vary between 0.15 and 3.5 l/s. EK-8, EK-10, EK-35 discharge from the Yörük member consisting of lacustrine limestone. EK-14, EK-36, EK-37, EK-44, and EK-45 discharge from the areas where the Yörük member and Örencik Formation, which comprises both limestone levels and loose conglomerate-sandstone levels, are tangled. EK-38, EK-39, EK-40, EK-43 and EK-46 discharge from the Örencik Formation consisting of conglomerate, sandstone, mudstone, siltstone and claystone. These waters are used as drinking water and domestic water. On the other hand, EK-47 is a well drilled in alluvium for drinking, domestic and irrigational purposes.

The wells located in the Örencik Formation were drilled in ancient years and there are no regular well logs. Nevertheless, in accordance with the information obtained from well owners and drilling companies, it is understood that the drilled lithologies of EK-40 (depth 37 m), EK-46 well (depth 40 m), and EK-39 well (depth 96 m) consist of an intercalation of poorly cemented coarse conglomerate, sandstone, siltstone and claystone. However, it is understood that the clayed levels at lower altitudes in EK-39 are more extensive and thicker, when compared with other wells. The fact that the flow rate of EK-40 and EK-46 wells range between 0.5 and 1.55 l/s and that the flow rate of EK-39 well is approximately 0.1 l/s (occasionally dry) supports this situation. The existence of lithologies of different thicknesses in wells that are close to each other indicates that the lithology is irregular.

NO<sub>3</sub> pollution is highest in the wells drilled in the clastic levels of the Örencik Formation (EK-39, EK-40, EK-46), at medium levels in wells and in springs discharging from areas featuring clastic and limestone levels of the Örencik Formation and drilled wells in alluvium, and at low levels in springs of the formation discharging from mainly limestone levels (Table 4). NO<sub>3</sub> concentration contours are given in Fig. 3. It is clear that NO<sub>3</sub> pollution is concentrated in Eskipazar and its vicinity, where intensive agricultural activities are carried out.

Nitrate (NO<sub>3</sub>) values of the springs and wells in the study area range between 0 and 135.2 mg/l. Cezaevi Well (EK-39) with a value of 57.7 mg/l, Yorgalar Well (EK-4) with a range of 121.5–135.2 mg/l, and Kurs Well (EK-46) with a range of 115.6–130.2 mg/l, exceed the Turkish Standards for Water Intended for Human Consumption (TS 266 2005) and the World Health Organization (WHO

**Table 1** Field measurement values of the springs discharging from Abant Formation, geothermal and/or mineral springs and rivers in which no nitrate pollution are observed

Water type	Elevation (m)	EC ( $\mu\text{S}/\text{cm}$ )			TDS (mg/l)			pH			Temperature ( $^{\circ}\text{C}$ )			Discharge (l/s)				
		Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average		
Springs	1,708	667	1,253	794	351	509	426	186	270	7.40	7.40	7.1	19	6.5	11.19	305	0.5	55.6
Geothermal and/or mineral springs	1,503	941	1,203	4,370	682	3,828	2,360	363	2,060	7.04	7.04	6.18	35	9.9	28.45	~0.3	~3	~1.72
Rivers	858	824	841	431	353	395	229	188	210	8.13	8.13	7.75	18.2	13.9	16.2	2,046	247	817

**Table 2** Chemical analysis results of the springs discharging from Abant Formation, geothermal and/or mineral springs and rivers in which no nitrate pollution are observed ( $\text{NO}_3$  mg/l, others meq/l)

Water type	Na		K		Mg		Ca	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Springs	0.99	0.05	0.2	0.08	2.33	0.22	0.7	5.5
Geothermal and/or mineral springs	32.25	0.38	23	2.32	21.11	1.83	10.9	16.9
Rivers	0.23	0.14	0.18	0.05	0.99	0.23	0.71	3.35
Water type	$\text{CO}_3 + \text{HCO}_3$		Cl		$\text{NO}_3$		$\text{SO}_4$	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Springs	6.45	2.70	4.7	0.24	3.72	<DL	0.62	0.76
Geothermal and/or mineral springs	46	5.85	38.1	6.0	<DL	<DL	<DL	2.74
Rivers	3.9	3.05	3.6	0.08	0.62	<DL	0.002	0.17
DL detection limit								

**Table 3** Field measurement values of the waters discharging from Örencik Formation and alluvium in which nitrate pollution are observed

Spring-Well no.	Spring-Well name	Formation-Member Name	Elevation (m)	Longitude	Latitude	Date	EC (µS/cm)	TDS (mg/l)	pH	Temperature (°C)	Discharge (l/s)
EK-8	Gökdere Spring	Yörük member	1,212	45,1,384	45,30867	24.07.2007	507	270	7.06	9.3	1
EK-10	Köpekler Çay Spring	Yörük member	875	45,5253	4,531,175	24.07.2007	506	269	7.09	13.4	2.5
EK-10	Köpekler Çay Spring	Yörük member	875	45,5253	4,531,175	20.04.2008	460	245	7.06	12.5	3.5
EK-10	Köpekler Çay Spring	Yörük member	875	45,5253	4,531,175	15.08.2008	476	254	7.37	12.6	3.25
EK-14	Çağlayan Spring	Örencik Form.-Yörük mem.	1,103	4,52,694	4,530,154	25.07.2007	440	235	7.22	11.2	1.8
EK-35	Hacıahmetler Mill Spring	Yörük member	826	4,56,525	4,530,473	28.07.2007	462	246	7.19	12.1	1
EK-36	Bahçepınar Spring (1)	Örencik Form.-Yörük mem.	778	4,59,203	4,532,200	20.08.2007	523	279	7.42	15.0	2.5
EK-36	Bahçepınar Spring (1)	Örencik Form.-Yörük mem.	778	4,59,203	4,532,200	19.10.2007	537	286	7.57	14.2	2
EK-36	Bahçepınar Spring (2)	Örencik Form.-Yörük mem.	789	4,58,656	4,531,995	19.10.2007	540	287	7.23	13.9	2
EK-36	Bahçepınar Spring (3)	Örencik Form.-Yörük mem.	767	4,59,305	4,53,2480	18.10.2007	572	280	7.60	(-)	(-)
EK-36	Bahçepınar Kaynağı (2)	Örencik Form.-Yörük mem.	767	4,59,305	4,53,2480	21.04.2008	497	264	7.05	13.6	3
EK-36	Bahçepınar Kaynağı (2)	Örencik Form.-Yörük mem.	767	4,59,305	4,53,2480	11.08.2008	502	268	7.25	14.7	2.5
EK-36	Bahçepınar Spring (1)	Örencik Form.-Yörük mem.	767	4,59,305	4,53,2480	09.12.2008	503	268	7.55	13	(-)
EK-37	Bahçepınar Well	Örencik Form.-Yörük mem.(well depth 30 m)	774	4,59,112	4,532,128	20.08.2007	658	350	7.04	15.9	0.75
EK-37	Bahçepınar Well	Örencik Form.-Yörük mem.(well depth 30 m)	774	4,59,112	4,532,128	04.10.2008	730	357	7.10	16.0	0.6
EK-38	Pazarbaşı Fountain	Örencik Form.	775	4,60,721	4,532,478	28.07.2007	790	420	7.15	16.5	0.4
EK-38	Pazarbaşı Fountain	Örencik Form.	775	4,60,721	4,532,478	21.04.2008	795	422	7.99	12.4	1
EK-38	Pazarbaşı Fountain	Örencik Form.	775	4,60,721	4,532,478	06.08.2008	793	421	7.15	16.8	0.4
EK-39	Cezaevi Well	Örencik Form.(well depth: 96 m)	816	4,60,846	4,531,474	16.10.2007	2,230	1,190	6.83	14.9	(-)
EK-39	Cezaevi Well	Örencik Form.(well depth: 96 m)	816	4,60,846	4,531,474	21.04.2008	2,660	1,420	6.66	18.9	(-)
EK-39	Cezaevi Well (4)	Örencik Form.(well depth: 96 m)	816	4,60,846	4,531,474	06.08.2008	1,090	580	7.47	18.3	(-)
EK-39	Cezaevi Well	Örencik Form.(well depth: 96 m)	816	4,60,846	4,531,474	06.12.2008	1,270	680	7.29	18.2	(-)
EK-40	Yorgalar Well	Örencik Form. (well depth: 37 m)	855	4,60,461	4,531,085	16.10.2007	1,130	600	7.16	13.4	0.5
EK-40	Yorgalar Well	Örencik Form. (well depth: 37 m)	855	4,60,461	4,531,085	21.04.2008	1,100	590	7.01	13.2	1.3
EK-40	Yorgalar Well	Örencik Form. (well depth: 37 m)	855	4,60,461	4,531,085	06.08.2008	1,160	610	7.20	14.3	1.4
EK-40	Yorgalar Well	Örencik Form. (well depth: 37 m)	855	4,60,461	4,531,085	06.12.2008	1,150	610	7.19	12.6	1.4
EK-43	Bahçelievler Fountain	Örencik Form.	758	4,60,728	4,532,624	06.08.2008	930	490	7.20	20.3	0.25
EK-44	Bahçepınar Pool Spring	Örencik Form.-Yörük mem.	767	4,59,310	4,532,485	11.08.2008	630	335	6.96	14.3	0.25
EK-45	Kölepinarı Fountain	Örencik Form.-Yörük mem.	812	4,58,716	4,532,576	11.08.2008	693	347	7.21	19.7	0.15
EK-46	Kurs Well	Örencik Form.(well depth: 40 m)	845	4,60,698	4,531,314	06.08.2008	1,006	560	7.34	14.4	1.5
EK-46	Kurs Well	Örencik Form.(well depth: 40 m)	845	4,60,698	4,531,314	06.12.2008	1,050	560	7.47	13.4	1.55



