

Fluoride and Arsenic in an Alluvial Aquifer System in Chihuahua, Mexico: Contaminant Levels, Potential Sources, and Co-occurrence

Víctor M. Reyes-Gómez ·
María Teresa Alarcón-Herrera ·
Mélida Gutiérrez · Daniel Núñez López

Received: 3 May 2012 / Accepted: 3 January 2013 / Published online: 19 January 2013
© Springer Science+Business Media Dordrecht 2013

Abstract The objectives of this study were to identify potential sources of As and F within an alluvial aquifer system in central Chihuahua, to evaluate their change in concentrations with time, and to determine their degree of co-occurrence. 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 was measured. From 34 wells sampled, seven had As levels above the Mexican maximum contaminant level of 0.025 mgL^{-1} , and 13 wells surpassed the F value of 1.5 mgL^{-1} , all of these near the town of Aldama. The surrounding rocks contained enough As

and F to support a geogenic origin of these contaminants, especially evident in rhyolites. A correlation between As and F suggests a co-occurrence of these two contaminants ($r=0.720$; $p<0.001$). The minor variations of As and F in the measured events indicate a stable evolution for As and F. Yearly monitoring the content of As and F is recommended, in order to observe the behavior of these elements within the aquifer, especially as land use is changing and the demand for groundwater (drinking water, irrigation) is increasing.

Keywords Arsenic · Fluoride · Alluvial aquifer · Conceptual model · Chihuahua · Mexico

V. M. Reyes-Gómez · D. N. López
Instituto de Ecología, A.C. Red Ambiente y
Sustentabilidad,
Miguel de Cervantes 120, Complejo Industrial Chihuahua,
31109 Chihuahua, Chihuahua, México

V. M. Reyes-Gómez
e-mail: victor.reyes@inecol.edu.mx

D. N. López
e-mail: daniel.nunez@inecol.edu.mx

M. T. Alarcón-Herrera
Renewable Energy and Environmental Protection,
Centro de Investigacion En Materiales Avanzados (CIMAV),
Miguel de Cervantes 120, Complejo Industrial Chihuahua,
31109 Chihuahua, Chihuahua, México
e-mail: teresa.alarcon@cimav.edu.mx

M. Gutiérrez (✉)
Missouri State University (MSU),
Springfield, MO 65897, USA
e-mail: mgutierrez@missouristate.edu

1 Introduction

In countries such as China, Japan, Pakistan, Australia, Argentina, Chile, and Mexico, the concern about mitigating the toxic effect of arsenic (As) and fluoride (F) in groundwater used as a source of drinking water has been on the rise (Alarcón-Herrera et al. 2001a; Carrillo-Rivera et al. 2002; Farooqi et al. 2007; Wang et al. 2009). The recommended limit for As by the World Health Organization and the US Environmental Protection Agency is 0.01 mgL^{-1} (SSA and Asistencia 2000; Ochoa Reyes et al. 2009). Presently, the drinking water limits in Mexico are 0.025 mgL^{-1} for As and 1.5 mgL^{-1} for F (NOM-127-SSA1-1994, Norma Oficial Mexicana. Salud ambiental 1994). Although there are many studies reporting either As or F, more are needed on the

combined presence and the combined toxic effect of these contaminants (Chouhan and Flora 2010). Groundwater with high As and F content have been reported in alluvial aquifers in northern Mexico (Piñón-Miramontes et al. 2003; Reyes-Gómez et al. 2010; González Dávila 2011), across the border with the USA in New Mexico (Deng et al. 2006), Arizona (Vinson et al. 2011), and Texas (Scanlon et al. 2009). These aquifers have similar geological characteristics (deep basins that formed as a result of Basin and Range extensional deformation that are now filled with unconsolidated sediments or alluvium) and desert climate. In addition, volcanic rocks such as rhyolites, tuff, and volcanic glass abound both in outcrops and as fill material. These rocks tend to have relatively high concentrations of As in their crystal lattices, which during their dissolution and hydrogeochemical evolution release As into the groundwater (Casentini et al. 2010; Vinson et al. 2011).

In Mexico, high concentrations of As and F have been reported for at least 36 aquifers spanning from Sonora and Baja California, to Puebla and Morelos (Table 1). In the north, northeast, and central parts of Mexico, the origin of As and F has been identified as mainly geogenic and associated with alluvial aquifers filled in part with volcanic material (Alarcón-Herrera et al. 2001b; Planer-Friedrich et al. 2001; Ortega-Guerrero 2009; Reyes-Gómez et al. 2010; Camacho et al. 2011). A second source in importance includes contamination by mining activities (Mendez and Armienta 2003; Razo et al. 2004), while a third source is the genesis of geothermal solutions (Birkle and Merkel 2000; Espino-Valdés et al. 2009; Camacho et al. 2011). In some aquifers, the origin of As and F has been highly controversial, as is the case of the Comarca Lagunera, where both natural and anthropogenic sources have been reported as their origin (Del Razo et al. 1993); however, only few studies address the source, and the origin of these contaminants has not been definitely established. The range of values for As and F reported for northern Mexico and the Southwest of USA commonly include concentrations above the recommended limits of 0.025 mgL^{-1} As and 1.5 mgL^{-1} F, in some places even reaching values as extreme as 11 mgL^{-1} As in the Comarca Lagunera in the Durango-Coahuila border, La Casita in Chihuahua, or Los Azufres in Michoacán (Del Razo, et al. 1993; Birkle and Merkel 2000; Ochoa Reyes et al. 2009). In the case of F, extreme values of 5 to 9.7 mgL^{-1} have been found in the states de Chihuahua, Aguascalientes, and Durango (Alarcón-Herrera et al. 2001b; Hernández-

Montoya et al. 2003; Mahlknecht et al. 2008). Co-occurrence of As and F has been reported for localities nearby our study area, in the Comarca Lagunera ($r^2=0.52$), Zacatecas ($r^2=0.91$), and San Luis Potosi ($r^2=0.68$), all with $p<0.05$ (Del Razo et al. 1993; Planer-Friedrich et al. 2001; González Dávila 2011; González Dávila et al. 2012).

A better understanding of the origin of contaminants and the hydrology of the aquifers are key factors toward implementing preventive as well as corrective measures in areas where groundwater supplies most of the drinking water to the population. The studies mentioned above each covered relatively small areas where high concentrations have been historically reported, leaving in between gaps in knowledge that impede a regional-scale view of possible contaminant sources and flow paths. The results obtained in this study will fill in some gaps, helping in the identification of possible sources and processes responsible for the presence of As and F applicable at a regional scale for alluvial aquifer systems that are common in arid lands.

In the southwest and central Chihuahua, high As and F concentrations have been found in groundwater and also in the river traversing it, the Rio Chuvíscar (Rodríguez Pineda et al. 2002; Reyes-Gómez et al. 2010). The content of As along the Rio Chuvíscar was found to increase downstream, and the main source of As was tied to wastes from urban centers and industries (Rodríguez Pineda et al. 2002), which may cause an increase in the concentration of As in the river channel sediments and therefore contribute to the contamination of the aquifer present at the influent zone of the Rio Chuvíscar (Chávez Aguirre 1993; Benavides et al. 2008; Hernández-García et al. 2008; Gutiérrez et al. 2009). Although the Rio Chuvíscar is an influent stream most of its length, it becomes an effluent stream at the in the southwest of Chihuahua city and the vicinity of the town of Aldama, making it difficult to infer the true origin and contributions of these contaminants. Because of the aforementioned problem, and with the purpose of validating the hypothesis that the origin of As and F in underlying aquifers is geogenic, the objectives of the study were set up to investigate the origin of As and F in groundwater and their co-occurrence, to better understand the hydrogeochemistry of the system, and to determine how much the levels of contamination of the aforementioned contaminants vary within a period of 7 years.

