

Occurrence of arsenic and related microbial signature of hydrothermal systems in Western Turkey

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ABSTRACT: The naturally occurring aqueous Arsenic (As) and other toxic elements are found around the world. The present study concentrates on arsenic concentrations, speciation and related microbial diversity in a hydrothermal system in Western Turkey. The surface temperatures of hot springs reach up to 90°C and deep well (reservoir) temperatures vary in the range of 40 to 230°C. The elements such as As, B, Br, Ba, Cr, Fe, Mn, V and Zn are found in high concentration in hydrothermal waters. Hydrogeochemically, Seferihisar hot spring exhibited a Na-Cl water type. On the other hand, Karahayıt, Pamukkale, Emirfakı, Alaşehir and Sart exhibit a Ca-HCO₃ water type and Çitgöl exhibited a Na-HCO₃-SO₄ water type. The arsenic (As) concentrations in geothermal waters of Western Anatolia have been detected to range from 0.03 mg/L to 1.5 mg/L, including Buharkent (İnaltı) (1.50 ± 0.005 mg/L), Kızıldere (1.13 ± 0.005 mg/L), Eynal (0.71 ± 0.005 mg/L) and Sarayköy (0.06 ± 0.004 mg/L). Arsenic (III) is the dominant species in geothermal water of Western Anatolia. The 16S rRNA gene sequences of bacterial diversity show that the thermophilic, sulfur/thiosulfate-oxidizing bacterium (*Thiobacter subterraneus*) is present in Kula geothermal water and mesophilic sulfur- and thiosulfate-oxidizing *Sulfurovum lithotrophicum* bacterium occurs in Sarayköy geothermal spring. Also, *Bacillus fumarioli*, (a thermophilic, aerobic endospore forming bacterium growing on (NH₄)₂ SO₄, MgSO₄ and MnSO₄ at 50–55°C), *Schlegelella thermodepolymerans* and *Methylocaldum szegediense* are rich in geothermal water.

1 INTRODUCTION

The metal-rich geothermal systems have been found throughout the world. In several geographical locations (Turkey, India, Bangladesh, and Taiwan), As occurs naturally in subsurface strata within volcanic and sedimentary formations.

The contamination of waters with heavy metals such as hydrothermally derived As is the most severe environmental impact in Western Turkey (Baba and Armannsson, 2006). The dominant As species in the environmental setting is controlled by many parameters, e.g. pH, Eh, temperature dependent microbial activity, precipitation, adsorption reactions. These are generally driven

by the presence of organic matter and inorganic electron donors (sulfide).

The aims of the present study were to establish the biogeochemical behavior and characteristics of arsenic in the hydrothermal waters of Western Turkey.

2 MATERIALS AND METHODS

2.1 Study area and sampling

The sampling points are shown in Figure 1. Water samples were filtered using 0.45 µm syringe filters in the field, collected in dark sterilized Vacutainer and stored at 4°C until analysis.



Figure 1. Location of the sampling points.

2.2 Physico-chemical analysis

Electrical Conductivity (EC), Total Dissolved Solids (TDS), Dissolved Oxygen (DO), temperature, salinity, pH, Eh were measured with portable multi parameter probe (Hach-Lange HQ40d). The major ions and trace elements were measured using Ion Chromatograph (IC) (Dionex, CA) and ICP-MS (Hewlett-Packard 4500), respectively.

2.3 Microbial analysis

A Genomic DNA extraction kit (Viogene, Taipei, Taiwan) was used to isolate the genomic DNA from hot spring water. DGGE was performed on a Dcode universal mutation detection system (Bio-Rad, Hercules, CA), 16S rDNA fragments were loaded onto an 8% polyacrylamide gel. The sequence fractures (~1500 bp) were doing blast in GeneBank of NCBI, to compare the difference for nucleotide sequences.