**Table 3** continued

Spring-Well no.	Spring-Well name	Formation-Member Name	Elevation (m)	Longitude	Latitude	Date	EC (µS/cm)	TDS (mg/l)	pH	Temperature (°C)	Discharge (l/s)
EK-46	Kurs Well (5)	Örencik Form.(well depth: 40 m)	845	4,60,698	4,531,314	06.08.2008	779	414	7.21	23.9	(-)
EK-46	Kurs Well	Örencik Form.(well depth: 40 m)	845	4,60,698	4,531,314	06.12.2008	103	54	6.7	14.9	(-)
EK-47	Üçevler Well	Alluvium (well depth: 72 m)	610	4,66,501	4,538,621	12.08.2008	3,000	1,640	6.94	15.9	1.2

(-) marking indicates that no measurement was made for the value in question

1 water reservoir, 2 catchment, 3 mains water, 4 mixing with city water, 5 after purification unit

2006) limit value of 50 mg/l. EK-39 is a well belonging to an open prison located in the region; the water is used for drinking, domestic and irrigational purposes, sometimes directly and sometimes by being mixed with city water by the prison officials and prisoners. EK-40 is privately owned and is sometimes used for drinking and domestic purposes. EK-46 is owned by a theological study center and the water is used by course attendees and students for drinking and domestic purposes, after passing through a purification unit. As it is seen in Table 4, the purification unit is not operated systematically and the necessary controls are not performed properly. Parts, such as filters, cartridges, etc. become dirty and are not replaced on schedule. As a result, the purification system can neither purify the water sufficiently nor reduce nitrates and other ions. Thus, nitrate levels at EK-46 considerably exceed the limit stipulated in the regulations. The nitrate values of Cezaevi Well (EK-39), Bahçepınar Spring (EK-36), Bahçepınar Well (EK-37), Pazarbaşı Fountain (EK-38) and Köpekler Çay Spring (EK-10) range between 32.9 and 57.7, 30.4 and 43.4, 21.1 and 36, 29.1 and 34.8, and 7.44 and 11.2 mg/l, respectively. The nitrate values of Kölepinar Fountain (EK-45), Bahçepınar Pool Spring (EK-44), Üçevler Well (EK-47), Bahçelievler Fountain (EK-43), and Gökdere Spring (EK-8) are 32.2, 27.3, 27.3, 24.2 and 12.4 mg/l, respectively. The majority of these waters are used continuously for drinking and domestic purposes without undergoing any operation such as purification and/or chlorination.

Nitrite and nitrate are inorganic ions produced during various stages of the nitrogen cycle. Nitrate is the predominant ion in well-oxygenated water, because of the rapid oxidation of nitrite. Nitrate is used mainly in inorganic fertilizers. Therefore, its concentration in groundwater and surface water is normally low; nitrate can reach high levels as a result of leaching or runoff from agricultural land or contamination by human or animal wastes (Ekmekçi 2005). Owing to its negative charge (NO<sub>3</sub><sup>-</sup>) is not held in the soil, the majority being leached to the saturated zone (Canter 1996; Novais et al. 2008).

It was found that nitrate pollution in waters in the study area comprises NO<sub>3</sub>, and NO<sub>2</sub> and NH<sub>3</sub> are absent or below detectable levels. This indicates that the pollution is not actual and that the areas from which the waters recharge are oxygen rich and feature an oxidizing environment, in terms of redox potential, that is sufficient to perform transition of NH<sub>3</sub> to NO<sub>3</sub> (NH<sub>4</sub><sup>+</sup> + 2O<sub>2</sub> = NO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O). This indicates that the irrigation water, rain and snow water do not reach the groundwater rapidly and therefore, the permeability of recharge areas of the waters is not very high. This indicates that the levels of mudstone, siltstone, and claystone cause a reduction in the permeability of loose conglomerate and sandstone levels in the Örencik Formation.