Table 1 Concentrations of F and As and their possible source in aquifers in Mexico

State	Range of values As (mgL ⁻¹)	Range of values F (mgL ⁻¹)	Origin	No. of wells	Reference
San. Luis Potosí	0.001–0.120	0.001–16.0	G	246	Ortega-Guerrero 2009
Chihuahua	0.034–0.344	0.800–9.70	G, Gth, A	35	Mahlknecht et al. 2008
San Luis Potosí	0.005–0.050	NA	G*	53	Planer-Friedrich et al. 2001
Aguascalientes	NA	1.500–5.100	G*	78b	Hernández-Montoya et al. 2003
San Luis Potosí	0.001–0.300	NA	G*	73	Carrillo-Rivera et al. 2002
Durango	NA	1.500–12.00	G*	74	Alarcón-Herrera et al. 2001a
Durango	0.005–0.167	NA	G	74	Alarcón-Herrera et al. 2001b
Chihuahua	0.001–0.045	NA	G	43	Reyes-Gómez et al. 2010
Chihuahua	0.015–0.370	NA	G, Gth, A	61	Espino-Valdés et al. 2009
Durango-Coah.	0.014–0.624	0.500–3.70	G, A*	128	Del Razo et al. 1993
San Luis Potosí	0.050–5.900	NA	A	7	Razo et al. 2004
Guanajuato	0.003–0.270	1.600–4.00	G, A	120	ESF-DMAE 2006
Chihuahua	NA	0.300–5.70	U	2	Ruiz-Payan et al. 2005
Chihuahua	7.000–11.00	NA	G*	1	Ochoa Reyes et al. 2009
Chihuahua	0.075–0.134	4.800–5.90	G, A	2	Piñón-Miramontes et al. 2003
Jalisco	0.014–0.260	NA	G, A	129	Hurtado-Jiménez and Gardea-Torresdey 2006
Sonora	0.003–0.048	NA	G*	2	Cantú-Soto et al. 2009
Sonora	0.018–0.062	0.500–3.50	G*	122	Westerhoff et al. 2004
Chihuahua	0.052–0.627	0.500–3.30	G*	24	Westerhoff et al. 2004
Chihuahua	0.002–0.220	NA	G, A	127	Arreguin- Cortéz et al. 2010
Baja California	0.043–0.244	NA	A	9	Naranjo-Pulido et al. 2000
Hidalgo	0.059–0.400	NA	A, G	5	Armienta and Segovia 2008
Puebla	0.003–0.760	NA	G	D	González Partida et al. 2001
Tlaxcala	0.014–0.940	NA	G, A	14	Briones Corona et al. 2009
Zacatecas	0.015–0.405	1.050–3.09	G, A	16	González Dávila 2011
Michoacán	5.100–24.00	9.000–17.00	Gth	36	Birkle and Merkel 2000

G geogenic, A anthropogenic, Gth Geothermic, G* possible geogenic, U unknown, NA not available

^a Water storage ponds

^b Household samples

2 Materials and Methods

2.1 Area of Study

The study was conducted in an area encompassing three contiguous aquifers: Tabalaopa–Aldama (ATA), Aldama–Dolores (AAD), and Laguna de Hormigas (ALH), an area with coordinates between 28°47' to 28°56' N and 105°57' to 106°05' W (Fig. 1) that will be henceforth referred to as VTAD. The aquifers are distributed under the valleys of Tabalaopa, Aldama, and

Dolores, which are separated by two small mountain ranges, El Cuervo and La Gloria. The valleys of Tabalaopa, Aldama, and Dolores have different draining regimes; the river Chuisca drains the valleys of Tabalaopa and Dolores while the Aldama valley has internal drainage, therefore forming a playa (El Cuervo). The climate is classified as arid with summer rains (García 2003) and has an annual mean temperature of 15.5 °C. The highest monthly mean temperatures occur in June, July, and August with an average of 27 °C, whereas the coldest temperatures occur in

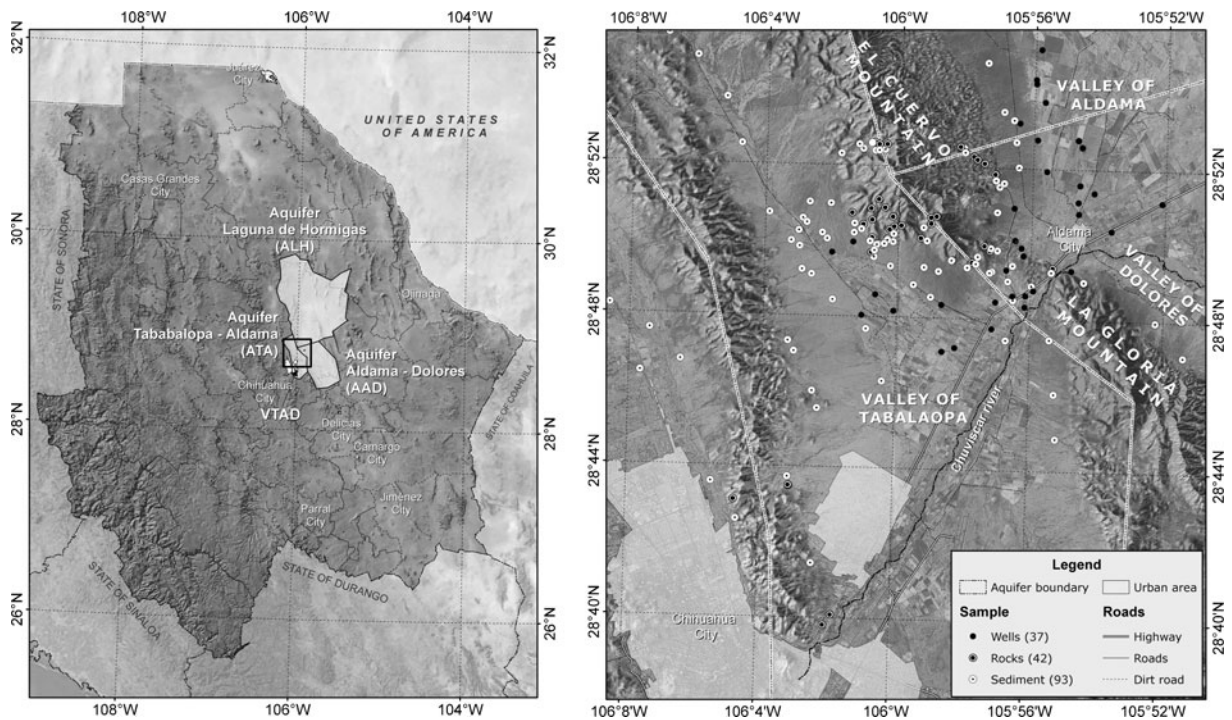


Fig. 1 Location of area of study

January with a mean value of 10 °C. The annual precipitation is 338 mm, with an evaporation rate above 2,400 mm (CONAGUA 2005). The elevations vary between 750 and 1,580 m above sea level.

The vegetation cover and land use are predominately xeric shrublands and pasture grasslands (Rzedowski 1983); the latter are used extensively in cattle grazing, although a small part of the study area is irrigated and grows pecan trees, alfalfa, cotton, and shade trees. The latter trees have been planted in support of recreational activities.

The three interconnected alluvial aquifers (ATA, ALH, and AAD) belong to the non-confined type for most of their extent, except in a few locations where they underlie or intertwine with clay lenses. These clay lenses have thicknesses up to 100 m and extend over large areas, which result in conditions of confinement (CONAGUA 2008).

ATA Aquifer This aquifer is composed from Quaternary alluvium; it is highly permeable with $0.012 \text{ m}^2 \text{ s}^{-1}$ transmissivity and a mean recharge rate of $76.5 \text{ Mm}^3 \text{ year}^{-1}$. This aquifer has a thickness of about 400 m that thins out to 200 m toward the valley of Aldama, at which

point the permeability becomes medium–high (Pérez Arambula 1996; Cruz Medina 2005). The total dissolved solid (TDS) values in the ATA aquifer vary between 500 and $2,000 \text{ mgL}^{-1}$ (CONAGUA 2008). The annual mean extraction of groundwater is 65.6 Mm^3 , drawn from 148 wells.

ALH Aquifer The transmissivity of the ALH aquifer is $0.0046 \text{ m}^2 \text{ s}^{-1}$, and the mean recharge rate for this aquifer is $25.6 \text{ Mm}^3 \text{ year}^{-1}$. The annual extraction volume is 1.5 Mm^3 . The water quality is mostly of good quality, with values of TDS between 400 and 800 mgL^{-1} except in the vicinity of the Aldama narrows at the convergence of the ALH and ATA aquifers, where the values increase up to $2,500 \text{ mgL}^{-1}$ (CONAGUA 2008).

AAD Aquifer This non-confined aquifer is composed of Quaternary alluvial and colluvial sediments and contains abundant lithic fragments of volcanic the volcanic rhyolite and tuff as well as of conglomerate and limestone. It has a transmissibility of $0.0033 \text{ m}^2 \text{ s}^{-1}$ and a mean recharge rate of $61 \text{ Mm}^3 \text{ year}^{-1}$. The thickness is about 300 m, and the mean extraction volume is about

20.9 Mm³ drawn from 128 wells (CONAGUA 2007). TDS values range between 300 to 500 mgL⁻¹, yielding the best quality water of the three aquifers.

