



Naturally occurring arsenic in terrestrial geothermal systems of western Anatolia, Turkey: Potential role in contamination of freshwater resources

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HIGHLIGHTS

- Potential environmental impact of high arsenic from geothermal sources was identified.
- Geothermal waters from deep wells are characterized by Na-HCO₃ type.
- Hot spring fluids are characterized by Ca-HCO₃ type.
- As(III) is the dominant species in both deep wells and hot spring fluids.
- Mixing of geothermal waters containing As is responsible for environmental impact.

ARTICLE INFO

Article history:

Received 3 September 2012

Received in revised form 7 January 2013

Accepted 17 January 2013

Available online 28 January 2013

Keywords:

Arsenic

Geothermal wells

Hot springs

Environmental contamination

Turkey

ABSTRACT

Arsenic (As) contamination in terrestrial geothermal systems has been identified in many countries worldwide. Concentrations higher than 0.01 mg/L are detrimental to human health. We examined potential consequences for As contamination of freshwater resources based on hydrogeochemical investigations of geothermal waters in deep wells and hot springs collected from western Anatolia, Turkey. We analyzed samples for major ions and trace element concentrations. Temperature of geothermal waters in deep wells showed extreme ranges (40 and 230 °C), while, temperature of hot spring fluids was up to 90 °C. The Piper plot illustrated two dominant water types: Na-HCO₃[−] type for geothermal waters in deep wells and Ca-HCO₃[−] type for hot spring fluids. Arsenic concentration ranged from 0.03 to 1.5 mg/L. Dominance of reduced As species, i.e., As(III), was observed in our samples. The Eh value ranged between −250 and 119 mV, which suggests diverse geochemical conditions. Some of the measured trace elements were found above the World Health Organization guidelines and Turkish national safe drinking water limits. The variation in pH (range: 6.4–9.3) and As in geothermal waters suggest mixing with groundwater. Mixing of geothermal waters is primarily responsible for contamination of freshwater resources and making them unsuitable for drinking or irrigation.

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1. Introduction

Arsenic (As) is a well-known toxic and carcinogenic metalloid found in a wide variety of chemical forms. Under changes in geochemical and microbiological conditions As can be transformed and mobilized in the environment. The presence of As, above the level safe for human consumption, has been detected widely in groundwater and hydrothermal systems, currently

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recognized as a major global public-health issue [1–3]. The occurrence of As in terrestrial geothermal systems has been identified in many areas of the world, including Alaska, western USA, Mexico, Central America, northern Chile, Kamchatka, Japan, Taiwan, Philippines, Indonesia, Papua New Guinea, New Zealand, Iceland and France [2,4]. It has also been recognized that both geogenic and anthropogenic processes control the occurrence on local and regional scales in different parts of the world [5–7].

In several geographical locations such as Turkey, India, Bangladesh and Taiwan, As occurs naturally in subsurface strata within the volcanic and sedimentary formations as well as in the areas of geothermal systems associated with tectonic activity. Arsenic concentrations found in geothermal waters are highly variable depending on the geological and tectonic setting, the hydrodynamic pattern, and the thermodynamic conditions especially pressure and temperature. The release of As in geothermal waters further depends on the availability of As source rocks and minerals (both primary and secondary), geochemical conditions (predominantly pH and redox state), and microbial activity [2,4]. In geothermal environments, mobility of As can be partly controlled by its chemical speciation. The dominant As species in a given environmental setting is controlled by many parameters, such as pH, temperature, adsorption and dissolution reactions and redox conditions which are driven by the presence of organic matter and inorganic electron donors such as sulfides [8–13]. Arsenic is generally released from the host rock by dissolution under reducing conditions, where high residence time, and high temperature and pressure of the fluids favor its mobilization [2,14]. The presence of As in geothermal systems, principally in geothermal deep wells and/or geothermal surface manifestations, such as hot springs, fumaroles and solfataras, may have severe environmental consequences, as the rising geothermal water may contaminate “cold” groundwater aquifers, vadose zone, surface waters, and other surface environments [2].

During last few decades, environmental impacts of geothermal energy production have become a key research topic in Turkey [15–17]. The contamination of surface waters and groundwaters with hydrothermally derived As is the most severe consequence of geothermal energy production [18,19]. Drinking and irrigation water resources, such as surface waters and groundwater near geothermal fields, have become polluted with significant levels of As and other toxic elements by the wastewater derived from geothermal plants [20–22]. Therefore, this study was aimed to investigate the geochemical behavior and characteristics of As in geothermal waters of western Anatolia, Turkey. This study also focuses on the behavior of contaminants in surface environments associated with mixing of geothermal waters with freshwater resources.

2. Geological setting of the study area

The study area, western Anatolia, Turkey, is located on a seismically active crust with N–S extensional regime [23]. Plate movements associated with tectonic activities have controlled the geography of the region. Under the extensional regime, the upper crust of western Anatolia is broken by normal faults that form E–W oriented graben systems (Fig. 1). The most important of these graben systems are Gediz, Simav, Küçük and Büyük [24,25].

The Gediz graben is 140 km long and 3–40 km wide where fractured rocks of the Menderes Massif (such as mica-schist, gneiss and marbles) form the reservoir rock. The cap rock of the geothermal waters include clay-rich intervals within the Neogene sedimentary units [26].

The Simav graben is located in the northeastern corner of the Simav plain. This is an E–W trending Pliocene to Quaternary

asymmetric depression that developed on the older NE–SW trending Miocene basin in Western Anatolia [27]. The graben is bounded from the south by the Simav fault, which is an active oblique-slip normal fault. The graben fill associated with the Simav fault is composed of semilithified boulder conglomerate and sandstone. The northern part of the Simav graben is known as Akdere basin, which consists of coarse clastics and Naşa volcanics. Three geothermal systems (Eynal, Naşa and Çitgöl) have formed in this graben.

