Arsenic Pollution in the Groundwater of Simav Plain, Turkey: Its Impact on Water Quality and Human Health

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Abstract In this research, geological and hydrogeo-logical studies were conducted to determine the source of high arsenic levels in the surficial aquifer of Simav Plain, Kutahya, Turkey. One of the two aquifer systems isolated in the study area was a deep confined aquifer composed of fractured metamorphic rocks that supply hot geothermal fluid. The other one was an unconfined alluvial aquifer, which developed within the graben area as a result of sediment deposition from the highlands. This aquifer serves as the primary water resource within the plain. A water quality sampling campaign conducted in 27 wells drilled in the surficial aquifer has yielded an average arsenic concentration of 99.1 μg/L with a maximum of 561.5 μg/L. Rock and sediment samples supported the fact that local metamorphic rocks contained significant amounts of sulfur minerals where arsenic-containing lenses are present inside. It was also determined that a Cu–Pb–Zn mine was operated in the past in the same formation. Arsenic-containing wastes of this mine were deposited near the Simav district center in an uncontrolled manner. This mined formation had arsenic levels reaching to levels as high as 660 mg/kg, which was found out to be the highest arsenic level in the area. Another potential arsenic source in the study area was the geothermal fluid that was used extensively in three geothermal fields with levels reaching to levels as high as 594 μg/L. Uncontrolled discharges of waste geothermal fluid and overexploitation of groundwater were also found to contribute to arsenic pollution in surface/subsurface waters of the plain. Thus, natural sources and anthropogenic influences of arsenic were found to create high concentrations in local water reserves of the area and influence human health. Consequently, death statistics from the 1995 to 2005 period collected from the area has revealed increased rates of gastrointestinal cancers above Turkish average.

Keywords Groundwater quality · Arsenic pollution · Rock–water interaction · Cu–Pb–Zn mine waste · Human health · Simav Plain—Turkey

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1 Introduction

Arsenic is a toxic chemical that is naturally found in the environment and is a proven carcinogen for humans when exposed thru oral, dermal, and inhalation pathways (NRC 1997; ATSDR 2000; WHO

2001). Typically, arsenic exposure occurs as a result of natural and anthropogenic sources (Wang and Mulligan 2006; O'Shea et al. 2007), where oral and dermal routes are the most significant intake mechanisms. Arsenic-containing groundwater is the primary medium of exposure in many areas of the world influencing large populations (Arsenic Project 2008). In many cases, local geological formations such as altered volcanic and metamorphic rocks with arsenic containing sulfide mineralizations as well as fossil beds containing petroleum and coal are among the major causes of high arsenic levels in groundwater resources (Wang and Mulligan 2006; Alverez et al. 2006; O'Shea et al. 2007).

In general, certain natural resources contain high risks for creating environmental pollution under human influence. Among these, one could possibly mention mine sites and geothermal fields as the most important ones with significant environmental consequences. Operation of sulfide containing mines with high arsenic levels and deposition of their wastes are considered to be important sources of arsenic-related problems (Lee et al. 2005; Alverez et al. 2006; Robles-Arenas et al. 2006). Similarly, development and operation of geothermal fields within arsenic-containing formations are also considered to cause arsenic-related contamination problems, particularly in groundwater reserves (Gemici and Tarcan 2004; Gunduz and Simsek 2007, Aksoy et al. 2009). In particular, very high arsenic levels (>1,000 µg/L) were previously reported in waters that receive waste geothermal fluid discharges (Stauffer and Thompson 1984; Ball et al. 1998). In areas with high tectonic activity, hot waters with elevated mineral content surface out from faulty and cracky zones and mix with cold water reserves. When these hot waters have deep circulation patterns, they demonstrate favorable conditions for extended rock–water interaction where mineral enrichment takes place (Gemici and Tarcan 2004). Another anthropogenic source for arsenic is the arsenic-containing pesticides that have also caused significant environmental pollution (Chatterjee and Mukherjee 1999).

High arsenic levels in parent rock are typically responsible for high concentrations in groundwater. When found in levels exceeding 10 µg/L in water and 90 µg/kg in soils, arsenic is proven to demonstrate toxic effects to human health (WHO 2001; EA 2002). Numerous studies are conducted throughout the world

regarding the human health impacts of arsenic exposure exceeding these standard limits. In one such study, Mazumder et al. (2000) have found that indigestion of arsenic-contaminated waters with levels exceeding 50 µg/L results in destructions in digestion and respiration systems as well as on skin. Similarly, Ayotte et al. (2003) have published on the occurrence, control mechanisms, and health effects of arsenic in New England groundwaters. Other studies by Das et al. (1995), Focazio et al. (2000), Ali and Tarafdar (2003), Fritzsche et al. (2006), and Liu et al. (2006) have all published similar results in areas with known arsenic problems such as Bangladesh, India, China, USA, and Taiwan. Particularly, in Bangladesh where Holocene-aged sedimentary formations are commonly observed, arsenic is found to be present in levels ranging between 3.6 and 26.0 mg/kg (Bibi et al. 2006).

Numerous cases of natural arsenic pollution have also been reported in Turkey within the last 10 years (Colak et al. 2003, Simsek 2005; Atabay 2005; Aksoy et al. 2009). Particularly, in Kutahya Province located in the western parts of central Anatolia, geological formations and geothermal activity create suitable conditions for arsenic contamination of surface and subsurface water resources. Arsenic-related health complaints have been reported in Emet and Simav districts of Kutahya. Simav Plain is thus selected as the study area for this particular research. This area is a graben basin with rich groundwater resources, typically extracted for drinking and agricultural purposes from a moderately thick alluvial layer. This layer is mostly formed from sandy material weathered from metamorphic and magmatic rocks of the surrounding mountains. In addition, three geothermal fields are currently active within the plain, which are used in domestic heating and in thermal spas. A previous study by the authors (Simsek and Gunduz 2007) has reported the presence of arsenic in Simav Plain groundwaters but did not propose any mechanisms for its source or contamination mechanisms. Therefore, it is vital to properly characterize its source, understand its current status, and assess its potential risks to human health. Based on these fundamentals, this study is intended to describe arsenic pollution in the groundwaters of Simav Plain, to illustrate possible mechanisms of contamination, and to evaluate associated health risks from exposure to arsenic-containing groundwater.

2 General Characteristics of the Study Area

Simav Plain is located within the boundaries of the District of Simav in Kutahya Province in western Anatolia. It is situated about 45 km southwest of Kutahya City (Fig. 1). Total population of the Simav district center and its villages was reported to be around 76,000 according to 2007 census results (TUIK 2007). In addition to Simav district center, Citgol, Nasa, Kelemyenice, Caysimav, Degirmenciler, Beyce, Orey, Golkoy, Bogazkoy, and Guney are among the other residential areas in the study area.The hot water springs situated in Nasa, Citgol, and Eynal are widely used in thermal tourism.

Simav Plain and its vicinity are considered to be situated in the central Aegean climate zone, which shows attributes of a transition region from Aegean climate to central Anatolian climate (Simsek and Gunduz 2007). Based on the data from the Simav Meteorological Station collected between 1991 and 2000, mean annual temperature of the region is 11.7°C. The hottest months are July and August with monthly averages of 21.9°C and 21.5°C, respectively, and the coldest months are January and February with monthly averages of 2.1°C and 2.7°C, respectively. According to 10 years of meteorological data, the region receives an average precipitation of 723 mm. Monthly averages of the highest and lowest precipitation occur in December and August with totals of 117.4 and 11.2 mm, respectively (DMI 2005).

