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Arsenic occurrence and water quality in recreational thermal springs at Araro, Mexico

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ABSTRACT

Arsenic content was evaluated in water from recreational thermal springs in Araro, at Cuitzeo basin, Michoacán State, Mexico. There were also analyzed physicochemical parameters and major components. Arsenic was determined by atomic absorption spectrometry within hydride generation. Physicochemical parameters and major components were analyzed by conventional laboratory methods. Arsenic concentration values found exceeded the Mexican regulation recommendations for drinking water use, indicating a potential risk for health. The metalloid content ranged between 0.01 and 6.26 mg/L. Results of physicochemical characterization revealed that eight of the analyzed parameters were found above the recommendations given by the Mexican regulation for drinking and domestic uses.

Keywords: *Arsenic, thermal springs, water quality, Cuitzeo.*

I. INTRODUCTION

The geological characteristics of aquifers are essential parameters generating differences between the concentration levels of the physical parameters and chemical species in the water in some areas, as the result of the geological composition, the arsenic concentration that exists naturally in groundwater is elevated. In Mexico, arsenic is naturally found in Coahuila, Durango and San Luis Potosi States in the North and also at the Center and South region of the country in Hidalgo, Michoacan and Guerrero States in concentrations exceeding the values recommended by the World Health Organization (WHO) [1]. In drinking water, it is rare to find more than 10 mg/L of arsenic, although values of up to 100 mg/L have been reported, whereas the guide value recommended by the WHO is 0.01 mg/L [2]. In Mexico, the maximum permissible level (MPL) of arsenic for drinking water is 0.025 mg/L [3]. According to the WHO, concentrations of 0.005 mg/L of arsenic in water have no effect on health and cancer risk is unknown. People that consume water with amounts higher than 0.05 mg/L of this element have shown incidence of skin and other types of cancer, increasing according to dosses and the age of the consumer [2].

Studies about the activity of the Quaternary period in the volcanic field of Michoacán and Guanajuato States, Mexico, indicate that the lacustrine river basins of this zone provide important information about the human impact on the environment [4]. According to previous studies [5, 6, 7], the abundance of arsenic in this region is significant and it could be considered as a potential health risk for inhabitants of this zone [8]. This investigation was focused on the study of arsenic levels and the water quality in water of recreational thermal springs located on Araro region at Cuitzeo basin at Michoacan, Mexico, by monitoring five of the most important thermal springs in the zone [3].

II. MATERIALS AND METHODS

Studied area

Araro region is located on the Cuitzeo basin at the northern part of Michoacán State, in Mexico (Fig. 1). The region belongs to the middle part of the Mexican Volcanic Belt [8, 9]. Cuitzeo Lake is one of the largest lakes of the country with an extension of 3977 km^2. The weather is moderate with summer rains (May–October), giving an average annual precipitation of 906 mm and a temperature range from 10◦C to 28◦C. Recent volcanism has occurred in this region; the youngest volcano, Paricutin, was born in 1943. The main regional geological formations are from Tertiary and Quaternary periods. Michoacan hydrology is composed by the upper Lerma river basin, the central lakes zone and the Balsas River. The main landform of the sampling zone is formed by the Cuitzeo depression. The southern region of the lake has been reported to have neutral-alkaline groundwater type [9].

Sampling

The sampling sites are located at Araro region, at the eastern part of Cuitzeo Lake, between 100° 49.5’ and 100° 52.25’ W and 19° 52.93’ and 19° 54.69 N, at an average altitude of 1850 m. The samples were obtained from Huingo, El Hervidero, La Playa, Manantiales Curativos and Atzimba (Zinapecuaro) recreational thermal springs (Figure 1, Table 1).

The sampling campaigns were performed from August to November 2009 according to the Mexican regulations [3] and the Standard Methods [10]. Four sampling campaigns to determine physicochemical parameters, coliform content and total arsenic in water were performed. The samples for physicochemical parameters were taken in 1L plastic polyethylene bottles filled and tightly closed to avoid degassing.