The Küçük Menderes Graben is 80 km long and 3–10 km wide system. This is a part of the horst-graben system of western Anatolia and is bounded by the Bozdağ horst to the north and the Aydın horst to the south.

The Büyük Menderes graben is 200 km long and 10–20 km wide system which is bordered by well-developed normal fault systems. Many geothermal springs are associated with the bounding normal faults. North striking transverse faults dissect the northern margin of the graben and commonly extend into the Menderes massif. Ten hottest geothermal systems in Turkey, Kizildere, Germencik, Yılmazköy, Sultanhisar, Atca, Kavaklıdere, Pamukoren, Umurlu, Hıdırbeyli, Guzelkoy are located in the Büyük Menderes graben. Most of the geothermal systems in this graben have two reservoirs. The reservoir fluid is contained mainly in Paleozoic fractured rocks consisting of quartz schist, gneiss, and karstic marbles of the Menderes Massif where the second fluid reservoir is contained in Neogene sandstones and conglomerates. The impermeable claystone and mudstone of Neogene age forms the cap rock. The heat source is a magmatic intrusion along the young faults related to graben tectonic activity.

3. Materials and methods

3.1. Sample collection and preservation

Geothermal waters were collected from different hot springs ($n = 12$) and deep geothermal wells ($n = 19$) of western Anatolia, Turkey. The locations of these sampling regions are given in Table 1 and are shown in Fig. 1. The samples were collected after filtering through 0.45 μm filter syringes, in a dark, sterilized glass (BD anaerobic Vacutainer) tubes. Parts of the samples were preserved with a few drops of concentrated nitric acid for cations and trace element analysis, whereas, un-preserved samples were collected for anion analysis. Electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), temperature, salinity, pH, and Eh were measured in the field. A portable multi parameter probe (Hach-Lange HQ40d) was used to measure all the field parameters.

3.2. Chemical analysis

The cation and anion concentrations were analyzed using an ion chromatograph (IC) (Dionex, CA, USA). Dissolved organic carbon (DOC) was measured using C/N analyzer (Model: 2100, Analytik, Jena), detection limit 0.5 mg/L. The trace element concentrations were analyzed using an Agilent 7500cs (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-MS). The detailed procedure was outlined previously by Nath et al. [5] and Liu et al. [28]. The speciation of arsenic among the arsenite (As-III), arsenate (As-V), monomethyl arsenic (MMA), dimethyl arsenic (DMA), and arsenobetaine (AsB) forms was measured by ICP-MS coupled with a HPLC system (Series 200, Perkin Elmer Inc., Shelton, CT) as described in Reuter et al. [29]. The detection limit was 0.001 mg/L. To note that we only observed As(III) and As(V) including some unquantifiable peaks in the chromatograms.

Analytical accuracy was checked with reference materials, and precision was ensured through repeated measurements of unknown samples. Standard reference materials (SRM 3103a and

Table 1
Physico-chemical characteristics of the deep geothermal wells (DW) and hot spring (S) fluids in western Turkey.