Prevailing climatic conditions of the area trigger land erosion. Hot and dry summers followed by cold and wet winters result in significant sediment transport from the highlands to Simav Plain. The rate of this process depends on seasonal vegetation cover and precipitation amounts as well as local topography. In particular, the southern slopes of the area have steep grades that create flash floods and high sediment transport (Fig. 1). The relatively thick alluvial layer in the plain (i.e., up to 90 m in thickness) is a clue for the rapid deposition of transported sediments.
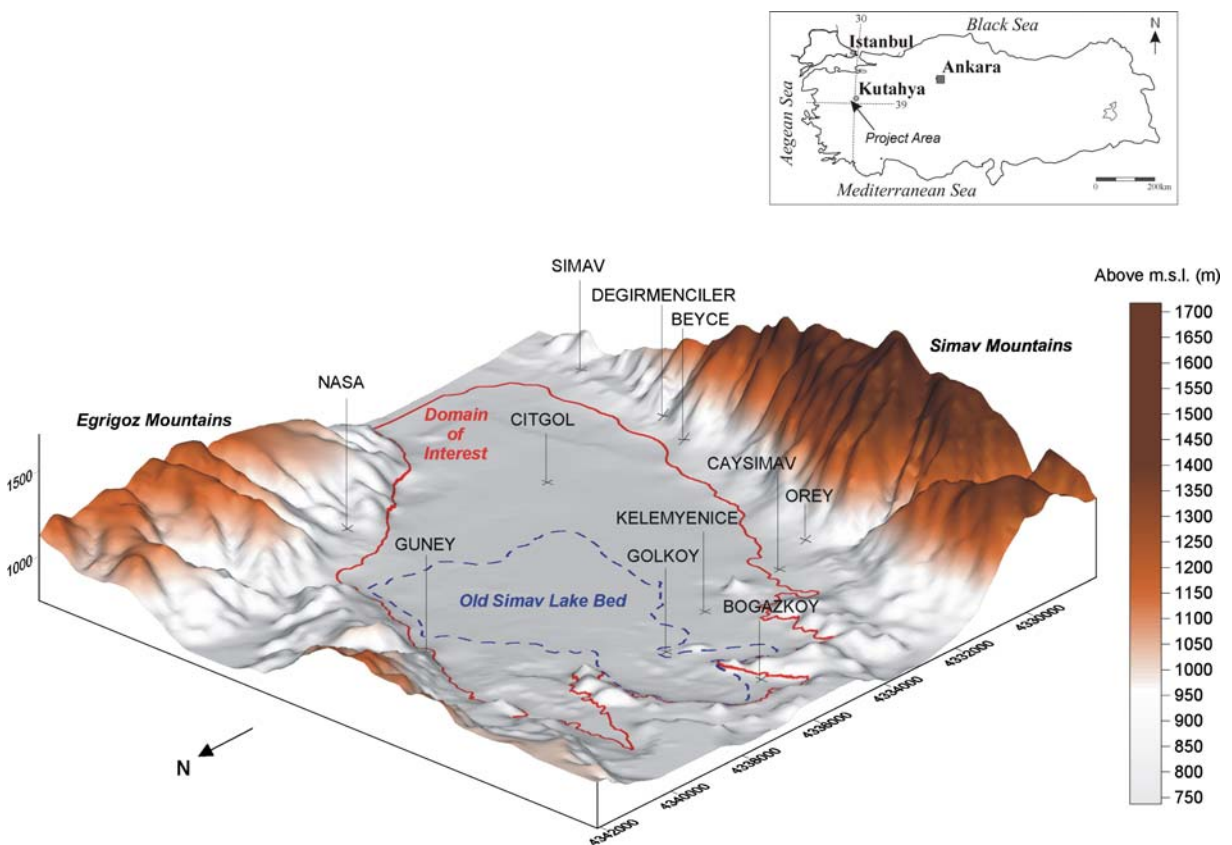
Fig. 1 Location map of the study area (Simsek and Gunduz 2007)

3 Geological and Hydrogeological Setting

Turkey is situated within the Alpine–Himalayan orogenic belt where east–west-directed horst-graben structures are typically observed particularly in the western parts of the country as a result of north–south-directed extensional tectonics (Sengor et al. 1984, 1985; Gemici and Tarcan 2002). Active normal faults are considered to be the major controlling mechanism for the formation of these horst-graben structures. As a consequence of the fracture of rocks with such normal faults, a number of depression zones are created, which are later filled with quaternary-aged alluvial sediments (Seyitoglu 1997). Being a good example to this formation mechanism, the geological map of Simav graben is presented in Fig. 2. As seen from the geological map, five major formations are observed in the study area including (a) the Paleozoic-aged Menderes metamorphics, (b) the Paleocene-aged Egrigoz granite, (c) the Neogene-aged Kizilbuk formation, (d) the Lower Quaternary-aged basalt, and (e) the Quaternary-aged alluvium (Akdeniz and Konak 1979; Hasozbek 2003; Akay 2009).

Metamorphic rocks of the study area belong to the Menderes metamorphics and are mainly composed of schists, gneiss, and marbles that experienced medium to high metamorphism. Schist includes mica and biotite and demonstrates well-developed foliation and lineation. Some marble bands are also observed in schists. Moreover, Pb–Zn and Sb-type sulfite minerals are also developed in schists due to hydrothermal alteration (Vedat and Erler 1999). An old mine (R-9) is observed in the schist of the study area located to the south of Degirmenciler Village near the Simav district center (Fig. 2). This mine was primarily used for lead and zinc production and was abandoned in early 1960s. Gneiss is another widely observed formation in the study area, which mostly includes quartz, feldspar, and plagioclase. Finally, marble unit is typically seen in upper layers in white and gray colors (Hasozbek 2003; Akay 2009).

Magmatic rocks of the study area belong to the Paleocene aged-Egrigoz magmatic complex and mainly consist of granite (Fig. 2). Egrigoz granite surfaces out by cutting the Menderes metamorphics and is frequently observed in the northwestern parts of the study area. Granites mostly consist of aplite and pegmatite dykes. Hydrothermal alteration is also observed along the boundaries of the magmatic rocks, with orthoclase and plagioclase as the major mineralogical content (Hasozbek 2003). Being considered as the primary rock cover of the study area, the Neogene-aged Kizilbuk formation overlies the Menderes metamorphics and the Egrigoz granite. It consists of claystone, conglomerate, sandstone, aglomerate, and tuff. This layer was observed until 435 m depth in a geothermal investigation borehole drilled in the eastern parts of the study area. Following this elevation, the borehole mainly cut metamorphic formations (MTA 1996). The Lower Quaternary-aged Nasa basalt is the youngest volcanic formation that is also considered to be the heat source for the geothermal fields in the study area (Ercan et al. 1984). Finally, the Quaternary-aged alluvium layer overlies these formations and forms the uppermost unit of the Simav graben plain (Fig. 2).

Based on these geological formations, the hydro-geology of the study area is governed by two major aquifer systems (Fig. 3). The first one of these aquifer systems is the alluvial surficial aquifer that supplies cold water. This system provides the majority of groundwater extracted for domestic, agricultural, and industrial use within the plain. The second aquifer, on the other hand, is a part of the local geothermal system formed along major fault lines that pass underneath Simav graben area (Figs. 2 and 3). In this system, hot geothermal waters emerge from the fault line and mix with surface and subsurface waters of the plain. This system resulted in three major geothermal fields located at Nasa, Eynal, and Citgol (Fig. 2). Currently, these fields are used as thermal spas and further supply hot water for the central heating system of the city of Simav.

The alluvial surficial aquifer is mainly composed of sedimentary sands and gravels. The aquifer reaches up to 90 m in thickness and provides the biggest portion of extracted groundwater. The groundwater depth range between 0.2 and 2.0 m, and general groundwater flow is from SE to NW. The depths of water supply wells vary between 15 and 90 m, and all irrigation and drinking water demands are supplied from this aquifer. Sediments of old Simav Lake demonstrate the characteristics of this alluvial layer. These sediments originate from different lithology rocks found in the vicinity of the study area. In particular, significant sediment influx is found to originate from highly weathered Menderes metamorphics located in higher elevations to the southwestern parts of the study area (Figs. 2 and 3). Thus,
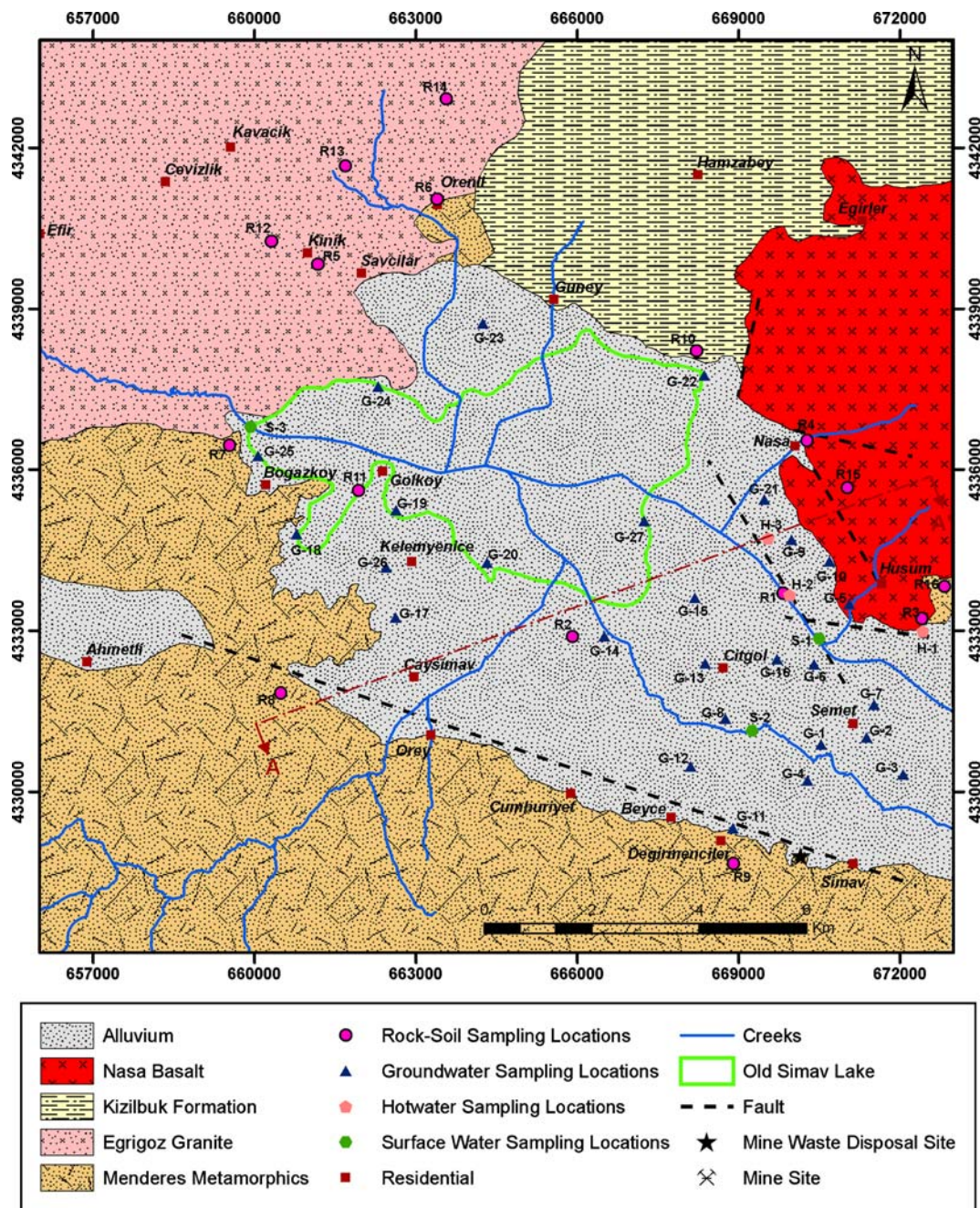
Fig. 2 Local geology and sampling locations map in Simav Plain

geochemical characteristics of samples collected from the alluvium layer are shown to be quite similar to the characteristics of samples from Menderes metamorphics, particularly with regards to trace elements and heavy metals.