The rocks that outcrop in the VTAD are igneous and sedimentary (Handschy and Dyer 1987) and are exposed in the La Gloria and El Cuervo mountains (Fig. 1). The rocks that predominate are rhyolitic tuffs, limestones, and shales in this order. Rhyolites, emplaced during the Tertiary, outcrop in both the El Cuervo and La Glorias mountains and are also the dominant lithology of the Sierra Madre Occidental, which occupies the western flank of the state of Chihuahua. The El Cuervo mountain is also characterized by intense deformation of its strata and for outcrops that have been dated as being between 1,025 and 1,037 million years old (INEGI 2004).

2.2 As and F in Rocks and Sediments

Between June of 2004 and June 2010, 42 rock and 93 sediment samples were collected throughout the study area (Fig. 1). Sediment samples were collected from the top 20 cm of depth and the rocks directly from fragments found on the ground (at least 5 kg sample). Rocks were taken to the laboratory where they were crushed and pulverized. Powdered samples were sent to a partner laboratory where they were digested and analyzed for As using an ICP spectrometer in accordance with the standard method EPA3050B. Ten sediment samples collected by the Servicio Geológico Mexicano and analyzed using the same standard methodology as above were added to the data set. The EPA3050B method applies to metals and does not apply for F, for which F was not determined in sediments; it was determined only in rock samples (petrographically) as described below.

Petrographic analyses were performed to 13 selected subsamples of rock to estimate the As and F concentrations based on their mineral content. The petrographic analyses included both polarized microscopy and X-ray powder diffraction, the latter utilizing a Siemens X-ray diffractometer model D-500. F was detected as the mineral fluorapatite. Petrographic methods were not as applicable as they were to F in order to determine As content since most of the As is present as volcanic glass. The total As content was instead determined by atomic absorption spectrophotometry after digestion of pulverized samples.

All sampling locations were georeferenced. The larger number of As samples allowed a contour map of As

content to be built, using the method of interpolation of square distances utilized in geostatistical techniques (Fig. 2). The highest concentrations (As > 300 mgkg⁻¹) were observed on the western flank of the El Cuervo Mountain and also on the northeast edge of the La Gloria Mountain (200–300 mgkg⁻¹), while the lowest values (As < 100 mgkg⁻¹) corresponded to the valley floors of VTAD.

2.3 As and F in Groundwater

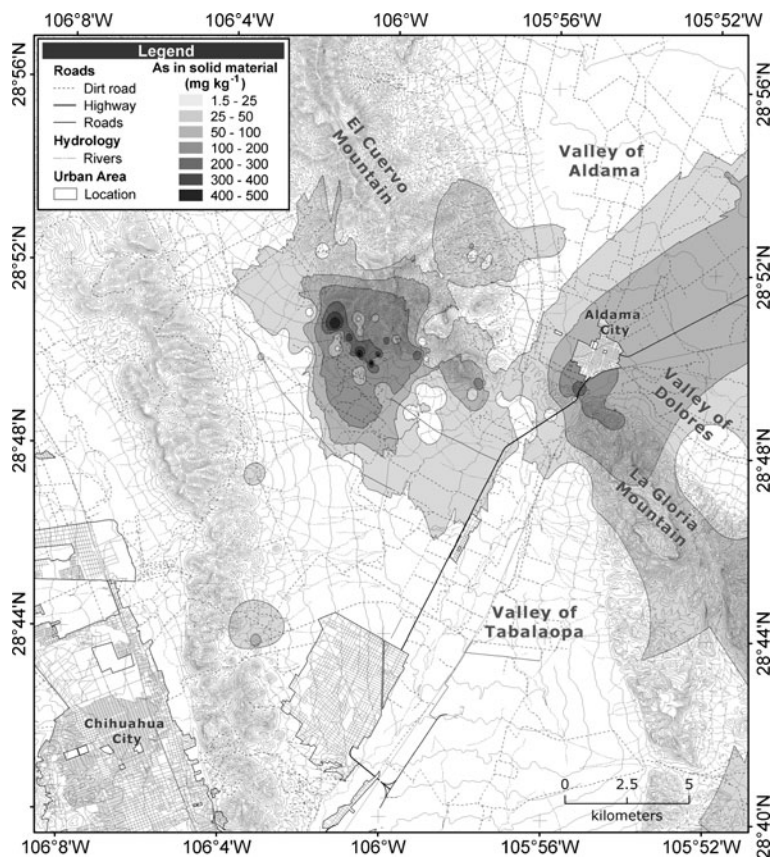
Samples collected in 2003 were analyzed for As only, while samples collected in 2007 and 2010 included analyses of F in addition to As (a total of 37 wells sampled). Arsenic levels in groundwater were determined using an ICP spectrometer in accordance with the standard method EPA3050B. The concentration of F was determined using an ion-selective electrode (ISE 9609BNWP-ThermoscientificTM) that was previously calibrated with standard solutions according to the method ASTM D 1179. At the time, groundwater samples were taken, the temperature (*T*), pH, redox potential (ORP), and electrical conductivity (EC) were measured, and their depth to the water table was recorded (Table 2). TDS were estimated from EC values using a factor of 0.65 mgL⁻¹/Scm⁻¹, reported for the Rio Conchos (Miyamoto et al. 1995). After 3 years from the first sampling, 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 except for ORP. During 2010, these wells were again sampled, and this time ORP was determined. 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 simple regression analysis was performed, using significance criteria for the coefficient of determination as well as its probability of error (Mayer and Butler 1993).

3 Results

3.1 As and F in the Solid Phase

The rock samples collected consisted of rhyolitic tuffs, felsic volcanic rocks, and shales. The dominant minerals in these rocks were, from most to least abundant, quartz, orthoclase, and volcanic glass (>25 %), followed by albite, sanidine, tridymite, clay minerals such as illite

Fig. 2 Spatial distribution of As content in rock, soil, and sediment



and montmorillonite (10–25 %), and in lesser amount biotite and hematite (0.1 to 10 %), as shown in Table 3. The As content of these rocks covered a broad range of values, from 2.3 to 540 mg kg⁻¹. Small amounts (0.1 to 1 %) of fluorapatite (Ca₅(PO₄)₃F) were detected in eight out of 13 rock samples, and although not a quantitative determination, even under the conservative assumption of 0.1 %, it would amount to a F content of 41 mg kg⁻¹.

3.2 Groundwater Flow Path

Potentiometric levels were used to generate a water table contour map, shown in Fig. 3. According to these values, the groundwater moves from the west through the Aldama narrows and then northeast. Although determining the recharge areas were not a part of this study, the topography of basin and range suggest that recharge likely takes place at the base of the mountains that surround the VTAD, where faults and/or alluvial fans are present. Alluvial fans are comprised of permeable, unconsolidated material (Pérez Arambula 1996; CONAGUA, 2007) that promotes infiltration

in these zones of bajada (nearly flat surface area consisting of confluent alluvial fans that make up the piedmont slope) and directs the flow toward the Rio Chuvísar.

3.3 Content and Evolution of As and F in Liquid Phase

From the 34 wells sampled in 2004, nine surpassed the 25- μgL^{-1} As, eight had concentrations between 20 and 24 μgL^{-1} (Fig. 4), and only ten had a concentration lower than the international maximum contaminant level (MCL) of 10 μgL^{-1} As. Wells with As concentration above 25 μgL^{-1} clustered in the south and northeastern parts of the VTAD, which correspond to areas more heavily pumped and near the town of Aldama. Three years later (in 2007), the As content decreased slightly for most wells, although four wells from the area of high As content that was identified in 2004 still had As concentrations above 25 μgL^{-1} . In 2010, the trend reversed and As concentrations increased

Table 2 Concentrations of F and As, temperature, pH, electric conductivity, and depth to water table in wells sampled within the VTAD

