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## Correlation of Arsenic and Fluoride in the groundwater for human consumption in a semiarid region of Mexico

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### Abstract

The measurement of the values of arsenic and fluoride becomes critical in the characterization of groundwater quality. Although there are anthropogenic sources, most large-scale pollution in groundwater have been documented of geological origin, the arsenic to the reaction of oxidation in sulfide minerals in metasedimentary rocks and the F<sup>-</sup> value is proportional to the degree of water-rock interaction with fluorite (CaF<sub>2</sub>), the concentration values are proportional to residence times in aquifers and generally are associated with regional flow systems. The objective of this research was to determine the current correlation of arsenic and fluoride with emphasis in the extraction points used for human consumption, due to the water-rock interaction in a semiarid region in México.

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### 1. Introduction

The presence of total inorganic arsenic (As) and fluoride (F<sup>-</sup>) in groundwater is frequently observed worldwide. A high As concentration in water for human consumption usually causes health problems. Besides this problem, the use of these waters for irrigation purposes could cause problems on crop production and the food chain [1]. Although there

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are anthropogenic sources, most large-scale pollution in groundwater has been documented of geological origin. The As is associated the reaction of oxidation of sulfide minerals in metasedimentary rocks, where those rocks have a greater variability in arsenic, with averages and ranges somewhat higher than those of igneous and metamorphic rocks, mainly shale, with mean values of 28 ppm in alluvial quaternary basins which causes a condition of occurrence of high concentrations in large areas [2]. Adverse effects on human health of high F<sup>-</sup> concentrations have been revised by different researchers [3-5]; one of the most noticeable effects is the occurrence of yellow spots in the teeth of people who drink this water for prolonged periods of time. The F<sup>-</sup> concentration values, generally associated with regional flow systems, are proportional to the degree of water-rock interaction with fluorite (CaF<sub>2</sub>) and the residence times in aquifers [6], where the metamorphic rocks could have a fluorine concentration from 100 ppm (regional metamorphism) up to more than 5000 ppm (contact metamorphism) and the original minerals are enriched with fluorine by metasomatic processes [7]. Other source of F<sup>-</sup> can be the soil contamination as a consequence of the use of fertilizers and phosphate pesticides reaching the groundwater [8]. In this context, the objective of this research was to determine the correlation between arsenic (As) and fluoride (F<sup>-</sup>) with emphasis in the extraction points used for human consumption, due to the water-rock interaction within aquifers of a semiarid region in México.

### 1.1 Description of the Study Area (SA)

The SA is located in the Sierra Madre Occidental volcanic terrain, which is within the southern part of a regional graben structure that gives origin to the Calera endorreic basin, characterized by ephemeral streams that are dry most of the year. The Zacatecas Formation (maximum elevation 2,700 m.a.s.l.) and the Chilitos Formation bound a flat area (2010 m.a.s.l.) in south-central part and other flat area (2100 m.a.s.l.) in the north; the soils are from 10 cm up to depths of 50 cm. In general, the SA is considered arid, the average annual temperature is estimated between 18 and 20 °C, with precipitation ranging from 400-450 mm, there are important surface runoffs, with small intermittent streams; runoff is toward the center of the study area to continue at north, with a few reservoirs of surface water with reduced capacity but of great importance for the area [9]. This zone encompasses two important cities of the Zacatecas state, where the main economic and social activities are established (Figure 1).

