



Arsenic in Latin America: A critical overview on the geochemistry of arsenic originating from geothermal features and volcanic emissions for solving its environmental consequences

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ABSTRACT

Geothermal fluids and volcanic emissions are important sources of arsenic (As), resulting in elevated concentrations of As in ground-, surface-water and soil, which may adversely affect the environment. Arsenic originating from geothermal features and volcanic activities are common in Latin America forming a serious threat on the livelihoods of millions of people. This review attempts to provide a critical overview of geochemistry of As originating from these sources in Latin America to understand what information exists and what needs to be done in future research. This study evaluated 15 countries in Latin America. In total, 423 sites were characterized with As originating from geothermal sources, mostly related to present volcanic activity ($0.001 < \text{As} < 73 \text{ mg/L}$, mean: 36.5 mg/L) and the transboundary Guarani Aquifer System ($0.001 < \text{As} < 0.114 \text{ mg/L}$, mean: 0.06 mg/L). Many of the geothermal systems and volcanoes discussed in this study are close to densely populated cities, including Bogota, Managua, San José, Guatemala City and Mexico City, where total As concentrations in natural ground- and surface- water exceeded the safe drinking water guideline of 0.01 mg/L , recommended by the World Health Organization (WHO). However, wide geographical occurrence of As in geothermal fluids and volcanic emissions of this region is by far not fully understood, so that development of geographical maps based on geographic information system (GIS) is an urgent necessity to understand the real nature of the problem. Studies on environmental risks assessment and potential human health impacts are scarce or missing, hence, such existing gaps need to be addressed by future research. The present holistic assessment of As originating from geothermal features and volcanic emissions along with its geochemistry, mobility and distribution would be a vital driving force to formulate a plan for establishing a sustainable As mitigation in vulnerable areas of Latin America in the near future.

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1. Introduction

Arsenic (As) originating from geothermal fluids and volcanic emissions can have a great impact on adjacent aquifers, surface wa-

ter bodies and other environments. This metalloide is commonly found in geothermal reservoirs, spring discharges, fumarolic gases and volcanic emissions. The concentrations of As and other elements associated with geothermal fluids are controlled by the type of host rock, temperature, water chemistry, boiling and mixing processes, and addition of vapor and volcanic gases into thermal waters (Aiuppa et al., 2006; Ellis and Mahon, 1977; Yokoyama et al., 1993). Geothermal fluids can arise from deep geothermal reservoirs, and volcanic gases tend to be discharged from magma chambers to the earth's surface. Along this ascent, As undergoes several geochemical processes,

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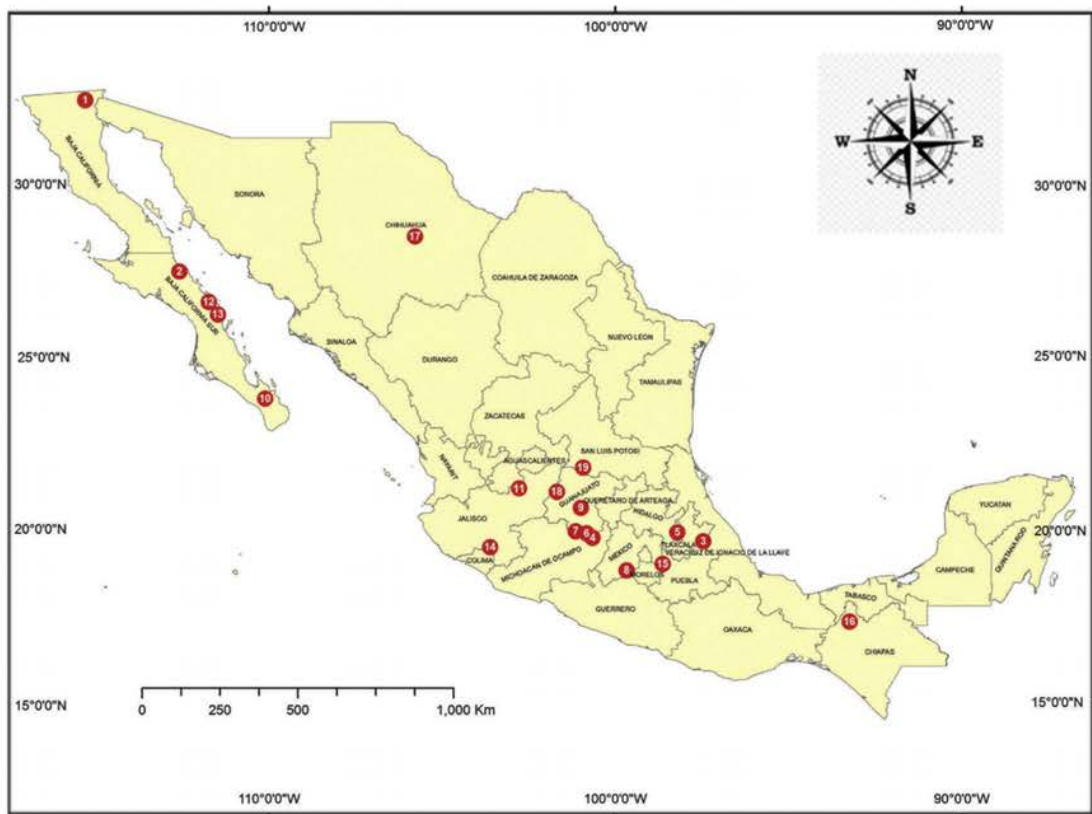


Fig. 2. Localities with arsenic presence related to geothermal and volcanic sources (red spots) in Mexico: 1. Cerro Prieto, Baja California Norte, 2. Las Tres Virgenes, Baja California Sur, 3. Los Humeros, Puebla, 4. Los Azufres, Michoacán, 5. Acoculco, Puebla, 6. Araró, Michoacán, 7. Cuitzeo del Porvenir, Michoacán, 8. Ixtapan de la Sal-Tonatico, Estado de México, 9. Santa Cruz de Juventino Rosas, Guanajuato, 10. El Triunfo, Baja California Sur, 11. Los Altos, Jalisco, 12. Bahía de Concepción, Baja California Sur, 13. San Juan Bautista Londó, Baja California Sur, 14. Volcán de Colima, Colima (gas condensates), 15. Popocatepetl, Puebla and Morelos (crater lake), 16. El Chichón, Chiapas (crater lake), 17. Central Chihuahua, Chihuahua, 18. Independencia basin, Guanajuato, 19. Villa de Reyes, San Luis Potosí. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

canic Belt, while up to 2 mg/L were measured in petroleum reservoirs. This summary reports As concentrations in the geothermal areas of Cerro Prieto, northern Baja California State, Las Tres Virgenes in Baja California Sur State, Los Humeros in Puebla State, and Los Azufres in Michoacán State. The latter two are located within the Transmexican Volcanic Belt, and have reported the As presence due to their specific sources. The mentioned review by Birkle et al. (2010) also indicates a distinct relation between As concentration behavior with temperature in magmatic and sedimentary types of geothermal reservoirs. Temperature was found to be irrelevant for As mobility in sedimentary type reservoirs, while temperatures above 230–250 °C were found to provide favorable conditions for As mobility in magmatic-type reservoirs. The general geological and hydrogeological characteristics of these main geothermal areas have been provided by López et al. (2012). In this paper, presence of As minerals or magmatic fluids input was not identified as an essential source for As occurrence in the geothermal fluids. The lowest As concentrations were measured in Cerro Prieto wells (non-volcanic), and the highest in the Los Humeros (volcanic) geothermal field. High As contents have also been reported in the spring waters at the volcanic caldera of Acoculco, Puebla (Quinto et al., 1995; Armienta and Segovia, 2008). Armienta et al. (2014) also reported As concentrations in geothermal wells of the Cerro Prieto geothermal field which is the most important geothermal energy source of the country and one of the top five of the world, ranging from 0.32 to 5.18 mg/L (measured by HGAAS) corroborating the relatively low levels previously reported by Birkle

low As levels (from <0.001 mg/L to 0.018 mg/L) were found in wells at the neighboring agricultural zone (Armienta et al., 2014).

2.1.2. Arsenic in geothermal springs and submarine hydrothermal vents

Arsenic occurrence in groundwater due to the mixing of geothermal water in sub-aerial springs and hydrothermal vents has also been studied in various sites of Mexico. One of them was the Araró hot springs region in the northern Michoacán State with up to 3.8 mg/L where the highest concentrations were measured at sites with temperatures close to the boiling point of water (Alarcón-Herrera et al., 2013). At Cuitzeo lake basin in Michoacán State, As concentrations (0.001 to 3.8 mg/L) were determined by HGAAS in thermal springs and drinking water wells (Páez-Sánchez et al., 2013).

Presence and sources of As and F⁻ were investigated in the low-temperature geothermal systems of Ixtapan de la Sal and Tonatico (IxS-T) and Santa Cruz de Juventino Rosas (JR), both located in the Trans-Mexican Volcanic Belt by Morales-Arredondo et al. (2018). The main ions were Na⁺ and Cl⁻ at IxS-T and Na⁺ and HCO₃⁻ at JR. At IxS-T increasing concentrations of As and F⁻ were reported by Morales-Arredondo et al. (2018) to correspond to the increase in TDS, Cl⁻, HCO₃⁻ and SiO₂. Silicate alteration of volcanic rocks (most probably rhyolites) and high temperature were associated with As and F⁻ occurrence at JR by Morales et al. (2015) and Morales-Arredondo et al. (2016). Concentrations up to 1.74 mg/L were measured (by ICP-OES) in thermal springs at IxS-T, while non-thermal

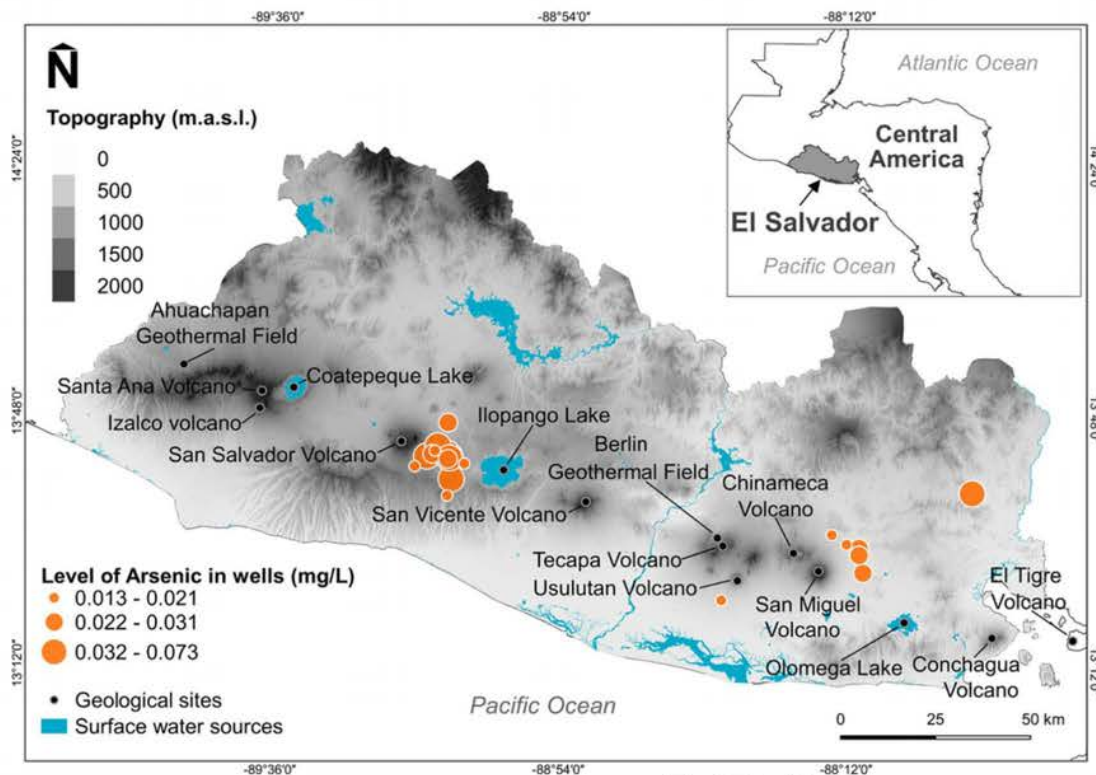


Fig. 3. Simplified map showing the volcanoes (Santa Ana, Izalco, San Salvador, San Vicente, Tecapa, Usulután, Chinameca, San Miguel, Conchagua, El Tigre), lakes (Coatepeque, Ilopango, Olomega) and hydrothermal systems (Ahuachapán and Berlin) of El Salvador. The level of arsenic concentration in water supply wells is shown in orange circles (mg/L). (Courtesy of the Administración Nacional de Acueductos y Alcantarillados de El Salvador - ANDA).

sured by HGAAS) were lower than those of IxS-T with up to 0.046 mg/L in thermal wells.

Although As presence in groundwater at the San Antonio-El Triunfo mining district in Baja California Sur State has been linked with mining activities (Carrillo-Chávez et al., 2000), the geothermal water in the area may be another source of As. However, hydrogeochemical results showing As concentrations <0.008 mg/L in alkaline geothermal waters with high concentrations of B and F⁻ led Wurl et al. (2014) to conclude that hydrothermal fluids do not have a significant impact on As occurrence in this area.

At the Los Altos de Jalisco area, western Mexico, As was analyzed by ICP-OES in 129 wells of the 17 municipal capitals; 44 of them exceeded the Mexican drinking water standard (0.025 mg/L), and 23 wells had a mean temperature higher than 30 °C. Arsenic content was explained by a geothermal component in the groundwater.

The composition of sediments collected at the intertidal hot spring zone and Santispac bight at Bahía Concepción, central Gulf of California, was studied by Leal-Acosta et al. (2010). The concentrations up to 111 mg/kg As (analyzed by HGAAS) were measured in the sediments near the surface of geothermal manifestations. However, a strong decrease was observed in the mangrove lagoon adjacent area (0.7–2.6 mg/kg). Leal Acosta et al. (2013) also determined the influence of shallow hydrothermal vents in sediments at Mapachitos, along the north-west coast of Bahía Concepción. Average concentrations were 60 mg/kg in the hydrothermal vents and 3.7 mg/kg in surface sediments of the adjacent area. However, principal component statistical analysis confirmed the influence of hydrothermal input in the sediments of the area close to the vents. Villanueva-Estrada et al. (2013) reported up to 0.78 mg/L of As in diffuse submarine vents and in hydrothermal fluids at the intertidal zone (up to 0.36 mg/L) of

the same bay. Analyses were done by ICP-MS on the samples collected using the displacement method. Sequential extraction of sediments obtained near the discharge areas showed that As was adsorbed on ferric oxyhydroxides. In addition, X-ray elemental maps of rocks indicated adsorption of arsenate on calcite surfaces. Wurl et al. (2013) indicated the presence of high As contents in geothermal influenced groundwater in the San Juan Bautista Londó aquifer, in Baja California Sur state. Although the value of As concentration was not reported, the authors indicated the importance of reducing the extraction rates to decrease groundwater contamination by thermal water.

2.1.3. Arsenic in active volcanoes

Arsenic concentrations have been measured in a few water and gas samples from the currently most active volcanoes in Mexico (Colima and Popocatepetl), and from the crater lake of El Chichón, the volcano producing the most devastating eruption of the 20th century in Mexico. Arsenic contents (analyzed by ICP-MS and HGAAS) were reported in the springs near Popocatepetl (up to 0.05 mg/L) and El Chichón volcanoes (up to 0.244 mg/L), and in El Chichón crater lake water (up to 0.17 mg/L) (López et al., 2012; Peiffer et al., 2011; Taran et al., 2008). The enrichment factor calculated for As in El Chichón lake water suggested a volatile input (Taran et al., 2008); however, since no strong enrichment was detected, Rouwet et al. (2009a) indicated the absence of a near-surface high temperature degassing magma batch. Volcanic gas condensates from Colima volcano had 0.53 mg/L As (López et al., 2012). Arsenic was also measured using HGAAS in the crater lake of Popocatepetl volcano (1.20 mg/L) that was present until 1994, before its disappearance due to the commencement of its ongoing eruption in December that year.

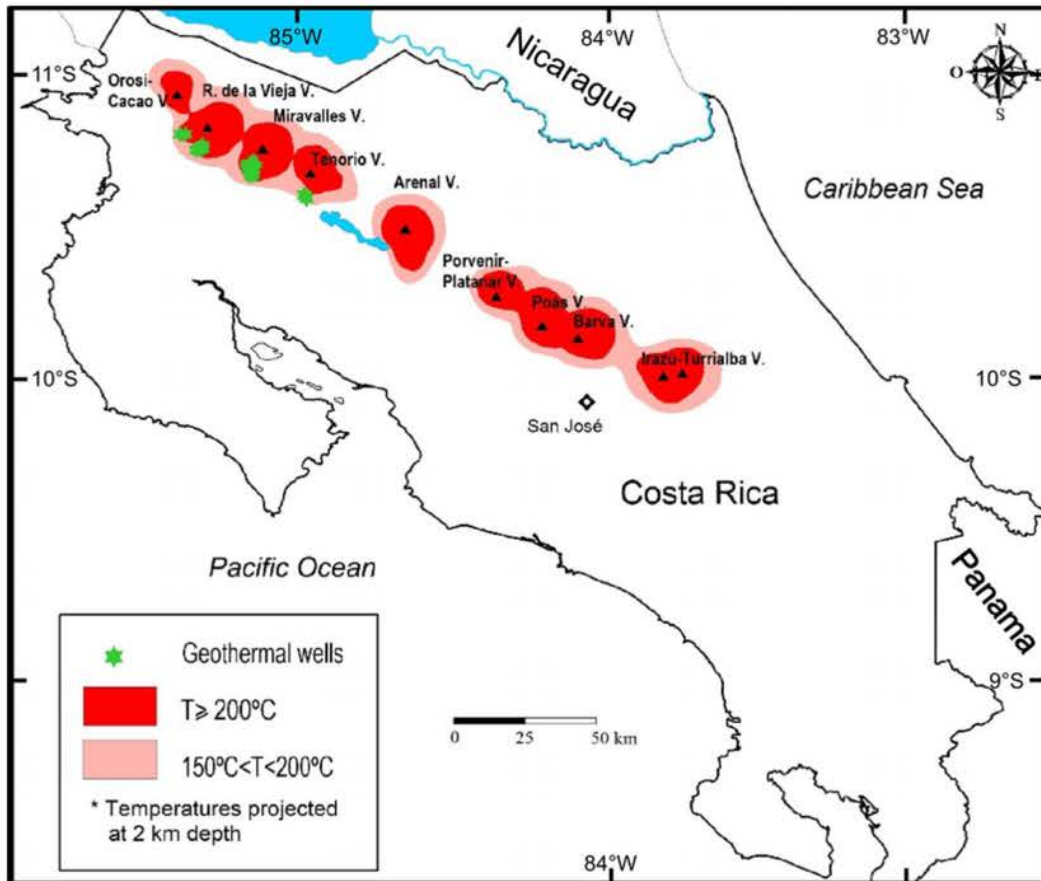


Fig. 4. Simplified map showing the projection of the isotherms distribution at 2 km depth based on the information from geothermal wells (green triangles) in northwestern Costa Rica and the location of the Poás and Turrialba volcanoes in Central Costa Rica (Courtesy of el Centro de Servicio Recursos Geotérmicos, Instituto Costarricense de Electricidad - ICE). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.1.4. Volcanic rocks as source for groundwater arsenic

Release of As from volcanic rocks, mainly rhyolites, has polluted groundwater in several parts of Mexico. Igneous rocks, conglomerates and alluvium were proposed as the As source in aquifers of Chihuahua, San Luis Potosí, Durango, and Sonora states (Alarcón-Herrera et al., 2013). In central Chihuahua, rhyolites enriched with As (measured by ICP-MS) were found as a source of releasing As to the alluvial aquifer system (Reyes-Gómez et al., 2013). Hydrological, isotopic and hydrochemical techniques applied to the study of the Independencia aquifer in Guanajuato State enabled the determination of the As (analyzed by ICP-MS) and fluoride (determined by IC) sources and enrichment mechanisms of the groundwater in this zone. Dissolution of rhyolites-ignimbrites in the fractured aquifer over nearly 35,000 years increased the concentrations of As (up to 0.12 mg/L) and fluoride (up to 16 mg/L) in the groundwater. In addition, intense pumping has transported As and F⁻ from the deep thermal fractured aquifer to the granular upper aquifer. Uranium (U) and As presence in groundwater was studied in the volcano-sedimentary aquifer of Villa de Reyes Graben, San Luis Potosí State. Arsenic concentrations (up to 0.0258 mg/L) above WHO drinking water guideline values pose a risk to the population. Congruent dissolution of volcanic glass that was enriched in incompatible trace elements during magmatic differentiation is the primary source of U and As in groundwater. In addition, As is mobilized from the sedimentary basin fill by meteoric decarbonatization of playa lake sediments and desorption from Fe-(hydr)oxides (Banning et al., 2012).

The semi-arid characteristics of the country along with the population increase, social, economic and political causes have led to the over exploitation of aquifers in many parts of Mexico. Esteller et al. (2012) remarked that the influence of this intensive aquifer exploitation on water quality in Mexico, causes the increase of As contents.

3. Central America

Because of Central America's location within the Pacific Rim volcanic zone, all of its countries — with the exception of Belize — are endowed with significant high- and low enthalpy convective geothermal systems related to active and past volcanism, receiving their heat from magmatic bodies and to non-volcanic deep circulating hydrothermal systems. They are the basis for many geothermal developmental activities for electricity generation, and direct uses of geothermal heat. Figure SM1 shows the Central American region with its volcanological and geotectonic setting, including the present-day active volcanic front, the secondary volcanic front and back-arc volcanoes (BVF), the last group including CM: Cerro Mercedes, AZ: Aguas Zarcas, GU: Guayacán and TO: Tortugero (Carr et al., 2007a).