**Table 4** Chemical analysis results of the waters discharging from Örencik Formation and alluvium in which nitrate pollution are observed (NO<sub>3</sub> mg/l, others meq/l)

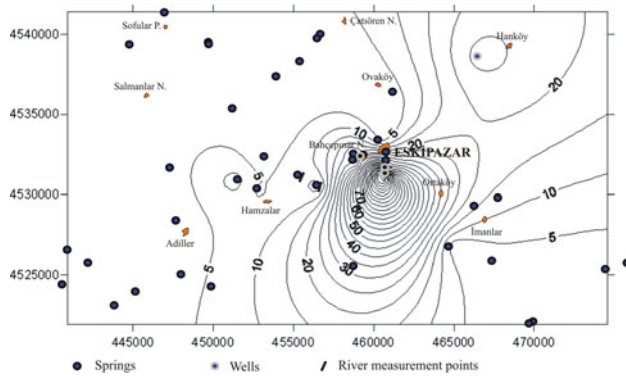
Spring-well no	Spring-well name	Date	EC (μS/cm)	Na	K	Mg	Ca	HCO <sub>3</sub>	F	Cl	NO <sub>3</sub>	SO <sub>4</sub>
EK-8	Gökdere Spring	24.07.2007	507	0.15	0.08	0.35	3.47	3.50	<DL	0.07	12.4	0.13
EK-10	Köpekler Çay Spring	24.07.2007	506	0.24	0.08	0.98	4.22	4.70	<DL	0.13	11.2	0.17
EK-10	Köpekler Çay Spring	20.04.2008	460	0.26	0.08	0.90	3.64	4.05	<DL	0.12	9.3	0.16
EK-10	Köpekler Çay Spring	15.08.2008	476	0.19	0.06	0.83	3.99	4.25	<DL	0.10	7.4	0.16
EK-14	Çağlayan Spring	25.07.2007	440	0.09	0.03	0.18	3.55	3.35	<DL	0.02	4.3	0.05
EK-35	Hacıahmetler Mill Spring	28.07.2007	462	0.32	0.06	1.23	3.14	4.20	<DL	0.09	1.2	0.30
EK-36	Bahçepınar Spring (1)	20.08.2007	523	0.59	0.08	0.95	4.02	4.45	0.003	0.29	37.8	0.24
EK-36	Bahçepınar Spring (1)	19.10.2007	537	0.63	0.09	0.96	4.08	4.10	0.012	0.31	43.4	0.26
EK-36	Bahçepınar Spring (2)	19.10.2007	540	0.60	0.08	0.95	4.03	4.00	0.000	0.30	43.4	0.25
EK-36	Bahçepınar Spring (3)	18.10.2007	572	0.62	0.08	0.95	3.95	4.00	0.000	0.30	43.4	0.25
EK-36	Bahçepınar Spring (2)	21.04.2008	497	0.06	0.09	0.94	3.93	3.75	0.005	0.26	31	0.24
EK-36	Bahçepınar Spring (2)	11.08.2008	502	0.59	0.07	0.85	3.91	4.00	0.026	0.28	33.5	0.26
EK-36	Bahçepınar Spring (1)	09.12.2008	503	0.57	0.06	0.81	3.89	4.25	<DL	0.23	30.4	0.24
EK-37	Bahçepınar Well	20.08.2007	658	0.88	<DL	1.31	5.00	5.80	0.005	0.26	21.1	0.34
EK-37	Bahçepınar Well	04.10.2008	730	0.82	<DL	1.23	5.21	5.85	0.026	0.49	36	0.37
EK-38	Pazarbaşı Fountain	28.07.2007	790	4.07	0.08	2.04	3.39	7.40	0.008	0.69	34.7	0.61
EK-38	Pazarbaşı Fountain	21.04.2008	795	4.00	0.08	1.95	3.25	6.50	0.008	0.66	29.1	0.62
EK-38	Pazarbaşı Fountain	06.08.2008	793	3.97	0.05	1.78	3.23	7.00	<DL	0.60	29.8	0.58
EK-39	Cezaevi Well	16.10.2007	2230	15.50	0.21	4.30	3.00	18.70	<DL	1.30	37.8	0.44
EK-39	Cezaevi Well	21.04.2008	2660	25.10	0.25	6.85	3.43	27.00	<DL	1.760	32.9	0.45
EK-39	Cezaevi Well (4)	06.08.2008	1090	6.79	0.08	2.73	1.91	7.55	<DL	1.140	57.7	0.59
EK-39	Cezaevi Well	06.12.2008	1270	8.8	0.11	2.9	2.36	10.65	<DL	1.171	47.1	0.57
EK-40	Yorgalar Well	16.10.2007	1130	2.76	0.10	4.98	3.93	6.65	<DL	1.33	123	0.79
EK-40	Yorgalar Well	21.04.2008	1100	2.86	0.11	5.26	4.00	6.85	<DL	1.33	122	0.79
EK-40	Yorgalar Well	06.08.2008	1160	2.78	0.08	5.26	2.92	6.90	<DL	1.49	135	0.90
EK-40	Yorgalar Well	06.12.2008	1150	2.74	0.07	4.98	4.08	7.4	<DL	1.52	133	0.85
EK-43	Bahçelievler Fountain	06.08.2008	930	4.35	0.06	2.01	2.65	7.05	<DL	0.74	24	0.66
EK-44	Bahçepınar Pool Spring	11.08.2008	630	0.85	0.02	1.06	4.84	5.10	<DL	0.28	27.3	0.31
EK-45	Kölepinarı Fountain	11.08.2008	693	1.66	0.02	1.08	3.76	5.05	0.044	0.47	32.2	0.48
EK-46	Kurs Well	06.08.2008	1006	3.41	0.08	1.28	4.25	6.00	<DL	1.59	130	0.68
EK-46	Kurs Well	06.12.2008	1050	3.09	0.07	3.78	3.82	6.8	0.019	1.55	116	0.65
EK-46	Kurs Well (5)	06.08.2008	779	2.65	0.07	2.98	2.50	4.85	<DL	1.13	99	0.46
EK-46	Kurs Well	06.12.2008	103	0.28	0.01	0.14	0.54	0.7	<DL	0.05	7.4	0.01
EK-47	Üçevler Well	12.08.2008	3000	8.02	0.18	9.21	19.61	4.75	<DL	0.50	27.3	35.00

1 Water reservoir, 2 Catchment, 3 Mains water, 4 Mixing with city water, 5 After purification unit, DL detection limit

### Trace element pollution

Most fertilizers contain small amounts of trace elements. Phosphorus (P) fertilizers such as triple superphosphates and calcium/magnesium phosphate contain varying concentrations of Cd, depending on the source of phosphate rock (Mortvedt and Beaton 1995; He et al. 2005). P fertilizers are among the other sources of heavy metal input into agricultural systems. On an average, phosphate rock contains 11, 25, 188, 32, 10, and 239 mg/kg of As, Cd, Cr, Cu, Pb and Zn, respectively (Mortvedt and Beaton 1995;

He et al. 2005). In the USA, the trace elements, such as Cu, Zn, B, Fe, and Mn were intentionally added to regular blend fertilizers to meet the requirement for these elements for plant growth. These fertilizers are important sources of trace elements for crops growing in soils which are severely deficient in these elements, such as sandy soils, peaty soil, and calcareous soils. Organic materials, such as farm manures, bio-solids or composts contain higher concentrations of trace elements than most agricultural soils. The use of bio-solids and composts was reported to increase total amounts of Cu, Zn, Pb, Cd, Fe, and Mn in



**Fig. 3** Nitrate concentration contours of the waters in the study area (mg/l)

soils (McBride 2004; He et al. 2005). The concentrations of trace metals in bio-solids/composts are given by Chaney et al. (2001), He et al. (2005) and Mikayilov and Acar (1998).