Sample ID	Longitude (in decimal degrees, WGS84)	Latitude (in decimal degrees, WGS84)	Type	Location	Depth (m)	Temp. (°C)	pH	Eh (mV)	EC (μS/cm)	DOC (mg/L)	DO (ppm)	Na ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	K ⁺ (mg/L)	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	F ⁻ (mg/L)	HCO ₃ ⁻ (mg/L)
P1	26.910	38.123	S	Seferihisar	Surface	57	6.45	-13	3330	3.70	bdl	6094	1088	598	889	55	3729	16.9	bdl	469
P2	27.626	37.933	S	Alangülü	Surface	38	6.85	-12	6920	4.79	0.06	1381	130	29	92	43	479	5.12	1.3	4400
P3	27.625	37.933	DW	Alangülü	47	39	7.29	95	6030	5.05	0.18	1124	159	65	100	6.3	387	3.42	1.1	3575
P4	27.583	37.886	DW	Hıdırbeyli	1900	130	8.30	32	6900	4.53	0.68	1467	11	16	98	14	598	4.76	1.7	3025
P5	28.099	37.880	DW	Salavatlı	1510	171	7.69	-222	4970	3.50	0.93	1152	18	13	96	63	111	2.31	6.2	3090
P6	28.095	37.876	DW	Salavatlı	1450	170	7.58	-250	4820	2.86	0.62	1134	11	15	90	63	112	3.19	8.1	3100
P7	28.829	37.921	DW	Sarayköy	300	120	8.77	-160	3890	3.36	0.77	841	105	18	103	497	39	3.51	4.9	1955
P8	28.828	37.921	S	Sarayköy	Surface	40	6.62	16	5450	3.48	0.24	892	333	112	92	993	81	3.71	5.3	3460
P9	28.808	37.927	S	Buharkent (İnaltı)	Surface	90	8.67	40	4360	3.81	0.68	953	22	15	94	870	43	3.53	6.3	1510
P10	28.774	37.933	S	Buharkent (Babacık)	Surface	60	6.67	-213	3610	3.38	0.76	523	405	95	51	767	30	4.04	2.2	2725
P11	28.846	37.960	DW	Kızıldere	510	193	8.57	-148	4070	1.09	0.48	1181	12	12	131	459	52	3.73	1.1	1907
P12	28.837	37.952	DW	Kızıldere	2250	190	8.13	-48	4720	2.06	0.88	1135	34	10	89	469	59	2.09	4.8	2306
P13	29.103	37.968	S	Karahayıt	Surface	40	6.59	13	2850	3.66	0.92	123	693	115	27	523	15	5.23	1.0	1964
P14	29.108	37.962	DW	Karahayıt	150	58	6.72	24	3010	3.21	0.73	110	657	109	25	507	13	3.15	1.1	2130
P15	29.126	37.926	S	Pamukkale	Surface	33	6.41	107	2520	3.41	0.84	45	736	97	7.9	391	8.0	3.43	0.60	2159
P16	28.747	38.650	S	Kula	Surface	60	7.06	-63	4480	2.82	0.04	936	67	91	92	62	96	1.92	0.80	3550
P17	28.747	38.650	DW	Kula	163	65	7.14	11	4270	3.34	0.45	966	150	101	95	61	99	4.45	0.80	3900
P18	28.960	39.142	DW	Naşa	N/A	85	7.61	109	1621	3.77	0.96	292	100	12	33	158	23	3.55	2.2	886
P19	28.966	39.134	DW	Çitgöl	N/A	95	7.62	109	1757	3.12	0.28	150	12	16	3.2	193	25	3.78	4.0	325
P20	28.995	39.127	DW	Eynal	N/A	160	9.30	-62	2940	1.71	0.20	659	21	11	77	332	43	3.42	1.1	1244
P21	29.257	38.940	DW	Gediz	N/A	85	7.15	94	3410	3.35	0.20	568	211	67	85	574	50	4.32	2.0	2035
P22	29.256	38.940	S	Gediz	Surface	75	7.09	119	2990	2.90	0.86	465	222	78	70	490	43	4.12	1.6	1975
P23	29.189	38.745	S	Emirfakı	Surface	39	6.56	39	2690	3.39	0.55	278	466	88	38	467	23	2.16	0.70	2605
P24	29.052	38.639	DW	Örencik	N/A	39	6.89	75	4120	4.34	0.06	831	255	71	91	176	38	3.14	0.40	3950
P25	28.521	38.332	S	Alaşehir	Surface	32	6.62	93	2460	4.07	0.13	245	248	141	17	106	32	2.51	0.20	2265
P26	28.368	38.407	DW	Kavaklıdere	N/A	213	6.98	-47	3210	3.21	0.70	727	17	11	79	10	89	4.53	1.4	2405
P27	28.115	38.451	DW	Salihli	N/A	84	7.66	-85	2340	3.72	0.97	433	126	22	56	29	39	3.78	1.0	1830
P28	28.082	38.512	DW	Bostan-Salihli	1100	80	7.78	-20	2114	3.96	0.88	527	13	14	11	27	45	3.73	0.20	1405
P29	28.048	38.456	S	Sart	Surface	52	6.59	-101	1575	2.85	0.78	148	289	35	22	29	15	4.06	0.40	1793
P30	27.840	38.571	DW	Urganlı	400	80	7.32	-75	2380	3.36	bdl	495	56	33	52	2.3	38	2.16	2.3	1500
P31	27.035	38.387	DW	Bağcova	371	102	7.68	-53	1823	3.25	0.82	348	55	15	32	84	89	1.38	3.3	1210

DW – deep geothermal wells; S – hot springs; N/A – not available; bdl – below detection limit.