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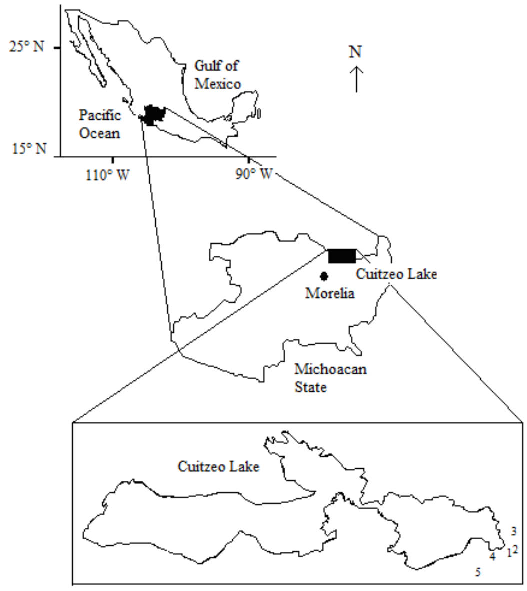

Figure 1. Sampling sites location, 1: Huingo (HU), 2: El Hervidero (EH), 3: La Playa (LP), 4: Manantiales Curativos (MC), 5: Atzimba (Zinapecuaro, ZI).

Samples for coliform content were taken in sterile plastic bags. To determine arsenic content, samples were taken in 120 mL polyethylene bottles, previously washed and decontaminated with HNO_3: one day before the sampling the bottles and covers were rinsed three times and filled with deionized water. At the field, two samples were taken at each site, one with the water sample and other with deionized water used as a field blank. The samples were acidified with ultrapure HNO_3.

Table 1. Location of the sampling sites at Araro recreational thermal springs, Mexico.

RECREATIONAL SPRING		LOCATION
1	Huingo (HU)	N 19° 54´ 15.23´´ W 100° 49´ 55.63´
2	El Hervidero (EH)	N 19° 54´ 16.9´ W 100° 49´ 54.7´´
3	La Playa (LP)	N 19° 54´ 59.4´ W 100° 49´ 52.6´´
4	Manantiales Curativos (MC)	N 19° 54´ 15.23´´ W 100° 50´ 41.22´
5	Atzimba (Zinapecuaro, ZI)	N 19° 52 0.93´´ W 100° 52´ 25.5´´

Measurement Techniques

In the field, pH, electrical conductivity, dissolved oxygen and salinity were determined with a Corning potentiometer calibrated before each measurement. Temperature was determined with by immersion with a Branan thermometer. Arsenic was analyzed using an atomic absorption spectrometer (PerkinElmer AAnalyst 200) with hydride generation system. Physicochemical parameters and major components were determined at the laboratory following the Mexican regulations and the Standard Methods [10].

III. RESULTS AND DISCUSSION

Physicochemical parameters

The results of physicochemical parameters for each sampling site: Huingo (HU), El Hervidero (EH), La Playa (LP), Manantiales Curativos (MC) and Atzimba (ZI), are shown in Tables 2 and 3.

Table 2. Turbidity, pH, water temperature (WT), electrical conductivity (EC), total solids (TS), total dissolved solids (TDS) and total alkalinity (TA) for each sampling site on the different sampling dates.