Well no.	June 2004						June 2007						February 2010					
	As (mg L ⁻¹)	T (°C)	pH	CE (μS cm ⁻¹)	Depth (m)		As (mg L ⁻¹)	T (°C)	pH	CE (μS cm ⁻¹)	Depth (m)		As (mg L ⁻¹)	T (°C)	pH	CE (μS cm ⁻¹)	Depth (m)	
1	n.d.	24.0	7.38	966	41.0	n.d.	n.d.	25.0	7.67	680	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
7	n.d.	25.0	7.40	690	53.4	n.d.	n.d.	25.0	7.82	570	69.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
10	0.027	25.8	7.71	576	87.9	0.005	0.92	23.0	7.47	710	103.0	1.06	0.008	23.2	7.42	989	120.0	
11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	21.4	7.27	1,027	n.d.	
14	0.028	31.4	7.46	871	42.0	0.026	3.30	30.0	7.37	740	58.0	4.40	0.034	20.2	7.46	889	79.0	
16	0.004	24.0	7.77	1,049	45.0	0.005	0.96	21.0	7.31	980	54.0	1.91	0.004	18.1	7.34	1,068	102.0	
17	0.026	33.1	7.55	659	44.7	0.024	3.66	33.0	7.22	520	50.6	4.47	0.021	26.4	7.46	705	51.6	
18	n.d.	29.5	7.88	831	44.0	n.d.	n.d.	30.0	7.47	490	50.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
20	0.020	26.0	7.56	578	69.7	0.019	2.34	33.0	7.73	410	71.0	3.62	0.025	16.6	7.77	535	130.5	
21	0.035	26.5	6.51	809	32.0	0.034	3.02	25.0	7.71	870	36.7	3.94	0.039	22.0	7.90	879	69.0	
25	0.027	21.0	7.16	2,320	5.5	n.d.	2.2	23.0	7.59	1,400	7.0	4.55	0.030	12.9	7.16	2,670	12.0	
28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18.3	7.57	1,843	13.0	
30	0.033	23.0	7.14	2,990	4.0	0.027	3.22	24.0	7.24	1,940	6.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
32	0.023	27.5	6.50	510	51.4	0.017	2.74	26.0	7.56	550	57.5	4.07	0.025	22.2	7.71	511	68.0	
33	0.022	30.0	6.47	627	80.0	0.009	2.72	30.0	7.54	490	78.2	3.59	0.026	26.1	7.58	629	90.4	
35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	26.0	7.73	587	80.8	
36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.33	1,037	90.0	
37	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	23.0	7.65	531	100.0	

Analytical errors: T (±0.1 °C); pH (±0.05); EC (±10 μS cm⁻¹)

Table 3 Mineral composition of rocks and their As content

Sample no. (rock)	Proportion of minerals (%)				As (mgkg ⁻¹)
	>25	10–25	1–10	0.1–1	
ECWR-66 (tertiary rhyolite)	Orthoclase Quartz Volcanic glass	Tridymite	Biotite	Fluorapatite	514.2 (14.7)
ECWR-69 (tertiary rhyolite)	Orthoclase Quartz Volcanic glass		Hematite Biotite		365.5 (14.2)
ECWR-93 (tertiary rhyolite)	Sanidine Volcanic glass	Quartz	Biotite Hematite		290.4 (10.1)
ECWR-77 (tertiary rhyolite)	Orthoclase Quartz Volcanic glass		Biotite	Fluorapatite	243.5 (8.04)
LMER-91 (tertiary rhyolite)	Sanidine Quartz Volcanic glass	Biotite	Hematite	Fluorapatite	173.4 (6.74)
ECWR-87 (tertiary rhyolite)	Orthoclase Volcanic glass	Quartz	Hematite	Fluorapatite	60.2 (4.80)
ECWR-30 (tertiary rhyolite)	Volcanic glass	Orthoclase Quartz	Biotite Montmorillonite Calcite, hematite		36.2 (1.67)
ECWR-44 (felsic volcanic)	Quartz	Hematite	Orthoclase Hornblende		30.7 (1.00)
ECWR-43 (shale)	Quartz Illite	Albite Montmorillonite	Hematite Kaolinite	Fluorapatite	28.6 (0.085)
NDWR-79 (tertiary rhyolite)	Quartz Volcanic glass	Albite	Hematite Calcite Biotite		15.8 (0.80)
ECWR-79 (tertiary rhyolite)	Sanidine Quartz Volcanic glass	Albite	Hematite		11.0 (0.04)
ECWR-27 (tertiary rhyolite)	Quartz Volcanic glass	Orthoclase	Biotite	Magnesite Fluorapatite	3.4 (0.30)
ECWR-80 (tertiary rhyolite)	Orthoclase Quartz Volcanic glass	Albite Biotite	Hematite Hornblende Montmorillonite	Fluorapatite	2.3 (0.09)

Errors of determination shown in parenthesis

again for the most part; this time, seven wells surpassed 25 µgL⁻¹ As (wells nos. 14, 20, 21, 25, 28, 32, 33). From the perspective of the international MCL, most of the wells analyzed in 2007 and 2010 surpassed the recommended limit for drinking water use.

Wells that reported high As content in 2004 were analyzed for F concentrations in 2007 and 2010. Out of 13 wells analyzed in 2007, ten surpassed the recommended limit of 1.5 mgL⁻¹ F (Fig. 5), reaching a total

average concentration value of 2.77 mgL⁻¹. Only four out of 24 total measurements made during these two sampling events were found to be below the recommended limit. The highest F levels were detected in the transition zone of ATA toward 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

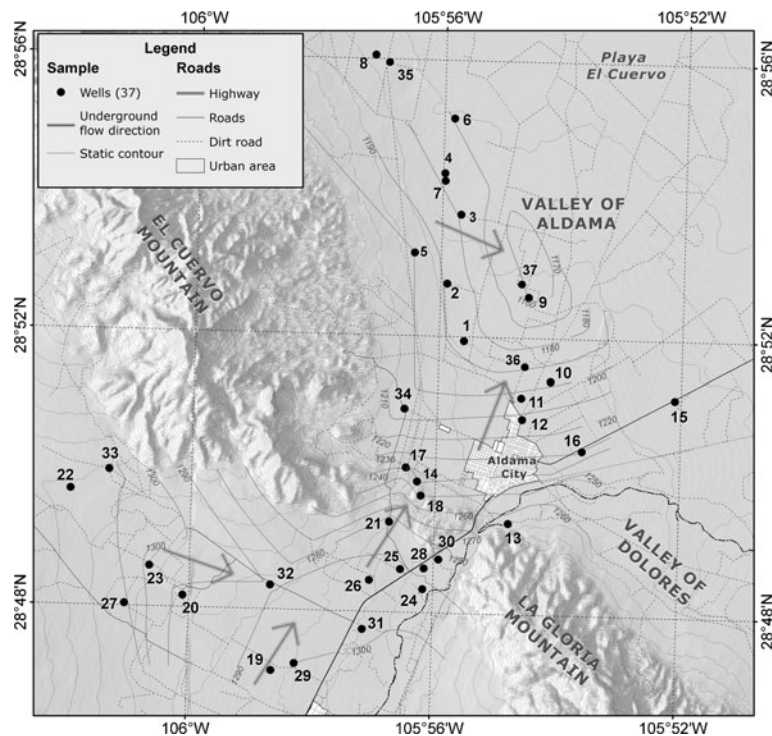


Fig. 3 Groundwater flow and location of wells sampled

MCL and was up to 106 % above their previously measured concentration (well no. 25).

3.4 Conceptual Model

In spite of the complexity involved in generating a model to represent the As and F contamination in aquifers (Reyes Cortés 1997; Bhattacharya et al. 2007; Benavides et al. 2008; Hernández-García et al. 2008), a hypothetical model for the VTAD was attempted here after adapting a previous model (Reyes-Gómez et al. 2010) to the verified contribution from rocks (As in crystal lattice of rhyolites, presence of fluorapatite in rocks collected within the study area) and the presence of F in groundwater (Fig. 6). The model states that the lithologies present at VTAD are able to release significant amounts of As and F (Table 2; Fig. 2) after a series of weathering processes such as fragmentation and dissolution and that the hydrogeochemical processes involved in the release of both As and F are similar. Other processes may have affected the form and the concentration at which these contaminants are present include adsorption/desorption from clays and iron oxides (Kau et al. 1997; Saalfeld and Bostick 2010), oxidation of any arsenopyrite present in the soil (Alaerts and Khouri

2004), and reaction to groundwater chemistry. Within the permeable material of the VTAD, liberated As and F ions may fixate via adsorption (Appelo and Postma 1993) to the surface of solids such as clay minerals which abound in the subsurface up to 100–200 m depth (Martínez Leyva et al. 1979), as well as to other types of solids, such as alluvium and clays, as shown in Fig. 6. Each of these has a preference for a particular solid surface and has also its own optimal sorption/desorption conditions (Gupta and Chen 1978; Plant et al. 2004). For example, As has great affinity for clay minerals and iron oxides (Smedley and Kinniburgh 2002; Ruiz-Payan et al. 2005; Hurtado-Jiménez and Gardea-Torresdey 2006; Armienta and Segovia 2008) whereas F shows preference for materials rich in aluminum such as bauxite and kaolinite (Peter 2009; Kau et al. 1997; Saxena and Ahmed 2003). These preferred materials (clays, iron oxides, and aluminum-rich silicates) comprise a large part of the fill of these alluvial aquifers.

