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## Geothermal arsenic: Occurrence, mobility and environmental implications



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### ABSTRACT

Arsenic (As) contamination in geothermal systems has been identified in many areas of the world. Arsenic mobilization from rocks and mineral phases into geothermal fluids depends on available As sources, geochemical conditions and microbiological activity. In deep geothermal reservoirs As mobilization is predominantly from As-bearing pyrite at temperatures of 150–250 °C, and at higher temperatures also from arsenopyrite. Highest As concentrations, mostly in the range of thousands to tens of thousands of µg/L and in case of Los Humeros (Mexico) even of up to 162,000 µg/L are found in volcanic geothermal systems whereas in low- and high-enthalpy sedimentary geothermal systems they reach only about 2000 µg/L. At many sites, uprising geothermal waters contaminate shallow water resources. From the geothermal springs, those with NaCl water type have the highest As concentrations; these waters correspond to original reservoir waters which were not significantly altered during its ascent. In the geothermal reservoir and deeper parts of hydrothermal system, As is predominantly present as neutral H<sub>3</sub>As(III)O<sub>3</sub> (arsenous acid) and under sulfidic conditions also as thioarsenites; close to the earth's surface oxidation through atmospheric oxygen to As(V) species may occur; however, this is a slow process. As(III) emerging in geothermal springs is oxidized quickly through microbial catalysis and often most As is present as As(V), at a distance of few meters from the spring outlet. This review highlights the occurrence and distribution of geothermal As worldwide, its sources and its mobilization and the presence of different As species in geothermal fluids considering different geological settings and processes involving geothermal fluids rising from deep geothermal reservoirs to the earth's surface where it may mix with shallow groundwater or surface waters and contaminate these resources. The microbial diversity of hot spring environments which plays an important role to mobilize the As by oxidation and reduction process in the geothermal system is also addressed.

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**1. Introduction**

Geothermal fluids and springs are found around the world. Arsenic (As) is a well-known toxic and carcinogenic metalloid that is found in a wide variety of chemical species throughout the environment and can be readily transformed and mobilized by microbes, changes in geochemical conditions, and other environmental processes. The release of As from rocks into geothermal fluids occurs predominantly along active tectonic plate boundaries [1]. The As is found in geothermal reservoir fluids and surface manifestations (hot springs, fumaroles, solfataras) in many geological settings and may contaminate “cold” aquifers, vadose zone, and surface waters [2].

Naturally occurring As in groundwaters associated with terrestrial geothermal activity is recognized to be significant and 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 [2–5]. Arsenic concentrations in water from the El Tatio (North Chile), Copper River (USA), Yellowstone National Park (USA), Azores (Portugal) and Los Humeros (Mexico) are reported to be as high as 48,000 µg/L, 48,200 µg/L, 15,000 µg/L, 9500 µg/L and 74,000 µg/L, respectively [6–11]. The As mobilization and concentrations in geothermal waters are highly variable depending on the reservoir rock composition, pressure, temperature, redox condition, pH, presence of gases and microbiological activity.

The contamination of surface and subsurface water by geothermal waters with As may result in a severe environmental impact of geothermal systems; pollution can occur either naturally by mixing or during geothermal energy exploitation if residual waters are not adequately re-injected into the deep underground; consequence may be the contamination of water resources used for drinking or irrigation purposes (ground and surface water) [12–16].

This paper reviews available data on As concentrations and species in terrestrial geothermal systems, chemical characteristics, surficial discharges and microbial activity, to identify processes that determine the As concentrations in these waters, and the mechanisms for immobilization or release of As into freshwater bodies. It is not possible to describe and to evaluate all the worldwide existing geothermal sites; reason is that from most of them As data are not available, or they are classified and not accessible. We address similarities and differences between As concentrations from geothermal systems of different geological and tectonic settings: (i) volcanic rocks at active plate boundaries, (ii) sedimentary rocks which derive their heat from deep igneous intrusions and (iii) aquifers with geothermal waters corresponding to shallow groundwater which is conductively heated or which receives heat by steam uprising from depth.