Site	Sampling date	Turbidity (UTN)	pH	T(°C)	EC (µS/cm)	TS (mg/L)	TDS (mg/L)	TA (mg/L)
HU	**Aug-09**	0.2	7.0	57.0	3920.0	2506.0	1887.0	166.0
	Sep-09	0.2	7.0	58.0	3570.0	2444.0	2070.0	178.0
	Oct-09	0.3	7.0	59.0	3800.0	2446.0	2.0	174.0
	Nov-09	0.1	6.9	58.0	3830.0	2346.0	2040.0	174.0
EH	**Aug-09**	1.6	7.0	89.0	3510.0	1816.0	1749.0	140.0
	Sep-09	0.3	6.8	89.0	3580.0	2370.0	1787.0	132.0
	Oct-09	0.9	6.9	93.0	nd	2380.0	nd	124.0
	Nov-09	0.3	6.8	89.0	3560.0	2380.0	1772.0	108.0
LP	**Aug-09**	0.2	7.2	35.0	289.0	268.0	140.0	110.0
	Sep-09	0.1	6.9	35.0	285.0	226.0	150.3	102.0
	Oct-09	0.7	7.5	33.0	274.0	236.0	147.6	108.0
	Nov-09	0.1	6.9	34.0	273.0	252.0	148.6	106.0
MC	**Aug-09**	0.2	6.9	38.4	1841.0	1218.0	864.0	148.0
	Sep-09	0.1	6.8	42.0	1849.0	1188.0	976.0	152.0
	Oct-09	0.3	7.4	36.0	1905.0	1254.0	1016.0	158.0
	Nov-09	0.1	6.9	41.0	1874.0	1198.0	988.0	156.0
ZI	**Sep-09**	0.2	7.0	31.0	151.6	168.0	80.5	76.0
	Oct-09	0.3	6.7	31.0	156.6	164.0	81.6	80.0
	Nov-09	0.1	6.2	32.0	153.9	178.0	81.2	74.0

nd: not determined

Turbidity ranged from 0.1 to 1.6 UTN, the lowest values were observed at HU, LP, MC and ZI on November and at LP and MC on November and September while the highest was observed in EH in August. Turbidity is generated because of the presence of suspended or dissolved particles. The determination of this parameter results useful as a water quality indicator and takes an important part of the water treatment control [8].

pH ranges between 6.2 and 7.5. ZI on November was the site where lowest pH was registered and LP in October, registered the highest value for this parameter (Table 2). According to NOM-127-SSA1-1994 regulation [3], pH in drinking water should range between 6.5 and 8.5. Almost all the sites in this study were in the permissible range for this parameter, excepting for ZI in just one collecting campaign.

Water temperature ranges between 31 and 93 ºC, the site where the lowest temperature was registered was ZI on September and October. The highest was registered in EH site on October (Table 2). There is no permissible limit in the current regulation for this parameter, nevertheless it is an important characteristic, because some uses are defined by it (i. e. warm and hot water is used for domestic and recreational purposes), and also because this parameter affects directly the chemical and biological reactions of organisms in water. The increase in temperature decreases the portability of water because at elevated temperature carbon dioxide and other volatile gases that impart taste are expelled [8, 11]. All water samples from wells were colorless, clear and odorless indicating the absence of colloidal substances, suspended and decomposed vegetation.

Electrical conductivity (EC) ranged between 151.6 and 3920 µS/cm (Table 2). ZI site on September presented the lowest EC value and HU site on August had the highest value for this parameter. There were three sites that stood out for the high EC they presented: HU, MC and EH. These sites presented significantly higher values during the entire studied period than LP and ZI. Electrical conductivity indicates the presence of dissolved ions and its determination is very important because it gives an idea of the degree of mineralization of water, and it is also related to the Total Dissolved Solids (TDS) in water as it can be clearly seen on Table 3. The presence of excessive solids in water indicates pollution that can lead to a laxative effect and their presence may be attributed to agricultural activities and geological parameters [11].

Total solids ranged between 164 and 2506 mg/L, finding the lowest concentration at ZI on October and the highest at HU on August. Total dissolved solids presented values from 80.5 to 2070 mg/L, being ZI the site with the lowest level and HU the highest, both on September. Three sites showed concentrations above the maximum recommended by the regulations of 1000 mg/L: HU, EH and MC, being this last above the limit only on October.

Total alkalinity showed concentrations between 74 and 178 mg/L $CaCO_3$. The lowest value was observed at ZI during November, while the highest one was found at HU during September. Alkalinity expresses the presence of substances that can be hydrolyzed in water and as a product of the hydrolysis they generate the hydroxyl ion (OH^-), like strong bases and the hydroxides of alkaline-earth metals, and also carbonates and phosphates. The presence of borates and silicates in high concentrations also contribute to the alkalinity of the water. High alkalinity values could lead to sour taste and salinity.