4 Discussion

A physical property that greatly influences the model is the granular nature of the alluvial fans/fill that comprises

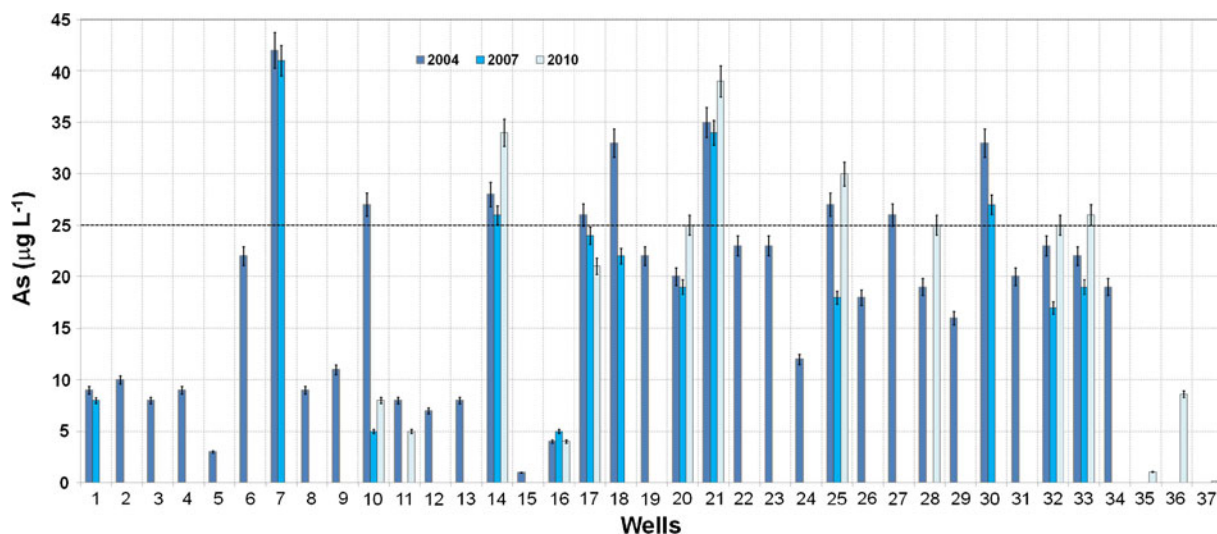


Fig. 4 Concentration for As in wells for the three sampling events

the aquifer (Pérez Arambula 1996; Rodríguez Pineda 2000; CONAGUA 2007). Both highly fractured exposed volcanic rock and alluvial fans at the base of the sierras (which are more conspicuous at the eastern flank of El Cuervo Mountain) likely recharge the aquifer. The volcanic (rhyolite) and sedimentary (shale) rocks (Martínez Leyva et al. 1979) that make up the alluvial fans contain, mixed with fine material, fragments of volcanic glass with high As content and fluoroapatite. Furthermore, the alluvial fans contain coarse material and dominate the bajadas of the VTAD and may extend to the plains near the main stream channel of the valley; these are important recharge zones that reinforce this

conceptual model (Chávez Aguirre 1993) by promoting infiltration and by facilitating the transport and dissolution of As and F into the aquifer, where further reactions take place, among them cationic exchange with fill material and with aqueous solutions (Wang et al. 2009).

The relation found for F in the presence of As is marked by a positive trend for both of the time periods, with $r=0.738$ in 2007 and $r=0.832$ in 2010 (probability of error EM=0.69 and 0.55, with $p<0.001$, in both cases), supporting the hypothesis of a co-occurrence of As/F (Scanlon et al. 2009). Considering that the wells were sampled in both June 2007 and February 2010 (Fig. 7), the co-occurrence stands at the same significant

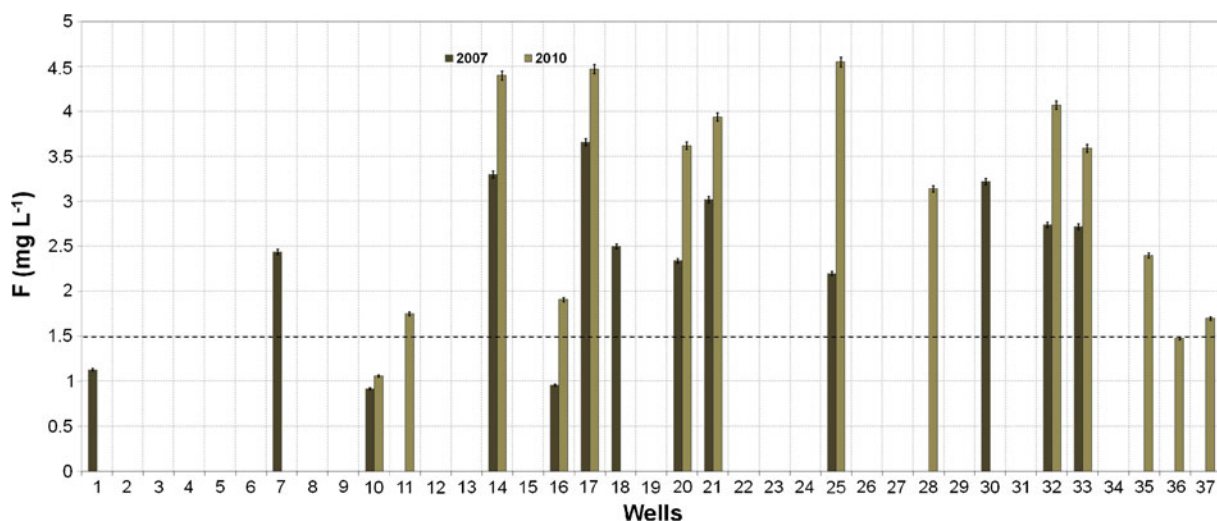


Fig. 5 Concentration of F in wells for 2007 and 2010

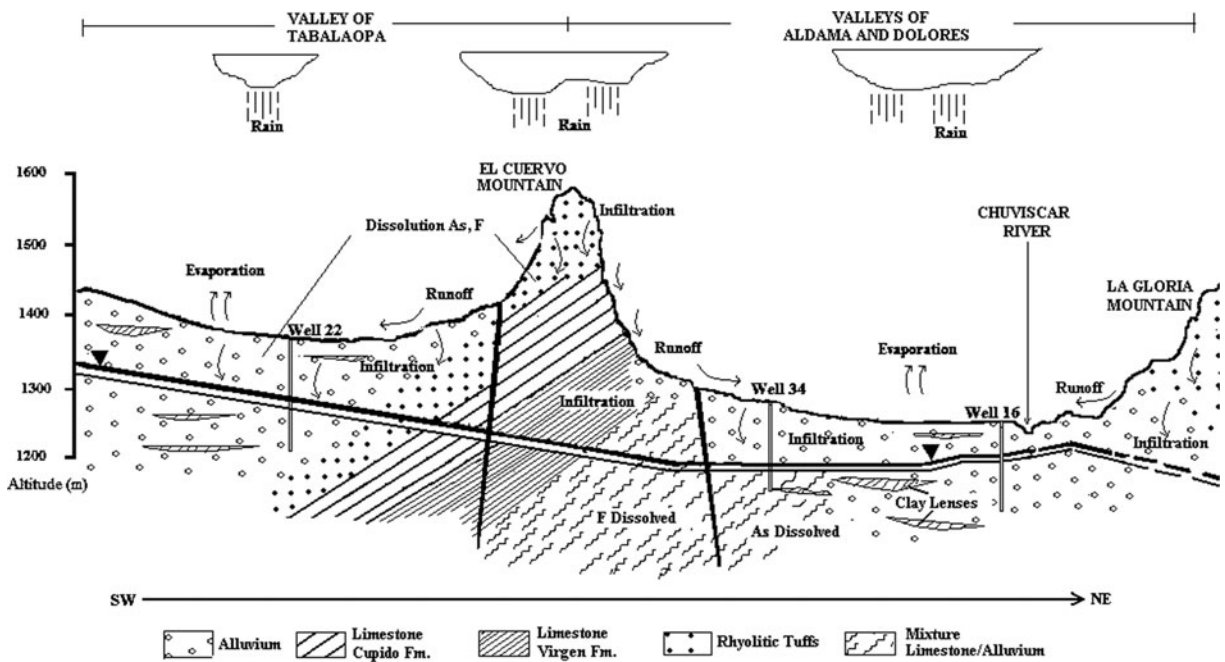


Fig. 6 Conceptual geochemical model of As and F mobility in the VTAD. The profile follows the flow of groundwater from left to right (SW to NE in Fig. 3)

level, with a value of r of 0.718 ($N=28$) and a low probability of error ($EM=0.50$ and $p<0.001$). A seasonal effect for groundwater temperature affecting the As/F correlation has been reported by Wang et al. (2009), but our data are insufficiently large to confirm this effect. Hence, it is necessary to keep monitoring yearly the concentrations of As and F in these wells in order to confirm if this relationship is permanent.