The reservoir rocks of geothermal field found underneath Simav Plain are composed of conglom-

erates, sandstones, limestones, schists, and marbles that belong to Kizikbuk formation and Menderes metamorphics. These rocks are broken with the movement of Simav graben faults and are transformed into a fractured structure that plays an important role in the formation and storage of hot waters. These formations demonstrate a productive aquifer, which

Fig. 3 Schematic cross-section of the Simav graben plain
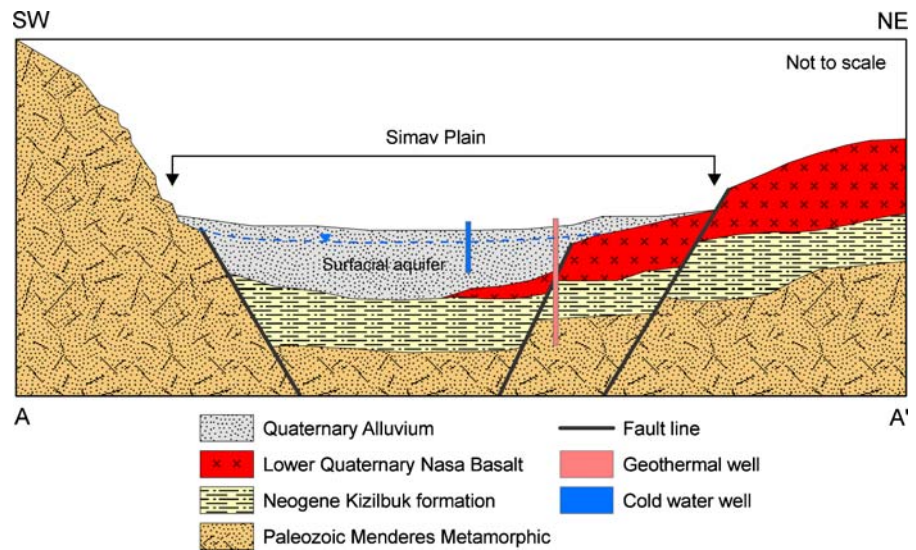
shows confined aquifer characteristics in many parts of the plain. In several geothermal boreholes drilled around Citgol and Eynal, this system exhibits free-flowing artesian characteristics.

4 Materials and Methods

A multidisciplinary research was conducted to understand the origin of high arsenic levels within the water resources of Simav Plain. A multimedia sampling program was conducted to assess the origin and contamination mechanisms of surface and subsurface water resources of the plain. Although the program was designed to achieve a general characterization of the area, it primarily focused on the source and the transport characteristics of trace elements with particular emphasis on arsenic. To achieve this objective, representative samples from regional rocks and soils, hot geothermal fluids, surface waters, and subsurface waters were collected as part of a field survey and were analyzed using standard techniques.

The rock–soil sampling program was performed with a total of 16 sampling stations as shown in Fig. 2. Samples are collected from different formations that characterize the regional geology of the study area. Of a total of 16 samples, five were taken from metamorphic rocks (R-6, R-7, R-8, R-9, and R-16); four were taken from granites (R-5, R-12, R-13, and R-14); three were taken from basalts (R-3, R-4, and R-15); three were taken from alluvial soils (R-1, R-2, and R-11); and one was taken from Neogene

formations (R-10). From each rock–soil sampling station, a total of 1-kg sample was collected and ground in the laboratory into powder form. Then, 1 g of the sample was taken and dissolved in an acid solution that contains 6 mL HF (40%) and 3 mL HCl (37%)/HNO$_3$ (67%), diluted at a ratio of 1:3. The mixture was held at 95°C for 1 h. Later, the solution was filtered and pure water was added until a 100-mL solution was obtained. The solution was then analyzed for dissolved trace and heavy metals at ACME Laboratories (Canada) via the inductively coupled plasma-mass spectrometry (ICP-MS) method.

The water quality sampling program was performed with a total of 33 sampling stations. Of these 33 stations, 27 were taken from cold groundwater production wells (G-1 through G-27) drilled in the alluvial surficial aquifer for domestic and irrigational water supply purposes; three were taken from deep geothermal wells (H-1, H-2, and H-3) that extracted hot geothermal fluid for three geothermal fields located in the plain; and the remaining three were taken from the drainage network (S-1, S-2, and S-3) to represent the quality pattern in surface waters (Fig. 2). Among the cold groundwater production wells, G-7, G-16, and G-17 were water supply wells for three residential areas (i.e., Simav district center, Citgol, and Kelemyenice villages, respectively). Selection of groundwater sampling points was performed such that an optimum homogeneous distribution was obtained to characterize the quality of groundwater in the surficial aquifer with the highest possible accuracy. Hydrogeochemical analysis of these

33 samples were undertaken to depict not only the overall quality pattern in the plain but also the general circulation and contamination mechanisms.

Prior to groundwater sampling, wells were operated for a minimum of 15 mins until electrical conductivity of water was stabilized. Then, two sets of samples were collected from each sampling station (i.e., 1,000 mL for standard anion and cation analysis and 50 mL for trace element and heavy metal analysis). All samples were filtered (0.45 μm) and stored at 4°C in polyethylene bottles until analysis. All 50-mL samples collected for trace element and heavy metal analysis were acidified to achieve pH value of less than 2. The pH (WTW-pH330), temperature (WTW-pH330), and electrical conductivity (EC) (WTW-EC330) measurements were conducted in the field with portable instruments. Cation and trace element analyses were performed with ICP-MS in ACME Laboratories (Canada). Chloride and bicarbonate ions were analyzed with titrimetric methods (EPA 325.3 and SM 2320); nitrate measurements were done by spectrophotometric methods (EPA 353.3), and sulfate analyses were conducted with gravimetric methods (EPA 375.3) in Dokuz Eylul University laboratories. All anion analyses were conducted with standart procedures with 2% analytical error. Aquachem v3.70 computer program was then used to conduct primary computations of water chemistry and correlation analysis between the parameters. Accordingly, the error in anion–cation balance was computed to be less than 2.5% in all groundwater samples.

A geographic information system (GIS) platform is then developed to provide a tool that would allow spatial analysis of parameter distributions within the study area. Parameter distribution maps are generated by implementing the built-in interpolation algorithm (i.e., inverse distance weighing) of the GIS platform (ArcGIS v9.1) used in this study. It must be mentioned, however, that a specific domain of interest is defined to include only the alluvial surficial aquifer considering the disperse locations of the wells used in groundwater sampling.

5 Results and Discussions

5.1 Rock Geochemistry

The results of the rock and sediment sampling program that was conducted to determine the geo-chemical features of rock lithologies which crop out in the project area are given in Table 1. In the study area, four rock groups were found to crop out. These are metamorphic rocks, magmatic rocks, cover sedimentary rocks, and alluvium which unconformably overlay the entire area as a result of physical weathering. The basement rocks of the area are metamorphic rocks, which are named as quartz–albite schist according to their biotite, muscovite, plagioclase, and quartz contents. The basement metamorphic formations are intrusively cut by the Egrigöz granite which forms the main magmatic unit of the area. The geochemical and geological features of the Egrigöz granite with its surrounding formations were previously studied in detail by Akay (2009). According to this study, these magmatic rocks are mainly made up of quartz, feldspar, plagioclase, biotite, and accessory minerals such as zircon, titanite, and in places tourmaline, demonstrating typical holocrystalline texture due to slow cooling processes of a magma in a shallow crust environment (Hasozbek 2003; Akay 2009).

In the detailed major element chemistry analysis, it has been found that SiO_2 is the most abundant specie in all rocks of the study area. Al_2O_3 is the second dominant specie with values ranging between 6.0% and 17.04% in metamorphic rocks, 8.02% and 16.38% in basalts, 12.9% and 20.39% in granites, and 1.18% and 12.99% in alluviums. Analysis of the correlation coefficients between oxide minerals of these rocks reveals that Al_2O_3 is negatively correlated with MnO and slightly positively correlated with Fe_2O_3, whereas Fe_2O_3 is positively correlated with TiO_2. These results point out the fact that hematite is dominant in the rocks of the study area. Na_2O and K_2O, respectively, range between 0.05–2.95% and 1.31–7.25% in metamorphic rocks, between 2.85–3.82% and 2.47–4.99% in granites, and between 0.01–2.58% and 0.41–3.61% in alluviums (Table 1). In particular, biotite, muscovite, and albite were found to be responsible from the moderately high values of Na and K in metamorphic rocks. In general, CaO values of all samples were low.