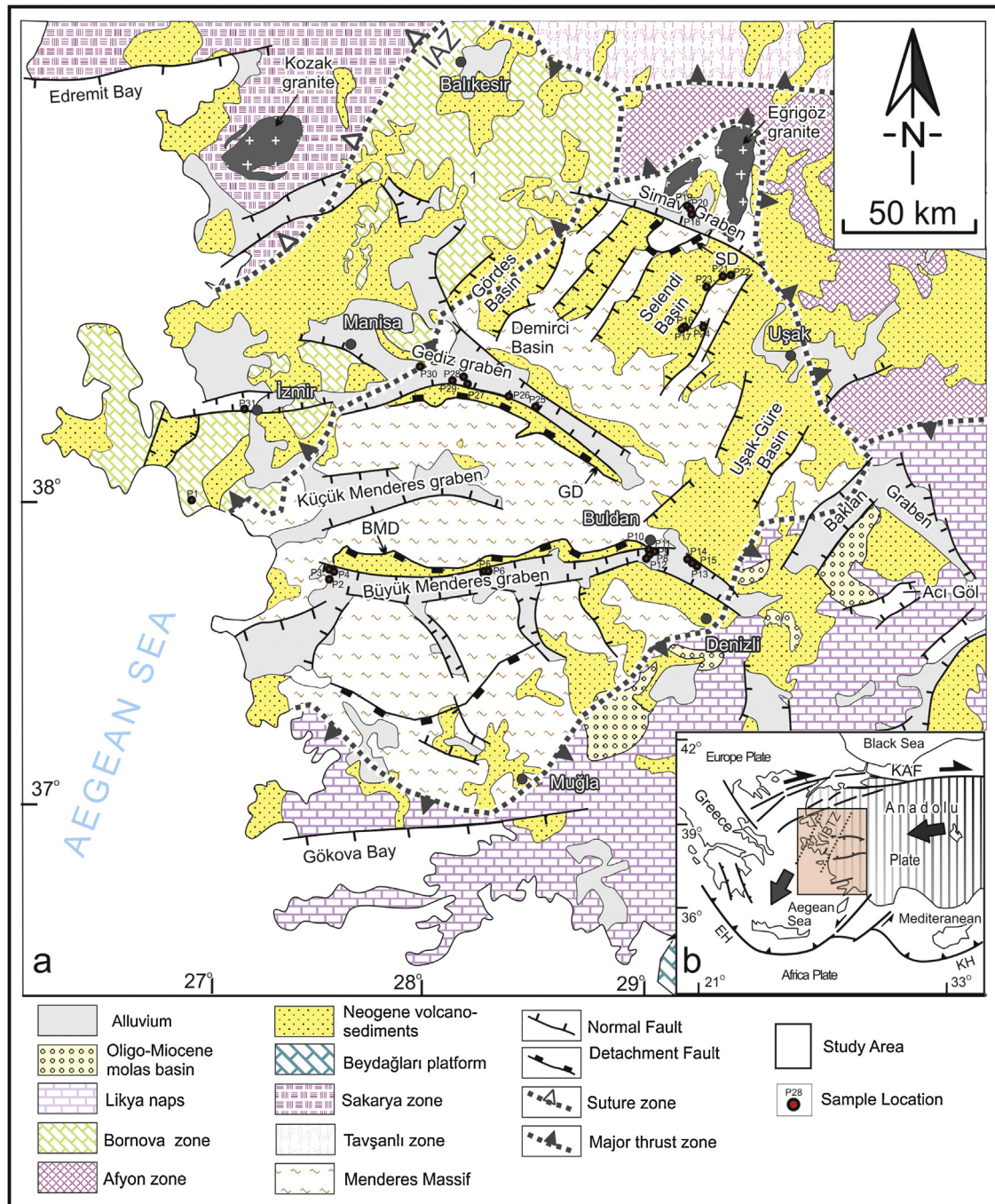


Fig. 1. Geological map of western Turkey (modified after Sözbilir et al. [40] and MTA [41]). The map also shows the location of sampling points and geothermal inventory.

1640a) from the National Institute of Standards and Technology (NIST) were used to achieve analytical accuracy. The detection limit for As and other analyzed trace element was 0.001 mg/L. The coefficient of variation (CV) was calculated to test the reliability of the data and was found to be <5% in all replicates.

3.3. Statistical analysis

Correlation statistics and the level of statistical significance were analyzed using statistical software SPSS 13.0 [30]. A p value <0.05 was considered to indicate the level of statistical significance.

Linear regression was used to observe the correlation of As with other elements.

4. Results and discussion

4.1. Physico-chemical characteristics of geothermal waters – deep wells and hot springs

The measured physico-chemical characteristics of geothermal waters are presented in Table 1. The measured temperature of geothermal waters in deep wells ranged between 39 and 213 °C with a median of 95 °C, whereas it was below the boiling point for

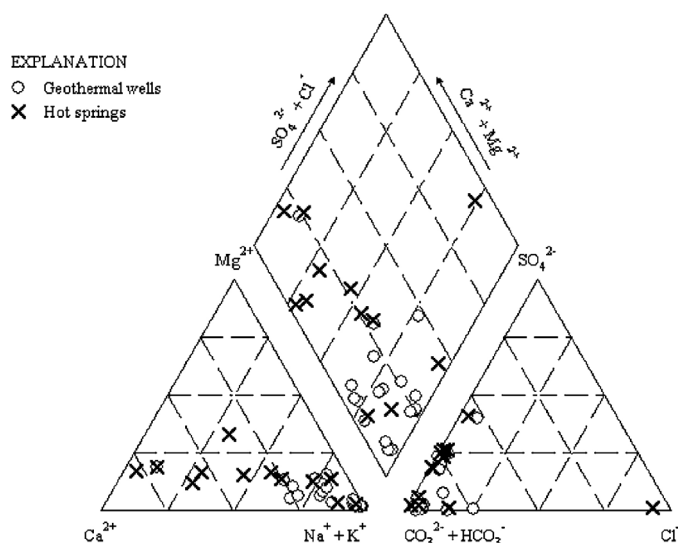


Fig. 2. Piper diagram illustrating major water types of geothermal wells and hot spring fluids of the study area.

hot spring fluids, ranged between 32 and 90 °C (median: 46 °C). The pH of geothermal waters in deep wells was slightly alkaline with a median of 7.6, whereas it was mostly neutral for hot spring fluids with a median of 6.6. The electrical conductivity ranged between 1621 and 6900 $\mu\text{S}/\text{cm}$ (median: 3410 $\mu\text{S}/\text{cm}$) in geothermal waters in deep wells. The hot spring fluids also show similar EC values with a median of 3160 $\mu\text{S}/\text{cm}$ (range: 1575–6920 $\mu\text{S}/\text{cm}$).

The Piper plot (Fig. 2) illustrates dominant hydrochemical features of geothermal waters in deep wells and hot springs in the study area. The geothermal waters in deep wells showed enriched concentration of Na^+ (median: 727 mg/L) relative to Ca^{2+} (median: 55 mg/L), whereas hot spring fluids showed enriched concentration of Ca^{2+} (median: 311 mg/L). The Ca^{2+} concentrations in hot spring fluids ranged between 22 and 1088 mg/L. However, Ca^{2+} concentrations were generally low, ranged between 1.9 and 657 mg/L in geothermal waters in deep wells. Geothermal waters in deep wells are of the Na-HCO_3^- type, whereas hot spring fluids are mostly of the Ca-HCO_3^- type (Fig. 2). The Seferihisar hot spring exhibited a Na-Cl type with high concentrations of Na^+ (6094 mg/L) and Cl^- (3729 mg/L) compared with other hot spring fluids and geothermal waters in deep wells of the studied region (Table 1). This is perhaps due to mixing and/or intrusion of seawater with rising geothermal waters. The SO_4^{2-} concentrations ranged between 2.3 and 574 mg/L (median: 84 mg/L) in geothermal deep wells, whereas slightly higher concentrations of SO_4^{2-} was observed in hot spring fluids (range: 29–993, median: 429 mg/L).