3.1. Geothermal systems in Guatemala

Thirteen geothermal areas were identified in Guatemala during the 1981 survey (Asturias, 2008); two of them (Zunil and Amatitlán) have been exploited (Fig. SM2). Other geothermal sources in north-

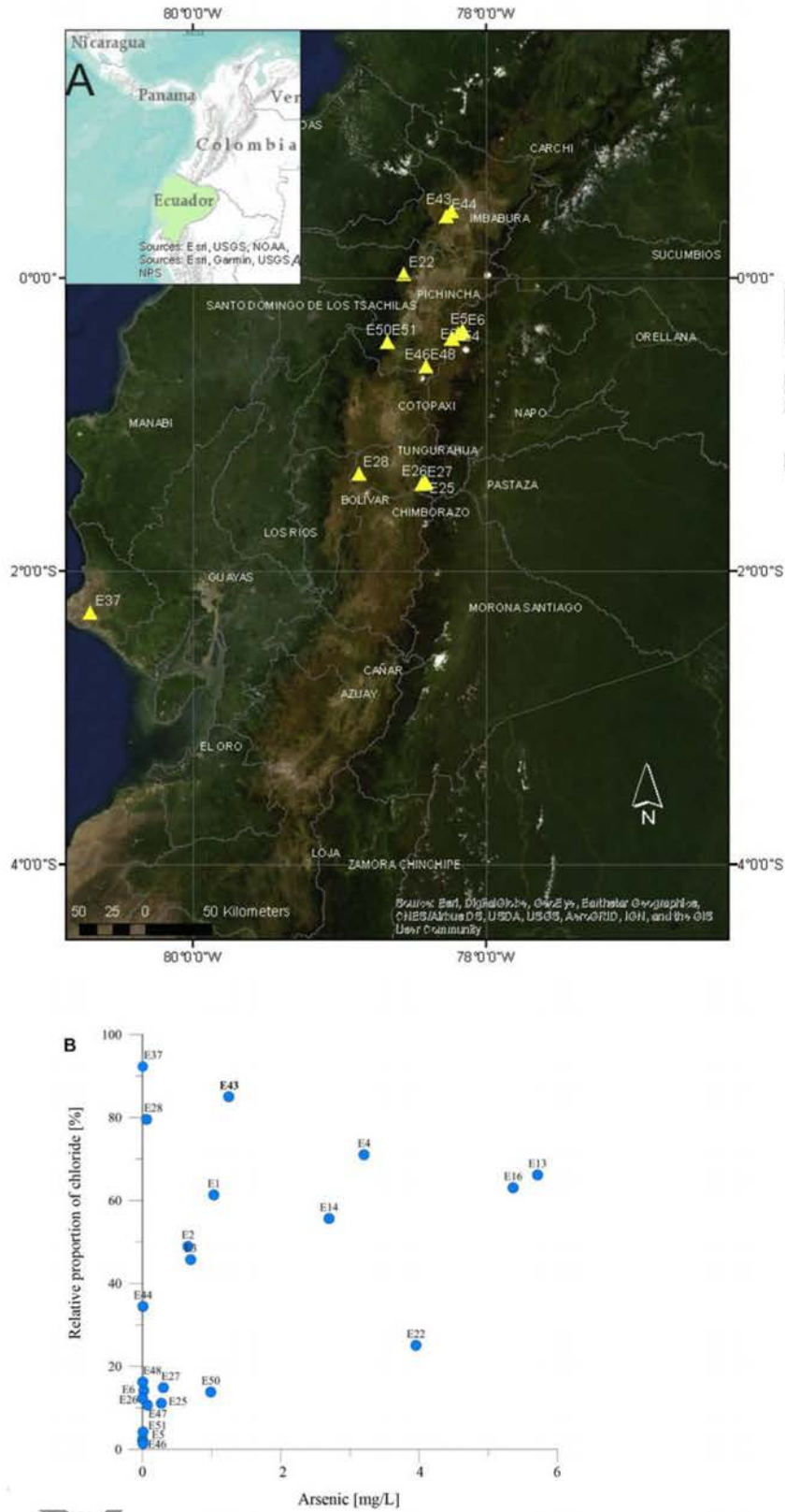


Fig. 5. (A) Location of sampled waters in Ecuador. Napo Province (E1-E3 Papallacta Terme, E4 Papallacta, E5-E6 Papallacta (up and down) of the terme, E13-E16 El Tambo Alto); Tungurahua Province (E-25-E27 Tungurahua volcano); Chimborazo Province (E28 Chimborazo volcano); Santa Elena Province (E37 Peninsula de Santa Elena); Imbabura



Province (E43-E44 Chachimbiro); Cotopaxi Province (E46-E48 Cotopaxi volcano); Pichincha Province (E22 Pichincha volcano, E50-E51 Atacazo). (B) Diagram with arsenic concentrations vs. relative proportion of chloride for the geothermal systems mentioned in (A).

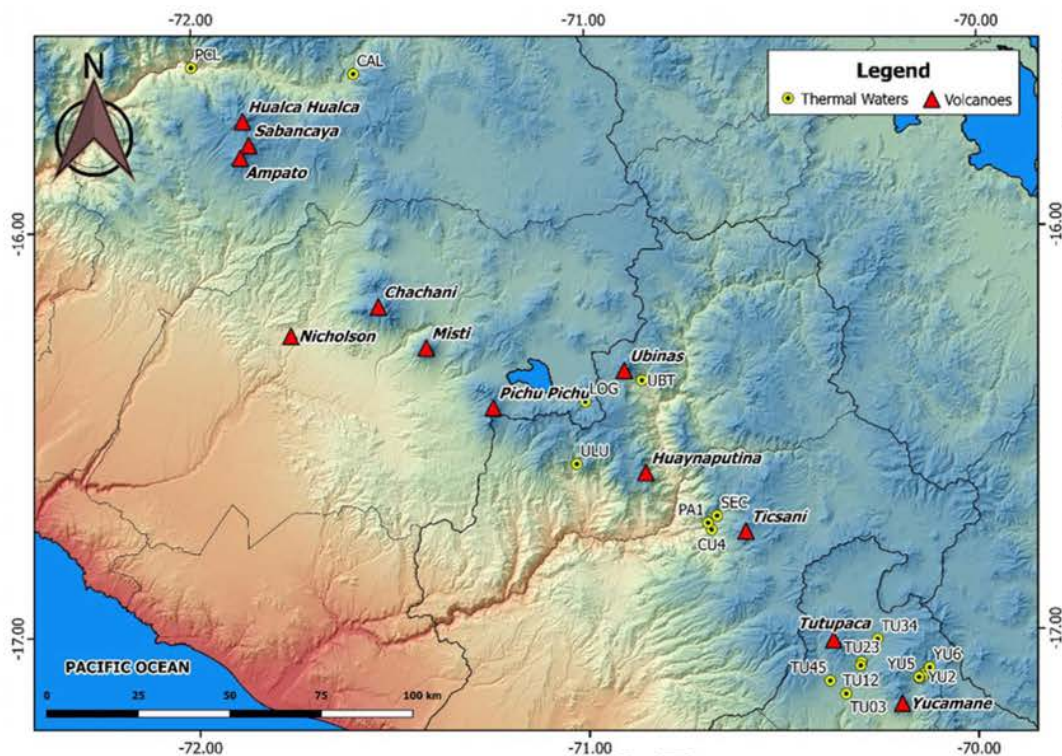


Fig. 6. Geological map and location of the geothermal systems in southern Peru, Sabancaya (Arequipa region), Ubinas, Huaynaputina, Ticsani (Moquegua region) and Yucamane (Tacna region).

mal system, where As concentrations range between 0.11 and 0.02 mg/L (Libbey et al., 2015) and the Tecuamburro volcano region in southeastern Guatemala with As contents between <0.05 and 2.0 mg/kg (Goff et al., 1989). Other studies that have reported As concentration of about 0.015 mg/L are from the public water supply system (groundwater) of the municipality of Mixco (29 km west of Guatemala City), the origin of which is natural due to leaching from volcanic rocks (Bundschuh et al., 2010, 2012; Cardoso et al., 2010), and the municipality of Chimaltenango (western Guatemala), with As concentrations of 0.06 mg/L (Lotter et al., 2014).

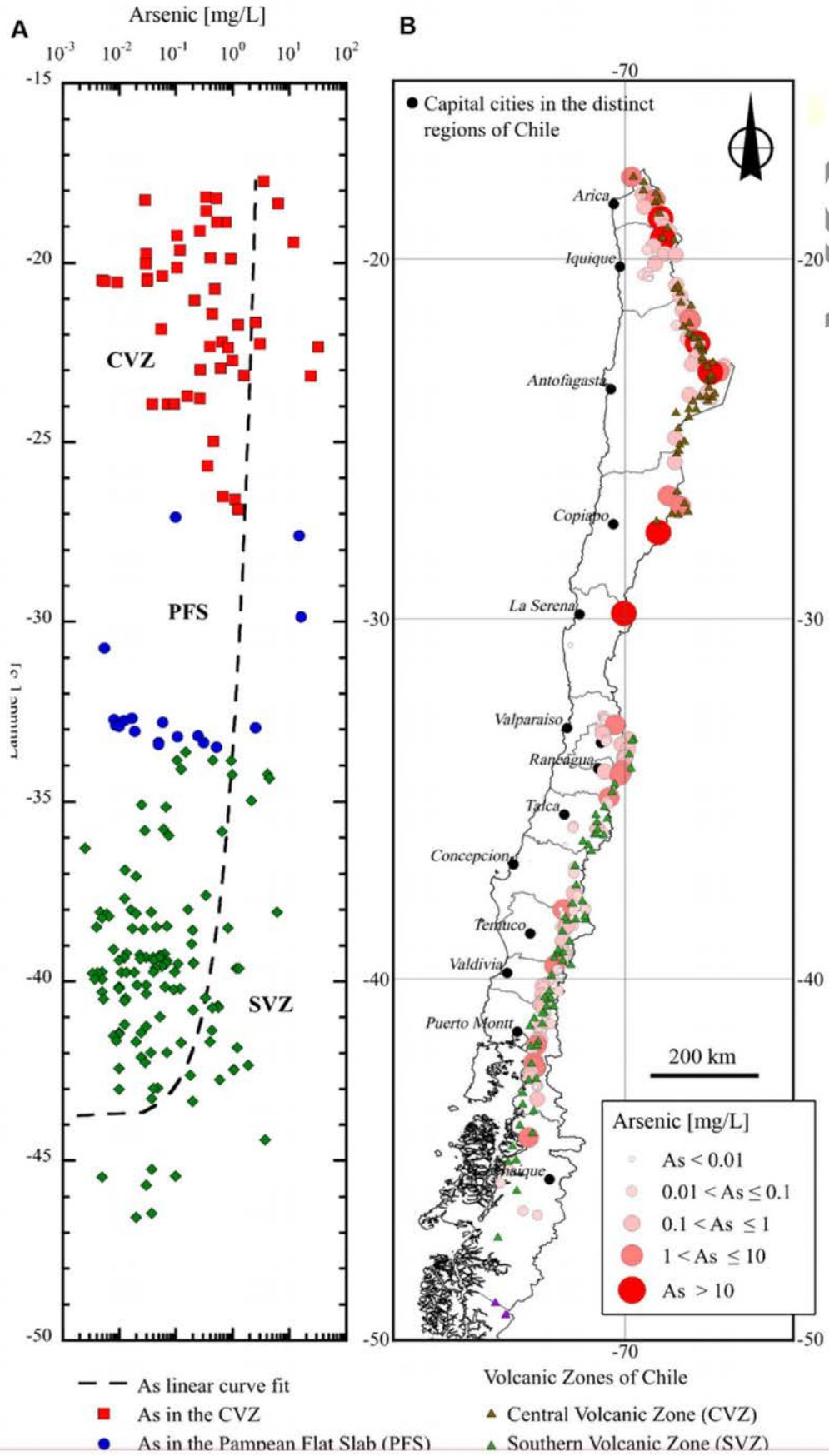
3.1.1. Geothermal systems of Zunil I and II (3542 m a.s.l.)

These geothermal systems are located in western Guatemala, adjacent to the active volcanic centers of Santa María and Cerro Quemado, inside a highly tectonic area, called the Zunil fault zone. This fault zone strikes NE-SW and is cut by a secondary NNW-SSE oriented fault system (Bennati et al., 2011; Lima Lobato and Palma, 2000). Samala River flows through the area and is surrounded on either side by the Zunil fault zone (Bennati et al., 2011). This tectonically complex zone is parallel and close to the eastern border of Xela caldera. Two regions of intense hydrothermal activity, Zunil I and II, are associated with these fault systems (Foley et al., 1990). The geothermal system lies on a surface of Quaternary and Tertiary volcanic rocks underlain by older igneous and metamorphic rocks (Adams et al., 1991; Foley et al., 1990). Sulfate and chloride waters are spatially confined to springs, wells and streams of the Zunil and Zunil-II geothermal fields on the flanks of the Cerro Quemado dome complex (Walker et al., 2006). According to Adams et al. (1991), As concentration ranges between 0.31 mg/L in geothermal waters to 4.8 mg/L in

(Table SM1). From the geothermometry of the neutral chloride type hot springs, the temperature of subsurface fluids near the confluence of Samala and neighboring rivers is about 210 °C, while the gas geothermometry in fumarolic gases (Azufrales and Fuente Georginas) revealed temperatures of 230 to 290 °C (Lima Lobato and Palma, 2000).

3.1.2. Tecuamburro geothermal system

This geothermal system is located 50 km southeast of Guatemala City, on the northern flank of the Tecuamburro volcano, a large andesitic composite cone with a complex geological history (Asturias, 2008). The region contains several volcanic centers of the Pleistocene age that are associated with seismically active faults and a wide variety of hot springs and fumaroles and an acid crater lake (Laguna Ixpaco). North- and WNW- trending normal faults are common within the Tecuamburro graben, with many thermal manifestations located along them. Vents of the Tecuamburro dome complex are aligned along the WNW trend and electrical resistivity data defines a WNW-trending conductive zone that passes through Laguna Ixpaco and fumaroles located west of the lagoon (Heiken and Duffield, 1990). Three types of thermal waters are distinguished in the area: steam-heated springs, acid-sulfate springs and neutral-chloride springs. The water of steam heated springs in the northern highlands within the graben have As concentrations of <0.06 mg/L (T: 69.1 °C, pH 5.7; for 4 samples). Those of the acid-sulfate springs in the Laguna Ixpaco (Chupadero crater) area have As concentrations of 0.05 mg/L (T: 55.3 °C, pH 3.3; for 9 samples). The neutral-chloride springs along the course of Río Los Esclavos have As concentrations of about



3.1.3. Joaquina geothermal system

The Joaquina geothermal system is classified as a non-magmatic, deep circulation-type, akin to Platanares and Azacualpa geothermal systems in Honduras (Libbey et al., 2015). The most prominent structures in the Joaquina area are steeply dipping, NE striking, left-lateral faults and moderately to steeply dipping ESE-WNW striking normal faults (Libbey et al., 2015). Arsenic concentrations in thermal springs can reach up to 0.7 mg/L (T: 74.5 °C, pH 8.3; for 7 sites) (Libbey et al., 2015). Meteoric waters penetrate deep into the subsurface and are heated to temperatures of around 180 °C. Geothermal fluids are Na-bicarbonate (sulfate) type with low Cl⁻ content, reflecting the lack of input of magmatic HCl and a chemical composition corresponding to the metamorphic host rocks (Libbey et al., 2015).

3.1.4. The Tacaná geothermal system

The Tacaná geothermal system is situated on the northwestern corner of the Central American Volcanic Arc at the Mexico and Guatemala border. It is associated with the Tacaná volcano (4100 m.a.s.l.), which hosts an active volcano-hydrothermal system (Rouwet et al., 2009b). The Tacaná complex rises above Mesozoic metamorphic and Tertiary plutonic and volcanic rocks (Mora et al., 2004), cut by three fault systems striking NW-SW, NE-SW and N-S. The last and youngest fault system may play an important role in the activity of the volcano (Mora et al., 2004). The Tacaná geothermal system is characterized by high temperature fumaroles in the summit (3600–3800 m.a.s.l.), and bubbling degassing thermal springs near its base (1000–2000 m.a.s.l.) (Rouwet et al., 2015). TDS values vary between 1400 and >2750 mg/L (hottest springs). Arsenic concentration in thermal spring waters ranges between 0.03 and 0.13 mg/L (T: 32–63 °C, pH 6.3–6.5; 6 samples), (Rouwet et al., 2009b, 2015). These thermal waters have also high contents of Sr, Fe, Mn and Al (Rouwet et al., 2009b). High Cl⁻ concentrations, in all springs, in particular for the hottest springs, probably derive from a deep geothermal aquifer hosting Na-Cl type waters (Rouwet et al., 2015).

3.2. Geothermal systems in El Salvador

The territory of El Salvador is characterized by numerous volcanoes, fumaroles and thermal springs (Armienta et al., 2008). This high thermal activity is the result of the geological setting of El Salvador with the boundary between the Cocos and Caribbean plates running parallel to the southern coast of the country and the boundary between the North American and Caribbean plates falling close to El Salvador's border with Guatemala (Motagua fault system). In El Salvador, the active volcanic chain runs east to west and it is marked by numerous volcanoes, some of which have recent eruptions (Santa Ana, Izalco, San Salvador and San Miguel volcanoes). High As concentrations are detected in surface water and groundwater (López et al., 2004a, 2009) which is due to the hydrothermal activity related to the volcanoes (e.g., Ahuachapán and Berlín geothermal fields). The high concentration of As is likely to be produced by the emissions of the magmatic gases from the active and dormant volcanoes that incorporate As to the groundwater overlying the magmatic chamber. The highly faulted terrane can channelize the hydrothermal fluids throughout faults and contacts to the surface or to the hydrothermal reservoirs and shallower groundwater. This is evident in the differ-

ent diffuse gas degassing studies that have been carried out in El Salvador (López et al., 2004b; Magaña et al., 2004; Pérez et al., 2004).

Geothermal waters discharging at the surface are generally rich in B, As, Li⁺, SO₄²⁻, CO₂ and Cl⁻ (e.g. Taran et al., 1998). This composition is the result of the interaction between magmatic system and the groundwater environment. El Salvador has many geothermal systems that discharge fluids to the surface and atmosphere (Fig. 3). Some of them are: (i) Ahuachapán and Chipilapa geothermal fields that are associated with the Concepción de Ataco caldera and the Laguna Verde, Laguna de las Ninfas and Hoyo del Cuajuste volcanoes; (ii) thermal springs located at the SW shore of Coatepeque lake that are related to Coatepeque caldera; (iii) thermal bicarbonate springs associated with San Salvador volcano; hot water seeps to the S of Ilopango lake that are produced by heat discharges from Ilopango caldera; (iv) the geothermal fields of Obrajuelo and San Vicente which are associated to San Vicente volcano; (v) the Berlín geothermal field associated with the Tecapa volcano; (vi) the Chinameca geothermal field which is associated with the Chinameca volcano; and (vii) thermal springs at Olomega lake. Ilopango and Coatepeque lakes form the largest bodies of fresh water in the country, and due to problems with the water supply systems in the country, there is some pressure in trying to make that water potable (e.g. Contrapunto, 2019; La Prensa Grafica, 2018, 2019).

Ahuachapán and Berlín geothermal fields are being exploited for electricity generation. The geothermal energy company (LaGeo) monitors the chemical composition of the geothermal waters, including As. Armienta et al. (2008) and López et al. (2012) reported that Ahuachapán geothermal field waters contain As at concentrations in the range of 0.01 to 0.21 mg/L, while for Berlín geothermal field, As concentrations in the range of 0.002 to 0.285 mg/L are reported, and for Las Burras wells, As concentration is 0.164 mg/L. Thermal discharges at Obrajuelo have As concentrations of 0.016 to 0.330 mg/L.

A number of different lakes have volcanic input and present high concentrations of As: the waters of lake Coatepeque have concentrations ranging from 0.09 to 1.19 mg/L and two hot springs to the S of the lake have As concentrations of 3.09 and 1.5 mg/L (López et al., 2012; McCutcheon, 1998). For the waters of Lake Ilopango, the As concentration ranges between 0.29 and 0.78 mg/L (López et al., 2009). Only one sample has been taken at Lake Olomega and the concentration has been reported as 4.21 mg/L, which is the highest As concentration measured in El Salvador (Armienta et al., 2008).

3.2.1. Volcanic rocks, arsenic and aquifers in El Salvador

Groundwater resources in El Salvador are formed by 71 aquifers of different size, with the more productive aquifers associated with volcanic centers in the country (MARN, 2017). The reason for this association is that the volcanic rocks normally present good hydrogeological properties due to fractures and easy water infiltration in blocky lava flows. Blocky flows occur in lavas of high silica content such as basaltic andesites and rhyolites. Basaltic andesites and andesites are common volcanic rock types in El Salvadorean volcanoes (Meyer-Abich, 1956). Some of the volcanoes that have extensive groundwater aquifers nested in the volcanic rocks are: Apaneca, Santa Ana, Izalco, San Salvador, San Vicente, Tecapa, Usulután, El Tigre, Chinameca, San Miguel and Conchagua volcanoes (MARN, 2017).