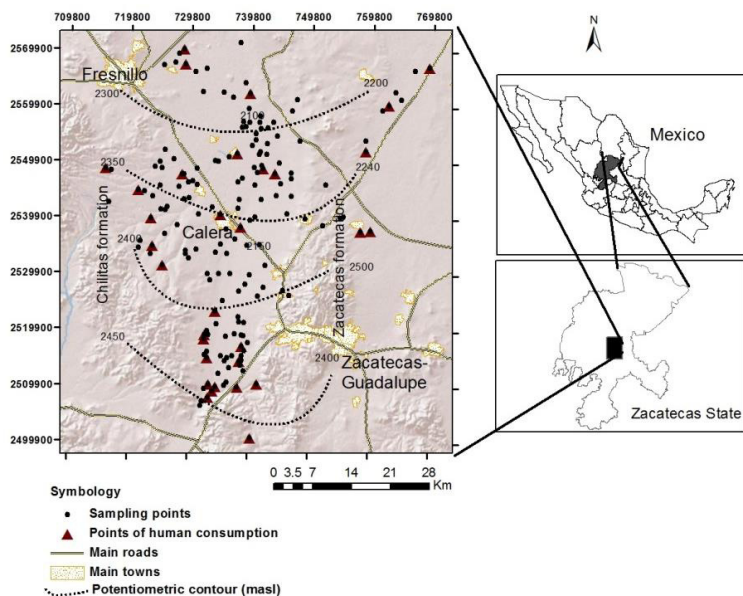


Fig. 1. Location of sampling points

Commerce in the form of animal breeding is a complementary occupation in the Zacatecas-Guadalupe metropolitan area. On the other hand, the mining activity has gained strength and has become an important influence on the groundwater quality in the last 30 years. With regards to industrial activity, a few companies extract a large amount groundwater and the 50 % of the total drinking water that is supplied to Calera, Morelos, and the Zacatecas-Guadalupe metropolitan area comes from the central and west part of the SA.

### 1.2 Geological setting

Sampling sites are located within the central and southern part of Zacatecas, Mexico, where the alluvium extends between tectonic pillars that consist mainly of metamorphic rocks of Zacatecas and Chilitos formations, from Triassic (volcanoclastic low grade metamorphic rocks) and Jurassic (metabasaltic and metandesitic pillow lava flows, volcano-sedimentary deposits) periods respectively, the Zacatecas Formation in the southeast of the SA, this is composed of feldspathic wacke, mudstone chert and discrete limestone lenses, accompanied by basaltic lava flows, rare dikes and hydrothermal vent-like structures.

In the Zacatecas formation, Las Pilas Complex is mainly composed of laccolithic intrusions and basaltic lava flows, interlayered with feldspathic and lithic wacke, mudstone chert and rare limestone; these units outcrop the east of the SA. In this case, lava flows are composed of plagioclase, clinopyroxene and rare quartz. This alteration developed chlorite, epidote, sericite and calcite together with quartz and calcite veinlets. At west, the Francisco I. Madero massive sulfide deposits developed in an island arc setting with intense mining activities, which evolves to Las Pilas Complex [10].

Geophysical surveys and direct drilling show that the aquifer is unconfined, semi-confined locally by interbedded clayey layers. The depth of the basement is considered between 400 and 500 m. it is constituted by a polymictic conglomerate, predominantly fragments of rhyolite and quartz, with clay cementing; with redeposit of argillaceous tuffs [11]. (Figure 2).