4.2. Arsenic species in geothermal waters – deep wells and hot springs

Table 2 shows measured concentrations of As, As(III) and As(V) in geothermal waters at each study locations. Table 2 also shows some unknown As species which was calculated as the difference between total As concentrations and sum of reported inorganic As species. Overall, the data showed As(III) as the dominant species in most of the samples. The reported unknown As species potentially represents As-sulfide (thioarsenic) species that could not be quantifiable using our method. However, Planar-Friedrich et al. [31] were able to quantify mono-, di-, tri-, and tetra-thioarsenate, as well as methylated As oxy- and thio-anions, besides As(III) and As(V) in geothermal waters of Yellowstone National Park. Therefore, our future work is directed to investigate the nature and occurrence of

these unknown As species in the study area and their importance on As biogeochemical processes.

In geothermal waters, As occurs mostly in inorganic forms, either as As(III) or As(V). Geothermal waters that emerged to the Earth's surface predominantly contain As(V) species. However, in deep geothermal reservoirs, As(III) is dominant, although, the dissolved inorganic As may change its oxidation states depending on the reservoir thermodynamic condition [2]. Generally, As(III) slowly oxidized to As(V) during the rise of geothermal waters from deep sources due to gradual increase in contact with atmospheric oxygen. The rate of As oxidation can be accelerated in the presence of microorganisms. For example, Wilkie and Hering [32] observed decrease in dissolved As(III) concentrations starting from the geothermal spring vent to 1.2 km downstream along with increase in As(V) concentrations, where stream macrophytes provided required microbial loads. Cumbal et al. [33] observed the dominance of As(III) (61–74% of the total As) in hot spring fluids characterized by low redox potential (Eh: –112 and –104 mV), whereas, As(V) dominance (67–68% of the total As) in hot spring fluids was characterized by higher redox potential (Eh: 9.2 and 7.3 mV). We also observed similar relation between As species and Eh values, for example, negative Eh values correspond to the dominance of As(III) whereas positive Eh values correspond to the dominance of As(V) in geothermal waters in deep wells and hot springs (Table 1).

4.3. Geochemical behavior of geothermal waters – deep wells and hot springs

The majority of trace elements found in the studied geothermal waters were above the World Health Organization (WHO) guidelines [34] and the national safe drinking water limits of Turkey. Arsenic concentrations were highly variable, and were mostly above the WHO drinking water guidelines (0.01 mg/L). Arsenic concentration in geothermal deep wells were found in the range of 0.03–1.1 mg/L (median: 0.26 mg/L), whereas in hot spring fluids, it ranged between 0.06 and 1.5 mg/L (median: 0.18 mg/L). The highest As concentration was found in the Buharkent (İnaltı) hot spring and Kızıldereli geothermal deep wells, with values of 1.5 and 1.1 mg/L, respectively. A strong positive correlation ($r^2 = 0.67$) was observed between As and Fe in geothermal waters in deep wells, whereas no correlation was observed in hot spring fluids (Fig. 3a). Similarly As and DOC have a strong negative correlation in geothermal waters in deep wells but no correlation was observed in hot spring fluids (Fig. 3b). The correlation between As and Mn was not significant (Fig. 3c).

We observed a good correlation between pH and As concentrations in geothermal waters in deep wells and hot springs with r^2 values of 0.50 and 0.81, respectively (Fig. 4a). Positive correlation was also observed for As(III) concentrations with measured pH in geothermal waters in deep wells and hot springs (Fig. 4b). Hot spring fluids also show a positive relationship between As(V) and pH but not with geothermal waters in deep wells (Fig. 4c). In general, pH and solubility of dissolved chemical constituents in geothermal waters often affected by the loss of CO_2 during adiabatic cooling of the ascending geothermal fluids [2]. However, As and other elements, such as Au, Sb and Hg, may remain dissolved under alkaline pH. Upon atmospheric contact, i.e., near the Earth's surface, the dissolved redox sensitive elements may precipitate or change its oxidation states. This is mainly due to the dominance of reducing condition along the pathways of ascending geothermal waters, however, oxidizing condition were dominant at or near the Earth's surface, due to availability of atmospheric O_2 . The exposure of geothermal waters to Earth's surface results in the oxidation of As(III) to As(V) and the precipitation of redox sensitive mineral phases such as Fe-oxides [35], which subsequently

Table 2
Arsenic species and trace element composition of the deep geothermal wells (DW) and hot spring (S) fluids in western Turkey.