Some of the well waters from these aquifers which are widely used for drinking water supply contain As concentrations higher than the standard for drinking water in El Salvador (0.010 mg/L), accord-

Fig. 7. Arsenic concentrations in surficial thermal water and their latitudinal distribution. (A) Arsenic concentrations in relation to the Central (CVZ) and Southern (SVZ) volcanic

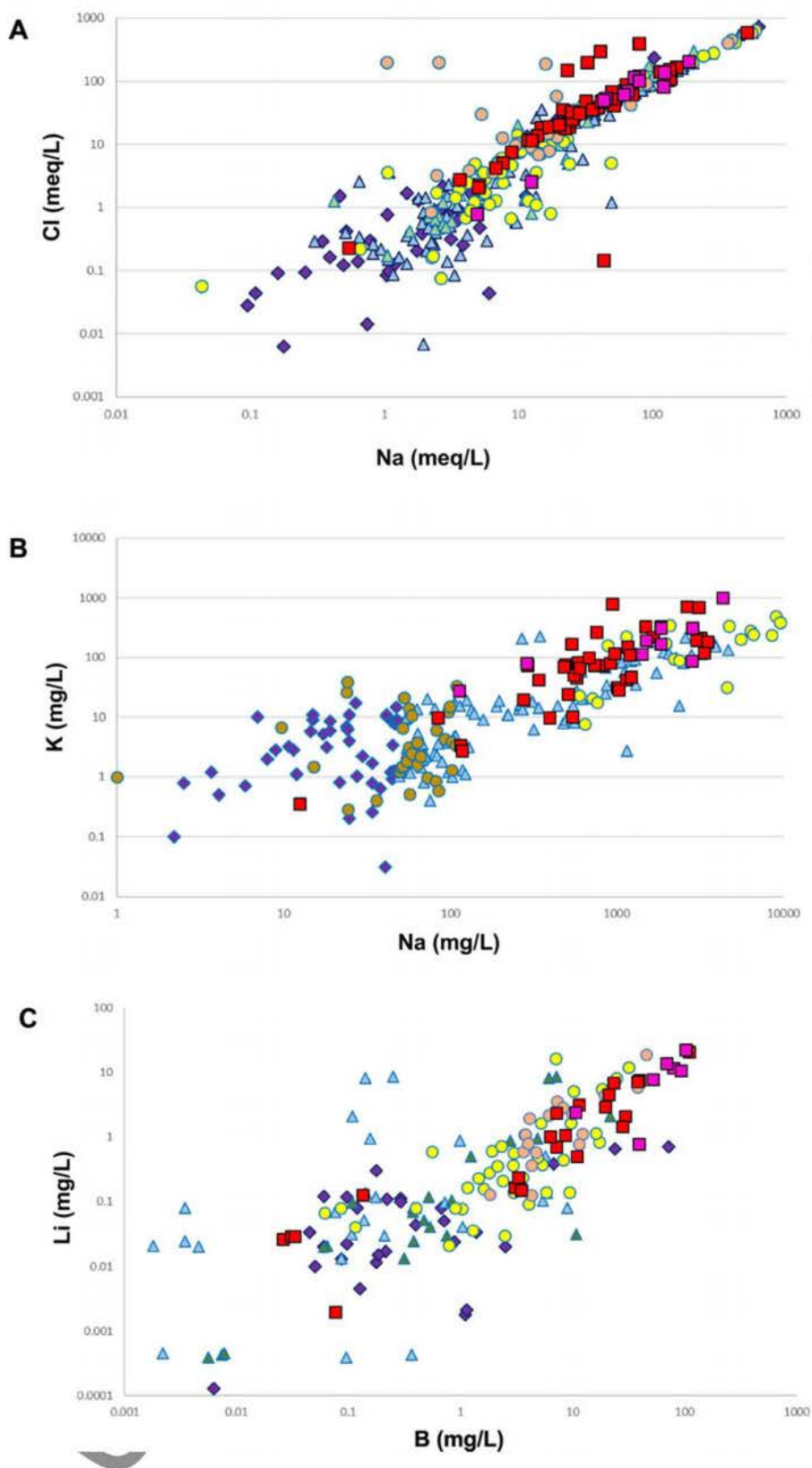


Fig. 8. Relationship between different major and minor elements plotted according to their As concentration in different groups: (A) sodium versus chloride, (B) sodium versus potassium, and (C) boron versus lithium.

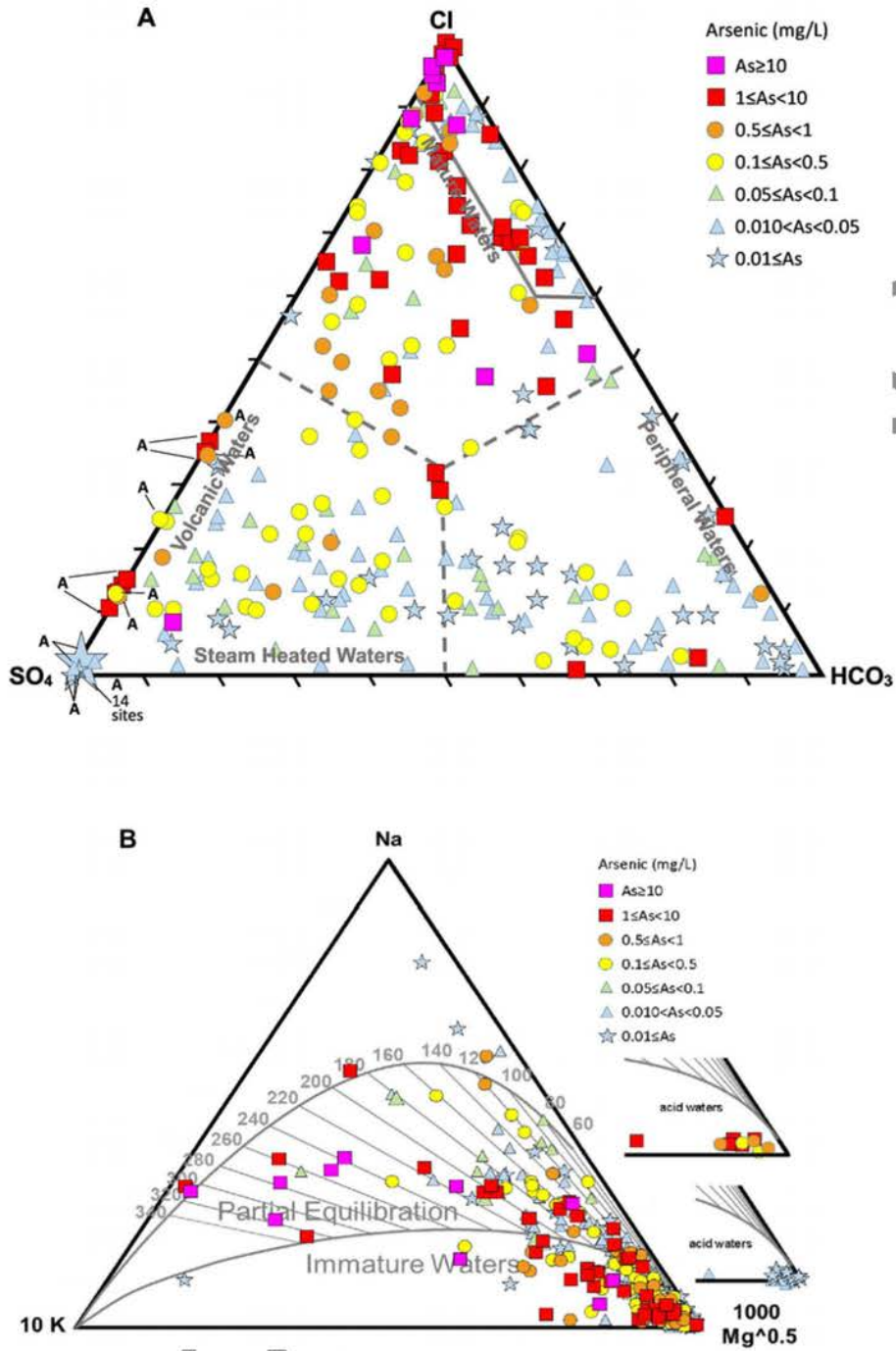


Fig. 9. Chemical characterization of geothermal waters (and related fluids) of Latin America compiled in Table SM1 (not including the Guarani Aquifer System). Data have been plotted according to their As concentration in different groups: (A) ternary main ion diagram (Cl-SO₄-HCO₃) diagram and (B) according to the Giggenbach (1991) diagram. In these diagrams, all the As groups have been included. For more clarity and further providing the site numbers (in A), in the supporting material (Figures SM1 and SM2), respective plots are individually provided for each As class.

ing to data provided by ANDA (Administración Nacional de Acueductos y Alcantarillados en El Salvador). In this case, such well water containing high As levels is diluted with water from another well with low As concentrations to comply with the national As standard for drinking water. Fig. 3 shows the locations of the wells and the concentration of As determined using atomic absorption spectroscopy. It can be observed in Fig. 3 that the majority of the wells with high As concentration is located in the aquifers related to

San Salvador and to San Miguel volcanoes, two of the most active volcanoes in the region. The four volcanoes that erupted during the last 112 years are Santa Ana, Izalco, San Salvador, and San Miguel. For the volcano aquifers of San Miguel and San Salvador, As inputs from the magmatic system can reach the shallower aquifers that are exploited for the water supply systems for the large cities of San Salvador and San Miguel. Arsenic concentrations for San Miguel's volcanic wells range from 0.013 to 0.031 mg/L. For San Salvador's vol-



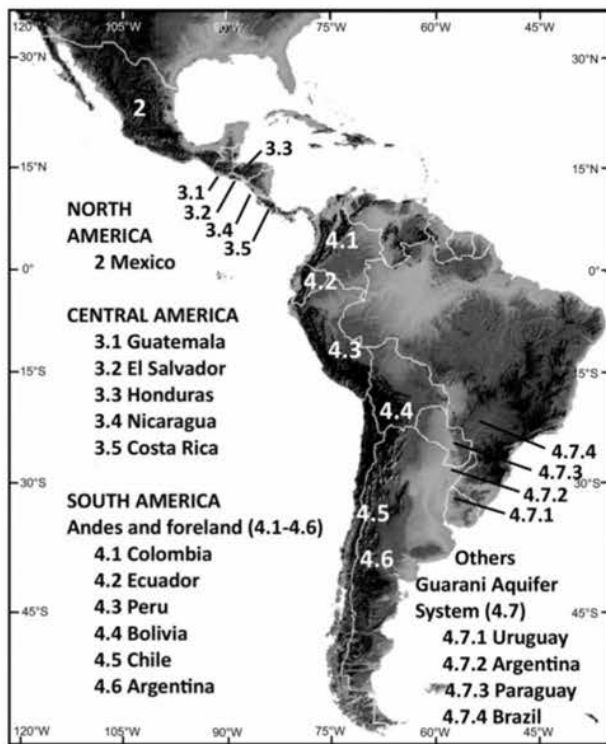


Fig. 1. Simplified location map of Latin America, showing the countries included in this paper and respective sections therein: North America: Mexico (2); Central America (3); South America (4): Colombia (4.1), Ecuador (4.2), Peru (4.3), Bolivia (4.4), Chile (4.5), Argentina (4.6), Guaraní Aquifer (4.7). The digital elevation model of the world PIA3388 (<http://photojournal.jpl.nasa.gov>) is courtesy of NASA/JPL-Caltech.

canic wells, the range of As concentrations is 0.015 to 0.064 mg/L. However, the highest As concentration of 0.073 mg/L is reported for a well located close to the town of Santa Rosa de Lima. This well also has the highest temperature (66 °C) of all the wells reported with high concentration of As, which suggests mixing of groundwater with geothermal water containing As.

The location of water supply wells containing As suggests that high concentrations of As are observed in the hydrothermal waters of El Salvador (e.g. Ahuachapán and Berlín geothermal fields) as well as in lower temperature waters of shallower aquifers located in volcanic rocks at two of the most active volcanoes in the country (San Miguel and San Salvador volcanoes).

For the two geothermal systems being exploited in El Salvador (Ahuachapán and Berlín), the hot waste waters, after the generation of the electrical energy, are injected back into regions of the deep hydrothermal aquifer. Water injection sites are selected in locations that can help to maintain the pressure, have a minimum effect on the temperature, and decrease the environmental impact to shallow groundwater and surface water systems. However, the natural discharges of geothermal fluids (e.g. from fumaroles and hot springs) have high As concentrations and can contaminate surface water and shallow groundwater. It is expected that high concentrations of iron (e.g. as iron hydroxide) in the river sediments can ameliorate and immobilize As through sorption and reduce the As content in the water (Herbel and Fendorf, 2006). However, the extent of the As contamination of streams in El Salvador by hydrothermal As has not yet been evaluated.

In some shallow volcanic aquifers, groundwater seems to be affected by As contamination such as is the case for the aquifers associ-

ior suggests that As is not only incorporated in the deeper geothermal system but it can be transferred by the mixing of As rich geothermal/magmatic fluids to shallower aquifers and even to the surface as in fumaroles and hot springs.

3.3. Geothermal systems in Honduras

Honduras is located in an inner part of the Caribbean plate, where most of the volcanic activity is from the Miocene age (Williams and McBirney, 1969). The active volcanic Pacific belt from Central America is only present in the Gulf of Fonseca, in the southern sector of the country. However, several surface manifestations (e.g. boiling mud pots, steaming ground, boiling springs, fumaroles) exist in the western and southern part of Honduras. These are most likely related to deep circulation of meteoric waters along fault systems (Heiken et al., 1991). The concentration of As in surface waters of 6 prospective hot spring sites (Platanares, 1.26 mg/L; Azacualpa, 0.07 mg/L; Pavana, 0.11 mg/L; San Ignacio, <0.05 mg/L; Sambo Creek, <0.05 mg/L; El Olivar <0.05 mg/L) and the temperature were measured for geothermal development during the late 1980s in response to the first global oil crisis (Goff et al., 1986). Geologic evidence in these investigations indicates that the hot spring systems in Honduras are not associated with silicic volcanism, which is abundant along the Central America volcanic front (Vogel et al., 2006). Rather water circulates deep into the earth, is heated conductively, and rises connectively along faults and fractures. Despite negative exploration results for finding suitable sites for geothermal resources for electricity generation with the existing technologies, further geochemical studies, including As sampling, were carried out until 2005 in the Platanares and Azacualpa geothermal fields (Fig. SM3). Other geochemical studies, including isotopic assessments on thermal waters have been performed in the present decade in NW Honduras (Capaccioni et al., 2014) and southern Honduras (Garcia et al., 2017) but the concentrations of As and other trace metals have not been reported.

3.3.1. Platanares geothermal system

The Platanares geothermal system (700 to 1300 m a.s.l.) is located close to Santa Rosa de Copán, Western Honduras. It lies within a graben that is complexly faulted and limited on the north by a highland of Paleozoic metamorphic rocks in contact with Cretaceous-Tertiary redbeds. These are unconformable, overlain by Tertiary andesitic lavas, rhyolitic ignimbrites, and associated sedimentary rocks (Heiken et al., 1986, 1991). This system is controlled by normal faulting within an active extensional tectonic setting, which has resulted in fractures that enable boiling fluids to reach the surface along the graben, depositing silica and altering preexisting rocks (Fercho et al., 2017). According to Barberi et al. (2013), the average total As (analyzed by ICP-OES) concentration in these fluids varies from 0.01 to 0.5 mg/L (boiling hot springs, 0.45 mg/L; non-boiling hot springs, 0.16 mg/L; cold meteoric water, 0.14 mg/L; exploration core hole, 0.33 mg/L), showing temperatures from 26.4 to 97.8 °C and pH values from 6.0 to 9.5 (Table SM1). Evaluation of all the data collected during the 1985 survey suggests that there are two levels of the geothermal reservoir at Platanares: a shallow (<700 m, 160–165 °C), and a deeper (>1.2 km, 225 °C) reservoir (Laughlin and Goff, 1991). This is confirmed by Barberi et al. (2013), who found that the geochemical geothermometers indicate a temperature for the deeper part of the geothermal reservoir close to 200 °C although it can reach temperatures of 270 °C and a mean of CO₂ flux of 17 g/m² day, probably because of the dominant silicate nature of the deeper reservoir.

3.3.2. Azacualpa geothermal system

this area, the predominant rock types are limestones of the Cretaceous age, red clastic strata, with minor volcanic rocks and a microdioritic intrusion of the Tertiary age (Finch, 1972). The most recent deposits are fluvial loose gravels and sands (Barberi et al., 2013). La Cueva spring is the main spring site in the Azacualpa thermal site, which is located at the interception of the Zacapa fault with the Jaitique River (Barberi et al., 2013; Capaccioni et al., 2014; Eppler et al., 1986). This N-NE-trending fault is one of the bordering faults of the Santa Barbara graben. The main branches of the Zacapa fault and their subsidiary fractures serve as conduits for thermal waters surfacing in the gorge of the Jaitique River (Eppler et al., 1986). The average total of As (analyzed by ICP-OES) is 0.08 mg/L (boiling springs 0.15 mg/L, non-boiling springs 0.08 mg/L, cold meteoric water 0.014 mg/L), with temperatures up to 98 °C and a pH of 7.2–9.0 and the geochemical geothermometers indicate a temperature for the deeper part of the geothermal reservoir between 150 and 170 °C and a CO₂ soil flux of 163 g/m² flux per day (Barberi et al., 2013).

3.4. Geothermal systems in Nicaragua

Nicaragua has an active volcanic belt that extends along the Pacific coast and comprises a NW-SE trending chain of volcanoes within the Nicaragua Depression, formed by the subduction of the Cocos Plate beneath the Caribbean plate along the Central America trench (DeMets, 2001; Carr et al., 2007b). The composition of the volcanic products varies from tholeiitic basalts to calc-alkaline acidic and intermediate rocks (van Wyk de Vries, 1993; Walker et al., 1990). The ignimbrite complexes represent the youngest structural surfaces located within the Nicaraguan Depression (Garofalo, 2006). In this volcanic range several important geothermal resources of high and low enthalpy have been identified but As data are sparse although hot springs, mud pots, gas discharges, zones of rock alteration are abundant in the Nicaraguan Depression (Zúñiga and Sánchez, 2003).

3.4.1. Momotombo geothermal plant

The Momotombo geothermal plant, is situated about 40 km NW of the city of Managua, on the NE shore of Lake Managua and the southern slope of the Momotombo volcano (Fig. SM4; Porras Cruz, 2012). This field is characterized mainly by three fault systems running NW-SE, NE-SW and N-S, allowing the circulation of fluids in the hydrothermal system (Porras et al., 2007; Porras Cruz, 2012). The Na/K and quartz geothermometry show aquifer temperatures around 200 °C and 271.9 °C. However, in some of the geothermal wells, there is a strong decline in temperature as a result of meteoric water infiltration (Porras Cruz, 2012). Parello et al. (2008) reported As concentrations of 2.09 mg/L (T: 79.7 °C, pH 8.3) and TDS values of about 4932.3 mg/L (for three sites) in the Na-Cl waters exploited by the Momotombo geothermal plant. The effect of active thermalism in groundwaters and the mixing of variable proportions of hyper-saline geothermal Na-Cl brines, explain the high salinities and high concentration of environmentally-relevant trace elements such as As, B, Fe and Mn in the Momotombo geothermal site (Parello et al., 2008). However, the release of As and other contaminants (e.g. Ni, Cu) from volcanic rocks into geothermal fluids occurs predominantly along active plate boundaries (Bundschuh and Prakash Maity, 2015; Parello et al., 2008).

3.4.2. Momotombo volcano and neighboring geothermal areas in the Managua region

The Momotombo volcano (1297 m.a.s.l.) is located on the NW shore of the Managua Lake, not far from the city of León (Fig. SM4). The volcano is an active old basaltic-andesitic stratovolcano. Surface

of the volcano, following hydrothermally active, NW-trending fractures (Wohletz, 1992). Total As concentration in the fumarole concentrates is about 0.79 mg/L (T: 472–776 °C) for 3 fumaroles (Table SM1), with emission rates of As of about 150 g/d (Garofalo, 2006). Metals emission fluxes at the Momotombo volcano are very low compared with the Masaya volcano, which has emissions of As, Cu, Zn, Tl, Rb and Cd each in excess of 10 kg/d (Martin et al., 2012; Wardell et al., 2004). According to Garofalo (2006) the fumarolic gases (containing e.g. As, Tl, Bi, Se, Mo, Sb, Hg, Au, W, Pb, Cd, Sn) are most likely to be of magmatic origin at the Momotombo volcano.

Near to the Momotombo volcano, Parello et al. (2008) collected a few acidic samples (between Mt. Galán caldera and the Asosca León volcano) with an As average of 0.112 mg/L (T: 45 °C, pH 6.6, TDS 1184 mg/L for 4 samples) and high salinities (up to 1356 mg/L) in HCO₃⁻-dominated groundwaters, reflecting extensive gas-water-rock interaction as a consequence of deeper/longer circulation paths. In the Momotombo area (Chilpete peninsula, near Xiloá lake), Parello et al. (2008) found As concentrations of 0.123 mg/L (T: 47 °C, pH 6.6, Eh -220 mV, TDS 4932 mg/L for 4 samples) and composition more or less similar to liquid samples extracted from the Momotombo geothermal plant in Na-Cl-dominated groundwaters. The temperature of the thermal springs on Xiloá lake shore are around 51 °C, pH 7.1, TDS 5105 mg/L under strongly reducing conditions (Eh < -300 mV), indicating the interaction with CO₂ and the H₂S-rich hydrothermal steam, feeding the nearby fumaroles.

Arsenic concentrations were also reported in SO₄²⁻-dominated waters in active faults and Na-Cl-waters in volcanic lakes. The SO₄²⁻-dominated waters have an As concentration of about 0.021 mg/L (T: 40.3 °C, pH 7, TDS 1202 mg/L for 4 sites), while the volcanic lakes (e.g. Apoyeque, Xiloá, Asosca de León, Asosca de Managua, Tiscapa, Nejapa, Monte Galán, Masaya and Apoyo) located within recently formed volcano-hosted depressions or calderas have As concentrations of 0.441 mg/L (T: 30 °C, pH 7.9, TDS 3958 mg/L for 18 samples) (Parello et al., 2008; Vázquez-Prada Baillet et al., 2008). The Nicaraguan lakes are a part of the Central American Quaternary volcanic belt, which is located at southwest of the Tertiary volcanic range, following the axis of the Nicaraguan Depression (McBirney and Williams, 1965).