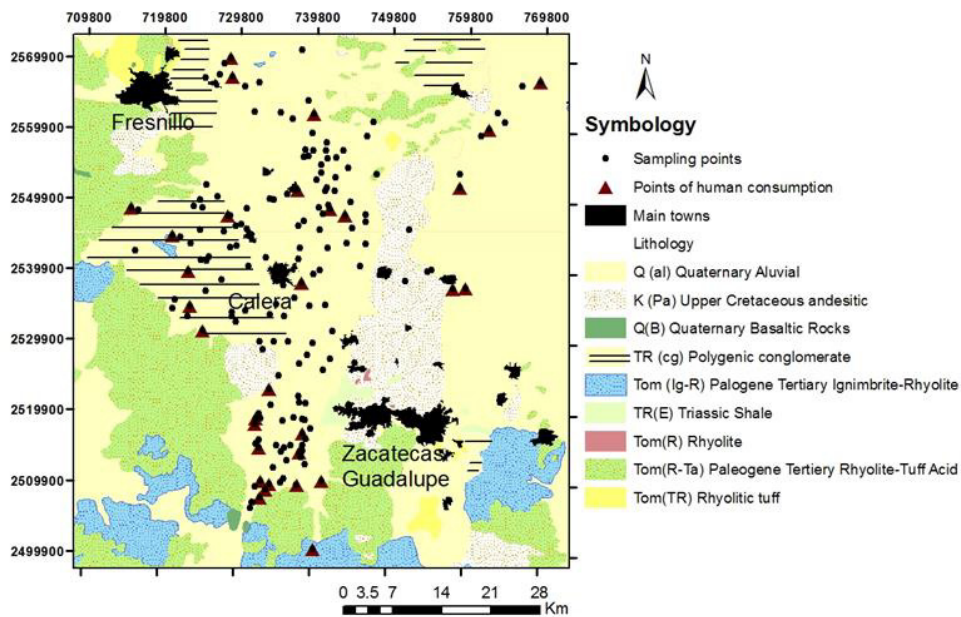


Fig. 2. Geology setting

## 1. Methodology

The determination of As and F<sup>-</sup> was done in 182 wells which were monitored during the period from April 2014 to August 2015, thirty-five of them are used for human consumption and their results were utilized for this research. The planning of sampling campaign was conducted with information from government offices ([12]). The electrical conductivity, pH, temperature, dissolved oxygen and alkalinity were sampled in situ. In the case of As, major ions and tracer elements, the samples were filtered (0.45 µm membrane filters) and acidified (1% v/v HNO<sub>3</sub>) in field. The F<sup>-</sup> samples were not treated. The analytical determinations were carried out in the Environmental Engineering Laboratory of the Autonomous University of Zacatecas.

The As was analyzed by atomic absorption spectrophotometry (Thermo Scientific ICE AA 3300) with hydride generation, steam generation increases the sensitivity of the atomic absorption technique, especially in those elements which are important as environmental pollutants or toxicology. The F<sup>-</sup> was determined by colorimetry by the reaction between fluoride and a zirconium-dye lake, knowing that the absorbance is inversely proportional to the concentration of fluorides, the reaction is carried out in acid medium.

In addition, the study was completed with determinations of major ions Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup>, they were analyzed in the same equipment used for As. Chloride was determined by titration using AgNO<sub>3</sub> and K<sub>2</sub>CrO<sub>4</sub> indicators. Other anions were determined by colorimetry, SO<sub>4</sub><sup>2-</sup> by precipitation of BaSO<sub>4</sub>, N-NO<sub>3</sub><sup>-</sup> by automated cadmium reduction method. SiO<sub>2</sub> was determined by the spectrophotometric method. Total alkalinity as HCO<sub>3</sub><sup>-</sup> was determined by titration using H<sub>2</sub>SO<sub>4</sub>, phenolphthalein and bromophenol blue indicators. Calibrations for atomic absorption spectrophotometry and automated colorimetry were performed using appropriately dilution standard, both laboratory and international reference material were used as checks of accuracy (4 sigma). Additional control includes the ionic balance; the balance lies below ± 7%. All the determinations were conducted under the guidelines described in APHA-SMWW 2006 [13] and applicable Mexican regulations.

A geostatistical analysis was made using the Geographic Information System ArcGIS 10.0. In this research the x Inverse Distance weighted tool was used for interpolation and spatial analysis for two parameters. This type of tool comprises a set of techniques for describing and modeling spatial data. This origins spatial patterns, distributions, trend and relationships [14].

The analysis of the obtained data was carried out in AquaChem2015. It is a program designed by Waterloo Hydrogeologic for numerical and graphical analysis used to interpret water quality data. It contains a fully modifiable data base and includes an important set of data analysis tools for water quality. Specific functions contained in this program are among others:

- Unit conversions
- Ionic balances
- Comparison and classification of samples,
- Trend analysis
- Comparison with international standards.

The analytical capabilities are complemented by a complete set of graphical tools to represent the chemical characteristics of water, one of them is the correlation graph, this is considered the simplest approach to interpreting hydrochemical data and reveals statistical relations between two or more variables. In this research, the X-Y Scatter plots of the Aquachem were used to calculate correlation between the As y F<sup>-</sup>.