Bicarbonates ranged between 74 and 178 mg/L. The lowest value was found in ZI on November and the highest one in HU on September (Table 3). Bicarbonates were the predominant ions of the carbonate system in all the sites. Carbonates were not reported due to the fact that they are only found in water when its pH is over 8.3.

Total hardness (TH) ranged between 44.4 and 119.2 mg/L, the highest reported value where found in HU, on August and the lowest one where found in ZI on October (Table 3). Total hardness refers to the sum of concentrations of calcium and magnesium. High levels of hardness, may lead to heart diseases and kidney stone formation, making hard waters unsuitable for drinking, washing, cleaning and laundering [11]. On the other side, there is some indication that very soft waters may have an adverse effect on mineral balance [2].

Sulphate is one of the least toxic anions of which WHO does not have any recommended value for drinking water, but catharsis, dehydration and gastrointestinal irritation have been linked to high sulphate concentrations in drinking water [11]. In addition, values over 250 mg/L have a "purgative" effect [17]. In this study, sulfates ranged between 1.6 and 101.5 mg/L. The lowest value was found in ZI on November and the highest value corresponded to HU on August. All the sites showed lower values than the limits recommended by the Mexican regulations [3]. In the water systems for domestic use, sulfates do not produce an increase of corrosion on metallic accessories. Nevertheless, when sulfates concentrations are over 200 mg/L, the concentration of dissolved lead from lead pipelines is increased [8].

Table 3. Bicarbonates, carbonates, total hardness (TH), sulphates, chloride, nitrates, total (TC) and fecal (FC) coliforms for each site, for the samplings from August to November 2009.

Site	Sampling date	HCO_3^- (mg/L)	CO_3^{2-} (mg/L)	TH (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	N-NO_3^- (mg/L)	TC (NMP/100mL)	FC (NMP/100mL)
HU	Aug-09	166.0	<dl	119.2	101.5	849.7	1.5	<dl	<dl
	Sep-09	178.0	<dl	112.6	71.9	889.7	0.8	<dl	<dl
	Oct-09	174.0	<dl	114.0	72.4	949.7	1.1	<dl	<dl
	Nov-09	174.0	<dl	118.6	76.3	849.7	nd	<dl	<dl
EH	Aug-09	140.0	<dl	109.4	96.8	874.7	1.5	<dl	<dl
	Sep-09	132.0	<dl	102.2	72.2	889.7	0.9	<dl	<dl
	Oct-09	124.0	<dl	96.0	72.1	924.7	1.2	<dl	<dl
	Nov-09	108.0	<dl	100.0	73.6	874.8	nd	<dl	<dl
LP	Aug-09	110.0	<dl	85.2	10.0	15.5	3.1	>8	>8
	Sep-09	102.0	<dl	78.2	3.0	12.0	2.5	>8	5
	Oct-09	108.0	<dl	74.6	7.6	15.5	3.3	>8	>8
	Nov-09	106.0	<dl	88.4	6.8	10.5	nd	3	3
MC	Aug-09	148.0	<dl	98.2	53.3	424.9	1.5	5	5
	Sep-09	152.0	<dl	83.4	1.8	389.9	1.1	>8	>8
	Oct-09	158.0	<dl	92.2	39.7	459.9	1.1	>8	1
	Nov-09	156.0	<dl	87.0	36.4	759.8	nd	5	3
ZI	Sep-09	76.0	<dl	47.4	2.5	4.0	1.3	>8	3
	Oct-09	80.0	<dl	44.4	2.0	4.5	1.7	>8	>8
	Nov-09	74.0	<dl	53.2	1.6	5.0	nd	>8	>8

< ld: lower than detection limit
nd: not determined

Chloride occurs in all natural waters in varying concentrations. Concentration is usually greater in groundwater than surface water especially if salt deposits are in the area. Chloride in small concentrations are not harmful to humans in drinking water, and with some adaptation, the human body can tolerate water with as much as 200 mg/L chloride ions [12]. In sites from the study area, chlorides ranged between 1.3 to 949.7 mg/L. ZI site on September, presented the lowest value and HU site on October registered the highest value. Chlorides were the predominant ion in HU, EH and MC. Also, these three sites exceeded the maximum concentration allowed by the Mexican regulations (250 mg/L) [3]. High concentrations of chlorides can avoid the growth of plants and can cause damages to metallic structures by promoting corrosion of pipes, which could be potentially dangerous if pipes are made of toxic metals.