3.4.3. Telica municipality (Nicaragua depression)

Communities in the vicinity of the volcanic complex of Telica-Rota, located in the Nicaragua Depression, are supplied with groundwater in which in since 2006 elevated As concentrations have been found (Unión España, Nuevo Amanecer; Nuevas Esperanzas, 2010). Exploration for water supply in 2010, more wells with elevated As concentrations; 59 well water samples, 20 (34%) exceeded the regulatory limit of 0.010 mg/L set for drinking water (6, i.e. 10% were above 50 µg/L). A subsequent study in other communities (Bella Vista, Ocotón and Los Cementos – located north of Telica municipality analyzed As from 154 wells and springs; As concentrations ranged from 0.010 to 0.325 mg/L (OPS/OMS, Nuevas Esperanzas, 2011). The origin of the As has been attributed to geothermal activities in the region and As-rich thermal water locally ascending and mixing with the shallow groundwater; as indicated by local temperature anomalies in the shallow groundwater and the fact that waters sampled from the shallow groundwater with >50 µg/L of As also have elevated temperatures exceeding 33 °C.

3.5. Geothermal systems in Costa Rica

Arsenic concentrations in volcanic emissions have been determined only for a few volcanoes of Costa Rica, in spite of numerous

noes (Turrialba and Poás) in the Central Cordillera of Costa Rica and two important geothermal reservoirs (Rincón de la Vieja and Miravalles) under exploitation for electricity generation in northwestern Costa Rica (Fig. 4).

3.5.1. Turrialba volcano

Turrialba volcano (3,349 m.a.s.l.) is an active basaltic-stratovolcano and represents the southernmost volcanic edifice of Costa Rica (Fig. 4). It is part of the Irazú-Turrialba massif, the largest volcanic complex of Central America (Carr et al., 1990). Major and trace element geochemistry of selected volcanic rocks of Turrialba shows As concentrations of <5 mg/L, indicating that most of the observed chemical variability can be explained using a fractional crystallization process (Piazza et al., 2015). Lücke and Calderón (2016) identified As and Cl⁻ concentrations in ashes from the 2014–2015 Turrialba volcano eruptions by means of Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). Quantitative analysis of the clay coating of a sample (LQf2) showed an anomalously high content of As₂O₅ (4910 mg/kg), suggesting that the dust fraction (non-rinsed) of the volcanic ash may be enriched in As due to pervasive hydrothermal alterations. However, As and Cl⁻ are absent on the rinsed samples, which may indicate that they are associated with the dust fractions or that they are coating the coarser grains and may be removed by as a result of lixiviation. On the basis of this study, the authors concluded that no As is present imbedded in the matrix of the 2.7 diameter (0,15mm) fraction of the ashes. Further geochemical studies are necessary to understand As mobility and fate in the Central Valley of Costa Rica, where most of the country's population is concentrated.

3.5.2. Poás volcano

Poás volcano (2325 m.a.s.l.) is a broad, basaltic-andesitic stratovolcano (Fig. 4). The 1.3 km wide active crater hosts an acidic lake, known as Laguna Caliente (Casertano et al., 1987; Martínez Cruz, 2008). The acid sulfate waters of Laguna Caliente have a SO₄-Cl composition (Rodríguez and van Bergen, 2017). According to Giggenbach and Corrales Soto (1992) and Truesdell (1992), the high acidity of these waters is mainly caused by HSO₄⁻ and HCl(aq), products of the input of the magma-derived gases HCl and SO₂. Martínez Cruz (2008) reported As concentrations from 0.143 mg/kg on June 4, 2008 to 16,000 mg/kg on November 19, 1992 in the crater lake, where the lake temperature varied between 22 and 95 °C and pH from -0.97 to 1.75. Based on the geochemical data collected by Martínez Cruz (2008) for the Vulcanological and Seismological Observatory of Costa Rica (OVSICORI, based on the initials in Spanish), Keizer (2014) modeled the mobility of trace elements (B, Zn, As, Mo, Sn, Sb, Tl, Pb) in the crater lake and found that As concentrations have varied during the Poás volcano's development, being higher in some stages and lower in others, for example during November 7 and June 4, 2008 (the later part of stage 5, in Martínez Cruz, 2008 classification), the concentration of As decreased from 0.05 to 0.005 mg/L in the Poás crater lake, as well as those of Sb and Mo. It may be suggested that Mo, As, Sb are incorporated into native sulfur or sulfide precipitate (Africano et al., 2007, in Keizer, 2014). Arsenic concentrations in some fumarolic concentrates were also reported by Africano et al. (2007), cited in Keizer, 2014), and the highest values (86 mg/L) were found in November 05, 2002 at 122 °C. During this stage, enhanced subaqueous fumarolic discharge induced increased lake temperature, conductivity and concentration of dissolved chemical species, as well as a steady drop in pH throughout 2005 (Martínez Cruz, 2008). Details of the geochemical evolution of the acid crater

et al. (2000), Martínez Cruz (2008), and Africano et al. (2007) cited in Keizer (2014).

3.5.3. The Miravalles geothermal system

The Miravalles geothermal field lies in the northwestern part of Costa Rica inside the Guayabo caldera, which is a collapse structure of about 15 km diameter with an active hydrothermal system (Chiesa et al., 1992; ICE-ELC, 1983). It is a typical high-temperature liquid-dominated reservoir (Gherardi et al., 2002; Vallejos Ruiz, 2013). Inside the Guayabo caldera, four NW-SE, N-S, NE-SW and E-W trending structural systems have been defined, all contributing significantly to the permeability of the geothermal systems (Chavarria, 2003a, 2003b). On the surface, different eruptive vents have been observed, mainly NE-SW oriented (Alvarado, 1989). The largest thermal manifestation in the area is in the Hornillas zone on the flank of Miravalles volcano (Hammarlund and Piñones, 2009). The geothermal manifestations are lakes, acid-sulfate springs, steaming ground, fumaroles, small craters and mud volcanoes (Gherardi et al., 2002). Las Hornillas constitutes an important geothermal nature-close leisure site with natural thermal sauna and volcanic mud baths with therapeutic qualities, hot springs and simple lodging options. Arsenic concentrations (using ICP-OES) were measured in geothermal wells (11.9–29.1 mg/L), thermal springs (0.005–4.6 mg/L; T: 33.7–88.9 °C), and cold surface waters (0.005–0.007 mg/L, T: 14.2–23.6 °C, pH 6.6–7.2) (Hammarlund and Piñones, 2009).

3.5.4. The Rincón de la Vieja geothermal system

This geothermal system lies on the Pacific slope of the Rincón de la Vieja volcano, inside the Cañas Dulces caldera, northwest Costa Rica (Molina and Martí, 2016). The zone is characterized by several structures (e.g. dykes and plutonic intrusions) and mainly NE-SW and NW-SE striking fault systems (Curewitz and Karson, 1997) and two minor N-S and E-W trending systems with N-S and E-W orientations (Chavarria, 2003a, 2003b). The origin of geothermal fluids may be meteoric water, sea-water, magmatic water or mixtures of these (Curewitz and Karson, 1997; Giggenbach and Corrales Soto, 1992). Geothermal manifestations are characterized by fumaroles, silicified rocks, soils and thermal springs, mainly found in the sectors of Las Pailas and Borinquen. Arsenic concentrations (using ICP-OES) were measured for the geothermal wells (7.8–13.0 mg/L), thermal springs (0.005–10.9 mg/L; T: 26.0–91.0 °C) and cold surface waters (0.005 mg/L, T: 27.1 °C, pH 6.01) (Hammarlund and Piñones, 2009). Three type of waters are distinguished in the area: sulfate, bicarbonate and chloride waters (Molina and Martí, 2016).

4. South America

4.1. Geothermal systems in Colombia

The Colombian Andes are the result of the interaction between the Nazca plate, the Caribbean oceanic plate and the South American plate (Borrero et al., 2009; Pulido, 2003; Taboada et al., 2000). The country has 15 active volcanoes produced by the eastward subduction of the Nazca plate below the South American plate. Two main significant fault systems have been identified: the Romeral Fault System in the Central Range and the Frontal Fault System in the Eastern Range (Pulido, 2003; Villagómez et al., 2011). (Fig. SM5A), which play an important role in the landforms of the country.

4.1.1. Azufral geothermal system

The Azufral geothermal system is associated with the active Azufral volcano (4020 m.a.s.l.), located in the Western Cordillera of

and Bernal, 1998). The volcano is characterized by an acidic lake (Laguna Verde) inside the caldera. The geothermal surface manifestations are: thermal springs, acidic alteration zones and fumarolic activity (Alfaro et al., 2015).

Inguaggiato et al. (2017) collected 15 acidic lake waters along the shoreline of the lake and 1 near-neutral thermal spring (FT1) discharging its water into the lake. Arsenic concentrations in the lake range from 0.0005 to 0.001 mg/L (this work), with pH values around 2.2, total dissolved solids (TDS) around 0.7 g/L and Eh⁺ values around 220 mV. Lake water is Na-SO₄ dominated and the origin of SO₄²⁻ is due to the adsorption of S-bearing gases (Fig. SM5B, Table SM1). The physico-chemical parameters and the chemical composition of the lake water were constant in the samples collected along the shoreline. In Figure SM5B is shown the comparison of the lake water to the spring waters (FT1) of Na-HCO₃ type. Arsenic concentration in the thermal spring (FT1) is 0.0022 mg/L (this work), with a temperature of about 56.5 °C, pH 6 and Eh 35 mV.

4.1.2. Nevado del Ruiz geothermal system

Nevado del Ruiz geothermal system is associated with the Nevado del Ruiz volcano (5311 m a.s.l.), which is located in the northern part of the Andes chain in the Central Cordillera. The volcanic rocks are calc-alkaline ranging from andesitic to dacitic in composition (Borrero et al., 2009). In this area, 7 springs and 5 rivers were sampled (Federico et al., 2017; Inguaggiato et al., 2015). The waters in the studied area have highly variable pH (1–8.8), electrical conductivity (0.2 to 33.3 mS/cm) and temperature (6.8 to 79.5 °C) (Table SM1). Most of the waters with acidic pH values (<3.3) are steam-heated waters (Group 2a, 2b, Fig. SM5C; sulfate dominated), according to the classification of Giggenbach (1988), which can be explained by condensation of sulfur-bearing acidic gases (Federico et al., 2017) (Fig. SM5C). The most acidic samples are those with highest temperature and mineralization, the latter probably due to the intense leaching of the host rocks favored by the higher temperatures and water acidity. The near neutral waters are río Molinos and Botero Londoño, characterized by a higher proportion of C content and a higher proportion of Cl⁻, respectively (Group 1a; Fig. SM5C).

Arsenic concentration in the spring waters ranges from 0.009 to 2.75 mg/L (this work), while those in the rivers varies from 0.0006 to 0.46 mg/L (this work). Arsenic concentrations increase with decreasing pH in some springs, reaching the highest values in Hotel 2 and Hotel 1 springs (As 2.6 mg/L, T: 61 °C, pH 1.4) and the near-neutral Botero Londoño mature water (As 0.93 mg/L, T: 79.5 °C, pH 7.7) (Table SM1). Moreover, Inguaggiato et al. (2015) identified the nature of the suspended solid matter (SPM) in the spring and river waters of Nevado del Ruiz. The highest As concentration was found in Group 2b (acidic waters) (Fig. SM5C), where Inguaggiato et al. (2015) did not identify SPM on the filter 0.45 μm used to filtrate the waters in the field. However, acidic waters (Group 2a) with lower concentration of As with respect to the Group 2b, presented sulfate minerals, probably alunite and jarosite in the SPM. Waters with pH from near-neutral to alkaline were probably oversaturated in Fe and Mn and therefore precipitated the Fe-, Mn-oxhydroxides found in the SPM.

Waters of the Nevado del Ruiz geothermal system show higher concentrations of As in comparison to the waters in Azufral volcano (Laguna Verde lake and FT1). However, more studies are necessary on both geothermal systems in order to understand better the nature of As.

4.2. Geothermal systems in Ecuador

4.2.1. Geothermal fluids in Ecuador

The geodynamics of Ecuador are ruled by the subduction of the Nazca plate beneath the South American plate (Gutscher et al., 1999; Witt et al., 2006). This process generated the magmatism of the Andean volcanic arc, characterized in Ecuador by at least 60 volcanoes (Hall and Beate, 1991). The volcanoes are usually subdivided into 3 different domains following their physiographic distribution: 1) the volcanoes lying in the western part of the cordillera; 2) the inter-Andean valley volcanoes; and 3) the volcanoes built on the eastern part of the cordillera. The Quaternary active volcanoes are located to the north of 2° S (Inguaggiato et al., 2010; Fig. 5A). The studied thermal springs are divided in three zones: the northern region (Imbabura, Pichinga provinces), the central region (Cotopaxi, Napo, Tungurahua and Chimborazo); and the southwest region (Santa Elena province).

4.2.2. Imbabura province

Two geothermal springs, Chachimbiro and Pitzanzi, were sampled by Inguaggiato et al. (2010) in Imbabura province. The chemical composition of Chachimbiro spring water is of Na-Cl type, while Pitzanzi spring water is Na⁺ dominated with similar proportions of Cl⁻ and HCO₃⁻ of about 25 mmol/L (Inguaggiato et al., 2010). The waters have near-neutral pH and an electrical conductivity of about 5 mS/cm. Chachimbiro is characterized by a higher temperature (51.2 °C) with respect to Pitzanzi (31.8 °C). Arsenic concentrations in Chachimbiro and Pitzanzi are 1.25 and 0.0069 mg/L (this work), respectively. The highest As concentration (1.25 mg/L; this work) was found in a Chachimbiro sample characterized by higher temperature and higher Na⁺ and Cl⁻ concentration compared to Pitzanzi. Cumbal et al. (2009) reported As concentrations up to 0.974 mg/L in Chachimbiro geothermal springs, which are similar to the unpublished As concentration data presented here (Table SM1). Moreover, As concentrations reported in two sediment samples in Chachimbiro springs are 131.9 and 176.7 mg/L (Cumbal et al., 2010; López et al., 2012).

4.2.3. Pichincha geothermal province

Nono spring, Aguas Caliente spring and Río Quitasol waters were sampled in Pichincha province. The former was classified as bicarbonate earth-alkaline water with Na⁺ concentration of 22.3 mmol/L and Cl⁻ concentration of 17.7 mmol/L, pH 6.3, electrical conductivity 4.0 mS/cm and temperature 28 °C (Inguaggiato et al., 2010) and As concentrations of 3.95 mg/L (this work). Aguas Caliente and Río Quitasol are classified as bicarbonate alkaline waters with temperatures of 10.5 and 21.4 °C, pH of 6 and 8, electrical conductivity of 2.7 and 0.2 mS/cm and Eh of 7.6 and 132 mV, respectively. Aguas Caliente spring has higher As concentrations (0.99 mg/L) than Río Quitasol (0.008 mg/L). Nono spring is characterized by As concentration (3.95 mg/L; this work) higher than Aguas Caliente and Río Quitasol (Table SM1).

Cumbal et al. (2010) reported As concentrations in seven geothermal water localities in Pichincha province: Aracuco (<0.002 mg/L), El Tingo (0.1 mg/L), La Merced (0.101 mg/L), La Cununyacu (0.405 mg/L), Merced de Nono (0.403 mg/L) and Ilalo (0.272 mg/L) and San Guillermo (0.048 mg/L) springs. High As concentrations (379.7 mg/kg) were found in the sediments at Merced de Nono spring (Cumbal et al., 2009).

4.2.4. Napo province

Four (4) thermal springs (Papallacta Terme), 3 thermal springs located in the Tambo River and 2 samples of the Río Papallacta were

springs are characterized by temperatures spanning between 47 and 61 °C, pH from 6.2 to 7.1 and electrical conductivity from 2.2 to 6.8 mS/cm.

Papallacta Terme springs are Na-Cl dominated with variable concentrations of Ca^{2+} , SO_4^{2-} and HCO_3^- . Three thermal springs close to the Tambo River have a chemical composition of Na-Cl dominated, temperatures spanning between 40.5 and 64.6 °C, pH ranging from 6 and 6.5, electrical conductivity between 3.3 and 5.6 mS/cm and Eh values ranging from negative to positive ($36.5 < \text{Eh} < -125 \text{ mV}$). The 2 samples of Papallacta river show a major chemical composition that is Ca- HCO_3 dominated (Table SM1).

Arsenic concentrations in the water of the Papallacta thermal springs changes from 0.66 to 3.203 mg/L, with the higher As concentration in the Jamanco sample characterized by slightly negative Eh values (-39 mV) and higher electrical conductivity (6.8 mS/cm) than those of the other thermal springs. Arsenic concentrations range from 2.7 to 5.7 mg/L (this work) in the geothermal springs close to the Tambo River. The Cachiyacu terraza de travertino and Cachiyacu campamento springs have higher As concentrations than the Cachiyacu Cueva spring and are characterized by higher temperature and Na^+ and Cl^- concentrations. The Papallacta river shows much lower As concentrations (0.001–0.02 mg/L; this work) with respect to the thermal springs previously mentioned.

Cumbal et al. (2009) characterized Papallacta Lake and the thermal springs in its vicinity. Arsenic concentrations were reported between 1.09 and 7.9 mg/L in the thermal springs, between 0.22 and 0.37 mg/L in the Papallacta Lake and between 0.233 and 0.698 mg/L in the Tambo River (Cumbal et al., 2009). Moreover, As concentrations in the sediments of Tambo river and Papallacta Lake vary from 20 to 128 mg/kg and 60–623 mg/kg respectively (Cumbal et al., 2009) impacting on aquatic life.

4.2.5. Cotopaxi province

Two springs (El Salitre and Hummocks) were sampled by Inguaggiato et al. (2010), which are classified as bicarbonate alkaline waters. Arsenic concentrations in both springs are 0.009 and 0.004 mg/L (this work), respectively. Cumbal et al. (2010) found As concentrations in the range from 0.012 to 0.045 mg/L in springs from Altamira farm.

4.2.6. Tungurahua province

Three thermal waters (La Virgen, Santa Ana, El Salado) were collected in Tungurahua province (Eastern Cordillera) and classified as Cl- SO_4 earth alkaline waters, with HCO_3^- up to 26.2 mmol/L (1599 mg/L) and Na^+ up to 24.19 mmol/L (556 mg/L) (Inguaggiato et al., 2010). The waters have $\text{pH} \approx 6.5$, electrical conductivity ranging from 4.4 to 6.8 mS/cm and Eh values from -112 to 66 mV. Arsenic concentrations range from 0.07 to 0.30 mg/L (this work), with the highest concentration in El Salado spring (Table SM1).

Cumbal et al. (2009) analyzed Agua Santa (P45), El Salado (P47) and Cunungyacu (P48) and reported As concentrations of 0.114, 0.048 and 0.047 mg/L, respectively. Moreover, an As concentration of 198.7 mg/kg (P47) was found in the sediment of the El Salado geothermal spring, and can be explained by the sorption of the solid phases (ferric oxide concentrations in sediment of 128 mg Fe g^{-1} of sediment) (López et al., 2012)

4.2.7. Chimborazo province

Cununyacu thermal water (47 °C) was collected in Chimborazo province and classified as Na-Cl type with Ca^{2+} concentration of 68.98 mmol/L (2765 mg/L), pH of 8.4, electrical conductivity of 4.3 mS/cm, Eh of 89 mV (Inguaggiato et al., 2010) and As concentration

4.2.8. Santa Elena province

Another geothermal area, San Vicente, is located in the Santa Elena peninsula in the SW of the country (Fig. 5). This thermal spring water was classified as Na-Cl type with Ca^{2+} content of 68.9 mmol/L (2761 mg/L), temperature of 38 °C, pH 6.4 and electrical conductivity of 19.7 mS/cm. Arsenic concentration in San Vicente thermal spring is 0.004 mg/L. No recent volcanism is reported in the area and the water is likely to be heated up by the terrestrial heat flux due to deep circulation. The water of the springs is used for spas and mud baths (Beate and Salgado, 2010).

In summary, the amount of As in the water samples collected by Inguaggiato et al. (2010) in Ecuador shows a wide variability of As concentrations ranging from 0.001 to 5.712 mg/L. Fig. 5B shows the As concentrations versus the relative proportion of Cl^- (calculated considering the sum of the major anions). Generally, higher concentrations of As are found in water with relative high proportion of Cl^- . The highest As concentrations were found in waters with a chemical composition dominated by Na^+ and Cl^- (Na-Cl type water), representing the mature waters with a prolonged water-rock interaction in the hot deep geothermal reservoir (Giggenbach, 1988). This evidence is in agreement with previous studies on As concentrations in Latin America, where mature Na-Cl waters have the highest As concentrations due to the prolonged water-rock interaction in the hot deep geothermal reservoir (Cumbal et al., 2010; Giggenbach, 1988; López et al., 2012; Ormachea et al., 2015).

4.3. Geothermal systems in Peru

Peru has a significant geothermal potential because it is located within the Pacific Ring of Fire, where the subduction process occurs between the Nazca and South American plates. In Peru, two geothermal regions can be distinguished, the first system in northern Peru, which is controlled by the geothermal gradient and the second system in southern Peru, which is related to a number of volcanic centers. The southern Peruvian geothermal fields described are related to five active volcanic areas of Pleistocene age: the Sabancaya, (Arequipa region), the Ubinas, the Huaynaputina and Ticsani (Moquegua region) and Yucamane (Tacna region). This Quaternary volcanic range in southern Peru belongs to the Central Volcanic Zone of the Andes, where several geothermal manifestations can be found such as hot springs, fumaroles and geysers. The hot springs related to these volcanoes have an average of As of 0.17–10.8 mg/L, with a pH of 2.7–7.6 and temperatures from 27 to 94 °C (Table SM1; Fig. 6).