### 3. Results and discussion

The basic statistics for the chemical analysis and field measurements are shown in table 1, very similar results in mean and median indicate normal distribution for a sample population.

**Table 1.** Basic statistic of sampling points

	Min	Max	Mean	Med	Sdesv
T °C	21.0	34.7	26.1	26.1	2.8
pH	6.30	8.34	7.44	7.59	0.55
DO	2.2	12.4	5.7	5.8	1.8
Ec µs/cm	250	1811	519.1	481	271.0
Alkalinity	109.6	340.3	183.1	185.0	47.4
HCO <sub>3</sub> <sup>-</sup>	133.7	415.1	223.4	225.7	57.8
Cl <sup>-</sup>	6.5	193.6	27.8	17.4	39.4
SO <sub>4</sub> <sup>2-</sup>	2.0	102.0	29.1	24.0	25.1
N-NO <sub>3</sub> <sup>-</sup>	0.10	8.00	2.59	2.20	1.79
F <sup>-</sup>	<b>0.35</b>	<b>3.60</b>	<b>1.16</b>	<b>1.13</b>	<b>0.58</b>
Ca <sup>2+</sup>	15.8	99.5	42.5	39.9	19.5
Mg <sup>2+</sup>	0.3	115.8	15.7	6.5	21.9
Na <sup>+</sup>	12.4	118.0	49.6	52.0	27.6
K <sup>+</sup>	1.1	22.1	10.3	9.5	5.6
SiO <sub>2</sub>	13.3	43.2	29.0	29.0	8.3
TDS	240.0	752.7	431.6	421.9	122.7
TH	40.7	545.1	170.4	143.0	108.5
As	<b>0.0033</b>	<b>0.0754</b>	<b>0.0185</b>	<b>0.0137</b>	<b>0.0156</b>
Li	0.0004	0.0986	0.0448	0.0459	0.0224
Sr	0.0769	4.3424	0.4889	0.2639	0.8606

DO=Dissolve oxygen, EC=Electrical Conductivity, TDS=Total dissolved solids and TH=Total hardness, all parameters in mg/L (Except pH and T)

The As concentrations were between 0.0033 to 0.0754 mg/L. For this metalloid, the World Health Organization (WHO) established the maximum permissible value at 0.010 mg/L [15]. The results show 24 samples exceeds the drinking water guideline, with the knowledge and understanding that there are not studies that provide information of the degree of damage to the health to the population using this groundwater. Values above 0.010 mg/L are mainly related to mining activities where the presence of sulfide oxidation can cause the arsenic mobilization; it can be common in its form of arsenopyrite (AsFeS) related to the drawdown of the water table, caused by massive extraction of groundwater and the oxygen entering the anoxic aquifer. However, other areas with high natural concentrations are associated only to mineral components of the geological framework in the north, where the quaternary alluvial setting is present [2]. In this case, the spatial distribution shows both conditions, the anthropogenic and natural origins, on the central-west part of SA with a mining activities and the north part where there is a large area with a quaternary alluvial (Figure 3)