The mobility of metals depends not only on the total concentration in the soil, but also on soil properties, metal properties and environmental factors. The mobility and availability of trace elements are controlled by many chemical and biochemical processes, such as precipitation–dissolution, adsorption–desorption, complexation–dissociation, and oxidation–reduction. Not all the processes are equally important for each element, but all these processes are affected by soil pH and biological processes. Therefore, it is crucial to understand some major reactions in soils that control the release of a specific trace element in the soil and the environment to overcome problems related to deficiency and contamination of these elements (He et al. 2005). Heavy metals accumulate in soils in various forms: water soluble, exchangeable, carbonate associated, oxide associated, organic associated and residual forms. The metals present in these categories have different levels of mobility (Moore et al. 1998; Iyengar et al. 1981; Sims and Kline 1991; He et al. 2005). Water soluble and exchangeable fractions are readily released to the environment, whereas the residual fractions are immobile under natural conditions. Dowdy and Volk (1983) suggested that the movement of heavy metals in soils could occur in sandy, acid, low organic matter soil if subjected to heavy rainfall or irrigation (He et al. 2005). Increased anthropogenic inputs of heavy metals in soils have received considerable attention, because transport of the metals may result in an increased content of heavy metals in groundwater or surface water (Purves 1985; Moore et al. 1998; He et al. 2005).

Certain trace element pollutions are observed in the study area, especially in wells drilled in the clastic levels of the Örenlice Formation with the highest NO<sub>3</sub> concentration. Trace element analysis of geothermal and/or mineral

springs, springs discharging from the Abant Formation and rivers without observing NO<sub>3</sub> pollution are given in Table 5. Trace element analyses of waters featuring NO<sub>3</sub> pollution are given in Table 6. According to Tables 5 and 6, it can be seen that Se, Hg, Pb, Cu, Zn, Ga, Y, Pd, I, Ba, and U concentrations of EK-39 well in different periods are higher than the average values of springs discharging from the Abant Formation that provides materials to the Örencik Formation and geothermal and/or mineral springs in the study area (the reservoir rock of most geothermal and/or mineral springs is the Abant Formation). Se, Hg, Pb concentrations exceed the upper limit values within the Turkish Standards for Water Intended for Human Consumption (TS 266 2005) and World Health Organization regulations (WHO 2006). Furthermore, B, S, Cr, Mn, Fe, Br, and I concentrations in this well are higher than the concentrations in springs discharging from Abant Formation, and the B value exceeds the upper limit value stated in the World Health Organization regulations (WHO 2006).

Pb, Ga, Y, Pd, and U concentrations of well EK-40 are higher than the average values of springs and geothermal and/or mineral waters discharging from the Abant Formation at different periods, and Pb concentration in rainy periods is close to, but does not exceed the upper limits stated in Turkish Standards for Water Intended for Human Consumption (TS 266 2005) and World Health Organization Regulations (WHO 2006), Pd and U value of well EK-46 are higher than the values of other springs and geothermal waters, and the Mn value is higher than the concentrations of cold springs discharging from the Abant Formation (Tables 5, 6). Furthermore, B, S, Cr, Fe, Cu, Zn, Ga, Br, Y, I, Ba, Hg, and Pb values of other springs and wells discharging from the Örencik Formation are generally slightly higher than the concentrations of springs discharging from the Abant Formation in different periods.