Antimony has also been analyzed in the southern Peru hot springs. Antimony behaves in a similar manner as As in the environment, e.g. these two elements are commonly found together in point sources and in downstream waters for example in New Zealand, Iceland and the USA (Yellowstone) (Stauffer and Thompson, 1984; Welch and Stoltenwerk, 2003).

4.3.1. Sabancaya geothermal field, Caylloma province, Arequipa region

The thermal waters of Caylloma province are found around the Sabancaya volcano (Fig. 6), which is a dacite to andesite stratovolcano located in the Andean Central Volcanic Zone of southern Peru. The volcano is surrounded by an extensive system of active faults and lineaments. The regional tectonic setting of this area is characterized by E-W trending normal faults, but a link to the magmatic system is possible (Jay et al., 2015). The most important hot springs sampled around the Sabancaya volcano are Calera and Paclla. Calera hot spring (3625 m a.s.l.) discharges water that is heated by an andesitic intrusion called Cotallaulli, while Paclla (2179 m a.s.l.) is em-

River, which creates one of the deepest valleys of the Andes (Thouret et al., 2007). The mean total As concentration of the spring water is around 1.42 mg/L, with a temperature of 94 °C and a pH of 7.6. The main geothermal elements are Cl^- , Na^+ , SO_4^{2-} with low Li. The mean total As level in Calera spring water is 0.68 mg/L, with Cl^- , Na^+ as the major ions, and low B and Li contents. The spring water has a temperature of about 65 °C and a pH of 6.4.

4.3.2. Ubinas, Huaynapatina and Ticsani geothermal fields, General Sánchez Cerro province, Moquegua region

Several thermal manifestations are associated with the Ubinas, Huaynapatina, and Ticsani volcanic areas (Fig. 6). Ubinas volcano is historically the most active volcano in southern Peru. It is a composite cone with a roughly circular shape formed by Oligo-Miocene ignimbrites and intrusive rocks of the upper Tertiary age (Marocco and del Pino, 1966). The edifice has been developed mainly in Lower-Middle to Late Pleistocene times but has been persistently active to the present. The boundary of the thermal system is elongated towards the NNW, suggesting that the hot body (magma or hot fluid rising system) follows a regional NNW trend (Thouret et al., 2001). NNW-SSE fractures have been observed across the summit caldera wall and the SSE flank of the volcano, which may act as a path for fluid circulation (Thouret et al., 2001, 2005). Ubinas and Logen thermal springs have been sampled around the Ubinas volcano. Ubinas spring water (3329 m.a.s.l.) rises up to the surface at a temperature of 28 °C. The total As concentrations in the spring reach around 0.17 mg/L and contain Cl^- and Na^+ as the major elements while the springs contain low amounts of Li. Logen springs (4475 m.a.s.l.) are emplaced in the volcanic plains and show several thermal manifestations. The total As concentrations of these springs are 0.46 mg/L with temperatures of around 31 °C and pH of 4.2.

The thermal waters of Ullucán (2814 m.a.s.l.) are associated with the Huaynaputina volcano, which is a stratovolcano with several fumaroles in the crater and thermal waters discharging around the volcano. It is characterized by 4 fault systems and lineaments oriented N-S, NW-SW, W-W and NW-SE. The first two systems are associated with the Tambo River and the third and fourth systems consist of a series of strike-slip faults, parallel to the Central Volcanic Zone of the Andes. The sampled waters around the volcano host immature alkaline-chloride-sulfate waters and sulfate-chloride-alkaline waters, possibly of magmatic origin with a deep reservoir at a temperature of >200 °C (according to the Na-K-Mg geothermometer). As concentration is around 28.1 mg/L and it contains high Cl^- , Na^+ , Ca^{2+} , B and low Li concentrations, with pH of 6.6 and temperatures of around 74 °C. As concentration is around 28.1 mg/L and it contains high Cl^- , Na^+ , Ca^{2+} , SO_4^{2-} , B and low Li concentrations, with pH of 6.6 and temperatures of around 74 °C.

The main thermal manifestations associated with the Ticsani volcano are: Chuchumbaya, Putina Arriba and Secolaque. The oldest volcanic rocks, that form the substratum over which the lava and pyroclastic flows were deposited, are constituted by andesites, dacites, continental clastic sediments and rhyolitic ignimbrites. Two regional fault trends have been observed, one with Andean direction NW-SE, NNW-SSE and WNW-ESE, and the other with NNE-SSW and NE-SW direction. These thermal waters are of alkaline-chloride-sulfate water type and plot in the $\text{Cl}-\text{SO}_4-\text{HCO}_3$ diagram, which is typical for geothermal deep fluids (Cruz et al., 2013).

The Chuchumbaya hot spring is located close to the town of Soquesane and the homonymous stream. The total As concentration is around 2.5 mg/L, pH 6.2 and temperature about 50 °C. The Putina Arriba hot spring is located along the shore of the Putina river. It has an

C. The Secolaque hot spring is located along the shore of the Putina river. It has As concentration of about 2.17 mg/L and the main chemical tracers are Cl^- (491.0 mg/L) and Na^+ (321.0 mg/L). This spring has a pH of 6.8 and the temperature is 71 °C.

4.3.3. Yucamane and Tutupaca geothermal field, Candarave province, Tacna region

Eleven hot springs, including Yucamane 1–6 (Calientes geothermal system, ~4361 m.a.s.l.), TU45 (volcanic plain, 4152 m.a.s.l.), TUO3 (Turun geothermal system, 4010 m.a.s.l.), TU34 (NE flank of the Yucamane volcano, 4381 m.a.s.l.) and TU23 and TU12 (Sulfur stream, 4324 m.a.s.l.) associated with the Yucamane and Tutupaca volcanoes, have been sampled (Fig. 6). The volcano comprises andesitic lava and pyroclastic flows, associated with lava domes (Cruz, 2018). Yucamane and other volcanic structures in the Tacna region are strongly fractured and aligned in the direction NE-SW (Cruz et al., 2010a, 2010b), controlling the recharge, circulation and discharge of geothermal fluids (Cruz et al., 2010a, 2010b). The average concentration of As in this geothermal field ranges from 0.34 to 11.1 mg/L with a pH between 2.6 and 7.7 and temperatures from 46 to 87 °C, Cl^- (1099.5–1896.0 mg/L) and is the dominant ion of these waters. According to Cruz et al. (2010a, 2010b), the waters are mainly Na-Cl type, typical of deep geothermal fluids found in most high-temperature systems. The geothermometry enabled the estimation that Yucamane 1–6 in the Calientes field has the highest reservoir temperature ranging from 240 to 280 °C. In the ternary diagram $\text{Cl}-\text{SO}_4-\text{HCO}_3$ (Giggenbach, 1988) shows that the geothermal springs samples fall inside the deep chlorides waters group, typical of geothermal deep fluids in the most high-temperature systems (Cruz, 2018).

4.4. Geothermal systems in Bolivia

In Bolivia numerous hot springs were have been studied, which are located in different ecosystems within the Bolivian Altiplano (BA), nevertheless, only a few scientific publications describe As occurrences and geochemistry of these thermal waters.

The BA is an intra-mountain basin, enclosed by the eastern and western Cordillera of the Andes, which have different geological settings. High concentrations of As in hot springs and fumaroles were found in two different catchments; the Poopó lake catchment and the Coipasa and Uyuni salt plains catchment (Fig. SM6).

4.4.1. The Poopó lake catchment geothermal resources

The Poopó lake catchment (3686 m.a.s.l.) is a large plateau located in the central Bolivian Altiplano (PPO-3, 1996a, 1996b, 1996c). The Eastern Cordillera comprises Paleozoic and Mesozoic rocks, which were deposited on the Precambrian basement and deformed by multiple orogenic cycles from Paleozoic to Cenozoic. Principal rocks are Ordovician limestones, quartzites, slates and schists with low angle faults. Within the Poopó lake catchment, hot springs occur at the Altiplano border of the Eastern Cordillera (Huaranca Olivera and Neumann-Redlin, 2000). Structurally, the Altiplano corresponds to a graben-type continental basin that resulted from the displacement and uplift of the Paleozoic block of the Eastern Cordillera (Huaranca Olivera and Neumann-Redlin, 2000). The occurrence of hot springs near the border of Eastern Cordillera and the Altiplano corresponds to the face of a very deep fault line. The product of a normal heat flow at depths of 2000–3000 m, these hot waters take advantage of this fracture zone to rise up to the earth's surface. The origin of the thermal waters in the Eastern Cordillera is related to the complex structural setting of the Andes. The Andes have been subjected to several compressive stresses and are also affected by phases of plutonic mag-

folded Paleozoic strata and linked to local faults and fractures. There is no evidence of a direct relationship between geothermal waters to igneous bodies at the surface; although such a relationship is inferred to exist at depths such as magmatic chambers or heat-emitting nuclei (Huaranca Olivera and Neumann-Redlin, 2000). Large deposits of black or reddish sediments in the Poopó catchment area suggest the ongoing precipitation of sulfides and hydroxides from the thermal water of the springs (Lehrberg and Morteani, 1989).

Physicochemical characteristics of sixteen thermal water samples collected within the Poopó lake catchment showed a pH ranging from 6.3 to 8.3 (average 7.0) and a redox potential from +106 to +204 mV (average +172 mV). Temperature varies from 40 to 75 °C (average 56 °C) and electrical conductivity ranges from 1.8 to 75 mS/cm (average 13 mS/cm). Predominant major ions are sodium, chloride and bicarbonate. The thermal waters are of Na-Cl (37.5%) and Na-Cl-HCO₃ (37.5%) types that confirm both the influence of the geological formations dominated by carbonate and evaporate rocks and water uprising from deep geothermal reservoirs (Ormachea et al., 2015). Arsenic concentrations ranged from 0.008 to 0.07 mg/L and As speciation indicates the predominance of As(III) over As(V) species; however, thiolated As species have not been considered. Sediments collected from the outlets of thermal waters show a high iron content where ferric oxides and hydroxides are assumed to be the principal mineral phases for As attenuation by adsorption/co-precipitation processes. Arsenic concentrations (range <0.006–0.23 mg/L) in samples of groundwater used for drinking water supply collected from shallow drinking water wells are higher than those found in thermal springs.

It is likely that thermal water discharge is not the main source of high As content in the shallow aquifer waters, as they are very immature and may only have a small component corresponding to the deep reservoir (Ormachea et al., 2015).

4.4.2. Salars of Coipasa and Uyuni geothermal resources

Both Uyuni and Coipasa salt plains are located near the Western Cordillera, which is dominated by volcanoes, as well as extensive lava fields mainly comprising volcanic material accumulated in the Late Tertiary and Early Quaternary. Principal rocks are basalts, dacites, rhyodacites, and andesitic lavas while colluvium, alluvium and evaporites occur as valley fill deposits of the Quaternary age (YFPB and GEOBOL, 1996).

High As concentrations (up to 4.6 mg/L, with median of 0.034 mg/L) were found in catchments draining from areas of thermal springs and native fumarolic sulfur mineralization in the Western Cordillera. Arsenic in surface water is predominantly in the form of mobile As(V) and evapo-concentration appears to further increase As concentrations. A weak attenuation of As relative to chloride is noted downstream in hydrochemical river profiles, probably due to adsorption onto iron oxyhydroxide flocs, particulate coatings or precipitates (Banks et al., 2004).

4.5. Geothermal systems in Chile

Chile hosts 90 active volcanoes (Calderón et al., 2015), of which 45 are closely monitored by the National Geological and Mining Services (Sernageomin). >150 thermal springs exist throughout the country and geothermal activity is mostly controlled by volcanism and regional geologic structures such as the Puchuldiza fault in northern Chile (Tassi et al., 2010), the Infernillo and San Ramón-Pocuro fault systems in central Chile (Benavente et al., 2016), and the Liquiñe-Ofqui fault system in southern Chile (Aguilera et al., 2014; Romero et al., 2015; Wynn et al., 2017).

; Fernandez-Turiel et al., 2005; Campos et al., 2010); however its quantification in central and southern Chile has not received particular attention despite numerous natural sources of this element in those regions such as volcanoes, thermal springs, and volcanic rocks. Nonetheless, an important difference between the regions of southern and northern-central Chile (until 35° S; Fig. 7) is the presence of well-defined metallogenic belts. The Eocene-Oligocene belt is related to porphyry copper deposits with important concentrations of As which are reflected in the copper concentrates produced from those deposits (Fuentes et al., 2009). Additionally, epithermal deposits present along the eastern border of northern Chile are also known for their highly enriched As geochemical signature coupled with the presence of As-rich minerals such as enargite and tennantite (Jannas et al., 1990). In southern Chile, there are only a few polymetallic deposits that are being exploited such as the Toqui mine in the Aysen region. Other metal deposit types in this region, if present, have not been exploited or studied in detail.

High enthalpy geothermal systems are also found in the Aysen region, including the Puyuhuapi thermal springs with As concentrations of 3.8 mg/L (temperature 80 °C, pH 6.6), which are located along the Liquiñe Ofqui fault zone (Hauser, 1989, 1997).

Due to the differences between the volcanic zones in Chile, As values have been separated geographically between the Central Volcanic Zone (CVZ), the Pampean Flat Slab (PFS), and the Southern Volcanic Zone (SVZ) (Table SM1; Fig. 7). In the Northern (AVZ) only one hot spring (low As concentrations) has been poorly documented and cannot represent the geographical distribution. Statistical analysis, including correlations were done using the compiled data of 48, 17, and 120 hot springs in the CVZ, PFS, and SVZ, respectively. In Fig. 7, a linear fit is presented of As concentration data from thermal springs of Chile as a function of latitude. It is clear from this trendline that As concentrations generally increase from south to north, and this is believed to be due to geological differences as well as the crustal thickness which varies as a function of latitude.

4.5.1. The central volcanic zone: Puchuldiza geothermal field and Tatio geysers

4.5.1.1. Arsenic in hot springs of the central volcanic zone

The CVZ of Chile is located between latitude 14°S and 27°S (Stern, 2004). Most geothermal fields are located west of the CVZ at high elevations of generally >3000 m.a.s.l. and are structurally controlled by N-S and N-W trending grabens (Marinovich and Lahsen, 1984), as well as volcanic activity. The geology along the geothermal fields of this segment is relatively homogeneous and is constituted by Lower Miocene-Pleistocene ignimbrite deposits and andesitic-rhyolitic volcanic products that are overlying Middle Cretaceous-Upper Miocene volcano-sedimentary sequences (Marinovich and Lahsen, 1984; Tassi et al., 2010).

In this zone, water characteristics have been compiled for 48 thermal springs in which the temperature varies from 19.3 to 80.7 °C (average 38.7 °C), pH from 2.1 to 9.0 (average 7.1), and conductivity ranges from 0.095 to 32.20 mS/cm (average 1.511 mS/cm), (Hauser, 1997; Cortecci et al., 2005; Chong et al., 2010; Sánchez-Yanez et al., 2017). In general, thermal springs of the CVZ are enriched in As when compared to the other geological settings in Chile (0.005 to 26.0 mg/L, average 1.95 mg/L; Table SM1), and As is mostly found in its oxidized form As(V) (Fernandez-Turiel et al., 2005).

The As-enrichment of these thermal springs might be related to the crustal thickness of the CVZ which reaches over 70 km (Stern, 2004), facilitating conditions for geothermal fluids to be enriched in other elements as well. In support of this idea, Aguilera et al. (2016)

ally, saline precipitates near the río Negro hot springs (Tapia et al., 2018) and sinter structures (Nicolau et al., 2014; Sánchez-Yanez et al., 2017) of thermal springs of this segment contain increased values of As.

The only operational geothermal plant of Chile and South America is Cerro Pabellón, which is located in the CVZ segment of the Andes, specifically within the Antofagasta Region, at an elevation of 4500 m.a.s.l. Operations at this plant began in 2017 and it has an installed capacity of 48 MW (ENEL, 2017). In the vicinity of Cerro Pabellón, As concentrations of up to 4% have been found in pyrites (Román et al., 2019).

Two important geothermal fields in this segment of the Andes are the Puchuldiza geothermal field and Tatio geysers field.

4.5.1.2. Puchuldiza geothermal field

The Puchuldiza Geothermal Field (PGF) is located in the Tarapacá Region of northern Chile at an elevation of 4200 m.a.s.l. (Sánchez-Yanez et al., 2017). This field covers an approximate area of 1 km² and geothermal activity in the area is controlled by NW-SE reverse fault and NNE-SSW normal strike-slip fault systems that contain the Churicollo, Puchuldiza, and Tuja faults (Tassi et al., 2010).

In the PGF, 11 thermal water samples have discharge temperatures ranging from 54.4 to 87.8 °C (average 81 °C), pH from 6.2 to 8.8 (average 7.7) and, conductivity of 6.780 mS/cm (Hauser, 1997; Risacher and Hauser, 2008; Sánchez-Yanez et al., 2017). The PGF waters are of alkali-chloride type (Sánchez-Yanez et al., 2017). Arsenic values range from 10.7 to 13 mg/L (Hauser, 1997; Risacher and Hauser, 2008; Sánchez-Yanez et al., 2017), and As concentrations are positively correlated with K⁺, Li⁺ and Br⁺ (using the data of Hauser, 1997; Risacher and Hauser, 2008; Sánchez-Yanez et al., 2017).

Additionally, in the PGF, there are sinter structures where As and B⁺ are predominantly enriched in the amorphous phases (Sánchez-Yanez et al., 2017). Water and gas geothermometry show that the geothermal reservoir at Puchuldiza has high equilibrium temperatures (up to 270 °C) and is considered to be a promising geothermal field (Tassi et al., 2010).

4.5.1.3. The Tatio geysers field

The Tatio-Geysers Field (TGF, 4300 m.a.s.l.) is one of the most studied geothermal systems in Chile and is the principal natural source of As for the Loa river, the main surface water resource in the hyper-arid Atacama desert (Alsina et al., 2014; Muñoz-Saéz et al., 2015). Loa is also used for the water supply of the coastal city of Antofagasta (Romero et al., 2003) after As has been removed in several treatment facilities. The input of As from the Tatio geysers field into Loa river is through its tributary the Salado river. Contents of As reach up to 11,000 mg/kg in the river sediments close to El Tatio springs and still amount about 700 mg/kg at the mouth of Loa river where it discharges into the Pacific Ocean. Due to dilution and adsorption of As onto solid materials, the concentration of As, which is dissolved in the water of Salado river decrease downstream due but still amounts 1.2 mg/L at its confluence with Loa river (López et al., 2012; Romero et al., 2003). From there on it decreases further to about 0.1 mg/L at its mouth at the Pacific Ocean.

In the TGF, hydrothermal activity is centered in three major zones: the Upper, Middle, and Lower Basins, which collectively cover an area of approximately 30 km² (Alsina et al., 2014).

The surface water of geysers and pools in the TGF has registered two distinct ranges of As concentrations based on the present geologic units. The first sample group, found above ignimbrites, presents discharge temperatures ranging from 49.8 to 82.3 °C (average 73.4 °C), pH from 5.9 to 7.6 (average 7.8), and conductivity from

over 20 mg/L of As (data from Cortecci et al., 2005; Risacher and Hauser, 2008) which is closely positively correlated with Si and F⁻. The second group, found above alluvial deposits, presents discharge temperature ranging from 36.2 to 80.7 °C (average 66.4 °C), pH from 3.0 to 7.4 (average 5.5), and conductivity from 0.481 to 3.940 mS/cm (average 2.010 mS/cm) (Cortecci et al., 2005; Risacher and Hauser, 2008). These waters have lower As concentrations varying from 0.03 to 2.36 mg/L, and As is closely positively correlated with CO₃²⁻ and HCO₃⁻ (using data from Cortecci et al., 2005; Risacher and Hauser, 2008; Table SM1).

Isotopic data of the TGF indicate that hydrothermal fluids are controlled by water-rock interactions and complex mixing processes associated with meteoric and local groundwater (Giggenbach, 1978), CO₂ or H₂S, and hydrocarbon-rich magmatic fluids (Tassi et al., 2005).

Additionally, the TGF exhibits sinter structures where As is present as arsenate sorbed to hydrous ferric oxide in the form of nodular arsenide microminerals (Alsina et al., 2014). It is also found as caninite (Ca₄B₂As₂O₁₂•4H₂O) which precipitates through the evaporation of thermal waters that are highly enriched in As, B, and Ca²⁺ (Nicolau et al., 2014). Studies of solid-state partitioning in sediments of this area have shown that As is mostly associated with carbonates (Wilson, 2011).

4.5.2. The Pampean flat slab: Socos and Toro thermal springs

The Pampean Flat Slab (PFS) is located between 27° and 33° 30' S, and the most elevated segment of the Andes is found within the central portion of the PFS (Ramos and Folguera, 2009). In the Pampean flat slab there are 17 poorly documented thermal springs (Hauser, 1997; Risacher and Hauser, 2008). Temperatures and As values are highly variable and in general are similar to those of the CVZ (0.006 to 16.2 mg/L, average 2070 mg/L). Two examples located within the PFS are found in the Coquimbo region of north-central Chile and correspond to the Toro and Socos thermal springs.

4.5.2.1. The Toro and the Socos thermal springs

The Toro hot spring is located below the northern limit of the PFS at an elevation of approximately 3500 m.a.s.l. The temperature of this hot spring is 54.4 °C on average, pH is near neutral (6.84), the electrical conductivity corresponds to 7.660 mS/cm and As concentrations are on average 16.2 mg/L (Hauser, 1997; Risacher and Hauser, 2008). On the contrary, the Socos thermal spring is one of the few geothermal expressions in this segment of Chile that is located far from the Andes Mountains and at low elevations (88 m.a.s.l.). The water temperature is close to 27 °C and is alkaline (pH 9.74). In addition, the conductivity is 1686 mg/L and measured As concentrations are low (0.006 mg/L on average) (Hauser, 1997; Risacher and Hauser, 2008).