Sampling ID	Type	As (mg/L)	As (III) (mg/L)	As (V) (mg/L)	Unknown As (mg/L)	Fe (mg/L)	Mn (mg/L)	Al (mg/L)	B (mg/L)	Rb (mg/L)	Ba (mg/L)	Sr (mg/L)	Br (mg/L)	Cr (mg/L)	Ni (mg/L)	Zn (mg/L)	Se (mg/L)	Sb (mg/L)	Ge (mg/L)	Cs (mg/L)
P1	S	0.21	0.03	0.09	0.09	0.24	0.19	bdl	0.01	bdl	0.05	bdl	bdl	0.02	0.12	0.02	bdl	0.001	0.001	0.15
P2	S	0.19	0.08	0.04	0.07	0.14	0.12	bdl	0.01	bdl	0.03	bdl	bdl	bdl	bdl	0.09	bdl	bdl	0.005	0.05
P3	DW	0.08	bdl	0.02	0.06	0.05	0.01	0.42	0.72	0.24	0.30	0.62	3.34	bdl	0.13	0.11	0.008	bdl	0.006	0.04
P4	DW	0.15	0.08	0.03	0.04	0.12	0.01	0.06	2.91	0.03	0.08	0.11	0.98	0.03	0.26	0.05	0.002	0.028	0.009	0.06
P5	DW	0.29	0.11	0.03	0.15	0.57	bdl	0.05	2.68	0.04	0.02	0.18	0.99	0.03	0.27	0.11	0.001	0.009	0.006	0.04
P6	DW	0.29	0.03	0.03	0.23	0.26	0.01	0.08	3.79	0.04	0.03	0.15	1.36	0.02	0.18	0.15	0.009	0.004	0.006	0.04
P7	DW	0.60	0.43	0.04	0.13	0.13	0.01	0.08	3.51	0.02	bdl	0.07	0.64	0.03	0.09	0.02	bdl	0.009	0.003	0.02
P8	S	0.43	0.26	0.04	0.13	0.41	0.09	0.11	4.05	0.02	0.01	0.06	1.04	bdl	0.06	0.03	bdl	0.003	0.002	0.02
P9	S	1.50	1.0	0.14	0.36	0.56	bdl	0.07	1.05	0.03	bdl	0.31	0.80	bdl	0.12	0.05	bdl	0.018	0.003	0.01
P10	S	0.16	0.04	0.02	0.10	0.29	0.09	0.08	0.92	0.03	bdl	0.48	0.67	bdl	bdl	bdl	bdl	bdl	bdl	bdl
P11	DW	1.13	0.89	0.12	0.12	1.25	bdl	0.08	1.27	0.03	0.01	0.28	0.73	0.01	bdl	0.06	bdl	0.015	0.004	0.02
P12	DW	1.08	0.87	0.11	0.10	1.45	bdl	bdl	3.78	bdl	bdl	bdl	bdl	0.01	bdl	0.05	bdl	0.005	0.003	0.01
P13	S	0.13	0.04	0.02	0.07	0.59	0.04	0.09	1.28	0.04	bdl	0.09	0.33	0.02	0.23	0.05	bdl	bdl	bdl	bdl
P14	DW	0.13	0.02	0.01	0.10	0.19	0.03	0.08	0.86	0.02	bdl	0.12	0.42	0.01	bdl	0.07	bdl	bdl	bdl	bdl
P15	S	0.12	bdl	0.01	0.11	0.29	0.01	0.03	0.12	0.01	bdl	0.46	0.37	0.02	0.24	0.12	bdl	bdl	bdl	bdl
P16	S	0.09	bdl	bdl	0.09	0.15	bdl	0.03	0.09	0.01	0.02	0.43	0.28	bdl	bdl	0.05	bdl	bdl	0.002	0.01
P17	DW	0.03	bdl	bdl	0.03	0.13	0.03	0.05	0.05	bdl	0.02	0.32	0.42	bdl	0.09	0.01	bdl	bdl	0.001	0.01
P18	DW	0.42	0.02	0.24	0.16	0.24	0.23	0.06	0.38	0.02	0.01	0.11	0.47	bdl	0.06	0.02	bdl	0.003	0.002	0.01
P19	DW	0.38	bdl	0.22	0.16	0.51	0.09	0.06	0.38	0.03	0.01	0.15	0.50	bdl	bdl	0.01	bdl	0.002	0.002	0.01
P20	DW	0.71	0.23	0.07	0.41	0.85	0.01	0.04	0.15	0.01	0.01	0.05	0.27	bdl	bdl	0.04	bdl	0.002	0.002	0.02
P21	DW	0.21	0.09	0.06	0.06	0.35	0.02	0.05	0.21	0.02	bdl	0.03	0.48	0.01	0.23	0.01	bdl	bdl	0.001	0.01
P22	S	0.24	bdl	0.15	0.09	0.46	0.08	0.05	0.31	0.03	bdl	0.03	0.28	0.01	0.26	0.01	bdl	bdl	0.001	0.01
P23	S	0.29	0.11	0.04	0.14	0.81	0.02	0.03	0.26	0.02	bdl	0.17	0.27	0.01	0.02	0.01	bdl	bdl	bdl	bdl
P24	DW	0.08	0.03	0.02	0.03	0.25	0.02	0.04	0.24	0.02	bdl	0.17	0.28	bdl	bdl	0.01	bdl	bdl	0.001	0.01
P25	S	0.06	0.02	0.01	0.03	0.35	0.08	0.03	0.07	0.01	0.01	0.21	0.25	0.01	0.01	0.01	bdl	0.005	0.001	0.01
P26	DW	0.18	0.10	0.02	0.06	0.39	0.04	0.03	0.15	0.02	0.07	0.20	0.39	bdl	bdl	0.02	bdl	bdl	0.007	0.03
P27	DW	0.35	0.27	0.04	0.04	0.67	0.01	0.03	0.78	bdl	0.01	0.06	0.36	bdl	bdl	0.02	bdl	0.001	0.004	0.03
P28	DW	0.18	0.06	0.08	0.04	0.31	0.01	0.06	4.04	0.03	0.01	0.02	0.48	bdl	bdl	0.03	bdl	0.001	0.001	bdl
P29	S	0.09	0.06	0.02	0.01	0.21	0.15	0.06	2.01	0.02	0.01	0.06	0.61	bdl	bdl	0.03	bdl	bdl	0.001	0.01
P30	DW	0.09	bdl	0.01	0.08	0.37	0.01	0.06	1.02	bdl	0.07	0.02	0.54	bdl	0.01	0.03	bdl	bdl	0.002	0.01
P31	DW	0.26	0.11	0.05	0.10	0.86	0.04	0.05	0.52	0.01	0.01	0.06	0.47	0.01	bdl	0.04	bdl	0.008	0.001	0.02

DW – deep geothermal wells; S – hot springs; bdl – below detection limit.