Large amounts of boron (B) may result in indigestion and affect the central nervous system (Department of National Health and Welfare 1979; McNeely et al. 1979). Lead (Pb) has a considerable toxic effect. It penetrates into red blood cells in the body and emits the iron from the cell, and thus may lead to anemia due to iron deficiency (Peker 1970; Atabey 2005a, b). Furthermore, it is stated that the lead accumulated in bones dissolves over time and may lead to inflammation in kidneys and abnormalities brain and nervous system functions, and that IQ levels of children decrease due to the increase of lead in blood (Kahvecioğlu et al. 2003). Daniş (2005) indicated that lead exceeding the regulatory limits may result in diseases, such as metabolic intoxication, fatigue, anemia and nervousness (Atabey 2005a, b). Excessive intakes of mercury may lead to physiological and neurological diseases, such as central nervous system failures (Appleton 2001). Increased mercury concentration causes considerable damage in the

**Table 5** Trace element analysis results of the springs discharging from Abant Formation, geothermal and/or mineral springs and rivers in which no nitrate pollution are observed (ppb)

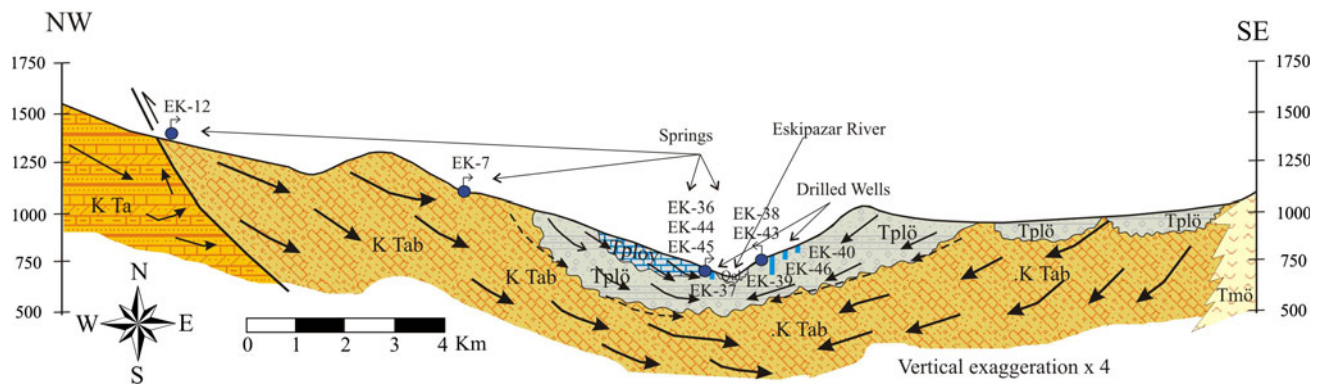
Water type	<sup>7</sup> Li			<sup>10-11</sup> B			<sup>27</sup> Al			<sup>29</sup> Si			<sup>33</sup> S			<sup>47</sup> Ti			<sup>51</sup> V			<sup>52</sup> Cr		
	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average
A	<DL	3.97	317	10.5	64.3	124	<DL	71.2	8.473	538	4.279	95,610	85,660	69,072	3.21	<DL	1.73	2.55	0.01	0.41	5.3	0.47	2.74	
B	1.056	21	392	27,010	278	9,602	977	130	335	46,220	2,524	23,269	8,492,000	6,53,800	8,20,600	16.1	<DL	8.01	3.84	<DL	1.26	45.4	4.2	14
C	4.8	3.22	3.99	137	60.6	98.6	120	95.4	108	5,517	5,528	5,622	(-)	(-)	3.1	2.21	2.67	0.43	0.34	0.38	3.27	2.4	2.81	
Water type	<sup>55</sup> Mn			<sup>56</sup> Fe			<sup>59</sup> Co			<sup>60-62</sup> Ni			<sup>63</sup> Cu			<sup>66</sup> Zn			<sup>69</sup> Ca			<sup>72</sup> Ge		
A	29.9	<DL	4.46	223	<DL	58.8	0.66	0.04	0.23	6.7	<DL	1.35	12.97	<DL	4.80	13.6	<DL	5.76	9.68	0.56	2.78	0.30	<DL	0.06
B	808	<DL	164	15830	20	3459	6.01	1.2	2.13	50	<DL	13.7	74.2	<DL	20.1	52.8	<DL	22.3	70.71	1	22.6	7.61	0.33	3.5
C	6.5	4.6	5.54	91.7	58.7	75.2	0.13	0.05	0.09	0.05	<DL	0.02	13.2	5.84	9.53	8.1	7.3	7.68	2.4	1.8	2.12	0.02	<DL	0.01
Water type	<sup>75</sup> As			<sup>81</sup> Br			<sup>82</sup> Se			<sup>86</sup> Rb			<sup>88</sup> Sr			<sup>89</sup> Y			<sup>90-92</sup> Zr			<sup>101</sup> Ru		
A	1.36	<DL	0.19	46	1.63	16.8	5.04	<DL	0.95	2.22	0.21	0.64	1385	96.6	405	135	<DL	18.07	0.76	<DL	0.45	0.022	<DL	0.01
B	783	<DL	203	574	4.4	323	31.9	<DL	8.05	261	1.8	124	4935	425	2195	594	<DL	116	9.95	<DL	2.46	0.13	0.02	0.06
C	0.36	0.34	0.35	7.6	5.4	6.46	0.28	0.16	0.22	0.54	0.37	0.46	339	329	334	0.19	0.18	0.18	0.7	0.69	0.69	0.01	0.004	0.01
Water type	<sup>105</sup> Pd			<sup>112</sup> Cd			<sup>118</sup> Sn			<sup>121</sup> Sb			<sup>127</sup> I			<sup>133</sup> Cs			<sup>137</sup> Ba			<sup>147</sup> Sm		
A	40.4	0.29	5.04	0.09	<DL	0.01	1.2	<DL	0.37	0.8	<DL	0.19	7.4	0.39	1.17	0.87	<DL	0.12	305	13.7	71.7	0.023	<DL	0
B	210	2.3	53	0.3	<DL	0.07	4.5	<DL	1.48	0.66	<DL	0.1	197	3.4	87.6	366	0.02	13.6	1001	29.5	410	0.17	<DL	0.04
C	1.08	0.89	0.98	<DL	<DL	0	0.43	0.31	0.37	<DL	<DL	0	0.62	0.48	0.55	0.01	0.003	0.01	70.4	54	62.2	0.008	0.006	0.01
Water type	<sup>153</sup> Eu			<sup>163</sup> Dy			<sup>166</sup> Er			<sup>172</sup> Yb			<sup>178</sup> Hf			<sup>181</sup> Ta			<sup>195</sup> Pt			<sup>197</sup> Au		
A	0.048	0.003	0.02	0.016	<DL	0	0.01	<DL	0	0.016	<DL	0	0.02	<DL	0.01	19.4	<DL	2.02	0.07	<DL	0.02	7.3	1.39	5.08
B	0.6	<DL	0.21	0.36	<DL	0.05	0.26	<DL	0.03	0.19	<DL	0.02	0.13	<DL	0.05	28.1	<DL	6.26	0.22	<DL	0.08	32.5	1.9	21.1
C	0.01	0.007	0.01	0.002	<DL	0	0.001	<DL	0	0.001	<DL	0	0.01	0.01	0.01	5.12	<DL	2.56	0.06	0.02	0.04	6.7	6.2	6.45
Water type	<sup>198-202</sup> Hg			<sup>208</sup> Pb			<sup>232</sup> Th			<sup>238</sup> U														
A	0.78	0.06	0.37	1.92	0.46	1.07	0.01	<DL	0	3.66	0.07	0.45												
B	1.2	0.12	0.57	7.7	3.1	5.34	0.05	<DL	1.6	<DL	0.22													
C	0.53	<DL	0.53	1.5	0.87	1.2	0.004	0.004	0.43	0.41	0.42													