General dominance of feldspar and biotite minerals in meramorphic rocks as well as the development of Fe oxidation is considered to be a strong indication for hydrothermal alteration in the study area based on the general assessment of rock geochemistry given in Table 1. Presence of hydrothermal alteration and the

Table 1 Geochemical results of rock and sediment samples

Rock–soil sample	X	Y	Formation	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	MgO (%)	CaO (%)	Na$_2$O (%)	K$_2$O (%)	TiO$_2$ (%)	P$_2$O$_5$ (%)	MnO (%)	Cr$_2$O$_3$ (%)	As (ppm)	Au (ppb)	Ba (ppm)	Co (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
R-1	669825	4333702	Alluvium	12.99	4.82	1.96	5	2.58	2.5	0.93	0.24	0.08	0.041	57.6	1.9	499.6	13.3	15.3	1.1	73.2	26.8	1.8	49.0
R-2	665910	4332887	Alluvium	14.7	5.31	1.94	2.48	1.91	3.61	0.53	0.17	0.16	0.02	87.1	3.7	736	17.3	33	1.9	101.5	33	3.4	75.0
R-3	672411	4333229	Basalt	8.02	3.88	1.27	3.07	1.17	1.99	0.61	0.33	0.07	0.019	6.1	2.2	681.3	16.3	19.3	0.5	68.7	4.2	0.2	32.0
R-4	670267	4336541	Basalt	15.84	7.08	3.54	7.21	2.71	3.93	1.14	0.7	0.16	0.026	5.5	75	1,285.7	24.1	45.4	1	72.8	9.7	0.2	69.0
R-5	661178	4339825	Granite	20.39	5.41	1.36	4.55	3.82	2.47	0.54	0.51	0.07	0.001	4.1	10.2	1,054.3	5.9	22.9	0.2	8.1	14.6	0.2	74.0
R-6	663391	4341033	Metamorphics	17.04	8.48	2.01	1.32	2.34	3.17	0.79	0.28	0.11	0.006	89.3	9.8	792.4	28.6	180.9	0.6	35.5	24.3	0.6	74.0
R-7	659537	4336458	Metamorphics	13.54	1.43	0.26	0.77	2.95	4.83	0.15	0.29	0.01	0.001	10.4	7.4	273.2	1.6	8.9	0.3	4.1	4	0.1	11.0
R-8	660488	4331839	Metamorphics	6.0	6.18	1.04	0.09	0.05	1.4	0.62	0.17	0.02	0.011	95.2	5.7	379.6	6.3	5.1	0.5	15.4	5.4	0.2	19.0
R-9	668903	4328664	Metamorphics (mine)	9.04	2.98	0.97	0.66	0.06	1.31	0.55	0.07	0.01	0.011	660.1	281.6	86.8	0.9	13.9	14.6	2.9	20.3	440.3	16.0
R-10	668215	4338210	Tuff	13.25	1.55	0.94	3.17	1.97	2.45	0.22	0.06	0.02	0.004	8.3	6.1	953.8	2	8.6	0.2	3.6	48.6	1.5	16.0
R-11	661935	4335611	Alluvium	1.18	3.51	0.85	0.49	0.01	0.41	0.08	0.07	0.05	0.004	31.6	1.4	119.8	14.1	39.3	3.4	43.6	32.1	2.9	91.4
R-12	660312	4340245	Granite	12.9	1.17	0.22	0.81	2.85	4.99	0.13	0.03	0.02	0.005	9.7	1.5	329	2.4	1.4	0.4	1.3	9.2	0.7	10.0
R-13	661690	4341655	Granite	15.9	3.51	1.24	3.67	3.37	2.7	0.37	0.17	0.07	<0.001	0.7	0.9	754	5.1	3.7	0.1	5.2	3.5	0.1	42.0
R-14	663563	4342900	Granite	14	1.15	0.32	1.39	3.69	3.89	0.16	0.05	0.02	<0.001	0.8	1.5	911	1	1.2	0.1	1.1	8.3	0.1	12.0
R-15	671018	4335660	Basalt	16.38	3.8	1.32	3.73	3.28	3.22	0.42	0.24	0.07	<0.001	0.5	<0.5	1090	5.1	3.2	<.1	1.7	2.6	0.1	43.0
R-16	672825	4333820	Metamorphics	13.1	1.73	0.71	0.48	1.57	7.25	0.23	0.05	0.03	<0.001	20.9	0.5	770	3	1.3	0.5	2.3	9.1	9.5	34.0

associated metal formation were also reported by previous mineralogical studies (Vedat and Erler 1999). Since the majority of alteration was observed in metamorphic rocks of the study area, it was concluded that this formation is the primary source of sediments deposited in the Simav graben plain. Furthermore, there were similarities between geochemical compositions of metamorphic rocks (Fig. 4) and alluvial sediments (Fig. 5). Thin section analysis conducted on the rocks of the study area exhibits Fe oxidation particularly in metamorphic and magmatic rocks (Fig. 4).

Elemental analysis conducted to isolate the source of arsenic in rock samples has revealed values that range between 20.9 and 660.1 mg/kg in metamorphic rocks, 0.8–9.7 mg/kg in granites, 0.5–5.5 mg/kg in basalts, and 31.6–87.1 mg/kg in alluvial sediments. As seen from Table 1 and shown in Fig. 6, the highest arsenic composition was detected within metamorphic rocks and in a sample (R-9) collected from the old Cu–Pb–Zn mine. The strong positive correlation between arsenic and Fe, Cu, Sb, and Pb demonstrates a situation where arsenic and other elements have developed as a consequence of arsenic containing iron and sulfur oxidation. In particular, arsenopyrites (FeAsS), chalcopyrites ($CuFeS_2$), galenas (PbS), sphalerites (ZnS), hematites (Fe_2O_3), proustites


Fig. 5 Fe-oxidizing layer in alluvial sediments

(Ag_3AsS_3), and marcasite (FeS_2) are among the commonly observed minerals within or near hydrothermal and epithermal zones (Guilbert and Park 2007). Iron and sulfur oxidation is thus considered to be the main source of arsenic and other trace and heavy metal occurrences. The Fe_2O_3 composition of rocks is, therefore, believed to control the contents of some metals in the study area. In particular, the positive correlation of Cu, Pb, and Zn with Fe show the dominant influence of Fe oxidation in metamorphic rocks. This finding also explains the presence of

Fig. 4 Fe oxidation in gneiss (a), metamorphic (b), and volcanic (c, d) rocks in thin sections
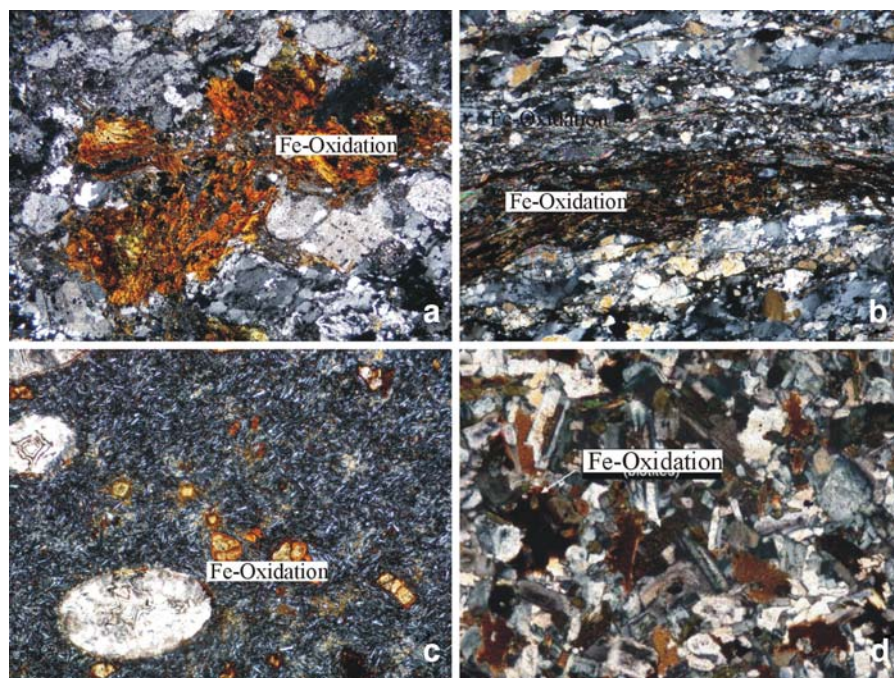
Fig. 6 Distribution of trace element composition in rock samples
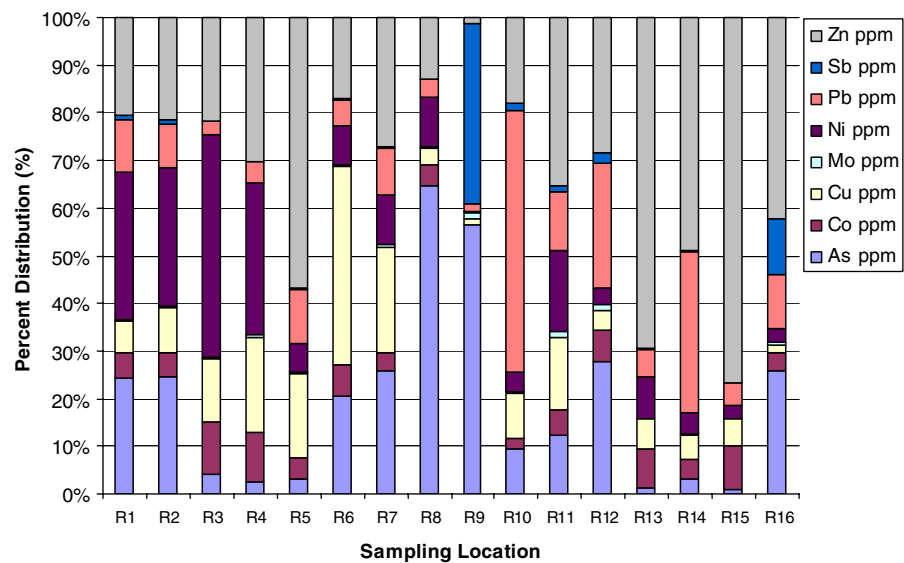
Cu–Pb–Zn mine sites within this rock formation such as the one close to the Simav district center shown in Fig. 2.