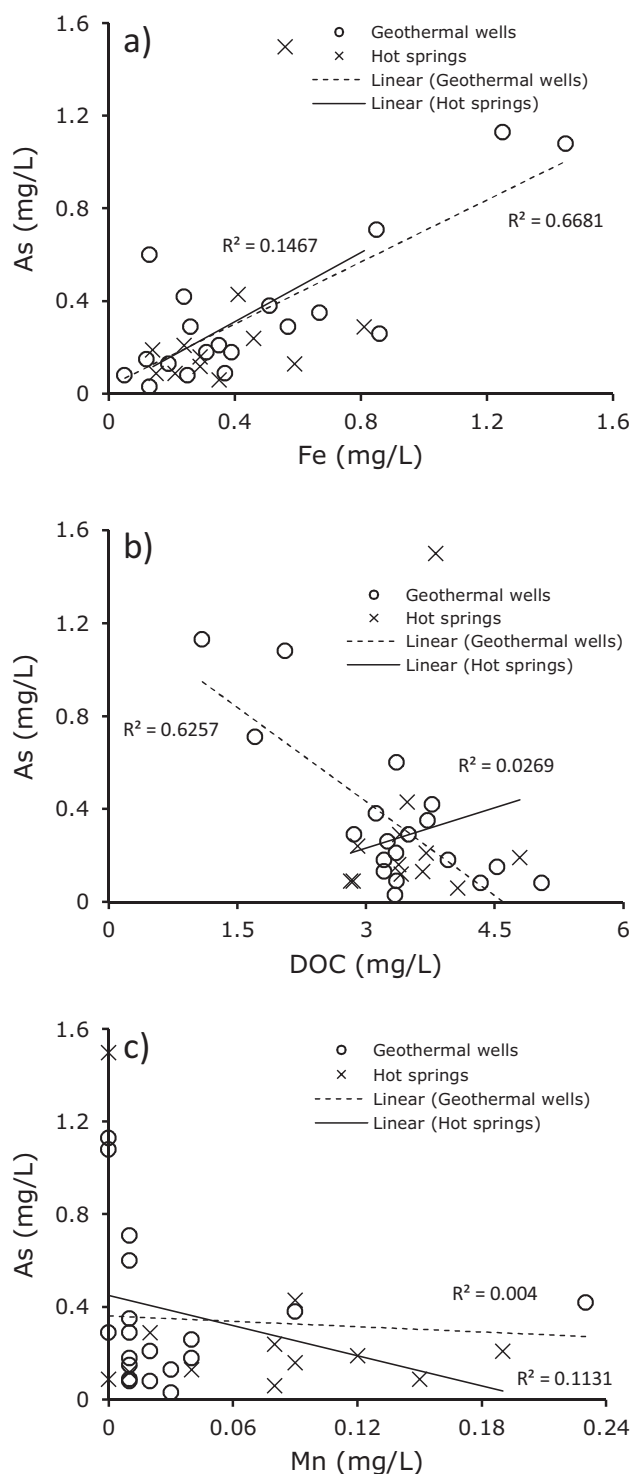


Fig. 3. Correlation between (a) As vs. Fe, (b) As vs. DOC and (c) As vs. Mn in geothermal wells and hot spring fluids of the study area.

sequester As from the water to variable extents. The sorption of As onto Fe oxyhydroxides is especially dominant in near-neutral pH and Na-Cl-HCO₃⁻ type waters [2,35] and thus controls As mobility. Such behavior of geothermal waters largely controls the relationship between pH and As species in the studied area (Fig. 4b and c).

Typically, geothermal waters contained elevated levels of B. In deep geothermal wells, B concentrations were found in the range between 0.05 and 4.0 mg/L (median: 0.78 mg/L), whereas, it was in the range between 0.01 and 4.05 mg/L (median: 0.29 mg/L) in hot spring fluids. The molar ratios of Cl/B in high temperature