4.5.3. Southern volcanic zone: Coñaripe, Rollizos and Puyehue thermal springs

The northern limit of the SVZ coincides with the subduction of the Juan Fernández ridge while the southern limit corresponds to the Chile Rise (Stern, 2004).

The thermal springs found in the SVZ are controlled by regional fault systems, namely the NNE Liquiñe Ofqui Fault System (LOFS; Ruiz and Morata, 2016; Wrage et al., 2017) and the WNW Andean Transverse Faults (ATF; Ruiz and Morata, 2016; Wrage et al., 2017). The LOFS is related to thermal springs located in the intertidal zone that have undergone a minor interaction with saline water and continental hot springs which exhibit important cation exchanges (Ruiz and Morata, 2016). Thermal springs controlled by the ATF are influenced by volcanic activity (Ruiz and Morata, 2016).

from 2.4 to 9.7 (average 7.7), and conductivity ranges from 0.124 to 52.100 mS/cm (average 4.556 mS/cm), respectively (Hauser, 1989, 1997; Pérez, 1999; Risacher and Hauser, 2008; Aguilera et al., 2014; Lemus et al., 2015; Wrage et al., 2017). In the thermal springs, three water types have been identified: (i) Na-Cl, the predominant water type, which is characterized as alkaline, with low temperatures (average 55 °C), controlled by water-rock interactions, and with important amounts of Cl^- , Na^+ , As, Li and Cs; (ii) acid-sulfate, which is related to volcanoes, is acidic ($\text{pH} < 4$), and exhibits high temperature (85 °C average) and high concentration of SO_4^{2-} , Mg^{2+} and Ba; and (iii) bicarbonate, with similar temperature and pH to those shown in Na-Cl waters; however it exhibits the highest values of HCO_3^- (>892 mg/L) and contains elevated concentrations of most cations (Ca^{2+} , K^+ , Na^+ , Mg^{2+} , Ba^{2+} , Sr^{2+} ; Wrage et al., 2017). The geothermal fields of this segment of the Andes in general present lower As concentration than the northern segments, ranging from 0.003 to 6.127 mg/L (average: 0.331 mg/L). The lower values of As in the SVZ could be related to the lower crust thickness (30 to 40 km) as well as to higher rates of precipitation which could act to dilute As concentrations at the surface.

Three different examples of thermal springs in the SVZ correspond to Coñaripe which is controlled by the ATF, Los Rollizos which has intertidal influence and is related to LOFS, and the Puyehue-Aguas Calientes geothermal system that is associated with LOFS in a continental setting.

4.5.3.1. Coñaripe thermal spring

The Coñaripe thermal springs are located in the Los Ríos region of southern Chile. These thermal springs are controlled by ATF (Wrage et al., 2017), and as suggested by Ruiz and Morata (2016), they are influenced by volcanic activity.

The data of 6 samples from the Coñaripe hot springs indicate that the discharge temperature ranges from 62.0 to 77.5 °C (average 69.7 °C), pH from 7.1 to 8.5 (average 7.8), and electrical conductivity from 0.496 to 0.532 mS/cm (average 0.511 mS/cm) (Lemus et al., 2015; Pérez, 1999; Risacher and Hauser, 2008; Wrage et al., 2017). In this case, thermal waters are of Na-Cl type (Wrage et al., 2017), while As concentrations varied from 0.94 to 2.09 mg/L (average 1.31 mg/L), and As is directly correlated to temperature, CO_3^{2-} , B, and Br^- (Table SM1).

4.5.3.2. Los Rollizos thermal springs

Los Rollizos thermal springs are located in Los Lagos Region of southern Chile. These thermal springs are controlled by the LOFS (Wrage et al., 2017) and have intertidal influence (Ruiz and Morata, 2016).

Data of 10 samples of the Los Rollizos thermal springs indicates that discharge temperature ranges from 23 to 35 °C (average 28.9 °C), pH from 6.4 to 7.8 (average 7.2) and conductivity is 2.107 mS/cm (Aguilera et al., 2014; Hauser, 1997; Pérez, 1999; Risacher and Hauser, 2008). In this setting As concentrations are low ranging from 0.01 to 0.05 mg/L (average 0.02 mg/L). In addition, As is correlated to pH, HCO_3^- , CO_3^{2-} and NO_3^- (Table SM1).

4.5.3.3. Puyehue-Aguas Calientes thermal springs

The Puyehue and Aguas Calientes thermal springs are located in the Los Lagos region of southern Chile in close proximity to each other. These springs are controlled by the LOFS (Wrage et al., 2017).

Data of 15 samples of these geothermal springs indicate that the discharge temperature ranges from 48 to 66 °C (average 58.3 °C), pH from 6.9 to 8.6 (average 7.8) and conductivity from 0.562 to 0.844 mS/cm (average 0.703 mS/cm) (Hauser, 1997; Pérez, 1999; Risacher

senic concentrations range from 0.37 to 0.74 mg/L (average 0.51 mg/L) and are directly positively correlated to pH, CO_3^{2-} and F^- .

4.5.4. Summary of thermal springs in Chile

In summary, the geothermal fields of the PFS and the AVZ are poorly studied, therefore additional research is needed to better characterize thermal springs in those areas. In northern Chile, thermal springs are located at high altitudes and As values are also elevated, exhibiting the maximum value at El Tatio geysers. In the SVZ, three different settings are defined for thermal springs. The highest values of As are related to Na-Cl water type and volcano-related, whereas thermal springs with intertidal influence present low As concentrations. In Chile, it is crucial to define the main oxidation state of As and its species in the CVZ, SVZ, AVZ, and in flat subduction zones.

4.6. Geothermal systems in Argentina

The geotectonic setting in the Argentinian-Chilean southern Andes is favorable for the presence of geothermal systems and active volcanoes in Argentina (and Chile). Subduction of the Nazca plate under the South American plate has produced thousands of volcanic structures.

Five zones located in the high altitude Puna plateau and two different geothermal systems with high As concentrations in this study from southern Argentina are considered in this study.

4.6.1. Arsenic in thermal fluids discharged from the Puna plateau

The Puna plateau (part of the Andean highland) is located in the back-arc area of the CVZ, where the subduction of the Nazca plate beneath the South American plate takes place (Allmendinger et al., 1997; Bermúdez et al., 2002; Caselli et al., 2012; Chiodini et al., 2014; Chmielowski et al., 1999; Folguera et al., 2007, 2016). A seismic anomaly in the middle crust, between 22°S and 24.5°S, was interpreted as related to the presence of a ~1 km thick sill-like igneous body, namely Altiplano Puna Magmatic Body (APMB) (Chmielowski et al., 1999; Ward et al., 2014; Zandt et al., 2003).

Geochemical and isotopic features of thermal fluids discharged from five zones located in the high altitude Puna plateau (Jujuy province between S22°20'–23°20' and W66°–67°), namely Granada, Vilama, Pairique, Coranzulí and Olaroz were reported by Peralta Arnold et al. (2017). The highest values of As were measured in the Na-Cl type waters and they were dominated by Fe, As and Ba (9.62, 6.17 and 3.3 mg/L, respectively).

4.6.2. Arsenic in the Copahue volcano and adjacent geothermal areas

Copahue volcano is located in the Southern Volcanic Zone of the Andes, and although it is not aligned to the volcanic arc, its geology and local structural controls do not differ from the other nearby active volcanic centers (Fig. SM7; Folguera et al., 2016). Its particular geological record and eastern longitudinal position indicate that Copahue was probably part of the Late Pliocene-Pleistocene Arc mostly developed in the axial and eastern Andes (Pesicek et al., 2012). Reasons for this long-lived eruptive history at Copahue volcano could be related to the particular geometry of the active Liquiñe-Ofqui dextral strike-slip fault system that runs through the arc front from S to N where it penetrates the back-arc area at the latitude of Copahue volcano (Lavenu and Cembrano, 1999; Melnick et al., 2006).

Copahue volcano is one of the most active volcanoes of the central sector of the volcanic chain along the border between Argentina and Chile (Fig. SM7A). Frequent phreatic to phreato-magmatic eruptions have recently occurred (e.g. Bermúdez et al., 2002; Delpino and

cano is generally characterized by a relatively high temperature (up

to 63 °C) and low pH (<1), although in the last two decades these two chemical-physical parameters have shown strong variations probably related to the changes of the volcanic activity (Agusto et al., 2013; Tassi et al., 2016; Varekamp, 2008; Varekamp et al., 2001). Two thermal springs located on the eastern flank of the volcano, at a short distance from the active crater rim, discharge hot (up to 80 °C) and acidic (pH=1–2) water giving rise to the Agrio river that flows down to the Caviahue lake (Parker et al., 2008; Varekamp et al., 2001, 2009). On the other hand, there are five different areas on the northern and northeastern sectors of the external flanks of the volcanic edifice: Las Máquinas, Las Maquinitas, Termas de Copahue, Anfiteatro, and Chanco-Co. These natural manifestations have discharge temperatures (up to 95 °C) approaching that of boiling water at the altitude of the emissions (2000 m.a.s.l.), with the exception of one jet fumarole at La Maquinitas, where temperatures up to 140 °C were measured. The hydrogeochemical studies carried out in the crater lake, thermal springs, Agrio river and adjacent geothermal areas have not been focused on As, resulting in little concentration data on As. Water samples collected between March 1997 and November 2004 from the thermal springs (northern and southern springs) vary between 7.3 and 2.91 mg/L of As, reaching a value of 10.98 mg/L a month before the 2000 eruption (Varekamp et al., 2009). These authors also analyzed samples taken near the mouth of the Agrio river (in the Villa Caviahue) and in the Caviahue lake, yielding values between 0.04 and 0.64 mg/L and 0.03–0.04 mg/L, respectively. The As and Cl⁻ concentrations correlate positively, suggesting close to conservative behavior from the thermal springs to Caviahue lake. Arsenic behaves conservatively from the very concentrated thermal waters to the rather dilute Caviahue lake waters. Only three water samples of the crater lake and one thermal spring sample show evidence for As loss, probably through precipitation and/or adsorption (Varekamp, 2008). The hydrogeochemical studies carried out in geothermal areas between May 2004 and April 2005 (not published) indicate values of As of 0.002–0.011 mg/L, 0.004–0.011 mg/L and 0.005–0.017 mg/L for Las Máquinas, Las Maquinitas and Termas Copahue, respectively (Caselli, pers. commun., 2008). For the same period, As concentrations were measured in the crater lake (0.89–5.75 mg/L), southern spring (4.192–4.392 mg/L), northern spring (2.864–6.437 mg/L) of the volcano and Agrio river (0.12–0.58 mg/L) and Caviahue lake (0.022–0.039 mg/L); while in the thermal waters of Chanco-co was measured 0.040 mg/L (Caselli, pers. commun., 2008). Termas Copahue, includes a sophisticated medical center for medical treatments, combining baths with modern balneotherapy having a daily capacity for thousands of baths. Professional management and treatment supervision is assured by doctors, kinesiologists, physical education teachers, balneotherapy auxiliaries, etc.

4.6.3. Arsenic in the Domuyo geothermal field

The Domuyo volcanic complex (Neuquén province) hosts one of the most promising geothermal systems of Patagonia, giving rise to thermal manifestations discharging hot and Cl⁻-rich fluids (JICA, 1983, 1984; Chiodini et al., 2014; Tassi et al., 2016). Cerro Domuyo (2.5±0.5 My) is a wide rhyolitic dome unconformably emplaced in a N-S oriented anticline (Folguera et al., 2007; Groeber, 1947; Llambias et al., 1978; Miranda et al., 2006). Younger domes (720–110 ky) extruded according to a sub-circular geometry in the southwestern sector of Cerro Domuyo, whereas a minor intrusive body, generated by the last magmatic pulse in the Late Pleistocene (Miranda et al., 2006), outcrops on the southern flank (Fig. SM7B).

Geothermal resources related to the possible occurrence of two hydrothermal aquifers are located at depths of ≤600 and 2000–3000 m. The Domuyo geothermal field is recognized as the site of

an important hydrothermal activity characterized by four thermal spring discharges: El Humazo, Los Tachos, Las Olletas and Agua Caliente (Palacio and Llambias, 1978). These thermal manifestations are linked to the streams Manchana Covunco, Agua Caliente and Covunco, all tributaries of the Varvarco river. Although there are some hydrochemical studies of the thermal sources, the As concentrations are not published. However, data on the content of As are available in these streams and the Varvarco river, downstream of the mentioned tributary streams. Arsenic concentrations measured during the period 2010–2013 of the Varvarco river, vary between 0.036 and 0.152 mg/L (AIC, 2015). Arsenic concentrations measured for Manchana Covunco, Agua Caliente and Covunco, tributaries of the Varvarco river were 0.47, 0.66, 0.403 mg/L respectively (Ministerio Salud Neuquen, 2015).

4.6.4. Volcanic ashes impacting groundwater on a regional scale with arsenic

Groundwater with high As concentrations is known to occur in the aquifers of many regions of the Chaco-Pampean Plain of Argentina (Nicolli et al., 2012). Previous studies speculated that the As mobilization in these groundwaters was a direct result of their elevated pH and oxidizing conditions which favors As from the aquifer material. The volcanic glass present as distinct layers or distributed in the aquifer matrix was hypothesized as one of the possible sources of As found in the groundwater. This region has been delineated to be a part of the foreland basin of Andean orogenic belt. Volcanism in the Andean arc leads to deposition of this volcanic ash during different geological ages. Arsenic concentration in groundwater varies from <0.010 to >5 mg/L, and highest values are from shallow aquifers of La Pampa (<0.004–5.280 mg/L; Smedley et al., 2002) whereas groundwater from other provinces show lower As concentrations: Salta province (0.010–0.210 mg/L), Tucumán province (0.011–1.660 mg/L), Santiago del Estero province (0.002–3.280 mg/L), Córdoba province (0.018–1.100 mg/L), Santa Fe province (0.018–0.780 mg/L), Buenos Aires province (0.010–1.300 mg/L) (Nicolli et al., 2012) and San Juan Province (0.009–0.357 mg/L) (O'Reilly et al., 2010). Due to the prevailing oxidizing conditions (Eh 100–525 mV) most As is present as As(V). Arsenic concentrations in groundwater are positively correlated to electrical conductivity (0.112–23.800 mS/cm) and those of U (<dl-0.515 mg/L), Se (<dl-0.498), Mo (<dl-6.280 mg/L) and V (<dl-430 mg/L), which indicate a common primary source, i.e. the volcanic ash (Bundschuh et al., 2012; Nicolli et al., 2012).

As mentioned above, volcanic ashes have been traditionally considered important carriers of As to aquatic environments affected by volcanic ash fall. Low As concentrations have also been measured in aqueous leachates of tephros. Samples of volcanic ashes collected after eruptions of the Hudson (1991), Chaitén (2008) and Cordón Caulle-Puyehue (2011) volcanoes (Bia et al., 2015) showed that As-bearing phases were closely linked with the release of this element to the aqueous media. The most available species are those concentrated onto the grain surface, consisting of thin coatings of As(III)-S compounds, probably arsenian pyrite, and As(V)-O compounds, present as adsorbed/precipitated arsenate species. The most stable As-bearing phase is Al-silicate glass, where As is included within the structure. The release of As from this phase at the pH conditions dominating the aqueous reservoirs represents <1% of the total As measured in the bulk samples, while more mobile surficial phases may release up to 6% (Bia et al., 2015). Arsenic concentrations were also measured in aqueous leachates of tephros emitted by the Copahue volcano in November 2016, giving a value of 0.14 mg/L (Caselli and Páez, 2017).

4.7. The Guarani aquifer geothermal system (Uruguay, Argentina, Paraguay, Brazil)

The Guarani Aquifer System (GAS) is situated in the eastern and southern central portion of South America (Fig. SM8). It consists of a sequence of sandy layers of Triassic-Early Cretaceous age, deposited in continental, eolic, fluvial and lagoon environments, above a regional erosional surface and below an extensive layer of Cretaceous basalts (Sindico et al., 2018). This Aquifer system (GAS) represents one of the most important transboundary aquifers in South America shared by four countries: Uruguay, Argentina, Paraguay and Brazil (Bonotto and Elliot, 2017; Elliot and Bonotto, 2017; Foster et al., 2009; Gastmans et al., 2017; Manzano and Guimaraens, 2012; Sindico et al., 2018), and its waters are used extensively for potable supply. Several tectonic structures and numerous volcanic dikes cut through the GAS rock sequence (Foster et al., 2009; Manzano and Guimaraens, 2012). The aquifer consists of several geological units, including the formations: Misiones (Argentina and Paraguay); Botucatu, Pirambóla, Caturrita, Santa Maria (Brazil); and Tacuarembó (Uruguay) (Araújo et al., 1999; Carrión and Massa, 2010; Sindico et al., 2018), which have been developed due to complex episodes of geologic and tectonic activity (Carrión and Massa, 2010; Gastmans et al., 2012; Manzano and Guimaraens, 2012).

According to Manzano and Guimaraens (2012), geochemical evolution of GAS groundwater could be summarized in three main facies, which are found downstream from the outcropping recharge areas towards the confined sectors in the center of the basin: facies A (Ca-HCO₃ and Mg-HCO₃ water), facies B (Na-HCO₃ type water), and facies C (Na-HCO₃-SO₄-Cl to Na-Cl or Na-SO₄ type water); a fourth facies, D (Ca-Cl and Mg-Cl type water) has been identified in southern GAS in urban areas. Types A and B are slightly mineralized and most of the type C groundwaters are mineralized to a moderate degree. Several studies, for example LEBAC (2008), Foster et al. (2009), Manzano and Guimaraens (2012), Sindico et al. (2018) and others, found that water quality analysis of diverse wells in GAS are of good quality for human consumption, except in regions such as the SW zone of the aquifer of Argentina, where salinity can be very high, and in isolated areas of southern Brazil. Significant increases in trace elements have been found, especially F and more locally As, in certain areas of the aquifer (LEBAC, 2008; Foster et al., 2009). The highest fluoride contents seem to be associated with deep, saline groundwater with Cl⁻/SO₄²⁻, where fluorite may be the source of F⁻ (Manzano and Guimaraens, 2012). Arsenic may be released to groundwater by desorption from iron oxides/hydroxides, as result of the higher pH of the waters that underlie GAS units. Increased concentrations of Cr and U isotopes, radium and radon gas are also related to high pH groundwaters (Foster et al., 2009; Gastmans et al., 2010). The low-temperature geothermal sites, especially, along the boundary between Argentina and Uruguay are used for therapeutic and recreational facilities.

4.7.1. The thermal waters of Uruguay

The geothermal potential of the northern basin of Uruguay is related to the Guarani Aquifer system, where the sedimentary fill is of the Early Devonian to the Late Cretaceous age (Morales and Pérez, 2014). This thermal corridor is located in the triple border of Argentina, Brazil and Uruguay, and shows an intense economic thermal tourism activity (Gastmans et al., 2010; Pesce, 2010).

In the area, there are several thermal artesian wells that were drilled for oil exploration purposes many years ago but during the last 10 to 15 years, the commercial exploration of thermal aquifers (30–50 °C) along the Argentina and Uruguayan sides of the Uruguay river

mal wells including GAS and pre-GAS aquifers are: Arapey (As >0.01 mg/L); Daymán, Salto (As 0.04 mg/L); Fuente Nueva, Salto (As 0.032 mg/L); Posada del Siglo XIX, Salto (As 0.034 mg/L); San Nicanor, Salto (As 0.044 mg/L); Perf. OSE Salto, Salto-inactive (As 0.023 mg/L); Club Remeros, Salto (As 0.032 mg/L); Hotel H. Quiroga (As 0.035 mg/L); Termas Guaviyú, Guaviyú (As >0.04 mg/L); Termas Almirón, Guichón (As >0.01 mg/L) and Test Well-Abandoned, Paso Ullestie (As >0.01 mg/L) (Table SM2). Guichón and Paso Ullestie obtain their water from deeper aquifers, underlying the GAS rock formations (A. Manganelli, pers. commun., 2018). The thermal resorts with more possibilities for development are Guaviyú (temperature 40 °C, pH 9.1), and Arapey (temperature 38.0 °C, pH 8.4) (LAVALIN, 2008; Quintana, 2014); the first is one of the thermal sites with major dimensions in the department of Paysandú, NW Uruguay. This thermal well has a depth of 1109 m, TDS values of 1032 mg/L, and EC is 1.198 mS/cm (Carrión and Massa, 2010). Scientific research of geogenic As levels in groundwater indicates As levels above those recommended by the WHO for drinking water (0.01 mg/L; Mañay et al., 2019). The well was drilled in 1957 and since then, the Termas de Guaviyú have been in development during several years, in order to increase the local, national and international market. Arsenic occurrence is associated with sodium bicarbonate type groundwater with pH values over 8.0, which is released to groundwater by desorption from iron oxides/hydroxides, as result of the higher pH of these waters, indicating that As is released from the units that underlie the GAS and the pre-GAS (Carrión and Massa, 2010; Gastmans et al., 2010, 2012). Under natural conditions the magnitude of the upward flows seems scarcely relevant but uncontrolled groundwater exploitation may lead to increased flow rates and to the pollution of large aquifer areas caused by inflow of groundwater from layers below the GAS aquifers (Manzano and Guimaraens, 2012).

