

Arsenic in geothermal sources at the Northern-Center Andean Region of Ecuador: Monitoring concentrations and mobility

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Abstract

This study aims to identify and determine arsenic content in geothermal sources, rivers, creeks, and sediments at the Northern-Center Andean (Sierra) Region of Ecuador. This region covers approximately 31477 km² and has a population of 370,000 inhabitants. The assessment of arsenic concentration and sources was conducted by taking samples of water and sediments in strategic points on thermal springs and along rivers and creeks to evaluate its impact on surface waters quality. Geothermal waters at El Carchi, Imbabura, Pichincha, Cotopaxi, and Tungurahua Provinces show levels of arsenic from 113 to 969 µg As/L. Surface waters of El Angel River, Cachiycu Creek, San Pedro River, Pichan River, and Ilalo Creek that receive thermal waters from the sources and thermal residuals from recreational complexes, have arsenic in the range of 2 to 171 µg/L. On the other hand, sediments at the geothermal springs and downstream of rivers and creeks contain arsenic from 2.8 to 717.6 mg/kg. Sediments with a significant organic matter content capture arsenic to some extent while sediments holding Fe(III) oxyhydroxides strongly uptake all arsenic species forming inner-sphere complexes. These sorption mechanisms partially explain the variability of arsenic concentrations found in rivers and creeks and arsenic content present in their sediments.

Resumen

Este estudio pretende identificar y determinar el contenido de arsénico en fuentes geotérmicas, ríos, quebradas y sedimentos en la Sierra Centro-Norte del Ecuador. Esta región cubre aproximadamente 31477 km² y tiene una población de 3700.000 habitantes. La cuantificación de la concentración de arsénico y las fuentes fue llevada a cabo tomando muestras de agua y sedimentos en puntos estratégicos de las fuentes termales y a lo largo de los ríos y quebradas a fin de evaluar su impacto en la calidad de las aguas superficiales. Las aguas geotérmicas en las provincias de El Carchi, Imbabura, Pichincha, Cotopaxi y Tungurahua muestran niveles de arsénico de 113 a 969 µg As/L. Mientras que las aguas superficiales de los ríos El Ángel, San Pedro y Pichán y las quebradas Cachiycu e Ilalo que reciben aguas termales provenientes de las fuentes y aguas termales residuales de los balnearios localizados en esta región, contienen arsénico en el rango de 2 a 171 µg/L. Por otro lado, los sedimentos cercanos a las fuentes geotérmicas y aguas abajo de los ríos y quebradas contienen arsénico de 2,8 a 717,6 mg/kg. Los sedimentos con un contenido significativo de materia orgánica capturan algo de arsénico mientras que los sedimentos que tienen oxihidróxidos de Fe(III) retienen fuertemente todas las especies arsenicales formando complejos de esfera interna. Estos mecanismos de sorción explican parcialmente la variabilidad de las concentraciones de arsénico encontradas en las aguas de los ríos y quebradas y el contenido arsenical presente en sus sedimentos.

1 Introduction

The problem of arsenic (As) contamination of groundwaters has been under extensive discussion during the recent years because of its adverse effects on human health. A number of world-wide aquifers have been identified with As occurring at concentrations exceeding the World Health Organization Standard (10 µg/L) [1]. Although records of affected aquifers are incomplete, the majority of As present in groundwaters is of geochemical origin. Arsenic

associated with thermal groundwaters has been reported in various parts of the world, including hot springs in the United States, Japan, New Zealand, Chile, Iceland, France, Argentina, and Dominica, [2,3]. Ball et al. reported values up to 2830 $\mu\text{g/L}$ of As at geothermal waters in Yellowstone National Park [4]. Robinson et al. evaluated the arsenic concentration in waste geothermal brine at the Wairakei geothermal field in New Zealand and found a value of 3800 $\mu\text{g/L}$ [5]. High As concentrations have also been found in geothermal waters from the El Tatio system in the Antofagasta region of Chile. As concentration of waters were reported to be in the range 45,000–50,000 $\mu\text{g/L}$ [6]. Elevated As levels have also been detected in geothermal springs in the area of Papallacta, Ecuador. Cumbal et al. reported high As concentrations in thermal waters of El Tambo swimming pool, reservoir of Jamanco, Papallacta Termas, and in the upper watershed of the Tambo River [7].