A Springs discharging from Abant Formation (15 springs), B Geothermal and/or mineral springs (7 springs), C Rivers (2 rivers measurement point) DL detection limit

**Table 6** Trace element analysis results of the waters discharging from Örencik Formation and alluvium in which nitrate pollution are observed (ppb)

Water no	Date	<sup>7</sup> Li	<sup>10-11</sup> B	<sup>27</sup> Al	<sup>29</sup> Si	<sup>33</sup> S	<sup>47</sup> Ti	<sup>51</sup> V	<sup>52</sup> Cr	<sup>55</sup> Mn	<sup>56</sup> Fe	<sup>59</sup> Co	<sup>60-62</sup> Ni	<sup>63</sup> Cu	<sup>66</sup> Zn	<sup>69</sup> Ga	<sup>72</sup> Ge	<sup>75</sup> As	<sup>81</sup> Br	<sup>82</sup> Se	<sup>85</sup> Rb	<sup>88</sup> Sr	<sup>89</sup> Y
EK-8	24.07.2007	0.42	34.3	113.7	5,514	(-)	2.38	0.52	6.44	5.12	78.6	0.16	<DL	6.73	8.30	1.19	0.02	0.31	6.5	0.84	0.56	114.1	0.18
EK-10	24.07.2007	5.75	66.1	115.9	6,971	(-)	2.66	1.42	3.18	5.84	86.7	0.14	<DL	7.53	9.80	2.10	<DL	0.65	11.2	0.14	0.42	403.7	0.20
EK-10	20.04.2008	(-)	(-)	15.3	883	97,180	0.97	1.27	4.88	<DL	<DL	0.51	4.86	<DL	<DL	3.76	0.22	0.18	47.3	<DL	0.50	402.6	84.60
EK-14	25.07.2007	<DL	31.6	99.3	4,796	(-)	2.50	0.11	1.79	4.54	50.6	0.08	<DL	5.90	8.16	0.50	0.02	<DL	4.9	<DL	0.15	73.1	0.16
EK-35	28.07.2007	7.08	180	95.4	5,868	(-)	2.08	0.26	3.81	5.06	87.8	0.05	<DL	55.61	12.62	3.00	0.02	0.15	6.0	0.38	0.24	311.7	0.16
EK-36	20.08.2007	6.29	80.1	92.8	7,666	(-)	2.55	1.44	3.81	4.34	45.7	0.06	<DL	6.47	7.87	2.20	<DL	0.51	47.6	<DL	0.53	458.6	0.18
EK-36	21.04.2008	(-)	(-)	14.0	987	1,24,700	1.41	1.48	5.99	<DL	46.2	0.50	3.31	<DL	<DL	4.76	0.19	0.28	72.7	<DL	0.67	462.6	72.33
EK-38	21.04.2008	(-)	(-)	15.3	1,189	1,61,800	1.75	6.01	6.59	0.44	65.7	0.43	2.33	<DL	1.18	6.99	0.27	0.67	80.5	0.56	0.32	493.8	148.80
EK-39	16.10.2007	(-)	628.2	<DL	114.90	(-)	<DL	7.10	3.78	11.39	48.46	0.9	<DL	<DL	<DL	12.27	0.22	1.36	164	23.86	3.24	2,112	0.1
EK-39	21.04.2008	(-)	(-)	130.0	3,614	8,62,600	3.79	3.88	26.72	48.81	127.20	1.5	3.62	65.75	71.33	30.73	0.61	<DL	292	<DL	4.58	1,588	692.9
EK-39	06.12.2008	(-)	(-)	19	(-)	(-)	0.78	4.76	4.08	2.58	20.58	0.39	1.58	28.05	47.21	18.53	0.21	0.7	(-)	1.22	2.44	1,593	0.1
EK-40	21.04.2008	(-)	(-)	130.8	2,631	7,19,400	2.00	5.95	7.16	0.16	176.0	0.57	<DL	<DL	0.21	12.52	0.71	<DL	180	<DL	0.95	1,672	228.70
EK-40	06.12.2008	(-)	(-)	20.35	(-)	(-)	1.94	5.96	0.054	0.19	20.72	0.41	8.94	0.99	<DL	19.55	0.30	0.31	(-)	0.22	0.97	1,671	0.06
EK-46	06.12.2008	(-)	(-)	134.8	(-)	(-)	3.26	5.67	0.45	10.14	<DL	0.73	1.59	<DL	0.7	14.55	0.21	0.27	(-)	0.76	0.93	1,135	0.33
Water no	Date	<sup>90-94</sup> Zr	<sup>101</sup> Ru	<sup>105</sup> Pd	<sup>112</sup> Cd	<sup>118</sup> Sn	<sup>121</sup> Sb	<sup>127</sup> I	<sup>133</sup> Cs	<sup>137</sup> Ba	<sup>147</sup> Sm	<sup>153</sup> Eu	<sup>163</sup> Dy	<sup>166</sup> Er	<sup>172</sup> Yb	<sup>178</sup> Hf	<sup>181</sup> Ta	<sup>195</sup> Pt	<sup>197</sup> Au	<sup>198-202</sup> Hg	<sup>208</sup> Pb	<sup>232</sup> Th	<sup>238</sup> U
EK-8	24.07.2007	0.67	0.000	0.42	<DL	0.33	<DL	1.02	0.01	35.1	0.006	0.009	0.007	0.000	0.002	0.01	0.45	0.06	7.2	(-)	1.14	0.01	0.28
EK-10	24.07.2007	0.63	0.004	1.24	<DL	0.50	<DL	2.33	0.00	66.8	0.003	0.012	0.006	0.001	0.002	0.01	2.25	0.02	6.9	(-)	1.36	0.01	0.52
EK-10	20.04.2008	<DL	0.012	17.67	0.05	<DL	0.76	2.11	0.05	53.0	0.003	0.029	0.001	0.003	0.003	<DL	0.39	0.04	2.2	0.06	1.41	<DL	0.44
EK-14	25.07.2007	0.67	0.000	0.10	<DL	0.44	<DL	1.91	<DL	14.7	<DL	0.002	0.003	0.000	<DL	0.01	<DL	0.01	6.7	0.61	0.80	0.001	0.14
EK-35	28.07.2007	0.67	0.01	0.91	<DL	1.22	<DL	0.55	0.000	90.0	0.001	0.02	<DL	<DL	0.001	0.02	<DL	0.02	6.4	0.52	3.08	0.001	0.47
EK-36	20.08.2007	0.70	0.00	1.28	<DL	0.39	<DL	4.16	0.002	66.0	0.003	0.01	0.001	0.000	<DL	0.02	<DL	0.002	6.8	0.37	0.83	0.002	0.74
EK-36	21.04.2008	<DL	0.01	20.65	0.01	<DL	0.72	4.43	0.036	66.1	0.006	0.04	0.002	0.001	<DL	<DL	0.56	0.001	2.4	0.03	0.63	<DL	0.76
EK-38	21.04.2008	<DL	0.02	47.85	0.03	<DL	0.65	3.97	0.045	98.2	0.005	0.06	0.004	<DL	<DL	<DL	0.57	0.031	2.3	0.06	0.79	<DL	2.79
EK-39	16.10.2007	<DL	0.05	35.74	0.15	0.43	<DL	32.69	1.40	214.4	0.006	0.15	0.009	0.002	0.011	<DL	5.50	0.21	23	1.43	10.86	<DL	7.13
EK-39	21.04.2008	3.15	0.13	163.10	0.03	<DL	0.78	162.5	0.30	428.1	0.025	0.25	0.017	0.009	0.007	<DL	2.45	0.07	11	0.15	8.83	<DL	6.72
EK-39	06.12.2008	0.043	0.017	88.68	0.17	0.135	0.72	(-)	0.32	170.3	0.013	0.061	0.008	0.004	0.006	<DL	2.56	0.033	<DL	0.017	2.5	<DL	3.16
EK-40	21.04.2008	<DL	0.05	78.38	0.14	<DL	0.53	4.27	0.23	173.9	<DL	0.09	0.01	0.00	<DL	<DL	2.87	<DL	10	0.32	7.29	<DL	1.90
EK-40	06.12.2008	<DL	0.038	88.89	0.05	<DL	0.6	(-)	0.31	171.3	0	0.071	0.005	0	<DL	<DL	2.1	<DL	<DL	0.025	1.78	<DL	1.73
EK-46	06.12.2008	<DL	0.021	68.78	0.21	<DL	0.5	(-)	0.31	130.5	0.053	0.049	0.038	0.019	0.028	<DL	0.30	<DL	<DL	0.015	2.33	0.02	1.41

(-) marking indicates that no measurement was made for the value in question, DL detection limit



**Fig. 4** Geological–hydrogeological cross section of the study area

brain and kidneys and may lead to increasing blood pressure, heart attack, rashes, wound formation and damage to the eyes (Güven et al. 2004; Atabey 2005a, b). High intakes of selenium may be toxic and result in diseases such as anorexia (Güven et al. 2004; ATSDR 2003; Atabey 2005a, b).

### General evaluations

Figure 4 illustrates a horizontal geologic–hydrogeologic section of the springs discharging from the Abant Formation, where no pollution is observed, and; springs and wells discharging from the Örenlice Formation, where  $\text{NO}_3$  and trace element pollution are observed.

Evaluation of the probable flow paths in Fig. 4, together with the factors given below shows that the main cause of  $\text{NO}_3$  and trace element pollution is agricultural activities. These factors are (1) in the study area,  $\text{NO}_3$  and trace element pollutions are observed in springs and wells discharging from areas of intensive agricultural activities, which utilize various types of pesticides and fertilizers (ammonium nitrate, ammonium sulfate, diammonium phosphate, urea (nitrogenous fertilizer),  $20 \times 20$ ,  $15 \times 15 \times 15$ , barnyard manure etc.). (2) There is no significant  $\text{NO}_3$  and trace element pollution in springs discharging from Abant Formation, which is the source rock of clastic levels of the Örenlice Formation. (3) In wells with the highest  $\text{NO}_3$  concentrations, concentrations of certain trace elements are mostly higher than in cold and geothermal and/or mineral waters within the study area (Tables 4, 5). (4) There is mudstones in the base of the Örencik Formation (Şaroğlu et al. 1995), which reduces the possibility for deeper circulating water to get mixed into the wells. (5) There are no polluting sources (waste disposal area, industrial center, mineralization, etc.) within the recharge area of waters; and the sewage system of the study area is fully operational.