High As concentrations have also been reported in the Mercedes (As 0.023 mg/L, pH 7.7, T: 18.5 °C for 10 samples), Raigón, (As 0.013 mg/L, pH 8.0, T: 17.0 °C for 14 samples) and Chui (As 0.021 mg/L, pH 8.0, T: 21.5 °C) aquifers (SW Uruguay), which have calcium bicarbonate, sodic bicarbonate and sodium bicarbonate type water. Two of the 10 samples of the Mercedes aquifer in the vicinity of Nueva Palmira city contained As in concentrations of 0.05 and 0.06 mg/L, respectively (Manganelli et al., 2007a, 2007b). Arsenic concentrations in Raigón and Chuy aquifers may be due to the fluvial and marine influence of the sediments.

4.7.2. The thermal waters of Argentina

The most important wells in the different levels of the Guarani aquifer and underlain aquifers are: Colón (As >0.01 mg/L); Chajarí (As 0.02 mg/L); Federación (As 0.03 mg/L); Concordia (As 0.04–0.06 mg/L); Villa Elisa (As <0.01 mg/L) (Table SM2). These thermal waters are of sodium bicarbonate-sodium chloride (e.g. Colón, Chajarí, Federación), sodium bicarbonate (e.g. Concordia) and sodium sulfate-sodium chloride (Villa Elisa) type. There are other thermal waters including Aguas Claras Termas, Concepcion de Uruguay (As 0.04 mg/L); Tambo Vecino Termas, María Grande (As 0.06 mg/L); Molino Vecino Termal (As 0.114 mg/L); En Predio Termal, María Grande (As 0.07 mg/L); Termas San José (As 0.101 mg/L) and Privado Termal, María Grande (As 0.06 mg/L), which are not mentioned in the cited literature, but are considered in the present work because they contain concentrations of As >0.01 mg/L (Table SM2; LEBAC, 2008). As mentioned previously, there is an extensive area in the southwest of the aquifer in Argentina, where the confined GAS aquifer contains groundwater of high salinity. These waters are used

4.7.3. The thermal waters of Paraguay

The Guarani Aquifer in Paraguay comprises layers of Permian and Triassic (Misiones Formation) sandstones, which are confined by Cretaceous basalts (Alto Paraná Formation) (Farina et al., 2004). In the 2004 survey carried out by Vassolo (2005), some wells for water supply were sampled in the southern part of the Guarani-Aquifer in Paraguay. These wells showed elevated As concentrations of 0.02–0.05 mg/L in some locations in the southwestern part of the Guarani aquifer, where the Triassic and Permian sandstones crop out. According to Vassolo (2005), As is released in consequence of the reduction of goethite, to which As was sorbed. Similar geochemical behavior is found in the state of São Paulo (Brazil). Most waters of this aquifer system are classified as HCO₃-Ca-Mg-type or HCO₃-Na type (Schmidt, 2005). In the surroundings of Ciudad del Este, the sandstone is confined by very thick layers of basalt leading to artesian boreholes with highly saline thermal waters of sulfate-sodium-chloride type, with a high content of fluoride (Farina et al., 2004).

4.7.4. The thermal waters of Brazil

Few geochemical studies have reported the concentration of As in the geothermal fluids in Brazil, however, geochemical studies carried out in the GAS (tube wells drilled in 10 cities) in São Paulo state during 2009, have reported increased concentrations of Al, Li, F, Br, As (As 0.02 mg/L) and Mo in hyperthermal waters (T: >38 °C) from the Paraguaçu Paulista, in comparison with cold/hypothermal waters (25–33 °C). These cold/hypothermal waters showed lower B and Sr contents in the site (Bonotto and Elliot, 2017). The identified hyperthermal waters exceeding the maximum allowable As and F concentrations for drinking water in Paraguaçu Paulista site are used for recreation purposes (thermal swimming pools) and they have also potential for industrial and space heating (Vieira et al., 2015).

5. Results and discussion

In this section, compiled data related to geochemical aspects of As in geothermal fluids and volcanic emissions from Latin America (428) are discussed. Most of the sites (~93%) are from active (e.g. Sabancaya, Villarrica, Copahue, Colima) and past (Platanares, Azcualpa, Los Humeros) volcanic areas. These volcanic areas correspond to the sites of geothermal springs (319), geothermal wells (10), crater lakes (14), surface waters (lakes, rivers) (33) and fumaroles (1) (Table SM1). Among all the sites, geothermal waters related to plutonic intrusions have been reported only from Cerro Prieto (As: 0.32–5.18 mg/L) in northern Mexico and have been included in Table SM1. Data from geothermal waters not related to volcanism or plutonism reported from Guarani Aquifer System are separately listed in Table SM2 (25 sites). All these data are used to delimit and characterize the different geoenvironments from which As is mobilized in Latin America through geothermal and volcanic processes.

This section further elaborates on different types of As sources along with As mobilization mechanisms which may involve controlling the levels of As in different compartments and fluids of geothermal/volcanic systems in Latin America. The last part of this section evaluates the environmental impacts due to high levels of As in geothermal fluids and volcanic emissions together with actions that need to be taken to reduce such consequences. It must be considered that the availability of data for each country or geothermal site is highly variable with regard to the number of samples and frequency of sampling, completeness of parameters and chemical species assessed, quality and accuracy of analyses, etc. in particular, the absence or limitation of data for minor and trace elements, redox potential and

pose. Therefore, results and conclusions, comparisons in particular, need to be interpreted with due caution.

5.1. Geoenvironmental and geothermal settings containing arsenic

In Latin America, different types of principal geological settings have been identified hosting As and release it to different surface-near environments through geothermal fluids and volcanic emissions. Thereby hydrothermal and volcanic systems can be related to:

- Active volcanism (magmatic–volcanic type; volcanic geothermal reservoirs in predominantly andesitic and basaltic host rocks; volcanic emissions);
- Past, mostly andesitic and basaltic, volcanism (volcanic geothermal reservoirs with remaining hot magmatic chambers at depth; fossil geothermal springs or volcanic hydrothermal systems);
- Plutonic intrusions of acidic magma bodies which heat up overlying sediments (i.e. non-volcanic sedimentary reservoirs); and
- Geothermal reservoirs (not related to volcanism) involving deep circulating meteoric water which is conductively heated up in depth by the terrestrial heat flow.

The first group comprises most of the sites described from Latin America. They are the best studied group, including in respect to As. However, it must be considered that Latin America is a host of significant areas with the other mentioned geoenvironments, such as the mostly low-enthalpy geothermal sites in areas of past volcanism (which covers a large area since it follows as a belt behind the active volcanic zone), plutonic intrusions, and non-volcanic hydrothermal systems which - with very few exceptions - have not even been considered for geothermal exploitation and much less for studying As. The same applies for fossil hydrothermal systems, which are former hydrothermal/volcanic systems commonly found in the past volcanic areas. They are of interest for metal-mining and are well-known source of As.

5.1.1. Arsenic in geothermal reservoirs related to active volcanism

In Latin America, 11 countries (out of 20) including Mexico, Guatemala, El Salvador, Nicaragua, Costa Rica, Colombia, Ecuador, Peru, Bolivia, Chile and Argentina count on areas of active volcanism. From this area, about 170 active volcanoes are known where corresponding geothermal reservoirs can be formed at depths of a few kilometers under favorable conditions. These show respective variable chemical compositions due to variable host rock materials; however, all can be considered as mature systems with chemical equilibrium between the host rock and the geothermal fluids of the reservoir. These areas are related to subduction zones along the Pacific coast where oceanic plates are subducted below continental plates. These processes are the origin of active volcanism generating numerous high- and low-enthalpy geothermal systems. These are characterized by high temperature and pressure which favors rock-water interactions resulting in high As concentrations in geothermal fluids (2.09–73.6 mg/L). These geothermal fluids, and the volcanic emissions, which release gases or solid particles, can form important sources of As and respective release impacts different close-surface environments. Surface manifestations of these geothermal systems include geothermal springs, fumaroles and steam fields.

5.1.2. Arsenic in areas of past volcanism: present and fossil geothermal reservoirs

Geothermal reservoirs are also found in formerly active volcanic systems where magma bodies still contain residual heat able to warm up water. These geothermal reservoirs are of low-enthalpy and due to

mal systems of this type are generally found in the areas behind those of active volcanism, i.e. in the east of the present active volcanic zones of Latin America's active volcanic front. Geothermal manifestations, in particular thermal springs where deep circulating meteoric water emerges are frequent. Examples from Honduras are Platanares (boiling hot springs and exploration well, As: 0.45 and 0.35 mg/L), Azacualpa springs (As: 0.08 mg/L) and from Chile is the Tatio geyser field (As: 0.59–20 mg/L).

In addition, in these areas of former volcanism, there is another important potential As source related to this past volcanic activity. This source is the fossil geothermal/volcanic systems which include precipitated As-rich minerals. These can locally form important mineral deposits such as gold ore deposits. Here rocks have been altered by fossil geothermal systems, thermal spring deposits and stockworks, volcanic sulfide deposits, and epithermal veins or vein-breccias where geothermal fluids have formerly entered faults and shear structures carrying As, Hg, and Sb (Nelson, 1990). High As concentrations in veins and stockworks have for example been reported from Nicaraguan deposits: Matagalpa (As: 39–91 mg/kg), La Libertad (As: <20–41 mg/kg), Bonanza (As: 20–380 mg/kg), and Siuna-Rosita (As: <20–120 mg/kg (Sundblad and Swedish Geological Company, 1985). Through natural dissolution or accelerated by mining activities they can impact ground- and surface water, leading to important enrichment of As in groundwater and other environments.

5.1.3. Arsenic in geothermal reservoirs of plutonic intrusions

In addition to geothermal reservoirs related to volcanic magmatic intrusions, plutonic intrusions can also lead to the formation of geothermal reservoirs. Heat is generated by minerals of the intrusions of granites or other acidic rocks, which possess high contents of radioactive elements such as uranium (U), thorium (Th), and potassium (K). These intrusions can form important geothermal reservoirs if a sealing cover such as sedimentary rocks is present. Further, water in fractured sedimentary rocks overlying the intrusive body can itself be heated by conduction from below and form a geothermal reservoir. The last is the case at Cerro Prieto (Mexico) which is the largest of the geothermal plants globally (by installed capacity), located in an extensional sedimentary basin with subsequent pluton intrusions ("pull-apart" basin). This sedimentary reservoir has high temperatures (280–350 °C) similar to those in active volcanic zones but lower As contents ranging from 0.32 to 5.18 mg/L. This is mainly due to the occurrence of different host rocks in both types of geothermal systems. The geothermal reservoirs in active volcanic zones have volcanic rocks as host, containing As-rich minerals such as arsenopyrite. In contrast to the sedimentary host rocks, geothermal fluid generally contains less As and the dissolution by water-rock interaction even at similar temperature results in lower As concentrations. This kind of geothermal system can result in geothermal springs as well. However, in most cases, such geothermal systems are of low-enthalpy.

5.1.4. Arsenic in hydrothermal basins which are not related to volcanism and plutonism

There are some other geothermal systems which are not related to volcanic or plutonic magmatism. These are low-enthalpy hydrothermal systems heated through conductive heat flux from the earth's interior. They are typically found in areas where the earth's crust is thin and the heat flow and geothermal gradient significantly exceed those of the respective average continental crust. High temperatures of generated geothermal reservoir and favorable mineralogical and (hydro)geochemical conditions can increase rock-water interactions leading to increasing dissolution of mineral/rocks and As mobilization. This for example is the case of (normally on regional scale)

ing As as found in the Guarani aquifer. This transboundary aquifer system is shared between Argentina Brazil, Paraguay and Uruguay (covering 1,200,000 km²). Recharge area and discharge area are thousands of kilometers apart from each other and groundwater reaches depths of over 1000 m below the earth's surface (Foster et al., 2009).

5.2. Arsenic sources and ways of mobilization within the geochemical framework of volcanic (and plutonic) geothermal systems

Geothermal/volcanic systems constitute a complex system involving different geodynamical, fluid-dynamical, physical, chemical and thermodynamic processes. Their roles and shares vary from site to site and within the same site in the respective three-dimensional structure (with high variability in horizontal distance around the volcanic center). They involve transport of fluids (water, gases and their phase changes), solutes, and heat (by conduction and convection). This involves uprising of geothermal fluids (water, gases) and interrelated chemical processes such as rock-water interactions at wall rocks controlled by thermodynamic processes and contact time. Cooling may lead to condensation of volcanic gases. These uprising fluids interact with the environments close to or at the earth's surface, e.g. when mixing with waters of shallow aquifers and surface water bodies and can impact groundwater and surface water, together with soils and sediments. The contact of close-surface freshwater with condensed volcanic gases and inflowing deep geothermal waters impact on their hydrochemistry and water quality. These processes can occur simultaneously or subsequently and As levels and their speciation depend on the respective individual shares and the chemistry of the different impacting water and gas components. A principal As source is the geothermal reservoirs with their As-rich reservoir rocks (especially in volcanic rocks). Other As sources are the volcanic rocks where the dissolution of rocks and transfer/mobilization of As into the liquid/aquatic phase is favored even at the earth's surface, in particular at high temperatures or under acidic conditions. Input of As through volcanic gases rising up from depth is another As source. In addition, there are volcanic exhalations of As-rich gases and particles into the atmosphere. The last involves volcanic ash particles on which additionally As-containing gas can condensate and be transported in the atmosphere over large distances.

Fig. 8 shows various effects of the presence of other metal ions (Na⁺, Cl⁻, Na⁺, K⁺, etc.) on the occurrence of As in geothermal and related waters of Latin America (excluding the waters from the Guarani Aquifer System). In this scattered plot, the data summarized in Table SM1 are plotted in different ranges of As: As ≤ 0.01 (WHO guideline for drinking water), 0.010 < As < 0.05, 0.05 ≤ As < 0.1, 0.1 ≤ As < 0.5, 0.5 ≤ As < 1, 1 ≤ As < 10 and As ≥ 10 mg/L.

The Cl⁻—Na diagram (Fig. 8A) depicts a strong positive correlation between Cl⁻ and Na⁺ at high Cl⁻ and Na⁺ concentrations (>10 meq/L) with a normal ratio of 1:1 for those samples with a high As concentration of >1 mg/L (n=80). Exceptions in this concentration range (>10 meq/L) are 4 samples with a Cl⁻/Na⁺ ratio significantly higher than 1. The 1:1 Cl⁻/Na⁺ ratio indicates a large seawater component for these elements in the geothermal reservoir waters. The additional Cl⁻ enrichment in the geothermal reservoir fluids may come from host rock-interactions, and/or dissolution of magmatic HCl gas. Despite the observed positive correlation between As and Cl⁻, seawater is excluded as a significant As source. The reason is that the content of As in seawater is very low (0.0026 mg/L) and it would need an evaporative concentration increase by a factor of more than about 400 to reach even 1 mg/L of As.

Fig. 8B shows that for most of the sites with As > 1 mg/L, Na⁺ and K⁺ concentrations are higher than 275 and 10 mg/L, respectively. A

groups (>1.0 mg/L) shows the following concentrations for the other main ions (Ca^{2+} : 1.2–1250 mg/L, mean: 202.8 mg/L, median: 105.2 mg/L; Mg^{2+} : 0.01–2520 mg/L, mean: 177.7 mg/L, median: 28.2 mg/L; SO_4^{2-} : 3.0–64,000 mg/L, mean: 2139 mg/L, median: 178 mg/L; HCO_3^- : 9.8–1980 mg/L, mean: 389 mg/L, median: 170 mg/L). In contrast, waters with lower As concentrations (<1 mg/L) are characteristic with generally lower concentrations of the aforementioned main ions (Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , HCO_4^-) and more scattering of respective data when correlating them (data from Table SM1). Fig. 8B shows that for As >1 mg/L, B and Li concentrations are higher than 3.0 and 0.1 mg/L, respectively. Exceptions are four samples where especially B is depleted to <0.13 mg/L even at As >1 mg/L. These depleted B values can be explained by differences in the host rocks or previous removal of the highly soluble B (e.g. from rocks in contact with the geothermal water). Water-rock interactions (leaching) is the principal mechanism of the enrichment of these ions; and the positive correlation of B and Li with As concentrations indicates that rock-leaching is the main source for As in geothermal reservoirs.

In the following sections (6.2.1–6.2.5), we applied the ternary $\text{Cl}-\text{SO}_4-\text{HCO}_3$ diagram to classify the samplers from 398 sites (Table SM1) compiled from Latin America (not included the Guarani Aquifer System). These comprise: geothermal wells ($n=10$, $2.09 \leq \text{As} \leq 73.6$ mg/L), springs ($n=319$, $0.0004 \leq \text{As} \leq 63.0$ mg/L), lakes ($n=19$, $0.0005 \leq \text{As} \leq 0.80$ mg/L), rivers ($n=14$, $0.001 \leq \text{As} \leq 2.86$ mg/L), crater lakes ($n=14$, $0.17 \leq \text{As} \leq 3.9$ mg/L), fumaroles/condensates/gases ($n=1$, $\text{As}=0.79$ mg/L) and (fresh)water wells ($n=21$, $0.02 \leq \text{As} \leq 0.44$ mg/L). In addition, the same samples were subjected to the Giggenbach diagram ($\text{Na}-10\text{K}-\text{Mg}^{0.5}$ ternary diagram) to obtain information relating to their equilibrium state for given temperatures. Both diagrams distinguish the samples according to the previously mentioned As concentration classes in which they fall to obtain insights in geological controls in order to explain their As content. Fig. 9A and B show the plots of $\text{Cl}-\text{SO}_4-\text{HCO}_3$ and Giggenbach diagrams. These two plots combine data points of all respective As ranges, respectively. However, the data plotted for each As class individually are included in the supplementary material (Fig. SM9A and B, respectively). In addition, in Fig. SM9A, the sampling sites are numbered according to Table SM1.

5.2.1. The deep geothermal reservoirs as a principal arsenic source

Most of the well known, and all high-enthalpy geothermal reservoirs of Latin America are found at several kilometers of depth in active volcanic systems along the Pacific coast between southern Chile and northern Mexico and within the Trans-Mexican volcanic belt. Outside of these areas, the Las Tres Vírgenes geothermal field (As: 6.7 mg/L) is found in northwestern Mexico. In contrast to other active volcanic areas, this site has been interpreted as a section of a hydrothermal regime that has developed in a post-subduction volcanic zone (Birkle et al., 2016). An exception is also the high-enthalpy sedimentary geothermal reservoir of Cerro Prieto in northern Mexico, which is the only known high enthalpy field in Latin America related to a plutonic intrusion, rather than magmatic volcanism. With few exceptions, water samples collected from the limited number of geothermal reservoirs where wells allowed direct access to geothermal reservoirs contain typically mature near-neutral waters of Na-Cl water type. The exceptions of these are limited areas within geothermal reservoirs where degassing of H_2S and HCl gases have produced acid Na-Cl waters as they are found in a sector of the Miravalles geothermal field, Costa Rica (pH 2.0–3.3). Reservoir waters have generally high salinity (TDS: 4000–40,000 mg/L), are high in Si (200–500 mg/L) and have a high $\text{Cl}^-/\text{SO}_4^{2-}$ ratio (>10). An exception to these is Los

Humeros. Fluid from this reservoir varies significantly from those of other evaluated geothermal reservoirs which can be explained in terms of different host rocks. With the exception of the Los Humeros, all geothermal reservoir waters plot into the Cl^- corner of mature waters or in the Cl^- field ($\text{Cl}^- > 50\%$) in the ternary main anion diagram (Fig. 9A). These waters are of (or close to) full equilibrium with the reservoir host rock as shown in the Giggenbach diagram (Fig. 9B). All reservoir waters have generally high As concentration ranging from several to several 10s of mg/L (Table SM1). Examples of these are (in decreasing order of concentration): Los Humeros, Los Azufres and Las Tres Vírgenes from Mexico (As: 73.6, 29.5 and 6.7 mg/L, respectively), Miravalles and Rincón de la Vieja in Costa Rica (As: 25.4 and 10.0 mg/L, respectively), Berlín, El Salvador (As: 11.7 mg/L), Zunil, Guatemala (As: 4.8 mg/L), Momotombo, Nicaragua (As: 2.09 mg/L). Similar to the chemical composition of geothermal reservoir fluids, As concentrations depend particularly on reservoir temperature and pressure, host rock composition and contact time between rock and water (i.e. time available for reactions). Arsenic-rich volcanic reservoir rocks such as andesites and basalts (containing As-bearing pyrite, arsenopyrite, Webster and Nordstrom, 2003; Pokrovski et al., 2002a, 2002b) are evidences for the existence of highest As concentrations in volcanic geothermal reservoirs compared to those of other geothermal reservoir types. Such other high-enthalpy and mature geothermal reservoirs which also have Na-Cl water include Cerro Prieto (Section 2.1.1) where a sedimentary geothermal reservoir is heated from below by an intruded acidic plutonic magma body. Due to the sedimentary characteristic of the geothermal reservoir and respective lower availability of As, the reservoir fluids contain only 0.32–5.18 mg/L of As. However, in contrast to Mexico and Central America, direct access to water of the geothermal reservoirs by deep wells is very limited in South America. Geothermal wells exists only in Argentina (but no As data could be found) and the Chile, e.g. El Tatio well (As: 26.4 mg/L), (Sections 4.6.2 and 4.5.1.3, respectively).