The climatic conditions of the study area cause high temperatures of the surface water during the summer ($T>30\text{ }^{\circ}\text{C}$) and low temperatures in the winter ($T<15\text{ }^{\circ}\text{C}$), and it is also prone to intense droughts (Reyes-Gómez et al. 2006; Núñez-López et al. 2007). Increased groundwater withdrawals during extremely dry or/and hot days promote the enrichment of As and F in the groundwater (Armienta and Segovia 2008; Wang et al. 2009), while

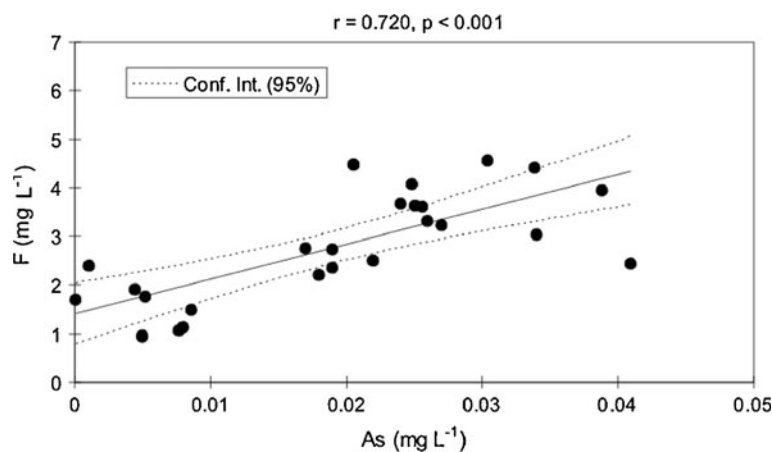


Fig. 7 Change of As concentration with F concentration

high temperatures at the top parts of the aquifer especially in the summer months may favoring further dissolution of As and F (Deming et al. 1992; Carrillo-Rivera et al. 2002; Espino-Valdés et al. 2009). The potentiometric levels in 2007 did not change drastically compared to those measured in 2004, but they dropped considerably in 2010 as compared to either 2004 or 2007, indicating smaller recharge and/or larger groundwater withdrawals for 2010. For example, between 2004 and 2010, the depth to the water table in well no. 10 dropped from 88 to 120 m and well no. 20 from 70 to 130 m.

At the tri-annual scale, the dynamic of the aquifer contamination seemed to evolve in small steps during the times of sampling. For example, at the zone of transition from the Tabaalopa Valley toward Aldama, differences in As concentrations between 0.090 and 0.022 mgL⁻¹ were observed, maybe as a result of varying water quality in the horizon from which water is extracted and the increased depth to water table, e.g., for well no. 16, it dropped from 54 m in 2007 to 102 m in 2010. The As levels in 2010 were higher in six out of nine wells while the F levels increased in all nine. The location of these wells near urban areas and/or the Chuvíscar river (Fig. 3) suggests dissolution of As or contributions from external sources such as runoff from upstream the rivers Chuvíscar and Sacramento (Gutiérrez et al. 2009) or the effects of the elevated dissolution of fragmented minerals by mining activities recently introduced. It is also possible that this water was older than that from other parts of the aquifer and that the prolonged contact of the water and rock rich in As and/or F had produced a more concentrated solution. With respect to F, the increase in concentrations may be the result of groundwater level decline during periods of drought (Pauwels and Ahmed 2007) that promote evaporation and increased groundwater extractions (e.g., wells nos. 10, 17, 20, and 21) and which may be exposing deeper layers with a higher F concentration. Other possible contributions include contaminated water reaching the aquifers near urban areas (wells nos. 16, 25, and 30), the Chuvíscar river (wells nos. 16, 25, and 30), or agricultural areas (wells nos. 10, 14, 17, 20, 21, 32, and 33) and remobilization of contaminants after drilling of new wells (Saxena and Ahmed 2003).

At the dates of the analyses (2004, 2007, and 2010), the pH varied between 6.5 and 7.9 (Table 3) and ORP between 156 and 313 mV, which allowed the identification of the possible ionic species of As that predominated in the water as HAsO₄²⁻, which coincides with

studies conducted in other semiarid regions (Saxena et al. 2004). The EC values fluctuated between 410 and 2,670 μS cm⁻¹; such difference indicates spatial and temporal variations of salinity within the aquifers, most likely due to contributions after dissolutions of Ca and Na salts of surface horizons within the VTAD during wet years (Chávez Aguirre 1993) as the EC dropped in 2007 in some wells and then increased again in 2010. The TDS during the first year of the study were found in general at low levels indicating that the water can be used directly by cattle to drink and in agriculture, except for a few wells near the Rio Chuvíscar (wells nos. 16, 25 and 30), where the values of TSD were higher than 500 mgL⁻¹. The spatial and temporal variations in the water chemistry can also imply contamination of anthropogenic origin such as domestic wastewater discharge into the Rio Chuvíscar. Infiltration and runoff of water contaminated upstream of the river and into the aquifer as source of As/F cannot be ruled out either, as there are agricultural and industrial practices that use herbicides and pesticides containing As (Rodríguez Pineda et al. 2002; Bhattacharya et al. 2007). In the case of VTAD and until 2008, there were no industries or new agriculture fields; however, in the last few years, two mining companies initiated operations and have been fragmenting the rocks of the western flank of El Cuervo Mountain. Also, within the northern side of the ALH aquifer, the land use has been recently changed; new settlements of Menonite farmers began plowing and cultivating the land using an agriculture-intensive technique and water from the aquifer to irrigate their crops (CONAGUA, 2010). All these new changes in industrial and agricultural practices could be affecting the patterns of flow and contamination. These possible new paths of As and F contamination of the system, as well as the possibility of contribution of contaminants by wind-blown material, need to be clarified a posteriori in future investigations, in order to take preventive or corrective measures to assure that the water quality is acceptable for different uses and also to protect the environment, for example, monitoring the amount of groundwater withdrawal and by better planning any newer human settlements.

The results obtained in this study allowed for the detection of the risk of exposure of the inhabitants by drinking water with high concentration of both contaminants in this zone and in particular of the town of Aldama and its surroundings. For example, average concentrations of 0.035 mgL⁻¹ As and 3–4 mgL⁻¹ F (well

no. 21, Figs. 4 and 5) detected at a shelter for children located 1 km southeast of Aldama prompted the shelter to install a reverse osmosis filter to treat its well water.

5 Conclusions

This study demonstrated the presence of As and F above the recommended limits for drinking water in many of the wells analyzed within the VTAD and identified of the parts of VTAD where the concentrations are persistently the highest. The geochemical characteristics of rocks, sediment, and groundwater supported the hypothesis of geogenic origin of As and F in the system, based on the presence of As in the rhyolite and shales that outcrop in the area, which also contain secondary accumulation of fluorapatite (source of F). A significant co-occurrence of As and F was found. The relatively stable As and F concentrations with time indicated a chemical stability with the surrounding rocks and supported the theory about the geogenic origin of the contaminant. A few wells that departed from reporting stable concentrations plotted close to the town of Aldama, an area of intensive groundwater extraction, and also where the highest concentrations of As and F were found. The results draw attention to the necessity to widen the studies in order to find other possible source of contamination, especially from the fragmentation and dispersion of mining wastes, wind derived material, and runoff which are generated, at least in part, by local industries, as well as changes in land use in the northern and central part of this alluvial system.