5.2 Water Geochemistry

A statistical overview of the results of water sampling program is given in Table 2. The water samples were previously grouped into three categories: (a) surface water samples, (b) groundwater samples, and (c) geothermal fluid samples. This categorization provided an opportunity to not only demonstrate the separate quality patterns in these waters but also to show the potential interactions between the three systems with regards to arsenic characterization and contamination.

Based on the Piper diagram given in Fig. 7, the surface and subsurface water samples collected from the plain are typically Ca-HCO$_3$- and Na-HCO$_3$-type waters, whereas hot geothermal fluid samples are Na-HCO$_3$-type waters. The results obtained from the sample collected from the shallow G-15 sampling station (<30 m) and the sample collected from the moderately deep G-19 sampling station (>100 m) demonstrate similar facies characteristics to hot geothermal fluid samples. The hot water samples were obtained from three geothermal fields (i.e., Eynal, Citgol, and Nasa) in the plain and had temperature values ranging between 76.6°C and 114.0°C. The pH and electrical conductivity values of these samples were between 7.30 and 8.32, and

1,460 and 2,357 μS/cm, respectively, demonstrating the characteristics of slightly alkaline high mineral content hot waters. Surface and subsurface samples, on the other hand, were low temperature waters with mostly neutral pH values. The electrical conductivity values of surface and groundwater samples range between 875–1,243 and 82–1,789 μS/cm, respectively, as shown in Fig. 8. The high conductivity value measured in surface waters was recorded a point downstream the discharge point of waste geothermal fluid of Eynal geothermal field. Similarly, high conductivity values measured in groundwater samples were also recorded in G-9, G-15, and G-25 sampling stations, all of which were water supply wells drilled deep to maximize water production.

With regards to major ion results given in Table 2, hot water samples were found to differ from surface and subsurface waters. While Na and K were the dominant species in hot waters, Ca and Mg were the major ions in surface water and in groundwater samples. In hot waters, Ca and Mg concentrations were lower than the national drinking water limits, whereas Na and K were above these limits as shown in Table 2. In surface and subsurface samples, major ion values were below the national limits. Nevertheless, these ions were found to be comparably high in areas of high electrical conductivity as a result of the fairly high correlation coefficients between electrical conductivity and these ions.

The results of elemental analysis covered toxic and trace elements found in hot geothermal fluids, surface

Table 2 Statistical summary of water quality monitoring in Simav Plain

Parameter	Unit	Surface water samples (N=3)				Ground water samples (N=27)				Geothermal water samples (N=3)				Water quality standards		
		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	ITASHY[a]	EPA[b]	WHO[c]
Temperature	°C	18.1	22.5	19.9	2.3	12.5	25.7	17.6	2.9	76.6	114.0	91.5	19.8	–	–	–
pH	–	7.0	7.9	7.4	0.45	6.4	7.6	7.2	0.3	7.3	8.3	7.9	0.5	6.5–9.5	6.5–8.5	6.5–8.5
EC	µS/cm	875	1,243	1,105.3	200.7	82	1,789	693.5	394.7	1,460	2,357	2,039.0	502.2	2,500	–	–
Ca^{+2}	mg/L	76.5	104.9	89.9	14.3	8.5	286.1	91.0	54.8	11.6	50.4	25.4	21.7	200	–	–
Mg^{+2}	mg/L	25.0	36.0	29.6	5.7	3.1	57.2	24.3	13.1	0.2	8.5	3.3	4.5	50	–	–
Na^+	mg/L	46.3	137.8	104.5	50.6	5.7	297.0	41.8	68.6	312.4	536.3	420.0	112.2	200	–	200
K^+	mg/L	18.2	149.3	91.0	66.7	0.1	31.0	4.9	7.4	34.0	63.4	45.7	15.6	10	–	–
Cl^-	mg/L	18.0	42.0	26.3	13.6	8.0	65.0	21.4	18.0	45.0	84.0	67.7	20.3	250	250	250
NO_3^-	mg/L	1.9	12.5	6.7	5.4	0.0	17.8	2.9	4.3	0.3	0.8	0.6	0.4	50	44.3	50
SO_4^{-2}	mg/L	127.0	145.5	135.0	9.5	28.0	474.8	130.4	114.4	215.0	423.1	335.2	107.8	250	250	250
HCO_3^-	mg/L	391.2	685.0	565.9	154.6	85.4	693.6	325.8	151.6	487.9	715.7	619.4	117.9	–	–	–
Al	µg/L	93.0	1,552.0	645.3	791.4	1.0	469.0	91.7	130.1	12.0	265.0	103.7	140.2	200	200	200
As	µg/L	60.0	179.2	124.6	60.2	0.5	561.5	99.1	138.0	436.7	594.0	502.5	81.7	10	10	10
B	µg/L	345.0	1,065.0	743.7	366.2	20.0	2,538.0	205.4	573.8	2,999.0	4,381.0	3,597.0	709.5	1,000	–	500
Cu	µg/L	1.9	6.4	4.1	2.3	0.5	35.5	4.4	8.5	2.2	6.4	4.7	2.2	2,000	1,000	2,000
Fe	µg/L	428.0	1,694.0	1,191.3	672.1	10.0	14,551.0	1,766.6	3,382.3	10.0	122.0	59.0	57.3	200	300	200
Li	µg/L	17.4	317.2	206.7	164.7	0.6	869.2	77.2	221.5	950.0	1,828.6	1,298.1	466.8	–	–	–
Mn	µg/L	414.7	545.8	473.8	66.5	0.5	3,356.4	941.4	1,073.3	10.9	290.8	106.1	159.9	50	50	400
Pb	µg/L	1.0	3.6	2.7	1.5	0.1	2.9	0.9	0.9	0.1	5.4	1.9	3.0	10	15	10
Sb	µg/L	0.3	3.4	2.0	1.6	0.1	4.0	0.5	0.9	4.4	63.6	32.6	29.7	5	6	20
Zn	µg/L	11.2	74.9	39.9	32.3	0.8	3,451.8	151.7	660.7	9.6	385.3	153.5	202.7	–	5,000	5,000

[a] ITASHY (2005)
[b] EPA (2003)
[c] WHO (2004)

Fig. 7 Distribution of water samples in Piper diagram
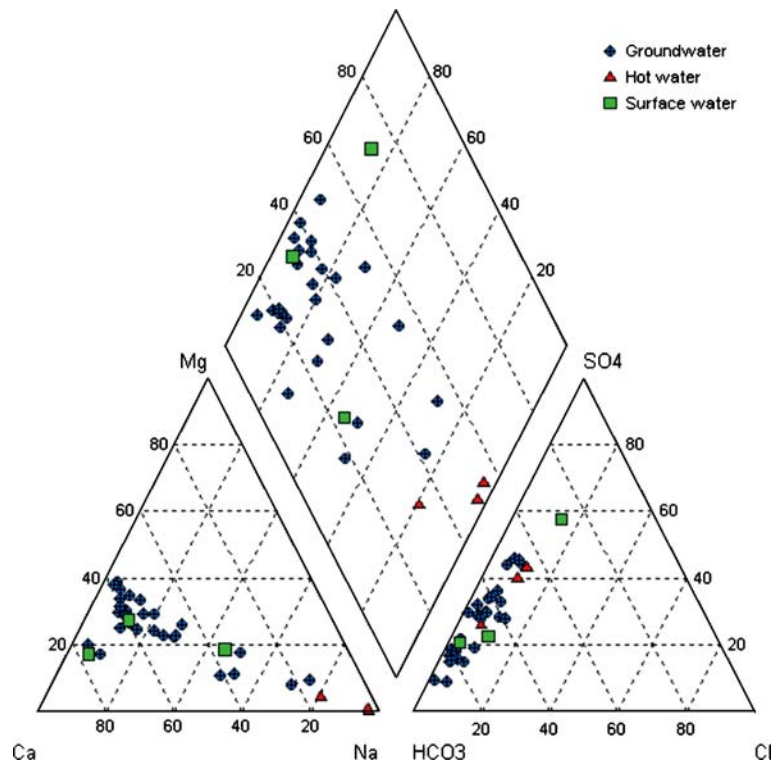
waters, and groundwaters of Simav Plain (Table 2). The results indicated a mixing pattern between hot geothermal waters with cold waters resulting in an increase in trace and toxic element concentrations in cold waters. Particularly, Al, As, B, and Li were found to be well beyond the typical values that would normally be found in cold water reserves (Table 2). Al values were high in the deep geothermal well (i.e., >400 m) of the Eynal field (H1), and As, B, and Li values were high in all three geothermal wells. Hot waters were generally enriched with minerals due to rock–water interaction under high temperature and pressure in deep aquifer systems. As a result of this characteristic, hot geothermal waters typically contained more major ions and minor elements as opposed to cold surface and subsurface waters.