5.2.2. High and low-As geothermal Na—Cl reservoir fluids of varied genesis

The geothermal waters described in Section 5.2.1 can rise up (e.g. along tectonic faults and fractures) from the deep geothermal reservoir and emerge as thermal springs at the earth surface. If the ascent is fast without significant loss of heat (or there is only limited heat loss by conduction) as well as if reactions with the rocks or gases along the pathway can be neglected, their chemical composition will remain un-altered. In short, their chemical composition corresponds to those in the deep geothermal reservoir. Thermal waters migrate laterally and discharge at significant distance from the geothermal field or volcanic center. They can be considered as practically pure reservoir water if they are of neutral Na-Cl type, are high in Si and As, and have a $\text{Cl}^-/\text{SO}_4^{2-}$ ratio >1 . In the ternary main anion diagram (Fig. 9A), most waters with As >10 mg/L fall in the “mature waters” field or close to the Cl^- vertex. Waters with As concentrations of 1–10 mg/L are also concentrated in the field of “mature waters” and close to the Cl^- vertex but there are some with higher SO_4^{2-} and HCO_3^- content which fall still into the Cl^- area (i.e. $\text{Cl}^- > 50\%$) but farther away from the Cl^- vertex. All the aforementioned geothermal springs, where mature Na-Cl water with these properties emerges, have the same As concentration as the geothermal reservoir. This can be demonstrated in the sites where geothermal reservoir water as well as water from geothermal Na-Cl springs could be sampled and compared. This was for example the case at Rincón de La Vieja in Costa Rica where similar As contents in geothermal reservoir waters (7.8–13.0 mg/L, mean: 10.0 mg/L) and in water of geothermal Na-Cl

content (mean: 531 mg/L) similar to the other studied geother-

mal reservoirs (Hammarlund and Finones, 2009). Therefore, in ar-

eas without access to the geothermal reservoir itself, at sites with thermal springs with mature (or close to) Na-Cl water, it can be argued that their As concentrations correspond to those of the geothermal reservoir. This assumption is further reinforced if a correlation between As and a suite of elements/ions is found which are typical for geothermal reservoirs (e.g. B and Li). However, these types of geothermal waters are exceptions to emerge at the earth's surface. So, from the 319 listed springs from volcanic zones in Latin America, only 12 correspond to such types with highly saline mature Na-Cl waters (where the respective main anion concentrations are available), high As content (>1 mg/L) and the other mentioned characteristics. Latin America's geothermal springs with the highest As contents belong to this group of 12 thermal springs. Two of them discharge water with >10 mg/L (El Tatio, Chile: 26.4 mg/L and Puchuldiza in Chile: 12.09 mg/L). Capur spring, Chile plots very close to the "mature water" field and contains 38.0 mg/L of As, as well as the Ullucan spring, Peru with As concentration of 28.1 mg/L and the Araro spring, Michoacán, Mexico with 63.0 mg/L of As. This group also includes the springs Salitral las Lilas 1 and 2 from Rincón de La Vieja, Costa Rica (As: 10.9 and 10.6 mg/L, respectively) (Hammarlund and Piñones, 2009).

Most of the geothermal fluids undergo physicochemical changes (e.g. loss of heat and pressure and related elemental fractionation, steam loss together with rock-water interactions) along their pathway during their ascent to the surface. This results in different water types discharging at or found in the area near the surface. In the Giggenbach diagram (Fig. 9B), water of mixtures of geothermal water (fully equilibrated) and local groundwater fall in the field of "partially equilibrated" which also includes mixed waters. Mixing Na-Cl waters from the deep geothermal reservoir with HCO_3^- type waters of shallow aquifers is very common, much more frequent than high-As Na-Cl springs. These mixed waters are labelled in the main anion ternary diagram as peripheral waters (see Section 5.2.4). However, as the anion triangle illustrates, there is another – in respect to As clearly distinct – group of Na-Cl waters falling in the "mature water" field (Fig. 9A). With the exception of the As content they do not differ from the previous high-As water group (>1 mg/L). They have high TDS and do not differ in main, minor and trace element concentrations and physicochemical parameters, as far as the limited data available indicate. However, their As contents is by two orders of magnitude lower (As: <0.05 mg/L). This group of low-As waters also forms a well distinguished cluster in the Giggenbach diagram. All samples fall within the "partial equilibrated" field or are equilibrated (Fig. 9B). In contrast, the other samples in this low-As range (<0.05 mg/L) fall in the field of "immature", most of them close to the $\text{Mg}^{0.5}$ vertex. Since all of the geothermal fluids sampled from the wells drilled into the deep geothermal reservoirs have high As concentrations, exceeding 1 mg/L, it is unlikely that low-As waters are derived from the deep geothermal reservoirs. Examples for these $n=19$ (about 5% of all sites) waters are from geothermal springs found in Bolivia (7), Chile (3) and Argentina (6). The sample number is not high enough to argue whether it is a regional issue. However, different reasons could explain the low As contents: conductively or steam-heated shallow waters in contact with halite-rich/containing rocks, i.e. other Na^+ and Cl^- sources not from the geothermal reservoir but from other sources and the waters are partially recalibrated. As these sites are from active volcanic areas, and in all accessible geothermal reservoirs, the high As content in water has been explained by dissolution from host rocks, it seems unlikely that As contents in host rocks differs greatly, resulting in the low concentrations observed in this geothermal water group.

5.2.3. Mixing of volcanic gases with surface-close waters (volcanic waters)

The degassing of the active magmatic-hydrothermal system releases volcanic gases (CO_2 , SO_2 , H_2S , HF, HCl, HBr, etc.) and volatiles, such as As tend to be partitioned from magma into volcanic gases which can be transported through the hydrothermal system. However, in Latin America (and globally) very little data exist on this partition and the volatile As species in volcanic gases. More data are available on As in condensates of volcanic gases, e.g. Poás (As: 8.6 mg/L), Colima (As: 0.53 mg/L), Popocatepetl (As: 1.20 mg/L) and Cerro Negro volcano (As: 0.07 mg/L). However, these gases can condensate close to the earth's surface and form springs or other geothermal manifestations (e.g. fumaroles) with $\text{SO}_4^{2-} \gg \text{Cl}^-$, such as Popocatepetl (Mexico) and Caviahue crater lakes and Copahue volcano (Argentina) and TU12 and TU23 thermal springs (Peru). They can also mix with shallow groundwater or surface water bodies (which are mostly of HCO_3^- water type). Thereby they can alter their chemistry and enrich their water strongly in H^+ , SO_4^{2-} , Cl^- , F^- , Br^- and As. The impact of these chemical changes depends on the degassing dynamics, quantity (and species) of the gases released and the type of the receiving freshwater body. Resulted waters are mostly acidic (pH: 0–4). This low pH value can increase water-rock interactions and dissolve rocks and other volcanic materials leading to an additional mobilization of As into the water. The sites and (physico)chemistry of these type of waters are separately listed in Table SM3. In the main anion triangle, these waters fall in the field of "volcanic waters" between the SO_4^{2-} vertex and the 50% Cl^- isoline (Fig. 9A, Fig. SM9A). Acid waters in this diagram are identified by "A" (19 samples). In the Giggenbach diagram all fall at the $\text{Mg}^{0.5}$ vertex (see Fig. 9B and SM9B, where the acid waters are plotted separately in this corner).

The As content in these acid volcanic waters is highly variable as shown in Fig. 9A and SM9A. With regard to the As contents, two distinct water groups can be distinguished. From the 38 sites (here the 14 sampling points of Azufral Lake are combined and counted as one site), 22 have waters exceeding 0.34 mg/L with a maximum of 4.5 mg/L (Group 1). The rest of the sites with acid volcanic waters have As concentrations of more than an order of magnitude lower ranging from 0.04 down to <0.001 mg/L (Group 2). In active volcanic lakes (with water of meteoric origin) which have no outflow (except in some cases, where they discharge acid waters into rivers or creeks, the solutes can be accumulated (degassing from the water and evaporation is their only sink). In Latin America, evaluated acid crater lakes have high As concentrations (0.34–3.90 mg/L; Group 2) and very low pH values of <1.1 . Due to the highly variable gas dynamics values of As vary considerably in time. Examples are the crater lakes of the Poás volcano in Costa Rica (As: varies from 0.84 to 3.9 mg/L with increasing temperature from 27 to 55 °C), and the Copahue volcano, Argentina (As: 0.87 mg/L, T: 29 °C). Some of these acidic crater lakes discharge rivers or creeks with acid water and – depending on the mixture ratio with other water bodies – can significantly impact water quality on long distances along their courses. For example, the Río Agrío which originates from the Copahue volcano crater lake, 2.86 mg/L of As and afterwards discharges into Caviahue Lake, which has other river inlets and therefore As concentration is reduced to 0.58 mg/L). The high sulfate contents of the river and the lake can be attributed to sulfuric acid generated by the uptake of sulfurous gases in the crater lake of Copahue volcano (Pedrozo et al., 2001). At other volcanoes, water from crater lakes filtrates through the flanks of the volcano and emerges as springs with acidic water and high As concentrations (e.g. the Poás volcano, Costa Rica with As values of 3.9 mg/L; the Copahue volcano, Argentina with As of up to 4.5 mg/L).

are highly variable depending on their flow dynamics. In surface water bodies with naturally very low salinity, a low amount of condensing volcanic gases is enough to significantly impact its water. This can be shown by the acidic Lake of Azufral (pH: 2.2) and the Rivers Río Lagunillas (pH: 3.6) and Río Azufrado (pH: 3.4) in Colombia (Table SM3). Here, however, the component of volcanic gases is not high enough (or do not contain sufficient volatile As) to increase As contents which are <0.001 mg/L. The same applies for some of the acidic geothermal springs (Table SM3).

5.2.4. Mixing of deep geothermal waters with surface close waters and formation of peripheral HCO_3^- waters

There is a group of bicarbonate waters ($\text{HCO}_3^- > 50\%$) with very low SO_4^{2-} content (<10%) and variable Cl^- content of 0 to 50% (Fig. 9A). These waters correspond to peripheral waters in the anion triangle diagram which are most likely to be cold HCO_3^- -rich groundwater containing a small component of Na-Cl water from the deep geothermal reservoir which explains the elevated Cl^- and As content of up to 0.1 mg/L of As. There are 2 samples which also fall into the field of "peripheral water" but have higher As contents than previously mentioned waters. These are: the Nono spring at Pichincha volcano (As: 3.95 mg/L) and the Aguas Caliente river at Atacazo volcano (As: 0.99 mg/L) both in Ecuador.

5.2.5. Steam-heated and purely conductively heated shallow groundwater

Bicarbonate waters from shallow aquifers tend to be heated through a deep heat source (geothermal reservoir) via S-rich steam or purely conductive heat transport which heats up 'cold' local groundwater (i.e., no transport of geothermal water from depth). In the anion triangle, these waters fall in the "steam-heated" field (Fig. 9A). This may result in local groundwater temperature anomalies or geothermal springs. Two mechanisms can be distinguished. The first is that the steam condenses locally at shallow depth and can form hot condensation layers which can heat up overlying aquifers by pure conduction (if there is no hydraulic connection to the overlying shallow aquifer). The chemistry of such conductively generated geothermal water corresponds to the chemistry of the water from the heated aquifer. However, the increased temperature can result in increased rock-water reactions and respective increased concentrations of chemical elements including As. The second case is where a hydraulic connection exists, so the condensed steam can mix with the shallow groundwater, heat it up and directly alter its chemistry, including adding condensed volatile As. The condensed steam (hot water) contains high amounts of sulfate but little chloride. So, in particular the SO_4^{2-} of the shallow groundwater is altered whereas the Cl^- content is low (<10%). With the increasing steam component, the samples of the shallow groundwater move along the SO_4^{2-} - HCO_3^- base line towards the SO_4^{2-} vertex forming first HCO_3^- - SO_4 , then SO_4 - HCO_3 and finally SO_4 water types. This explains the observed wide variation (in SO_4^{2-} and HCO_3^-) of these steam-heated waters occupying area in between SO_4^{2-} and HCO_3^- apexes. Most of the geothermal waters (mostly from springs) within the As<0.01 mg/L class fall in the steam-heated field limited by the 10% Cl^- isoline. However, with increasing As content, the contents of Cl^- increases reaching up to 30% in waters of the 4 lowermost As concentration classes up to 0.5 mg/L (Fig. 9A, SM9A). This higher Cl^- content may be explained by the presence of a small component of water from the deep geothermal reservoir or by water-rock interactions between the thermal spring water and the surrounding volcanic rocks or precipitates which also may be responsible for the increased As content.

5.2.6. Arsenic mobilization through ash-producing volcanic eruptions

Arsenic emissions through volcanic gases have already been addressed in Section 5.2.3 in context with the genesis of "volcanic waters". In the present section we discuss the transport of As together with volcanic ash. Thereby two potential transport mechanisms need to be distinguished: (i) volatile As species are condensed as coatings on the volcanic ash particles as it is typical for hydrogen halides (HF, HCl, HBr); and (ii) As is included with other typical trace elements of volcanic emissions such as the metals V, Mo, U, etc. (Edmonds et al., 2018; Nicolli et al., 2012) and fluoride as observed in several areas in Latin America (Alarcón-Herrera et al., 2013; Morales et al., 2015; Reyes-Gómez et al., 2013) including Mexico, Argentina, Nicaragua and Chile. Present and past ash-producing volcanic activity can distribute As to areas close to the eruption site or hundreds or thousands of kilometers away where the ash is deposited over long (corresponding to long-term volcanic activity in a region, e.g. in the Andes) or short time (e.g. by a single volcanic event) as distinct layers or mixed with local sediments and soils. This can be expected to be an important process in several regions in Latin America where, however, with the exception of the Chaco-Pampean plain (central and northern Argentina, Section 4.6.4) where long-term deposition of volcanic ash derived from the Andes lasting over millions of years until today is well documented (Bundschuh et al., 2012; Nicolli et al., 2012 and references therein), no respective detailed studies have been performed so far. Here, ash resulting from the Andean volcanism has been deposited over millions of years and mixed with local sediments in an area covering over 1 million km^2 . An example for volcanic ash deposition through a single volcanic ash emission is the eruption of Copahue volcano (southern Argentina; Section 4.6.2) in the year 2002, where volcanic ash with As contents of 0.18–113 mg/kg were deposited.

5.3. Impacts of arsenic on environmental health

In Latin America, numerous sites with geothermal water and volcanic emissions have been outlined and characterized as result of the present review. There are different pathways through which these As sources, i.e. geothermal water and volcanic emissions can contaminate near-surface environments and freshwater resources vital for drinking and irrigation. The principal pathways of which the first two are the most important ones when considering Latin America as whole are:

- By deep As-rich geothermal fluids (with several or several 10s mg/L of As) ascending through faults or fractures mixing with and contaminating freshwater resources (groundwater and surface water) which are used for drinking and irrigation of agricultural areas;
- Ash emitted by volcanoes and deposited close or far from the respective volcano site and subsequent mobilization into water, especially into groundwater;

5.3.1. Geothermal fluids contaminating freshwater sources

5.3.1.1. Surface water

Geothermal discharges of As-rich water into surface water bodies have been reported in several places across Latin America. Most easily, they can be detected where water emerging from geothermal springs discharges into creeks, rivers and lakes. There are several examples, in particular in the volcanic areas of Latin America including Papallacta Lake (Ecuador; Section 4.2.4) where As from geothermal springs (As: 0.7–3.2 mg/L; Section 4.2.4) discharges first into the Tambo river (As: 2.7–5.7 mg/L) which then flows into Papallacta Lake (As: 0.22–0.37 mg/L). This water is an important drinking wa-

ter resource for the region with an As contaminant level above the WHO guideline limit of 0.01 mg/L and required mitigation methods. Sediments of river lake are further adversely impacted by the As from the geothermal springs Loa river (northern Chile, Section 4.1.5.3) and its sediments is impacted by geothermal waters discharging from the Tatio geyser field, with As concentrations exceeding 20 mg/L in thermal discharges being the principal As source which severely increases – together with other natural As sources in the river's recharge area - the As concentration of river water and sediments. Loa river is the main surface water resource of the region and also supplies the regional capital of Antofagasta at the Pacific coast (Alsina et al., 2014; López et al., 2012; Muñoz-Saéz et al., 2015; Romero et al., 2003) and had required installation of drinking water treatment plants. The environmental impact of As-rich sediments through Loa river into the Pacific Ocean is a further environmental concern. When the geothermal water is discharged directly in the underground into the surface water body, the process often remains unrecognized and only few examples have been described.

5.3.1.2. Groundwater

In several regions of Latin America, geothermal water with high As concentrations discharges into freshwater aquifers used for drinking water supply and/or irrigation have been identified or found most likely to be the reason for elevated As concentrations observed in the respective groundwater bodies. Since there are no surface manifestations, this process is difficult to recognize and in most cases it is overseen or misinterpreted. Some examples where the process has been recognized are in: Los Altos de Jalisco area (western Mexico) (As: 0.015–0.102 mg/L; Section: 2.1.2), where groundwater containing a geothermal component (as indicated by elevated temperatures) is predominantly used for irrigation (Hurtado-Jiménez and Gardea-Torresdey, 2006). In 34% of the sample, exceed the national drinking water limit for As (0.025 mg/L) and 92% exceeded the WHO guideline value (0.010 mg/L). Another example is the vicinity of the San Salvador and San Miguel volcanoes (El Salvador, Fig. 3; Section 3.2.1), where wells used for drinking water supply including those of large cities as the capital San Salvador and San Miguel, partly contain As in concentrations exceeding the 0.010 mg/L limit, which can be explained by As inputs from the magmatic system of these volcanoes. In the area of Telica (northwestern Nicaragua; Section 3.4.3), where geothermal impacted groundwater (As: 0.01–0.3 mg/L) is used for drinking purposes (Longley, 2010) is another example.

5.3.2. Volcanic ash emissions contaminating freshwater sources

As described in Section 5.2.6, volcanic ash due to past and present ash-producing volcanic activity can have significant impacts not only close to the eruption site but also hundreds or thousands of kilometers far away. After the deposition of the ash from the atmosphere, the coated ash particles or the highly soluble volcanic ash (mostly amorphous) itself can adversely impact drinking water sources and respective water supplies (predominantly groundwater sources), agricultural soils and crops. This can be expected to be an important process in several regions in Latin America. However, this issue so far has only been researched in detail from the Chaco-Pampean plain in Argentina where millions of people are affected (Niccolli et al., 2012; Bundschuh et al., 2012). In this region, ash resulting from the Andean volcanism has been deposited over millions of years and distributed within aquifer sediments in an area covering over 1 million km². By dissolution of the volcanic glass under respective favorable geochemical conditions, mobilization of As from volcanic glass and/or secondary formed As oxyhydroxides of Fe and Mn into groundwater exposes millions of people to As (Section 4.6.4). However, it does not require

ment but are generally limited in space and duration of impact. Normally their impacts are of short duration. For example, during the Copahue volcano eruption (year 2002), volcanic ash (As: 0.18–113 mg/kg) accumulated in the Río Agrío watershed, southern Argentina, contaminated the Caviahue Lake (used for drinking water supply) and neighboring areas (see Section 5.2.3). The impact of this single event showcases the magnitude of impact considering thousands or tens of thousands or more of such events taking place during millions of years impacting the Chaco-Pampean plain and potential (unknown) As inputs in groundwater system in other Latin American regions and countries.

6. Future needs

The present review clearly demonstrated the current knowledge on As originating from geothermal features and volcanic activities in Latin American region based on existing as well as unpublished data available to date. However, the scientific depth of the existing information regarding mobility, distribution and transformation of As over different environmental, geographical and biological systems in this region is scarce or not appropriate for a proper evaluation of its adverse consequences on the environment and human health. Because of the limited knowledge and slightest attention on these aspects, thousands to millions of people in this region are frequently getting exposed to high levels of As directly and indirectly through drinking and irrigation water, thermal spas with bathing pools as well as food products. Therefore, the development of geographical maps based on analytical, geochemical, statistical, social, and economical information by using modern geographic information systems (GIS) is an urgent necessity for a proper understanding of the extent of the threat on the economy, environment and human health. Further, freshwater resources contaminated with high As levels which are used for drinking and irrigation purposes have been reported in a few sites of this region, so that identification of more affected water resources is of critically important to minimize the human exposure to high amounts of As. The dilution is the main mitigation strategy that has been widely practiced to reduce the concentration of As in drinking and irrigation water in this region. However, this approach is unacceptable and not strong enough for reaching the demands of higher population. Therefore, the application of sustainable As mitigation strategies such as, large scale water purification systems, rain water harvesting systems, constructed wet lands, and safe drinking water tube wells would be more reliable to provide As-free drinking water for the population of this region. Furthermore, future research needs to be more inclined towards developing modern analytical instruments for the analysis of complexed As species including thio-As as well as other co-existing toxic metalloids (Se, Sb, etc.) present in geothermal fluids, volcanic emissions and affected aquifer sediments. Overall, the contents of this review would make a scientific sound to draw attention of local and international political communities which will pave the way to preserve the social and economical values of Latin American countries in near future.

7. Conclusion

This review paper critically deliberates the geochemical aspects of As in different geological and tectonic settings in Latin America in order to provide a rational assessment of what is existing and what needs to be done in future research. A large-scale As contamination of ground- and surface-water in these regions has placed this metalloid into the focus of public and scientific attention during the present decade. Hence, this study evaluated 15 countries in Latin America in-

tonism (1 country) and geothermal systems not related to volcanism (4 countries). Geothermal waters with the highest As levels were found to be of Na-Cl type. In these waters, the concentrations of geothermal As positively correlate with high concentrations of other toxic contaminants such as Fe, Mn, Pb, Zn, Cd. Although the presence of As in geothermal fluids and volcanic emissions is a well-known fact, its wide geographical appearance and potential environmental impacts are often neglected or underestimated. Environmental impacts of the contamination of freshwater sources by As-rich geothermal fluids and their mixing, e.g. with shallow groundwater have only been investigated in a few areas, including Jalisco in Mexico and the Managua area in Nicaragua. However, this process exists possibly in many other sites. In overall conclusion, holistic assessments of As derived from geothermal fluids and volcanic emissions are crucial in order to define and execute As mitigation strategies which will lead to the supply of As-safe drinking and irrigating water for the population of Latin America.

Uncited references

Antayhua Vera et al., 2010
Birkle and Bundschuh, 2007
NOM-127, 2000
Wang et al., 2012

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.135564>.

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