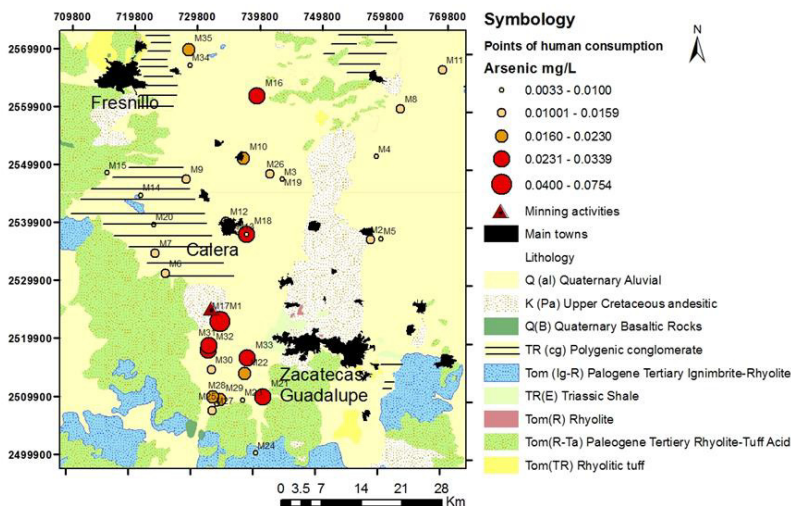


Fig. 3. Arsenic spatial distribution

The values of F<sup>-</sup> were between 0.35 and 3.6 mg/L. The WHO established the maximum permissible value at 1.5 mg/L. This value was exceeded in eight wells with a maximum of 2.20 mg/L. Actually; there is no evidence of health problems, specifically yellow spots in the teeth of population using this water. Values above the permissible limit occurred in the south where there is an intense agriculture activity and the use of the phosphate pesticides is a common practice, this situation has been occurring for the last three decades. The other zones are the northwest and south areas where the presence of water with sodium characteristics is causing those values of F<sup>-</sup>, as it has been reported in scientific literature [16] (Figure 4).

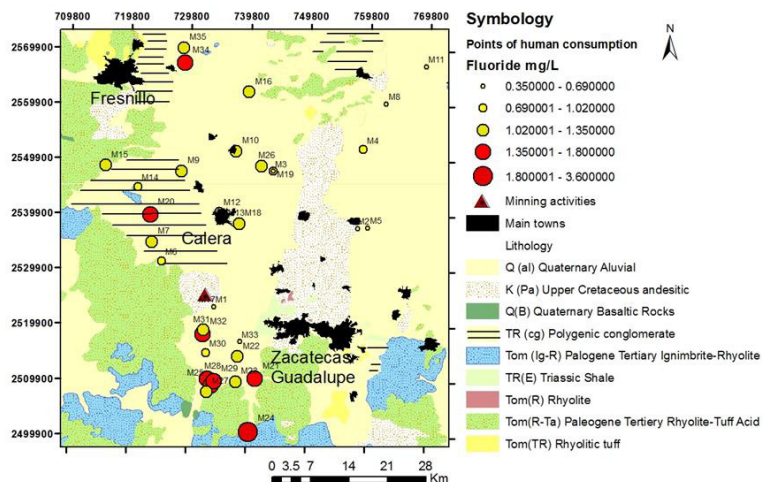


Fig. 4. Fluoride map contour

The correlation between the two analyzed parameters in this research was conducted with hydrochemical classification of dominant ions, recognizing the natural evolution of groundwater in the next sequence, an initial bacterial reduction of oxygen, nitrate and sulfate, followed by dissolution of sulfates and sulfides before the ion exchange of cations, with final mixture with a deep flow system [17]. This can be represented in the next way;  $\text{Ca}^{2+} \rightarrow \text{Mg}^{2+} \rightarrow \text{Na}^+$  (cations) and  $\text{HCO}_3^- \rightarrow \text{SO}_4^{2-} \rightarrow \text{Cl}^-$  (anions). The monitored points were classified by the dominant cation and anion, this analysis resulted in five types of groundwater, according to the values obtained for As and  $\text{F}^-$  did not show a positive correlation (Figure 5a)

In a further analysis, the correlation was reviewed independently for each type of groundwater type; where the cation dominant was calcium and values of As were relatively low, ( $\leq 0.030 \text{ mg/l}$ ) a positive correlation  $\text{F}^-$  was found, the highest values of arsenic did not show this behavior, these points are those that are influenced by mining activities (Figure 5b), this relationship was not present when calcium was not the dominant ion (Figure 5c), because there is an initial natural dissolution of  $\text{F}^-$  and later a precipitation of fluorite ( $\text{CaF}_2$ ), which makes an available cation by the ion exchange that took place in the geochemical evolution of groundwater in the SA, which in some way controls  $\text{F}^-$  concentration, a situation that has been tested in different geological settings [16].