Considering the fact that temperatures of hot geothermal waters within the reservoir were around 175–200°C (Gemici and Tarcan 2002), it could be concluded that the water chemistry was mostly controlled by temperature and pressure in a deep aquifer system. Among all minor elements, arsenic is particularly important due to its extreme toxicity for humans. Arsenic concentrations in hot water samples were measured to be between 436.7 and 594.0 μg/L,

which correspond to about 50 times the national and international standards (Table 2). Such high levels are extremely toxic in waters that are used for drinking purposes. Therefore, mixing of hot geothermal waters with cold water resources of the plain demonstrates a potential health risk for the inhabitants of the study area. The arsenic chemistry in hot waters of Simav Plain was found to be controlled primarily by the reservoir rock geochemistry and was further controlled by the dissolution of arsenic-containing iron and sulfur minerals found in metamorphic rocks. As a natural outcome of this situation, arsenic levels in cold surface and subsurface waters were also found to be above the national and international standards. A plot of arsenic distribution in surficial groundwater aquifer is presented in Fig. 9, which further demonstrates the above-standard situation in the plain. Possible reasons of this high arsenic occurrence in cold waters are given in the following section.

5.3 Source Characterization and Mixing Patterns of Arsenic in Simav Plain

Arsenic-containing iron and sulfur oxidation in local lithological units is the predominant mechanism for
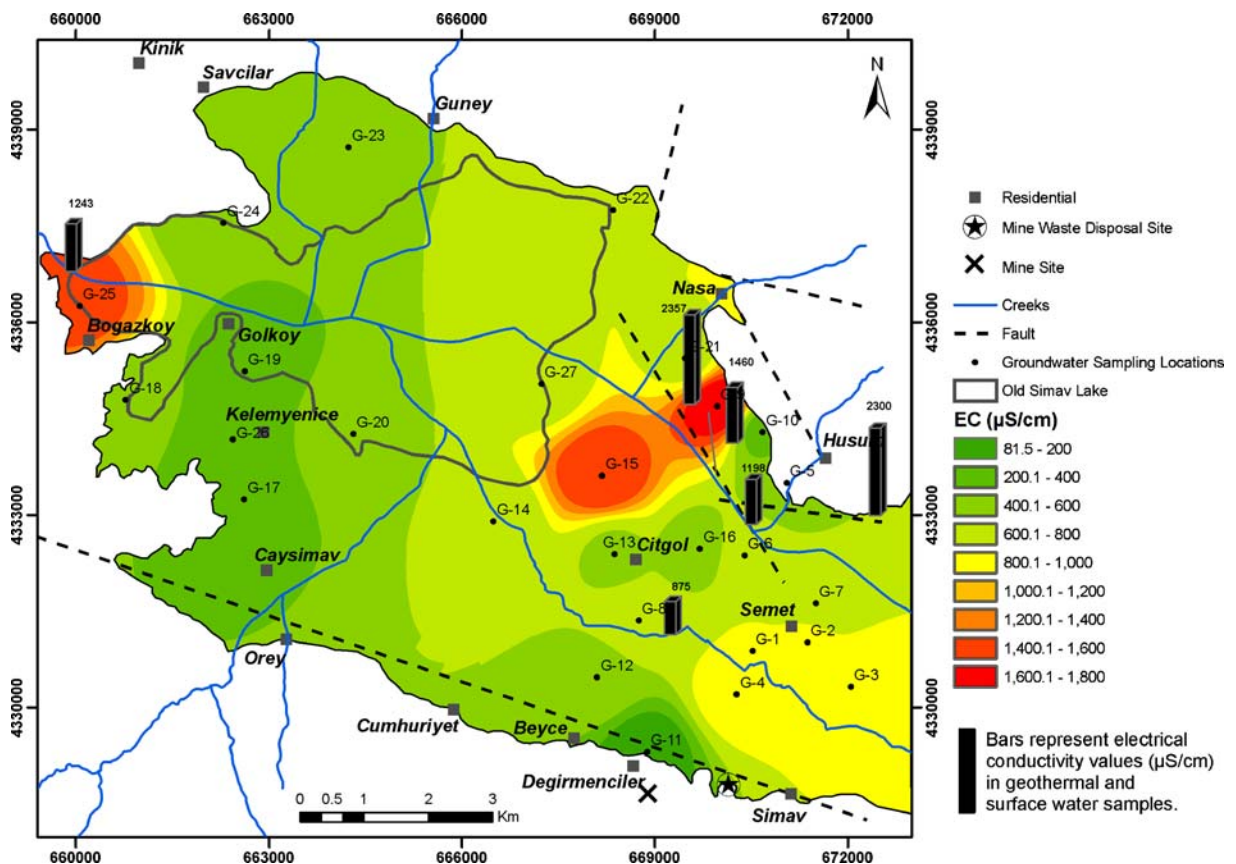
Fig. 8 EC distribution in alluvial aquifer

the release of arsenic into water column as discussed by McArthur et al. (2001). Based on the geochemical analysis conducted on local formations, iron and sulfur oxidation is dominant in metamorphic rocks (Fig. 4) and in the alluvial layers (Fig. 5) that are formed by the sediments of these rocks. The old Cu–Pb–Zn mine and its waste disposal site near the Simav district center are also considered to be other important sources of arsenic in the study area. This mine and its disposal site are situated on the northern slopes of the mountain range to the south of the plain. These slopes are extremely prone to water erosion and are believed to be a major source of the alluvial sediments deposited in the plain. Because of these two sources, the highest arsenic concentrations measured in groundwater were detected in two shallow wells (sampling stations G-4 and G-12) that are located in close proximity to these slopes and to the mine site (Fig. 9). These two wells collect water from a layer that contains sediments eroded from these slopes containing elevated levels of arsenic (Table 1).

Arsenic levels measured in these stations reached as high as 561.1 µg/L and corresponded to a value that is more than 50 times higher than the currently effective national (ITASHY 2005) and international standards (EPA 2003; WHO 2004). In general, only seven of the 27 wells sampled contained arsenic levels below the standard value of 10 µg/L. In all remaining wells, arsenic levels were recorded to exceed the standard level. The depths of these wells ranged between 50 and 130 m and are mainly drilled in the surficial alluvial aquifer.

Arsenic release from geological formations is considered to be the most important arsenic source in Simav Plain. Transported sediments from surrounding slopes are deposited within the plain to form the alluvial surface aquifer, which contains variable levels of iron oxide and arsenic along the vertical and horizontal cross-sections. In particular, the iron concentration distribution given in Fig. 10 demonstrates the fact that it is mostly observed in the centrals parts of the alluvial plain as well partly in the
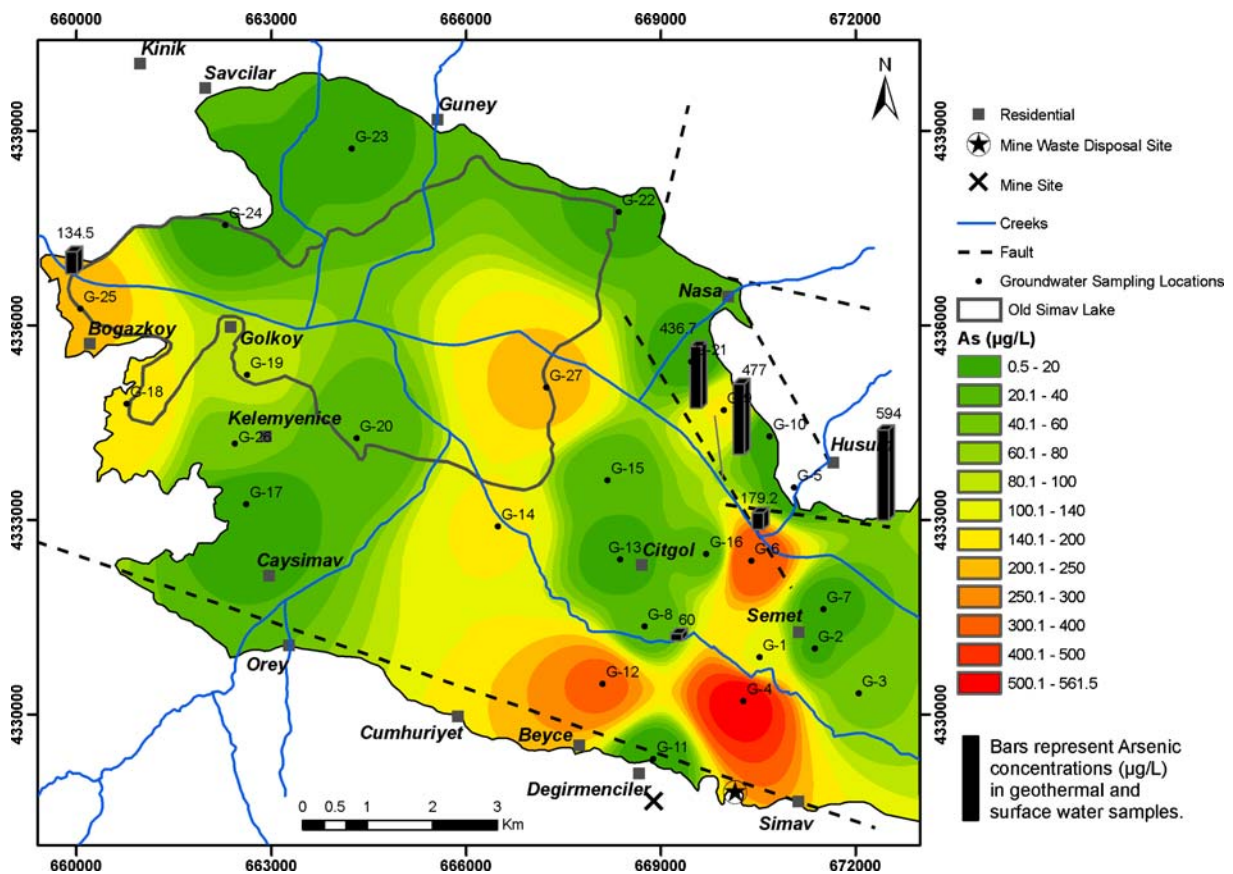
Fig. 9 As distribution in alluvial aquifer

vicinity of the mine site. Iron concentrations were found to be above standard levels in about 60% of all samples collected from the cold groundwaters of the surface aquifer.