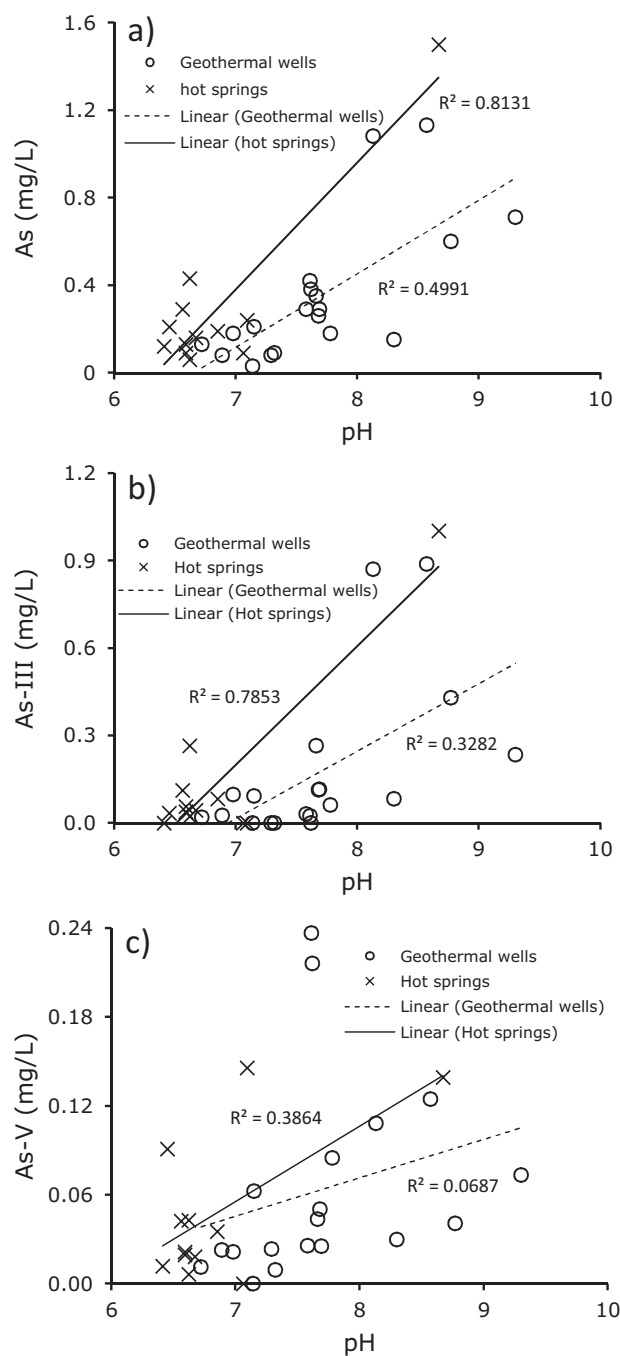


Fig. 4. Correlation between (a) As vs. pH, (b) As(III) vs. pH and (c) As(V) vs. pH in geothermal wells and hot spring fluids of the study area.

(>150 °C) fluids were low compared to low temperature fluids (<150 °C). Additionally in some geothermal waters in deep wells and hot spring fluids high concentrations of Sb (up to 0.028 and 0.018 mg/L, respectively) were observed. We observed no correlation between As and Sb in geothermal waters which suggests their co-occurrence. In addition to As, Sb is highly carcinogenic above the permissible drinking water limit of WHO (0.005 mg/L).

5. Potential consequences for contamination of local freshwater resources

The rising geothermal waters generally discharged into Earth's surface as a hot spring or mixed with shallow "cold" groundwater.

Either of these may result in contamination of groundwater and surface water with contaminants such as As [18,19]. The contamination of groundwater and/or surface water can occur additionally through geothermal energy exploitation if residual wastewaters are not adequately re-injected deep underground; this may result in severe environmental impact of contamination of freshwater resources used for drinking and irrigation [18,21,36]. Baba et al. [37] suggested two dominant behaviors which could potentially affecting the shallow groundwater quality in Tuzla geothermal region: (i) influx of salts and trace elements with geothermal brines during different seasons, and (ii) mixing of geothermal waters with shallow groundwater through fractures. Aksoy et al. [38] observed that the mixing of geothermal waters with “cold” shallow aquifers was mainly through the fractured zone, e.g. a fault line which conduit geothermal fluid. Similar observations were also reported from other parts of the world, such as an aqueduct in Los Angeles, USA, where high As concentrations (mean: 0.02 mg/L) were sourced from the geothermal activity in the Long valley, Mono county [32]. Tyrovala et al. [39] observed gradual decrease in As concentrations from the point of mixing of geothermal waters with shallow unconfined aquifers to the coastal area, approximately 7 km downstream. Such variations in As concentrations may relate to stratigraphy, depth of wells and redox status of the aquifer. Cumbal et al. [33] observed contamination of groundwater in Ecuador, where the discharge of geothermal water containing high concentrations of As (1.1–7.9 mg/L) has lead to a severe environmental exposure.

In our study area we observed high concentrations of As, Sb and B in the hot spring fluids which have a direct impact on human health through mixing with freshwater resources used for drinking and irrigation. For example, high As and Sb concentrations has carcinogenic effects to human health and potentially accumulate in agricultural produce. High B concentrations can cause human health effects. Additionally high B concentrations can have a detrimental effect to crops. Gunduz et al. [7] previously reported human health effects associated with the use of As contaminated local freshwater resources for drinking and irrigation. They also reported carcinogenic effects on people living in this region. Therefore, alternative drinking water sources need to be implemented in the study area to avoid further human health effects from drinking of As contaminated water. In addition to that proper management strategies should be adopted in order to avoid cross-contamination of fresh groundwater resources.

6. Conclusions

The studied geothermal waters contain higher concentrations of As, B, and other trace elements relative to WHO drinking water guidelines and the national drinking water safe limits of Turkey. The reduced As(III) is the dominant form of As found in the geothermal waters of the studied area, although some unknown As species were observed. We observed deterioration of local shallow freshwater resources through As and other trace element contamination due to mixing of geothermal waters and/or utilization of geothermal resources for energy regeneration [18,21]. Therefore, proper management and control strategy must be adopted in order to ascertain environmental safety to freshwater resources which is currently under threat from geothermal activity.

Acknowledgments

JB and PB thank the Strategic Environmental Research Foundation (Mistra) for the financial support extended to the KTH-International Groundwater Arsenic Research Group at the Department of Land and Water Resources Engineering, Royal

Institute of Technology, Stockholm, Sweden. PB also thanks the Swedish International Development Agency (Sida) for the financial support on global advocacy through the project Sustainable Arsenic Mitigation (SASMIT) (Sida Contribution 750000854) between 2007–2013. This work is partly supported by the Scientific and Technological Council of Turkey (TUBITAK) through project number 109Y029. JPM would like to thank the National Science Council of Taiwan for a postdoctoral position (NSC 100-2811-M-194-008). BN acknowledges The University of Sydney for Research Support Grant.

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