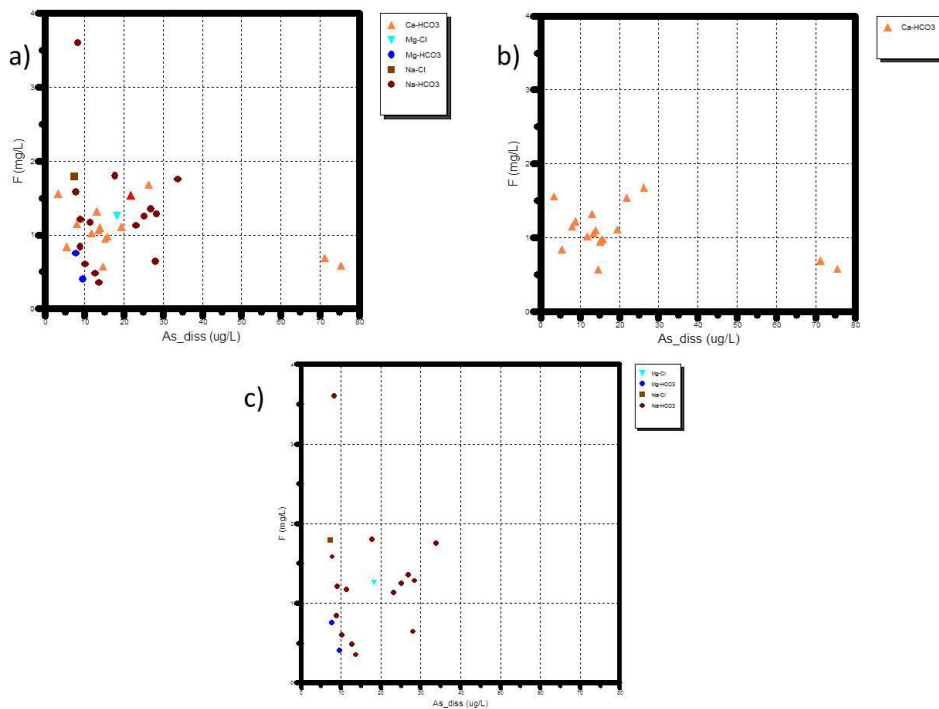


Figure 5. Correlation between  $\text{F}^-$  and As a) All types of groundwater, b) The calcium as dominant cation c) The other ions as dominant cations

#### 4. Conclusions and recommendations.

The groundwater quality analysis showed that in some sampled points the arsenic and fluoride concentrations were above the maximum permissible limits established by the WHO for human consumption. The origins for both parameters were defined: 1) anthropogenic, by mining activities for arsenic and the use of phosphate pesticides for fluoride 2) natural, the alluvial quaternary basin facilitates the dissolution of minerals containing arsenic, and the ion exchange with the increase of the precipitation of fluorite ( $\text{CaF}_2$ ).

Based on the ionic components of groundwater, there is a geological control over the concentration of F<sup>-</sup>, reason for the reduction of the positive correlation between fluoride and arsenic, however it is important a tracing to the south of the SA for the purpose of ensuring appropriate treatment in those wells with values above 1.5 mg / L.

In the case of Arsenic the mining activities in the southern part of SA combined with the type of rock and the intensive extraction of groundwater are causing mobility of this metalloid. A situation that has inhibited the taking appropriate action to attack this problem is that the Mexican legislation is 0,025 mg / L as the maximum permissible limit for human consumption.

The lack of knowledge existent of the groundwater consumption levels with values above levels considered safe for human health, since there is a tendency to consume bottled water for a negative perception of quality of the groundwater.

Further research should focus on three main points; 1) corroborate the temporary effect of groundwater extraction for agriculture in the zone of influence of mining activities to define its degree of impact, 2) begin studies of human health in communities with this situation and 3) establish a continuous monitoring program to corroborate the control of concentrations of F<sup>-</sup> that actually is naturally occurring.

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