Acknowledgments The study was supported by a grant from the Secretaría del Medio Ambiente y Recursos Naturales (SEMARNAT) and the Consejo Nacional de Ciencia y Tecnología (CONACYT) and received partial support by the Instituto de Ecología, A.C. (INECOL), the Centro de Investigación y Materiales Avanzados (CIMAV), and Missouri State University (MSU). Our special thanks to I.Q. Alejandro Benavides (CIMAV) for conducting the chemical analyses. Authors are thankful to anonymous reviewers for their valuable comments.

References

- Alaerts, G. J., & Khouri, N. (2004). Arsenic contamination of groundwater: mitigation strategies and policies. *Hydrogeology Journal*, *12*, 103–114.
- Alarcón-Herrera, M. T., Montenegro, I., Romero-Navar, P., Martín-Domínguez, I. T., & Vázquez, R. (2001a). Contenido del arsénico en el agua potable del Valle del Guadiana en México. *Ingeniería Hidráulica en México*, *XVI*(4), 63–70.
- Alarcón-Herrera, M. T., Martín-Domínguez, I. R., Trejo-Vazquez, R., & Rodríguez-Dozal, S. (2001b). Water fluoride, dental fluorosis, and bone fractures in the Guadiana Valley of Mexico. *Fluoride*, *34*(2), 139–149.
- Appelo, C. A. J., & Postma, D. (1993). *Geochemistry, groundwater and pollution*. Rotterdam: Balkema.
- Armienta, M. A., & Segovia, N. (2008). Arsenic and fluoride in the groundwater of Mexico. *Environmental Geochemistry and Health*, *30*, 345–353.
- Arreguin-Cortéz, F. I., Chávez Guillén, R., & Soto Navarro, P. R. (2010). Una revisión de la presencia de arsénico en el agua subterránea de México. *Revista Taloc AMH*, *45*, 1–11.
- Benavides, A., Moreno, M., Sosa, M., Puga, S., Alcalá, J., & Quintana, C. (2008). Evaluación de la calidad del agua en las principales Lagunas del Estado de Chihuahua. *Revista Latinoamericana de Recursos Naturales*, *4*(2), 84–88.
- Bhattacharya, P., Welch, A. H., Stollenwerk, K. N., McLaughlin, M. J., Bundschuh, J., & Panaullah, G. (2007). Arsenic in the environment; biology and chemistry. *Science of the Total Environment*, *379*, 109–120.
- Birkle, P., & Merkel, B. (2000). Environmental impact by spill of geothermal fluids at the geothermal field of Los Azufres, Michoacán, Mexico. *Water, Air, and Soil Pollution*, *124*, 371–410.
- Brones Corona, E., García Nieto, E., Juárez Santillán, L. F., Juárez santacruz, L., García Gallegos, E., Vazquez Cuechecha, O. G. (2009). Determinación de Arsénico en Agua del Sistema Hidrológico: Zahuapán-Atoyac. VIII Congreso Internacional de Ciencias Ambientales, XIV Congreso Nacional de Ciencias Ambientales. Academia Nacional de Ciencias Ambientales, Santa Cruz, Tlaxcala, México. CA 221-C, http://www.uaemex.mx/Red_Ambientales/docs/congresos/TLAXCALA%202009/MEMORIAS/Contaminacion%20Ambiental%20CARTEL/CA%20221-C.pdf.
- Camacho, L., Gutiérrez, M., Alarcón-Herrera, M. T., Villalba, M. L., & Deng, S. (2011). Occurrence and treatment of arsenic in groundwater and soil in northern Mexico and southwestern USA. *Chemosphere*, *83*, 211–225.
- Cantú-Soto, E. U., Harris, R., Ronerge, J., Klimecki, W. T., Félix-Fuentes, A., & Meza-Montenegro, M. M. (2009). Determinación de polimorfismos del gen Arsénico 3 Metiltransferasa (*As3MT*) asociado al metabolismo del arsénico en la población del Valle del Yaqui, Sonora, México. *Revista Latinoamericana de Recursos Naturales*, *5*(2), 155–160.
- Carrillo-Rivera, J. J., Cardona, A., & Edmunds, W. M. (2002). Use of abstraction regime and knowledge of hydrogeological conditions to control high-fluoride concentration in abstracted groundwater: San Luis Potosí basin, Mexico. *Journal of Hydrology*, *261*, 24–47.
- Casentini, B., Pettine, M., & Millero, F. (2010). Release of arsenic from volcanic rocks through interactions with inorganic anions and organic ligands. *Aquatic Geochemistry*, *16*, 373–393.
- Chávez Aguirre, R. (1993). *Hidrogeología Física y Química de la Porción Centro-Occidental del Valle de Tabalaopa-Aldama, Chihuahua*. M.Sc. thesis, Facultad de Ingeniería: Universidad Autónoma de Chihuahua.

- Chouhan, S., & Flora, S. J. S. (2010). Arsenic and fluoride: two major ground water pollutants. *Indian Journal of Experimental Biology*, 48, 666–678.
- CONAGUA, Comisión Nacional del Agua. (2007). *Determinación de la Disponibilidad de Agua en el Acuífero 0836 Aldama-San Diego, Estado de Chihuahua, Mexico*. México City: CONAGUA.
- CONAGUA, Comisión Nacional del Agua (2005). *Reporte Anual Hidrológico*, Mexico. México City: CONAGUA.
- CONAGUA, Comisión Nacional del Agua (2008). *Estudio de Disponibilidad de Agua en el Acuífero de Hormigas*, Mexico. México City: CONAGUA.
- CONAGUA, Comisión Nacional del Agua (2010). *Estadísticas del Agua en México*, Mexico. México City: CONAGUA.
- Cruz Medina, R. (2005). *Modelo Hidrogeoquímico del Arsénico en el Acuífero de Tabalaopa-Aldama-El Cuervo, Chihuahua, México*. M.Sc. thesis, Facultad de Ingeniería: Universidad Autónoma de Chihuahua.
- Del Razo, L. M., Corona, J. C., García Vargas, G., Albores, A., & Cebrián, M. E. (1993). Fluoride levels in well-water from a chronic arsenic area of northern Mexico. *Environmental Pollution*, 80, 91–94.
- Deming, D., Sass, J. H., Lachenbruch, A. H., & De Rito, R. F. (1992). Heat flow and subsurface temperature as evidence for basin-scale ground-water flow, north slope of Alaska. *Geological Society of America Bulletin*, 104, 528–542.
- Deng, S., Viswanathan, V., & Candelaria, D. (2006). Sol-gel derived mesoporous alumina for fluoride and arsenic removal from drinking water. *New Mexico Journal of Science*, 44, 183–202.
- Ecosystem Sciences Foundation (ESF)—Dirección de Medio Ambiente y Ecología (DMAE) (2006). Well water quality in San Miguel de Allende. Phase I: results and conclusions. 280 N 8th, St., Ste. 208 Boise, Idaho 83702. <http://www.ecosystemsciences.com/Portals/0/pdfs/Drinking%20Water%20Quality%20in%20San%20Miguel,%20Mexico.pdf>.
- Espino-Valdés, M. S., Barrera-Prieto, Y., & Herrera-Peraza, E. (2009). Presencia del arsénico en la sección norte del acuífero Meoqui-Delicias, del estado de Chihuahua, México. *Tecnociencia Chihuahua*, 3, 8–18.
- Farooqi, A., Masuda, H., & Firdous, N. (2007). Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. *Environmental Pollution*, 145, 839–849.
- García, E. (2003). Distribución de la precipitación en la República Mexicana. *Investigaciones Geográficas Boletín*, 50, 67–76.
- González Dávila, O. (2011). Water arsenic and fluoride contamination in Zacatecas Mexico: an exploratory study. In 8th international conference “Developments in Economic Theory and Policy.” The University of the Basque Country, Spain.
- González Dávila, O., Gómez-Bernal, J. M., and Ruiz-Huerta, E. A. (2012). Plants and soil contamination with heavy metals in agricultural areas of Guadalupe, Zacatecas, Mexico. In Srivastava, J. (Ed.). *Environmental contamination*. www.intechopen.com.
- González Partida, E., Tello Hinojosa, T., & Pal Verma, M. (2001). Interacción agua geotérmica-manantiales en el campo geotérmico de Los Humeros, Puebla, México. *Ingeniería Hidráulica en México*, XV(2), 185–194.
- Gupta, S. K., & Chen, K. Y. (1978). Arsenic removal by adsorption. *Journal of Water Pollution Control Federation*, 50(3), 493–506.
- Gutiérrez, M., Alarcón-Herrera, M. T., & Camacho, L. M. (2009). Geographical distribution of arsenic in sediments within the Rio Conchos Basin, Mexico. *Environmental Geology*, 57, 929–935.
- Handschy, J. W., & Dyer, R. (1987). Polyphase deformation in Sierra del Cuervo, Chihuahua, Mexico: evidence for ancestral Rocky Mountain tectonics in the Ouachita foreland of northern Mexico. *Geological Society of America Bulletin*, 99(5), 618–632.
- Hernández-García, Y., Sosa-Cerecedo, M., Moreno, M., Alcalá, J., & Puga, S. (2008). Evaluación de la contaminación por metales pesados y arsénico en sedimento en embalses del estado de Chihuahua, México. *Revista Latinoamericana de Recursos Naturales*, 4(2), 89–94.
- Hernández-Montoya, V., Bueno-López, J. I., Sánchez-Ruelas, A. M., García-Servín, J., Trejo-Vázquez, R., Bonilla-Petriciolet, A., & Márquez-Algara, C. (2003). Fluorosis y Caries Dental en Niños de 9 a 11 años del Estado de Aguascalientes, México. *Revista Internacional de Contaminación Ambiental*, 19(4), 197–204.
- Hurtado-Jiménez, R., & Gardea-Torresdey, J. L. (2006). Arsenic in drinking water in the Los Altos de Jalisco region of Mexico. *Revista Panamericana de Salud Pública*, 20(4), 236–247.
- INEGI, Instituto Nacional de Estadística Geográfica e Informática (2004). *Anuario Estadístico de Chihuahua, Mexico*. Aguascalientes: INEGI
- Kau, P. M. H., Smith, D. W., & Binning, P. (1997). Fluoride retention by kaolin clay. *Journal of Contaminant Hydrology*, 28, 267–288.
- Mahlknecht, J., Horst, A., Hernández, G., & Araventa, R. (2008). Groundwater geochemistry of the Chihuahua City region in the Rio Conchos Basin (northern Mexico) and implications for water resources management. *Hydrological Processes*, 22, 4736–4751.
- Martínez Leyva, P., De la Rosa Ambriz, A., Monsivais Santoyo, H., Charlez, J., Ramírez Baca, A., Bernal Prieto, M., Morales Montiel, A. (1979). *Estudio Geohidrológico del Valle de Chihuahua*. Reporte, Facultad de Ingeniería, Universidad Autónoma de Chihuahua.
- Mayer, D. G., & Butler, D. G. (1993). Statistical validation. *Ecological Modelling*, 68, 21–32.
- Mendez, M., & Armienta, M. A. (2003). Arsenic phase distribution in Zimapán mine tailings, Mexico. *Geofísica Internacional*, 42(1), 131–140.
- Miyamoto, S., Fenn, L. B., & Swietlik, D. (1995). *Flow, salts, and trace elements in the Rio Grande: a review*. College Station: Texas Agricultural Experimental Station.
- Naranjo-Pulido, A., Ortega-Rubio, A., Acosta-Vargas, B., Rodríguez-Mendez, L., Acevedo-Beltrán, M., Argüelles-Mendez, C. (2000). Mining activities and arsenic in a Baja California Sur Watershed. USDA Forest Service Proceedings RMRS-P-13. http://www.fs.fed.us/rm/pubs/rmrs_p013/rmrs_p013_392_394.pdf.
- NOM-127-SSA1-1994, Norma Oficial Mexicana. Salud ambiental (1994). Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización, Mexico.