2 Area of Study

The area of study is located in the Northern-Center Andean Region of Ecuador between $1^{\circ}11'$ N and $1^{\circ}30'$ S parallels and includes five provinces: El Carchi, Imbabura, Pichincha, Cotopaxi, and Tungurahua. This region covers 31477 km^2 and has a population of 370.000 inhabitants (Fig. 1). In this zone are predominantly tobas, acid pumice, ash, volcanic breccias and andesitic lavas. Because of its volcanic origin, the area of study is widespread with hot springs that are mainly used as medicinal baths and recreational complexes. Due to lack of treatment facilities, water residuals are commonly released to surrounding water bodies (i.e. rivers and creeks) from which water is taken for irrigation agriculture and as drinking water sources.

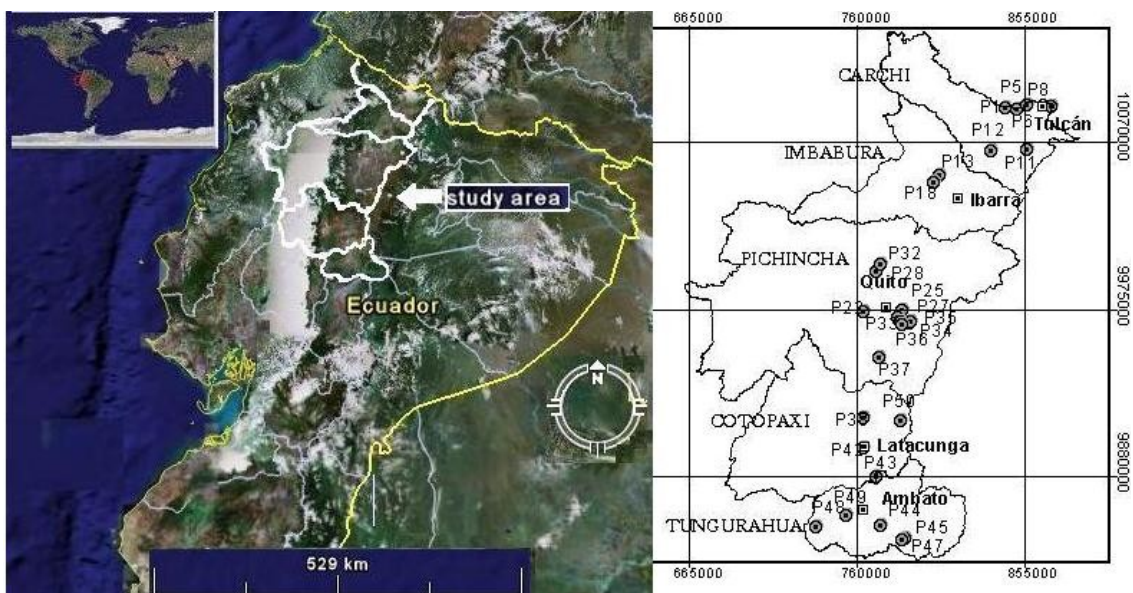


Figure 1 Study area at the Northern-Center Andean Region of Ecuador and location of sampling sites

3 Sampling and Analytical Procedures

3.1 Sampling

Samples of water and sediments were taken in geothermal springs, rivers, and creeks within the study area (for sampling points see Fig. 1). In rivers and creeks, sampling was carried out at distances wherever the topographical conditions allowed. Geothermal springs were sampled in their outlets and before arriving to the rivers. Field investigations included positioning the

sampling sites at geothermal springs and surrounding water bodies using a handheld global positioning system (GPS) and measurements of on-site parameters such as pH, temperature, dissolved oxygen, and electrical conductivity. Sampling of waters involved the collection of: i) filtered (0.45 μm , for anions analysis) and ii) filtered acidified samples (for As analysis). Samples were transported in a cooler to the laboratories of ESPE for detailed chemical analyses. Sediments sampling required the collection of a weight of approximately 0.5 kg from a point at 5 cm below surface. Samples then were stored in plastic containers and transported to the laboratories in a separated cooler.