Positive correlation values between arsenic and iron (0.35), manganese (0.68), and zinc (0.41) further support the fact that iron oxide-containing aquifer material is the predominant mechanism affecting water quality and arsenic contamination in the aquifer. Arsenic concentrations in the aquifer are partly controlled by its release from the arsenic-containing iron oxide zones of the alluvial layer under favorable redox potential values. In other studies regarding redox-dependent arsenic release, Hem (1985) has found that iron oxidation is high and could reach to levels as high as 10,000 μg/L under suitable redox conditions in sedimentary aquifers. Iron levels exceeding this level were recorded in Simav Plain, particularly in the vicinity of G-12 sampling station, which is believed to be associated with suitable redox

levels as a result of acidic mine drainage next to the waste dump area of the old mine site (Fig. 10).

In general, arsenic containing hot waters is another mechanism for arsenic release to the environment. As reported by Wilkie and Hering (1998), arsenic in geothermal waters could quickly oxidize from +3 to +5 form, the most stable form of arsenic in natural waters. From this point of view, it is also believed that the high arsenic levels in Eynal, Citgol, and Nasa geothermal fields are released into the environment upon oxidation to +5 form. These hot waters rich in arsenic have concentrations ranging between 476 and 594 μg/L, which are more than 50 times the standard value (Fig. 9 and Table 2). Mixing of these hot waters with cold water reserves of the plain via natural phenomena as well as thru anthropogenic intervention is believed to be responsible for elevated arsenic levels in a number of sampling stations including G-6, G-9, and G-25. Since EC, Li, and B are used as tracer compounds in hot geothermal waters of western
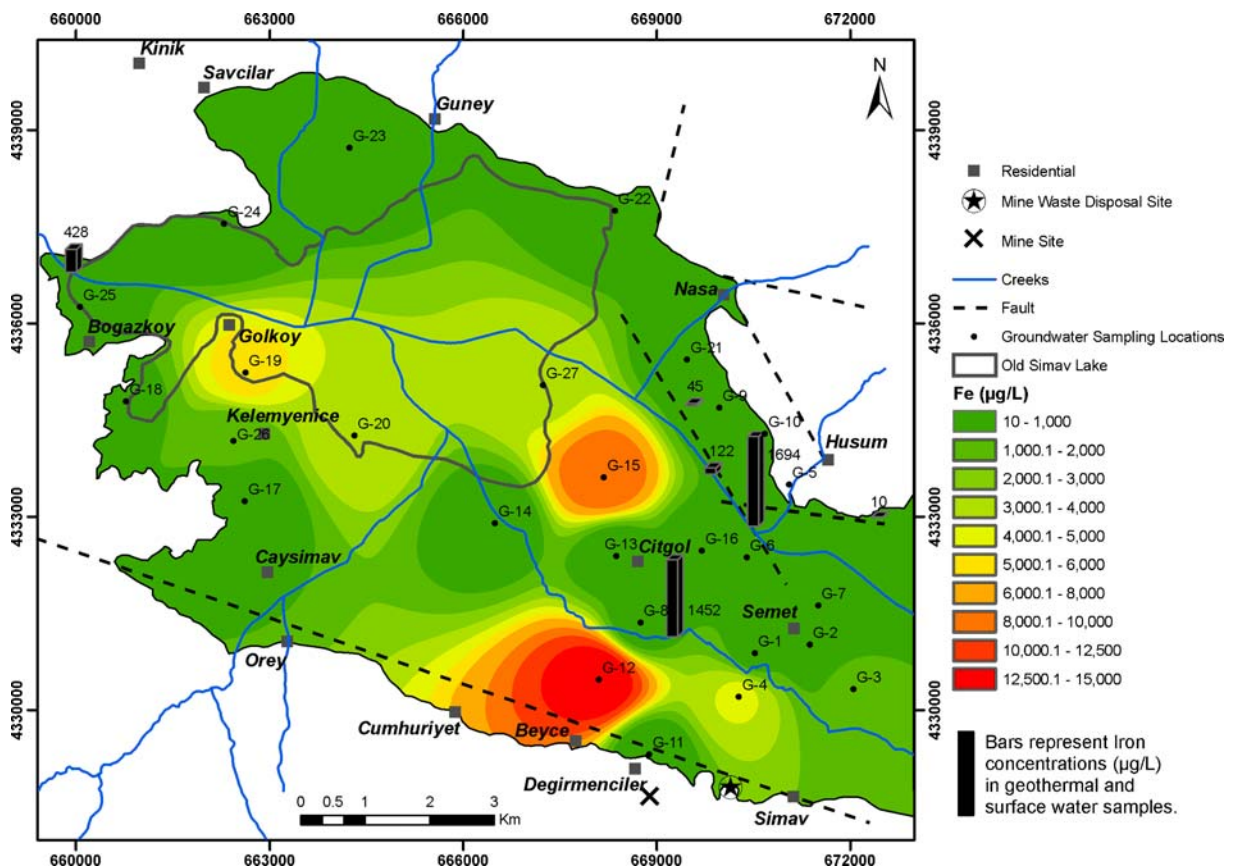
Fig. 10 Fe distribution in alluvial aquifer

Anatolia (Gemici and Tarcan 2004), areal distribution maps of these parameters were plotted in the surface aquifer. As seen from EC distribution given in Fig. 8 and the Li distribution given in Fig. 11, it could be hypothesized that one of the sources of high arsenic levels in the fresh aquifer waters (particularly in the wells G-6, G-9, G-18, and G-25) is the contamination by the hot geothermal fluid. Moreover, the groundwater temperature values in these wells were recorded to be 3–5°C higher than the typical groundwater temperature measured in other sampling stations, which is a further clue for hot water mixing into the surface aquifer. Since these wells were drilled deep into the unconfined aquifer and provide significant amounts of water for agricultural irrigation and domestic water supply, they operate intensively and overexploit the alluvium aquifer. The moderately high depths together with the overexploited operational patterns are believed to further accelerate the rate of hot water mixing into the surface aquifer from deeper layers. Overexploitation is a pure anthropogenic

influence on the aquifer, which increases the speed of contamination by hot geothermal fluid. Thus, hot water drilling activities in the plain coupled with overexploitation of the aquifer as well as the uncontrolled discharge of waste geothermal fluid into the surface drainage network are all considered to be possible mechanisms of contamination via anthropogenic influence. Nevertheless, this anthropogenic influence is still believed to be low compared to natural contamination originating from the local geological formation within the plain.

5.4 Health Effects and Risk Assessment

A statistical death analysis has been conducted in Simav Plain in order to search a clue regarding the influence of water quality in the increased rates of human health problems observed among the inhabitants of Simav Plain, particularly in areas such as Citgol, Kelemyenice, and Bogazkoy (Fig. 1). Within the scope of this analysis, the cause and age of deaths
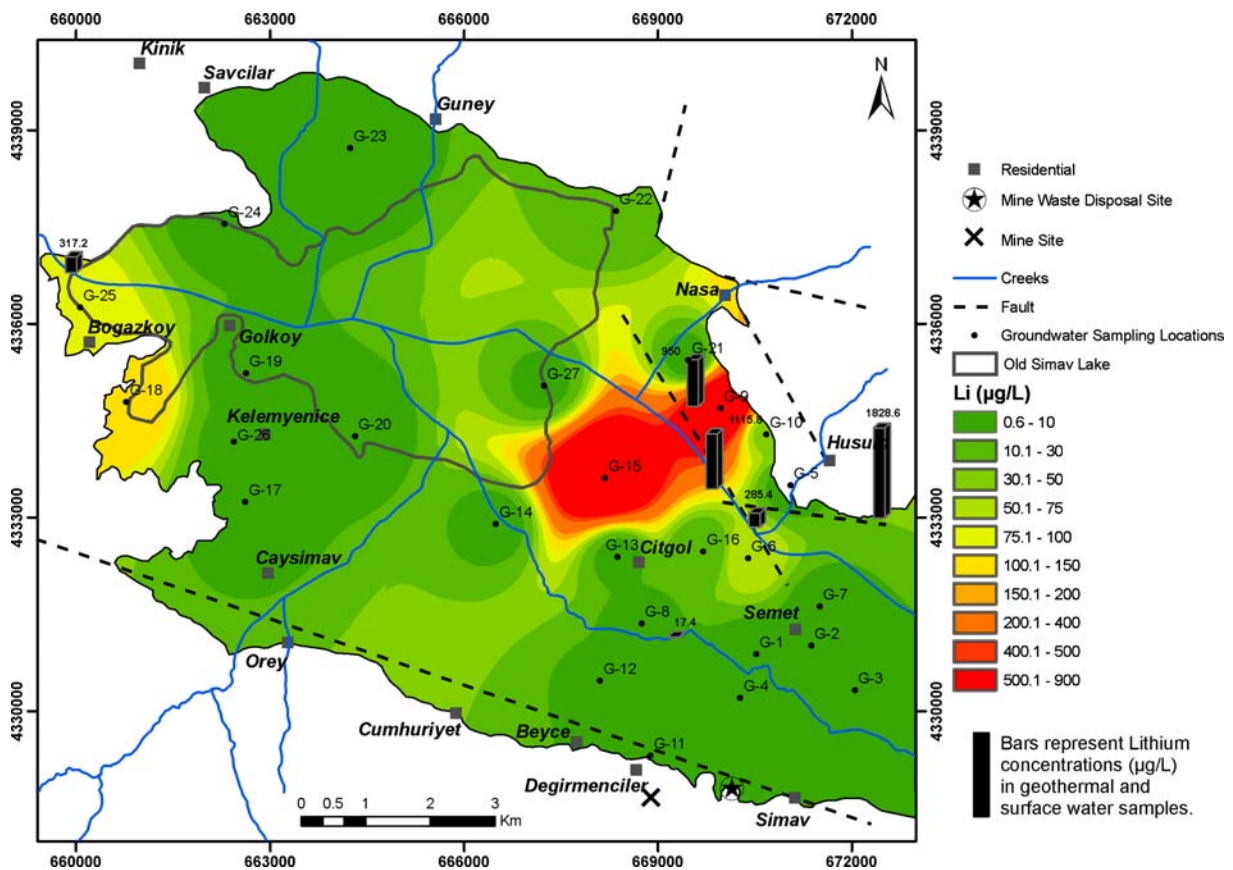
Fig. 11 Li distribution in alluvial aquifer

