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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-HCO_3 type.
- Hot spring fluids are characterized by Ca-HCO_3 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.

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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-HCO_3^- type for geothermal waters in deep wells and Ca-HCO_3^- 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.

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 Citgöl) 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