3 RESULTS AND DISCUSSION

3.1 Hydrochemistry and trace element in fluids

The major ions such as Na^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} were found within the range of 200 to 6000 mg/L, 50 to 1100 mg L^{-1} , 25 to 600 mg L^{-1} , 50 to 4000 mg L^{-1} and 10 to 1000 mg L^{-1} , respectively. Ca^{2+} concentrations in Karahayit, Pamukkale, Emirfakı, Alaşehir and Sart were determined to be very high. The water type of these hot springs was mainly Ca-HCO_3 . Çitgöl geothermal water exhibited Na-SO_4 water type. In general, hot springs of this study area were dominated by alkaline waters.

The alkaline spring waters show higher concentrations of Cr (0.01–0.03 mg L^{-1}), As (0.03–1.5 mg L^{-1}), B (0.01–4.05 mg L^{-1}), Mn (0.01–0.23 mg L^{-1}), S (3.05–103 mg L^{-1}), Rb (0.002–0.236 mg L^{-1}), Sr (0.01–0.62 mg L^{-1}), Sb (0.001–0.28 mg L^{-1}), and Ba (0.001–0.295 mg L^{-1}). The B concentrations were found to be very high in Salavatlı (3.79 ± 0.005 mg L^{-1}), Sarayköy (4.05 ± 0.005 mg L^{-1}) and Kızıldere (3.78 ± 0.005 mg L^{-1}) in comparison to other geothermal waters. As(III) was found to be the dominant species of geothermal waters in Alangülü (82 ± 0.002 $\mu\text{g L}^{-1}$), Salavatlı (115 ± 0.005 $\mu\text{g L}^{-1}$), Sarayköy (430 ± 0.006 $\mu\text{g L}^{-1}$) Buharkent (İnaltı) (1002 ± 0.02 $\mu\text{g L}^{-1}$), Buharkent (Babacık) (43 ± 0.007 $\mu\text{g L}^{-1}$), Kızıldere (889 ± 0.03 $\mu\text{g L}^{-1}$) and Karahayit (39 ± 0.01 $\mu\text{g L}^{-1}$).

3.2 Microbial diversity of geothermal water

The bacterial isolates from Kula geothermal water were assigned to be closely related to *T. subterraneus*, a thermophilic, obligately chemolithoautotrophic, sulfur/thiosulfate-oxidizing bacterium that survive in the temperature range of 60–65°C. This strain consumes thiosulfate during the growth and produces sulfate. The bacterial isolates from Buharkent, Babacık and Alangülü hot spring (60°C) were assigned to be closely related to *M. szegediense*, a methanophilic bacterium that is able to metabolize methane as their only source of carbon and energy. The bacterial isolates from Sarayköy hot spring were assigned to be closely related to *Sulfurovum lithotropicum*, a gram-negative, non-motile, coccoid to oval-shaped bacterium that experiences optimum growth around 40°C in the pH range 5.0–9.0. This strain survives chemolithoautotrophically with elemental sulfur or thiosulfate as a sole electron donor and oxygen or nitrate as an electron acceptor. Connon et al. (2008) were reported that the As(III) oxidation occurred within bacterial mats along geochemical gradients of temperature and pH. Due to As(III) oxidation in sulfate-chloride springs in the study area, As(V) is increased with the increase of O_2 concentration while dissolved sulfide decreased at the same time. As a result, active deposition of As(V)-Fe(III)-oxides occurred in the hot spring. Reduced sulfur compounds or organic compounds can serve as an electron donor for As(V) reduction while As(III) may drive the reduction of stronger oxidants such as oxygen or nitrate (Oremland and Stolz, 2003).

4 CONCLUSIONS

The geothermal waters were observed to contain high concentrations of As, B and other toxic

elements relative to WHO guidelines. Geothermal waters exhibited a diversity of water types such as Na-Cl, Ca-HCO₃ and Na-SO₄. As(III) predominated in comparison to other species. The geothermal waters were rich in bacterial diversity such as thermophilic and mesophilic, sulfur/thiosulfate-oxidizing bacterium, methanophilic bacterium and thermophilic, aerobic endospore forming bacterium. Chemolithoautotrophically and microbologically, the active deposition of As(V)-Fe(III)-oxides occurred in these hot springs. Microbial activity plays an important role in As transformation at the eruption point of geothermal water, as As(III) is transformed to As(V) by detoxification pathways of microorganisms.

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