3.2 Chemical Analysis

Acidified water samples and diluted extracts from sediments were analyzed for arsenic using a Perkin Elmer Hydride Generator (HG) coupled to a Perkin Elmer atomic absorption spectrometer, AA100. Results of chemical analyses were validated by comparing arsenic contents with standard solutions purchased to Sigma Aldrich. Analysis of phosphate was carried out in the laboratory in accordance with the 4500-P procedure of the Standard Methods.

3.3 Extraction of arsenic from sediments

For this test, each sample of sediment was dried in an oven for 12 hours at a temperature of 60 °C. Dried sediments were disaggregated using pestle and mortar and then sieved using a 0.2 mm sieve. The sieved samples (0.25 g) were attacked using 1 M $\text{Mg}(\text{NO}_3)_2$ solution, HCl and KI with a volumetric ratio of 1:5:5, respectively. Solutions were heated in a furnace for 6 h at 450°C and solid residues were dissolved in 10 mL 1 M HNO_3 . The acidified solution was filled with deionized water up to 25 mL and analyzed by HG-AAS. Since most of samples became brownish, a process for arsenic extraction bound to organic matter and sulphide was conducted. It was used 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 at pH 2, at 85 °C; then addition of a second 3 mL aliquot of 30% H_2O_2 at pH 2, and finally 5 mL of 3.2 M ammonium acetate (NH_4OAc) in 20% HNO_3 . Thereafter, the resulting solution was analyzed for arsenic.

5 Results

5.1 Arsenic in geothermal waters

Table 1 provides altitude, pH, temperature, electrical conductivity, alkalinity, and total arsenic concentrations at different sampling sites of the study area (for locations see Fig. 1). In El Carchi Province, Aguas Hediondas spring (P1) has a fairly high temperature (50°C), relatively low concentration of As (20 $\mu\text{g/L}$), and acidic pH of 4.8. At the Aguas Negras spring (P5) As concentration is the lowest of El Carchi Province (2 $\mu\text{g/L}$) and pH is close to 6.0. Temperature and electrical conductivity are 34.5°C and 1660 mg/L, respectively. Furthermore, in two other geothermal springs of El Carchi Province: Rumichaca and La Calera (P8 and P12), As contents are higher compared to other thermal waters, 403 $\mu\text{g/L}$ and 684 $\mu\text{g/L}$, respectively. Temperatures are 37.7°C and 30.9°C and pH is around 7.0. In the Imbabura Province, Chachimbiro geothermal field shows an average pH of 7.5 and a temperature around 41°C (P13-P15). Arsenic content reaches 976 $\mu\text{g/L}$ (876 $\mu\text{g/L}$ in average) and the electrical conductivity shows a value of 5920 mg/L. In contrast, As is very low (4 $\mu\text{g/L}$) at Timbuyacu spring (P18). Electrical conductivity, pH, and temperature values are 4660 mg/L, 6.5, and 39°C at this site. In the Pichincha Province, nine geothermal waters were analyzed. Among them, Arauco springs show no As content (P22) while springs at Cununyacu, La Merced of

Nono, and Ilalo show concentrations above 200 µg/L (P25, P28, P35). From field data, temperature of these springs is between 28,5°C and 37,7°C and pH is around neutral. Electrical conductivity is high at the La Merced of Nono (4120 mg/L) while at Cununyacu and Ilalo is moderate, 959 mg/L and 1604 mg/L, respectively. El Tingo and La Merced springs which are part of the Ilalo geothermal system (P33, P34) show As concentrations of 100 and 101 µg/L and temperatures of 42.6 and 36°C, respectively. At San Guillermo spring (P37), a source of bottled water, As content of 48 µg/L is observed.

Table 1. Water characterization of geothermal springs of the North-Center Andean Region of Ecuador (for location of sampling points see Fig. 1).