in the last 10 years were traced from hospital and health center records and were compared with the general averages of Turkey. According to the results of this analysis, it has been found that a total of 221 people have died in the three residential areas mentioned above between the period of 1998 and 2005. Of this total, 45.2% have died from cardiovascular diseases (primarily from heart attack), 15.8% have died from cancer, and 5.7% have died from respiratory depression. The remaining 33.3% have died from other causes including but not limited to apoplexy, senility, accidents, diabetes, and unknown causes. In particular, people who died from cancer aged between 35 and 80. Moreover, different cancer types were recorded in the area. Of all cancer deaths, 34.1% were from lung cancer, whereas 20.0% were from stomach cancer, 20.0% were from colon and prostate cancer, 17.1% were from liver cancer, and 8.8% were from skin and from other cancers. As seen from these figures, gastrointestinal cancers sum up to 40% of all cancer-related deaths in the area. When the

general death statistics of Turkey are considered, it is seen that 38% of all deaths are related to cardiovascular diseases where heart attack is the most important cause of death. Cancer has the second highest ratio with a total of 15%. Of this percentage, skin cancer and breast cancer take the highest ratios with 14.9% and 9.1%, respectively (Firat and Celik 1998; Sengelen 2002). When the death statistics of Turkey and the project area are compared, it is clearly seen that gastrointestinal cancers have the highest percentage in the project area despite the fact that they are of minor importance compared to other cancer types in Turkey.

It is known that arsenic and other toxic elements are among the primary causes of human cancers throughout the world (Mazumder et al. 1992; Smith et al. 1992; ATSDR 2000; WHO 2001). In this regard, numerous researches have been conducted in Bangladesh and other parts of the world where arsenic in drinking water was considered to be the major cause of cancer incidences. Studies conducted in Bangladesh and other areas facing arsenic problem has

reported values such as 10 μg/kg as the chronic arsenic exposure limit (Ali and Tarafdar 2003), 10–19 μg/kg as the daily upper limit for arsenic intake for adults and 5–15 μg/kg for acute or subchronic exposure limits for children aged between 0 and 6 (Tsuji et al. 2004).

In this particular study, average arsenic level in the groundwater was computed to be 99.2 μg/L in Simav Plain surface aquifer, from which drinking water is heavily extracted. With the assumption that an average 60-kg adult would intake a maximum of 2 L/day drinking water, an average exposure limit of 3.3 μg/kg was computed in Simav Plain. This value could reach to a level as high as 13 μg/kg in wells with the highest arsenic levels. Based on the slope factor value of 1.5 $(mg/kg/day)^{-1}$ for skin cancer risk, the average risk that a Simav Plain inhabitant would face is computed to be 4,950 in 1,000,000. This is an extremely high risk level for skin cancer development. Unfortunately, slope factors for gastrointestinal cancers are officially not released, and hence, the risks associated with these cancer types are not quantified. Nevertheless, the situation for skin cancer risk demonstrates the fact that risks for developing gastrointestinal cancers in Simav Plain would also be comparably high as indicated by the statistical death analysis results.

Considering the quality of groundwater in Simav Plain, it is possible to mention that the local inhabitants of Simav Plain are currently under increased risk of various cancer types. Although this finding is crucial with regards to source and cause identification, particularly when combined with the comparably high gastrointestinal cancer ratio in the area, it is not sufficient to conclude that arsenic is the primary triggering cause of gastrointestinal cancers in the project area. In this regard, detailed health surveys that specifically focus on death causes are to be conducted in the area to obtain more reliable death data.

6 Conclusions

This study is an example for high arsenic levels in groundwater originating primarily from local geological formations. Arsenic in the study area is higher than the levels given in international literature and thus demonstrates importance for the human health.

The aquifer material being composed of arsenic containing metamorphic rocks is considered to be a general mechanism for arsenic enrichment in aqueous phase. Arsenic levels in metamorphic rocks of the study area have been detected to range between 10.4 and 660.4 mg/kg, where the highest value was obtained in a sample collected from a former Cu–Pb–Zn mine site situated next to the Simav district center. As these rocks are highly altered and are located in high elevations of the project area, they serve as the main source of alluvial material deposited within the plain as a result of water and wind erosion. With local depths ranging as high as 100 m, the geochemistry of this alluvial layer represents similarities to the metamorphic rocks of the area with arsenic concentrations ranging between 31.6 and 87.1 mg/kg. Other rocks types of the project area such as the magmatic rocks, on the other hand, have lower arsenic levels when compared to the metamorphic rocks and the alluvial deposits.

Within this area of complex geology, three major geothermal fields have developed inside the geological formations of Simav Plain as a direct function of tectonism and magmatism. High temperatures of geothermal fluids originating from metamorphic rocks, which are essentially the reservoir rock for these fields, facilitate sulfur mineralization and result in high arsenic concentrations reaching to levels as high as 594 μg/L. Such high levels are about 60 times more than the allowable standard limit of 10 μg/L and serve as one of the major arsenic sources in the surface and subsurface waters of the plain.

These natural arsenic sources in solid and liquid media and the associated contamination from these sources are largely intensified as a result of human intervention. One of these anthropogenic influences is an old Cu–Pb–Zn mine and its waste disposal area situated in the vicinity of the Simav district center. The mine wastes that were deposited close to the alluvial aquifer as well as the geochemical transformations within this waste site are believed to be the major reasons for high arsenic concentrations in surface aquifer in the close vicinity of the waste disposal area. Another anthropogenic influence that increases the level of arsenic contamination in the plain is the deep boreholes drilled within three geothermal fields and the associated overexploitation of geothermal resources. As a result, arsenic containing hot geothermal fluid mixes with the cold water

resources of the plain and contaminates the surface aquifer. Moreover, uncontrolled disposal of waste geothermal fluid to the drainage network in the plain creates appropriate conditions for the rapid transport of the arsenic-containing waters within the plain due to the high hydraulic conductivity values of the alluvial layer underlying the drainage network. Accordingly, high arsenic levels were also detected in the surface waters of the plain.

Based on this characterization and source identification, the health effects of arsenic on local population were also investigated through risk analysis. Although there is no concrete evidence, the above-national average cancer rates were thought to be associated with direct indigestion of arsenic-contaminated groundwater as well as indirect consumption of foods irrigated with arsenic containing groundwaters of the plain. It has been found out through the analysis of the causes of human deaths in the plain that about 40% of the total cancer incidences were related to cancers of gastrointestinal tract and urinary system, which are among the most sensitive human systems to high arsenic levels. Thus, detailed health surveys coupled with death analysis would need to be conducted by health experts with special focus on dietary habits and nutritional practices of local inhabitants. Furthermore, an arsenic speciation study is to be conducted in Simav Plain groundwaters for identifying the relative contribution of various organic and inorganic arsenic species within the general total values presented in this study.

Considering the high risk for human health, certain measures are needed to be implemented immediately within the plain to protect the quality of groundwaters and to prevent further dispersion of arsenic-contaminated waters inside the aquifer. In this regard, operation of deep boreholes should be ceased immediately, overexploitation from these wells should be prevented, and no new boreholes should be drilled in areas with high health risks. Moreover, waste geothermal fluid should not be disposed to surface drainage network in an uncontrolled manner and should not be utilized in agricultural irrigation of edible crops. Arsenic removal measures should be implemented in boreholes that exceed the standard value. It is also thought that finding alternative water resources that are not influenced from arsenic pollution would need to be considered as the ultimate solution to arsenic problem in Simav Plain. It is also believed that such measures could also be applied in others parts of the world experiencing arsenic contamination through similar mechanisms.

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