**2. Occurrence and distribution of geothermal arsenic as function of geological setting**

High As concentrations in geothermal waters have been described over a century ago [17,18]. Since then, elevated As concentrations in geothermal reservoir waters have been reported from all inhabited continents. Common concentrations are in the range of thousands to tens of thousands of µg/L [7,19–24]. A world-wide overview of As concentrations in fluids of geothermal wells and springs is given in Tables 1 and 2, respectively. The fluids of geothermal reservoirs in

volcanic rocks along active plate boundaries have the highest As concentrations (typical range thousands to tens of thousands of µg/kg), but as high as 162,000 µg/kg at Los Humeros, Mexico [31,32]. Exceptions are the geothermal reservoirs of Hawaii and Iceland (< 0.1 µg/kg) despite that they are in volcanic rocks; these low concentrations may be explained by the presence of fresh basaltic reservoir host rocks with low As content [2] or with lower residence time compared to the other volcanic geothermal reservoirs (reduced time for water–rock interactions). Compared to reservoirs in volcanic rocks, much lower As concentrations (< 3–2010 µg/kg; Table 1) are found in fluids of reservoirs in sedimentary rocks comprising both high- (e.g. Cerro Prieto, Mexico: 250–500 µg/kg) and low-enthalpy geothermal reservoirs (SE Mexican oil fields: < 3–2010 µg/kg, Table 1) [35–38,52].

The As concentrations in fluids of geothermal springs are shown in Table 2; they are either similar as in the reservoir if they correspond to reservoir water or are lower if they are altered by dilution or chemical reactions or if they correspond to conductively-heated or steam-heated shallow groundwater. Spring waters of Wairakei, Waiotapu and Ohaaki/Broadlands (New Zealand), Mt Apo (Philippines) and Tibet contain 230–3000, 710–6500, 1000, 3100–6200 and 5700 µg/L, respectively [26,42,53–55]. The spring waters emerging from the geothermal systems of El Tatio (North Chile), Los Humeros (Mexico), and Yellowstone National Park (USA) contain up to 47,000–50,000, 3900, and 15,000, respectively [6,7,9,10]. Maity

**Table 1**  
Arsenic concentration in geothermal wells

Geothermal field/area	Arsenic (µg/L or µg/kg)	Ref	
Chile: El Tatio, Chile (VOL; H)	30,000–40,000	[25]	
	45,000–50,000	[26]	
Costa Rica: Miravalles (VOL; H)	11,900–29,100	[27]	
	Rincón de la Vieja (VOL; H)	6000–13,000	[27]
Mexico: Cerro Prieto (SED; H)	250–1500	[28,29]	
Los Azufres (VOL; H)	5100–49,600	[30,31]	
Los Humeros (VOL; H)	500–162,000	[30,32]	
Cactus-Sitio Grande (SED; L)	< 3–47	[33–35]	
Luna-Sen (SED; L)	< 3–548	[36–38]	
Jufo-Tecominoacán (SED, L)	< 3–1900	[39]	
Pol-Chuc-Abkatún (SED, L)	90–2010	[39]	
New Zealand: Broadlands (VOL; H)	5700–8900	[40]	
	Kawerau (VOL; H)	539–4860	[41]
	Orakei Korako (VOL; H)	599–802	[26]
	Waiotapu (VOL; H)	2900–3100	[26]
	Wairakei (VOL; H)	4100–4800	[26]
	1000–5200	[42]	
Philippines: Tongonan (VOL; H)	20,000–34,000	[43]	
	28,000 (mean)	[44]	
USA: Lassen Nat Park (VOL; H)	2000–19,000	[45]	
Russia: Kamchatka (VOL; H)	2000–30,000	[46]	
	Ebeko volcano, Kuril Is. (VOL)	190–28,000	[47]
Tibet: Yangbajing GTP (CC)	5700	[48]	
Japan: Hachoubaru GTP, Oita	3230	[49]	
Turkey: Kizildere GTP; wastewater	853	[50,51]	

Geological characterization of geothermal system after Chandrasekharam and Bundschuh [1]. VOL: volcanic rocks; CC: continental collision zone; L: low temperature reservoir,  $T < 150$  °C; H: high temperature reservoir,  $T > 150$  °C; mix: mixed with shallow groundwater or surface water; GTP: geothermal power plant; Is.: island.

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