Sample	Altitude (m a.s.l.)	pH	T (°C)	Conductivity (µS/cm)	Alkalinity (mg/L)	As _T (µg/L)
El Carchi Province						
P1	3610	4.8	54.0	1802	37	20
P5	3553	5.9	34.5	1660	98	2
P8	2801	6.9	37.7	320	317	403
P9	2805	6.2	20.8	506	146	49
P11	2778	6.6	32.7	2140	342	4
P12	2532	7.3	30.9	1019	183	684
Imbabura Province						
P13	2513	7.1	39.5	5920	780	969
P14	2513	7.7	43.5	5120	759	726
P15	2513	8.0	40.5	5340	695	976
P18	2693	6.5	39.0	4660	366	4
Pichincha Province						
P22	2763	6.5	34.5	2780	403	ND
P25	2349	7.4	28.5	959	146	389
P27	2382	7.7	31.3	923	171	11
P28	3143	6.3	30.5	4120	512	403
P32	2624	6.6	28.8	3430	329	28
P33	2461	7.1	42.6	3040	415	100
P34	2593	6.6	36.0	1008	183	101
P35	2564	6.5	37.7	1604	207	272
P37	2827	6.9	33.8	650	1098	48
Cotopaxi Province						
P38	2976	6.4	19.3	1524	525	45
P42	2795	6.7	33.8	496	634	40
P43	2574	7.6	27.6	250	170	31
P50	3656	7.4	34.1	1221	232	4
Tungurahua Province						
P44	2545	7.9	19.0	664	49	11
P45	1921	6.6	54.0	4990	415	114
P47	1935	6.4	48.9	740	403	48
P48	3200	8.3	42.6	422	49	47
P49	2865	7.6	23.9	445	98	6

5.2 Arsenic in sediments of geothermal springs

Arsenic content in sediments at the Aguas Hediondas increases downstream. In a sample taken at the geothermal discharge, As content is 170.7 mg/kg and in two sampling points at approximately 50 m and 200 m down are 286.6 and 717.6 mg/kg, respectively. As is also very high in the sediments at the outlet of El Baño spring (461 mg/kg) while at Aguas Negras, As is 92.5 mg/kg. Sediments at Chachimbiro springs contain As oscillating between 131.9 and 176.7 mg/kg as observed in Table 2. On the contrary, sediments at Timbuyacu springs have the lowest content of As among all samples analyzed at Imbabura Province (2.9-4.0 mg/kg). Sediments of three geothermal springs are analyzed for As in the Pichincha Province. At La Merced of Nono, sediments contain 329.7 mg/kg of arsenic while at Urauco arsenic concentration is quite low (2.8 mg/kg in average). The third sample of sediments (Cachaco spring) from Pichincha Province shows 69.5 mg/kg. At the Altamira farm in the Cotopaxi Province, sediments from two springs show high As concentrations (230 mg/kg in average).

Table 2. Arsenic in sediments of springs at the Northern-Center region of Ecuador (for location of sampling points see Fig. 1)

Sample	Location	As, mg/gk	Sample	Location	As, mg/kg
El Carchi Province			Pichincha Province		
P1	Aguas Hediondas	170.7	P22	Urauco spring 1	1.6
P2	spring	286.6	P23	Urauco spring 2	4.1
P3	50 m from spring	717.6	P28	La Merced of Nono spring	329.7
P5	200 m from spring	92.5	P32	Cachaco spring	69.5
P6	Aguas Negras spring El Baño spring	461.4			
Imbabura Province			Cotopaxi Province		
P16	Chachimbiro spring	176.7	P38	Altamira farm, spring 1	221.5
P17	Chachimbiro spring	131.9	P39	Altamira farm, spring 2	238.1
P18	Timbuyacu spring	2.9	Tungurahua Province		
P19	Spring in the border of Huarmiyahucu river	4.0	P43	Guapante spring	6.9
			P47	El Salado spring	198.7

6 Discussion

To determine processes that may control the As distribution in the sedimentary environments, geothermal sources, and rivers within the study area, data from the sediments and geothermal, river, and creek waters, are evaluated and interpreted, together with published experimental results. In general, it is observed that As content in sediments, geothermal sources, and rivers is dependent of the geographical location.

