# Temporal variation and Co-occurrence of fluoride and arsenic in aquifers of the central semi-arid region of Chihuahua, Mexico

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ABSTRACT: The objectives of this study were, to evaluate the change in concentrations of arsenic (As) and fluoride (F) in three aquifers located in the central semi-arid region of Chihuahua, at three different times within a seven year period. The As content in rock, sediment, and groundwater samples was first determined in 2004; later on, in 2007 and 2010, the content of As and F in groundwater were measured. In all three sampling episodes some wells had consistently As concentrations above 0.025 mg L<sup>-1</sup>. The F concentration surpassed the Mexican limit values of 1.5 mg L<sup>-1</sup> in 77% of the measured wells. The surrounding rocks contained enough As and F to support a geogenic origin of these contaminants and their higher concentrations within the rhyolites indicates a possible chemical association to these volcanic rocks. A correlation between As and F suggests a co-occurrence of these two contaminants ( $r^2 = 0.52$ , p < 0.001). The observed variations on the three-year concentrations of As and F in the three measured events indicate a stable evolution for As, and a dynamic increase evolution in the case of F.

Keywords: As and F, groundwater, temporal variation, co-occurrence As/F, Chihuahua, Mexico

#### 1 INTRODUCCION

Groundwater with high As and F content have been reported in aquifers within Chihuahua and adjacent states of Durango, Coahuila and San Luis Potosi () in Mexico, New Mexico and Texas in the U.S. (Armienta and Segovia, 2008, Camacho et al., 2011). The above aquifers have similar geological characteristics (deep basins filled with unconsolidated sediments that formed as a result of Basin and Range extensional deformation) and similar desert climate. A better understanding of the origin of contaminants and the hydrology of the aquifers are key factors towards being able to pinpoint preventive as well as corrective measures in these areas where groundwater supplies most of the drinking water to the population.

### 2. MATERIALS AND METHODS

*Area of study*. The study was conducted in an area encompassing three contiguous valleys: Tabalaopa, Aldama and Dolores (VTAD), (Fig. 1).



Figure 1. Location of area of study

Underlying the VTAD, the subsurface geohydrology is comprised of three aquifers: Tabalaopa (ATA), Las Hormigas (ALH) and San-Diego (ASD), which belong to the non-confined type for most of their extent, except in a few locations where they underlie or intertwine with clay lenses. The rocks that outcrop in the VTAD area are igneous and sedimentary and are exposed in the Sierra Las Glorias and Sierra El Cuervo (Fig.1). The rocks that predominate are rhyolitic tuffs, limestones and shales, in this order.

## 3. RESULTS

# As and F in rocks, sediments, and groundwater

In June of 2004, the concentration of As was analyzed for 142 rock, sediment, and groundwater samples distributed throughout the VTAD. The mineralogy was determined by X-ray diffraction and the concentration of As was analyzed using an ICP-MS spectrometer. Samples collected in 2007 and 2010 included analyses of F in addition to As. The concentration of F was determined using an ion-selective electrode. At the time groundwater samples were taken, the temperature (T), pH, redox potential (ORP) and electrical conductivity (EC) were measured, total dissolved solids (TDS) were determined, and the potentiometric surface of the wells were recorded. After three years, in June of 2007, nine wells that had surpassed the As permissible limit in the 2004 study, plus four other random wells, were analyzed for the same parameters. During 2010, these wells were again sampled. All sampling locations were georeferenced in order to construct contour maps showing the As content using the method of interpolation of square distances utilized in geostatistical techniques. Temporal and spatial distribution maps were constructed for each As and F. In order to evaluate the degree of co-occurrence of As and F, a regression analysis was performed, using significance criteria for the coefficient of determination as well as its probability of error ( $r^2 = 0.52$ , p <0.001).



Figure 2. Contour maps for the concentration of As in solid materials.

The results obtained during the 2004 groundwater sampling revealed that only ten out of the 34 wells sampled had a concentration lower than 0.01 mgL<sup>-1</sup>As. The spatial distribution of wells with As concentration above 0.025 mg L<sup>-1</sup> showed these wells clustering in the south and northeastern parts of the VTAD, which correspond to areas pumped more heavily and containing human settlements (town of Aldama and surroundings). Three years later (in 2007), the As content had not changed much in 77% of the wells. Four wells still had an As content higher than  $0.025 \text{ mg L}^{-1}$ , underlining that they maintained the same content and spatial distri-

bution as they had three years before. The As values for 2010 again revealed concentrations higher than 0.025 mg L<sup>-1</sup>. The F concentrations in groundwater collected in 2007 and 2010 revealed that 13 of the wells surpassed the recommended limit of 1.5 mg L<sup>-1</sup>, reaching an average concentration value of 2.77 mg  $L^{-1}$ . The highest F levels were detected in the transition zone of ATA towards ALH (encompassing the urban and suburban zones of Aldama) as well as in the southeast part of the study area, coinciding in a large extent with the location of the wells contaminated with As. The F content of the wells in 2010 surpassed the norm and was up to 106% above their previously measured concentration.

# 5. CONCLUSIONS

The observed variations on the three-year concentrations of As and F in the three measured events indicate a stable evolution for As with a few important changes in some wells, and a dynamic increase evolution in the case of F. A co-occurrence of As and F was also found. The As content of some wells after 7 years were found stable, indicating a chemical stability with the surrounding rocks.

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# Understanding the Geological and Medical Interface of Arsenic

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ARSENIC IN THE ENVIRONMENT PROCEEDINGS