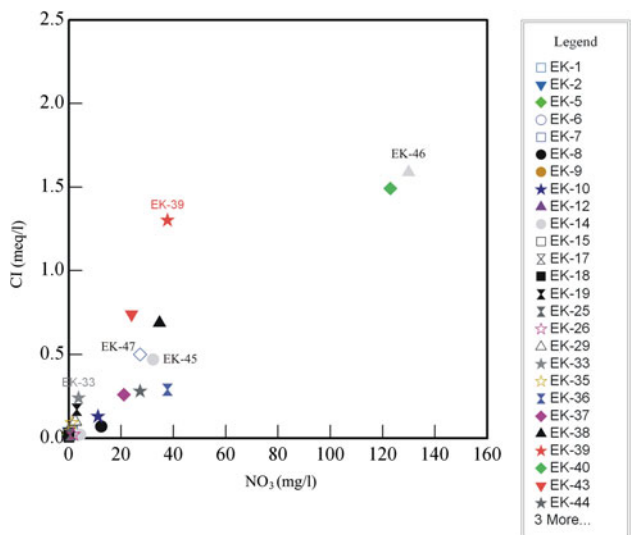
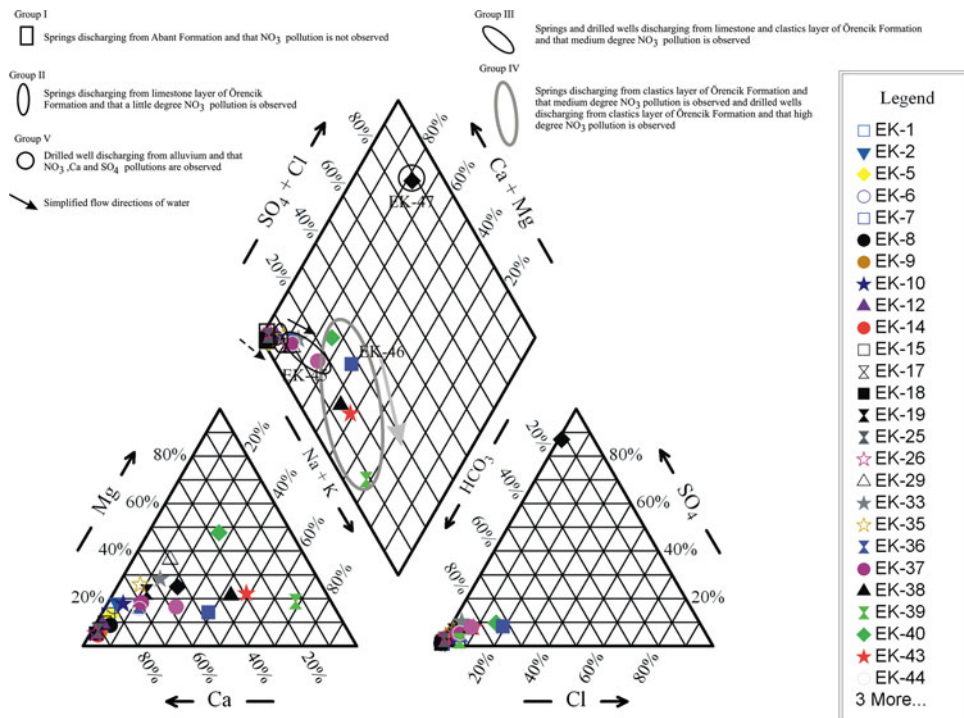
In well EK-39, Na pollution was observed in addition to  $\text{NO}_3$  and trace element pollution. Na pollution in this well

may be deemed to be due to the presence of higher levels of clay in EK-39 when compared with other wells, and from water–rock interaction, cation exchange with clayed levels and, to some extent, from fertilizers containing Na used in agricultural activities and the mixture of deep circulating water. In addition, the fact that Şaroğlu et al. (1995) mentioned the existence of mudstones in the base of formation hosting wells; that the discharge of the well is very low, that the well dries up periodically and the redundancy of clayed levels reduce the possibility for mixing of deep circulating water. In addition to  $\text{NO}_3$  pollution, Ca and  $\text{SO}_4$  pollutions were observed in the EK-40 well drilled in the alluvium. The fact that no units containing intensive  $\text{SO}_4$  such as gypsum were observed that no alteration that may lead to  $\text{SO}_4$  are observed within the recharge area of the well, and the fact that agricultural activities are conducted around the well suggest that this pollution may stem from agricultural activities. Unlike other wells in the vicinity of this well, fruit and vegetable farming that require high levels of irrigation are conducted, and fertilizers containing  $\text{SO}_4$ , Ca and Na in agricultural activities are used. The water returning from irrigation may lead to salinization in the soil and groundwater. Consequently, it is suggested that these pollutions in the well are due to agricultural practices.

Atabey (2005a, b) reported that water with a Na level above 200 mg/l presents a serious health risk for people with health conditions, nephropathy and circulatory problems. High rates of  $\text{NaSO}_4$  and  $\text{MgSO}_4$  in water may have a laxative effect on humans (Atabey 2005a, b). Excessive Ca loading may result in the formation of kidney stones and bone calcification (P.M. Journal 1995; Boz 2004; Atabey 2005a, b).

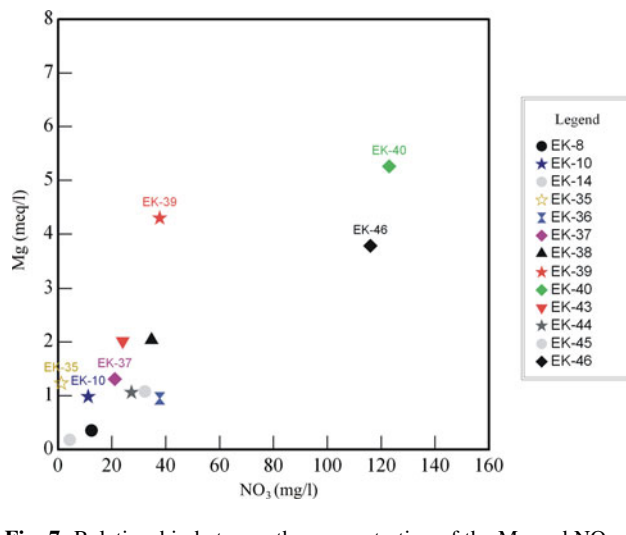
Elhatip et al. (2003) reported that high nitrate content and significant mineralization in the groundwater are probably due to contamination of the recharge to the aquifer by irrigation drainage, poorly maintained sewage networks, and septic tanks (APHA, AWWA, WPCF 1989; Elhatip et al. 2003). Previous research indicates some other

**Fig. 5** Piper diagram of the waters within the study area



**Fig. 6** Relationship between the concentration of the Cl and NO<sub>3</sub> of springs in the study area

inorganic constituents of groundwater that are present in agricultural additives including, Cl, K, Ca, Mg, and a variety of minor elements and agricultural sources of some of these elements and can dominate natural sources locally. In addition, it has been suggested that agricultural effects on the recharge fluxes of various ions such as NO<sub>3</sub> and H<sup>+</sup> can cause changes in weathering rates and ion-exchange equilibrium in the subsurface, thereby indirectly altering the concentrations of other constituents in groundwater. These indirect effects have important implications for geochemical studies of water–rock interactions and can



**Fig. 7** Relationship between the concentration of the Mg and NO<sub>3</sub> of water discharging from Örencik Formation

represent sources or sinks for a variety of problematic contaminants, such as nutrients and toxic trace elements (Elhatip et al. 2003). High NO<sub>3</sub> and NaCl concentrations in springs discharging from volcanic rocks located in Kayseri were stated to arise from agricultural wastes and waste water around the springs (Baba and Ayyıldız 2006). Novais et al. (2008) reported that NO<sub>3</sub> and Cl pollution in wells drilled in meta-sedimentary rocks in the Ervedosa region were due to agricultural and domestic wastewater.