6.1 Geothermal waters and sediments

In three samples of sediments downstream of Aguas Hediondas spring, the extractable As increases from 170.7 to 717.6 mg/kg (Table 2). Several factors can contribute to the buildup of As in sediments. It can be associated to: i) coprecipitation with calcite or calcium sulfate since concentrations of sulfate and calcium are oversaturated in the geothermal water ($\text{SO}_4^{2-} = 846$ mg/L; $\text{Ca}^{2+} = 96$ mg/L), ii) incorporation into the structure of an oxidation solid product of sulphide minerals (i.e. $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), and iii) sorption on Fe(III) and Al(III) oxides. Chemical analysis of sediment samples, carried out in a scanning electron microscope (SEM) confirms the presence of sulfur, iron, aluminum, and calcium (Si = 52.4%, S = 19%, Fe = 10.3%, Al = 9.3%, Ca = 5.3%, K = 3.6%). Therefore, the main mechanism of As binding can

be sorption on the mineral phases. This mechanism may also occur at Aguas Negras spring since sulfate and calcium are fairly high (702 and 95 mg/L). At this site, arsenic in the solid phase is 92.5 mg/kg while in the aqueous phase is 2 µg/L. Smedley and Kinniburgh report that sulphide minerals are not stable in aerobic systems and oxidize to Fe oxides with the release of large amounts of SO₄ and acidity [8]. On the contrary, sorption on Fe(III) oxyhydroxides is mainly the mechanism of arsenic reduction in water at El Baño spring. Chemical analyses report low dissolved Fe (1.5 mg/L) however large amounts of Fe(III) precipitates are noticeable in sediments (15%). Previous studies report that Fe(III) oxyhydroxides or hydrated Fe(III) oxides (HFO) particles have a large surface area to which As compounds bind forming stable inner-sphere complexes [9-12]. It is remarkable to note that As is high at the Chachimbiro geothermal waters (726 to 979 µg/L). A number of environmental conditions can contribute to maintain this high As concentration in water. It is most likely that high bicarbonate concentration in the springs (HCO₃⁻ = 616 mg/L in average) could trigger the formation of soluble arseno-carbonate complexes such as As(CO₃)²⁻, As(CO₃)(OH)²⁻, and AsCO³⁺ keeping As in water and hindering sorption of As in sediments. Indeed, As is not high in sediments at Chachimbiro springs (131.9 to 176.7 mg/kg) although they are in contact with As rich thermal waters. Kim et al. report that the release of As from the aquifer rock is strongly related to bicarbonate concentration in the leaching solution and the arseno-carbonate complexes formed are stable in geothermal water [13]. At Timbuyacu springs, located in the southern side of Chachimbiro geothermal field, extractable arsenic is between 2.9 and 4.0 mg/kg and dissolved arsenic is 4.0 µg/L. Results of mineralogical analyses reveal that sediments of Timbuyacu springs mainly contain andesitic ashes, volcanic glasses, and negligible fraction of metal oxides. This explains the low content of As in both water and sediments. These results are consistent with the findings of Baur & Onishi [14]. They report concentrations of As ranging from 0.5 to 5.8 mg/kg in andesitic sediments. However, analysis of soil samples taken at different depths in the geothermal source is needed to perform in order to measure soil's mineral composition. Data from the springs of Altamira farm show As concentrations above the value recommended by WHO (2001) for drinking water. They are in the range of 40 to 47 µg/L. On the other hand, the content of As in sediments is quite high (230 mg/kg in average) and the natural organic matter concentration is around 14.3%. The combination of these factors can certainly favor the formation of As-organic matter associations in the sediments. Wang & Mulligan report that natural organic matter commonly associated with soils and aquifer sediments have been shown to be significant As adsorbents [15]. However, they point out that the extent of sorption is influenced by As speciation and the site geochemical conditions such as pH, redox potential, and the co-occurring ions which have not been assessed in this investigation. High extractable As has also been measured in sediments of La Merced of Nono springs (329.7 mg/kg). The sorption mechanism and accumulation of arsenic in the solid phase is similar to the mechanism explained at El Baño spring. Nevertheless, the presence of high CO₂ concentration at this site (640 mg/L) may prevent the buildup of As in sediments due to the formation of arsenic-bicarbonate complex. Sahai et. al reveal that natural attenuation of As by simple adsorption on oxyhydroxides may be limited due to competing anions such as carbonate and phosphate [16].

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