Nitrogen from nitrates ranged between 0.8 and 3.3 mg/L. The lowest corresponded to HU on September and the highest was observed in LP on October.

Arsenic

The results for the content of arsenic for each sampling site, during the three samplings are shown in Table 4. The content of arsenic in HU, EH and MC was over the maximum permissible level indicated by the Mexican and international regulations for water destined for human use and consumption [2, 3]. Concentrations of arsenic ranged between 0.01 and 6.26 mg/L.

Table 4. Concentrations of as for each site of study in each sampling.

Site	Sampling date	As (mg/L)
HU	Aug-09	3.08
	Sep-09	4.04
	Oct-09	3.16
	Nov-09	3.92
EH	Aug-09	2.75
	Sep-09	6.09
	Oct-09	6.26
	Nov-09	5.32
LP	Aug-09	< dl
	Sep-09	0.02
	Oct-09	0.02
	Nov-09	0.01
MC	Aug-09	0.74
	Sep-09	2.25
	Oct-09	2.25
	Nov-09	2.88
ZI	Sep-09	0.01
	Oct-09	0.01
	Nov-09	0.01

The sites that presented the lowest value were LP on November and ZI in every sampling campaign (0.001 mg/L) and the one that presented the highest values was EH on September and October with levels above 6 mg/L, exceeding the maximum permissible limit for water destined for human use and consumption [2, 3] by several orders of magnitude in every sampling campaign.

The upgrade to the NOM-127-SSA1-1994 Mexican norm, regarding to environmental Health, water for human use and consumption, permissible limits of quality and treatments for water purification [19], indicates as maximum permissible limit a concentration of 0.025 mg/L of arsenic since 2006. Natural enrichment of groundwater by arsenic can arise in several ways like hydrothermal volcanism, oxidation of arsenical sulphide minerals, reduction of FeOOH and release of its sorbed load to groundwater, desorption of As from mineral sorption sites in response to increase of pH, and evaporative concentration; as well as anthropogenic sources like agricultural applications, wood preservation, glass production and mining activities [8, 20, 21, 22]. At the sites that exceeded the maximum limit recommendations there is not industrial or significant agricultural activities, therefore these sources can be discarded as pollution sources for this site. Besides, some studies have found presence of arsenic in groundwater near the studied area (used mainly for geothermal exploitation), relating As occurrence to the water-rock interaction and the geothermal nature of the zone [8, 23, 24]. Furthermore, a general relationship between As and salinity in geothermal waters from the USA has been reported [22, 25], where concentration greater than 1 mg/L of As mostly had Cl^- concentrations of 800 mg/L or more, which is the case of HU and EH sites in this study.

IV. CONCLUSIONS

HU, EH and MC sites presented several physicochemical parameters exceeding the Mexican and international recommendations for drinking water but, due to the fact that the use that is given to this water is only recreational, it does not represent a risk for health. The concentrations of chlorides found at HU and EH could cause damages on the pipelines and other metallic structures. Besides, the presence of arsenic at HU, EH and MC exceeded the permissible limit indicated by the Mexican and international regulations for recreational uses with contact, LP presented values under the Mexican regulations but exceeded the international, so these sites represent a risk for the health of the people who is in contact with this water. Therefore, a treatment process for the removal of arsenic is recommended. Hence, it is not recommended its use for any practical uses before a water treatment is applied. ZI site did not show parameters exceeding the Mexican or international regulations, so this water is considered totally suitable for any of the uses for which it is destined.

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