Figure 5 presents Piper (1944) diagrams demonstrating the major anion and cation percentages of the waters

discharging from the Abant Formation, Örencik Formation and alluvium. It can be seen from Fig. 5 that springs discharging from the Abant Formation and water discharging from the limestone levels of Yörük member (Örencik Formation) have Ca–HCO<sub>3</sub> facies. Waters discharging from areas where clastic levels of the Örencik Formation and limestones of the Yörük member (Örencik Formation) are located together have mainly Ca–HCO<sub>3</sub> facies and also high Na and Mg percentages. Water discharging from completely clastic levels of the Örencik Formation is mostly of the mixed type (Na–Ca–Mg–HCO<sub>3</sub>), whereas well EK-39 has NaHCO<sub>3</sub> facies. The well drilled in alluvium (EK-47) is of the CaSO<sub>4</sub> type and has high Mg and Na concentrations.

Five different primary groups are observed in the Piper diagram. Group I represents the water discharging from the Abant Formation with no NO<sub>3</sub> pollution; Group II represents water discharging predominantly from the limestone levels of the Örencik Formation (Yörük member), containing water with less NO<sub>3</sub> pollution; Group III represents water discharging from areas where limestone levels (Yörük member) and clastic levels of the Örencik Formation are located together containing water with medium level NO<sub>3</sub> pollution; Group IV represents water discharging from clastic levels of the Örencik Formation and water with high levels of NO<sub>3</sub> pollution; Group V represents water discharging from alluvium and water with NO<sub>3</sub>, Ca, and SO<sub>4</sub> pollution. Water in which NO<sub>3</sub> pollution is not observed and water in which NO<sub>3</sub> pollution is observed at different ratios are separated from each other in the diagram. Furthermore, the SO<sub>4</sub> pollution in EK-47 and Na pollution in EK-39 are clearly distinguished. When wells and springs are analyzed between each other, it can be seen from Table 4 that the total dissolved solids in the water increase throughout the general flow paths of each given group.

Figure 6 shows the NO<sub>3</sub>–Cl relationship of water in the study area and Fig. 7 shows the NO<sub>3</sub>–Mg relationship of water discharging from the Örencik Formation. It can be concluded from the figures that Cl and Mg concentrations increase along with the increase in NO<sub>3</sub>. Notwithstanding the few exceptions, because similar conditions are observed between Na, SO<sub>4</sub> and NO<sub>3</sub> concentrations (Table 4), it is thought that Ca, Na, Mg, Cl, and SO<sub>4</sub> ions may originate from fertilizers used in agricultural activities in addition to water–rock interaction. In the Piper diagram, this situation is reflected in the way that the water with high NO<sub>3</sub> concentrations is in the mixed type in terms of cations.

## Conclusions and recommendations

The aim of the present study was to make a contribution to research on NO<sub>3</sub> and trace element pollution. Investigations

were performed around Eskipazar (Karabük) and NO<sub>3</sub> pollution was recorded in water samples in areas where intensive agricultural activities are conducted. These waters are used for drinking, domestic and irrigation purposes. Pollution was particularly evident in the Örencik Formation and the Yörük member of the Örencik Formation consisting of conglomerate, sandstone, mudstone, siltstone and claystone alternations and intensive fractured-cracked limestone, and alluvium. Intensive forms of agriculture are practiced in these areas. In the wells drilled especially in the clastic levels of the formation, Na, B, Pb, Hg, Se pollutions were also detected in addition to NO<sub>3</sub>.

S, Cr, Mn, Fe, Cu, Zn, Ga, Br, Sr, Y, I, Ba, U concentrations in these waters with the highest level of NO<sub>3</sub> are at higher levels when compared with the average values of springs discharging from Abant Formation that provides material to the clastic levels of Örencik Formation. Furthermore, the concentrations of most of these elements are higher than the average concentrations within geothermal and/or mineral waters in the study area.

There is a high amount of NO<sub>3</sub> in EK-39, EK-40 and EK-46 wells drilled in the clastic levels of the Örencik Formation. The levels recorded are several times greater than the limit stated in the Turkish Standards for Water Intended for Human Consumption (TS 266 2005) and World Health Organization Regulations (WHO 2006). NO<sub>3</sub> concentrations in most springs within the formation are close to the upper limit. In addition, Na, B, Pb, Hg and Se concentrations in well EK-39 exceed the regulatory limits during different periods. Pb concentration in well EK-40 does not exceed the regulatory limit during rainy periods, but is very close to this value. In addition to NO<sub>3</sub> pollution, SO<sub>4</sub> and Ca pollution are also observed in well EK-47, which is drilled in the alluvium in an area where agricultural activities requiring intensive irrigation are conducted.

When the factors given below are evaluated in combination, it is concluded that the main cause of NO<sub>3</sub> and trace element pollution is agricultural activities; (1) in the study area, NO<sub>3</sub> and trace element pollutions are observed in springs and wells discharging from areas of intensive agricultural activities, which utilize various types of pesticides and fertilizers (ammonium nitrate, ammonium sulfate, diammonium phosphate, urea (nitrogenous fertilizer), 20 × 20, 15 × 15 × 15, barnyard manure etc.). (2) There is no significant NO<sub>3</sub> and trace element pollution in springs discharging from Abant Formation, which is the source rock of clastic levels of the Örenlice Formation. (3) In wells with the highest NO<sub>3</sub> concentrations, concentrations of certain trace elements are mostly higher than in cold and geothermal and/or mineral waters within the study area. (4) There is mudstones in the base of the Örencik Formation, which reduces the possibility for deeper circulating water to get mixed into the wells. (5) There are no polluting



sources (waste disposal area, industrial center, mineralization, etc.) within the recharge area of waters; and the sewage system of the study area is fully operational.

It is clear that these agricultural pollutants accumulating in the ground and reaching the groundwater through leaching may increase over time, depending on their usage, and may therefore constitute a significant environmental risk within the region in the future.

In the water within the study area,  $\text{NO}_3$  concentrations show a positive correlation with Mg and Cl concentrations. Notwithstanding a few exceptions, a similar correlation is observed between  $\text{NO}_3$  and Na,  $\text{SO}_4$ . This is reflected in Piper diagrams in a way that these waters are of mixed types, especially in terms of cations. The waters discharging from the Örencik Formation, where  $\text{NO}_3$  and trace element pollution observed are different facies from the waters discharging from the Abant Formation, where no pollution is observed. It is suggested that the diversity stemmed from agricultural fertilizers, containing Na, Mg, Cl and  $\text{SO}_4$  in addition to water–rock interaction. To fully explore such relationships, and to determine potential local and international effects, studies of surface water, groundwater, soil, rock, fertilizers, pesticides, and chemistry involving researchers from different disciplines should be conducted on a larger scale.

Current global population expansion increases the need for meeting basic nutritional requirements. Current intensive agricultural activities are highly dependent on the use of chemical fertilizers and pesticides. Many previous studies have demonstrated the significant negative effects of such chemicals in terms of water and soil pollution. Unless the use of fertilizers and pesticides are decreased, it is likely that levels of  $\text{NO}_3$ , trace elements and other pollutants in surface water, groundwater and soils will increase, and irreversible social, environmental and economic problems. Therefore, the appropriate element and compound and its amount which does not damage water quality should be determined; the proper dosages of chemicals required for every plant type should be established; conformity with standards for the use of fertilizers and pesticides should be strictly controlled; the public should be informed about the dosage use of fertilizers and pesticides, and necessary changes to agricultural methods should be immediately implemented.

Long-term monitoring studies should be carried out in regions where pollution arises from agricultural activity. Determination of the temporal distribution of  $\text{NO}_3$  and trace element increases are of crucial importance in terms of monitoring and maintaining the quality of surface and groundwater.

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