- Núñez-López, D., Muñoz, C. A., Gadsden, H., & Reyes-Gómez, V. M. (2007). Characterization of drought at different time scales in Chihuahua, Mexico. *Agrociencia*, *41*, 253–262.
- Ochoa Reyes, J., Vidal Lozano, A., Lerma Santana, A., Gómez Reza, L., Reta Sánchez, A., & Fernández Escajeda, D. (2009). Arsenicismo subagudo y crónico en una población rural. *Dermatología Revista Mexicana*, *53*(2), 63–69.
- Ortega-Guerrero, M. A. (2009). Presencia, distribución, hidrogeoquímica y origen de arsénico, fluoruro y otros elementos traza disueltos en agua subterránea, a escala de cuenca hidrológica tributaria de Lerma-Chapala, México. *Revista Mexicana de Ciencias Geológicas*, *26*(1), 143–161.
- Pauwels, H., & Ahmed, S. (2007). Fluoride in groundwater: origin and health impacts. *Géosciences*, *5*, 68–73. <http://www.brgm.fr/dcenewsFile?ID=315>.
- Pérez Arambula, J. M. (1996). *Determinación de la Geometría del Acuífero Tabalaopa-Aldama, Chihuahua*. M.Sc. thesis, Universidad Autónoma de Chihuahua, Ingeniería.
- Peter, K. H. (2009). Defluoridation of high fluoride waters from natural water sources by using soil rich in bauxite and kaolinite. *Journal of Engineering Applied Sciences*, *4*, 240–246.
- Piñón-Miramontes, M., Bautista-Margulis, R. G., & Pérez-Hernández, A. (2003). Removal of arsenic and fluoride from drinking water with cake alum and a polymeric anionic flocculent. *Fluoride*, *36*(2), 122–128.
- Planer-Friedrich, B., Armienta, M. A., & Merkel, B. J. (2001). Origin of arsenic in the groundwater of the Rio Verde basin Mexico. *Environmental Geology*, *40*, 1290–1298.
- Plant, J. A., Kinniburgh, D. G., Smedley, P. L., Fordyce, F. M., & Klinck, B. A. (2004). Arsenic and selenium. In Yurekian & Holland (Eds.), *Treatise in geochemistry*, *9*(9). the Netherlands: Elsevier.
- Razo, I., Carrizales, L., Castro, J., & Díaz-Barriga, F. (2004). Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. *Water, Air, and Soil Pollution*, *152*(1–4), 129–152.
- Reyes Cortés, I. (1997). *Geologic studies in the Sierra Peña Blanca, Chihuahua, Mexic*. Ph.D. thesis, University of Texas at El Paso.
- Reyes-Gómez, V. M., Núñez-López, D., Muñoz, C. A., Rodríguez, J. A., Gadsden, H., & López, M. (2006). Caractérisation de la sécheresse hydrologique dans le bassin-versant du Río Conchos (État de Chihuahua, Mexique). *Science et Changements Planétaires Sécheresse*, *17*, 475–484.
- Reyes-Gómez, V. M., Alarcón-Herrera, M. T., Núñez-López, D., & Cruz-Medina, R. (2010). Dinámica del arsénico en el Valle de Tabalaopa-Aldama-El Cuervo, en Chihuahua, México. *Revista Latinoamericana de Recursos Naturales*, *6*, 21–31.
- Rodríguez Pineda, J. A. (2000). *A geophysical, geochemical and remote sensing investigation of the water resources at the City of Chihuahua, Mexico*. Ph.D. thesis, University of Texas at El Paso.
- Rodríguez Pineda, J. A., Pingitore, N. E., Keller, R. (2002) Determinación de la génesis de contaminantes geológicos y urbanos en agua subterránea aplicando análisis discriminatorio multivariado en Chihuahua, México. *XXVIII Congreso Interamericano de Ingeniería Sanitaria y Ambiental*. México.
- Ruiz-Payan, A., Ortiz, M., & Duarte-Gardea, M. (2005). Determination of fluoride in drinking water and in urine of adolescents living in three counties in Northern Chihuahua Mexico using a fluoride ion selective electrode. *Microchemical Journal*, *81*, 19–22.
- Rzedowski, J. (1983). *Vegetación de México*. México: LIMUSA, IPN.
- Saalfield, S. L., & Bostick, B. C. (2010). Synergistic effect of calcium and bicarbonate in enhancing arsenate release from ferrihydrite. *Geochimica et Cosmochimica Acta*, *74*, 5171–5186.
- Saxena, V. K., & Ahmed, S. (2003). Inferring the chemical parameters for the dissolution of fluoride in groundwater. *Environmental Geology*, *43*, 731–736.
- Saxena, V. K., Kumar, S., & Singh, V. S. (2004). Occurrence, behaviour and speciation of arsenic in groundwater. *Current Science*, *86*(2), 281–284.
- Scanlon, B. R., Nicot, J. P., Reedy, R. C., Kurtzman, D., Mukherjee, A., & Nordstrom, D. K. (2009). Elevated naturally occurring arsenic in a semiarid oxidizing system, Southern High Plains aquifer, Texas, USA. *Applied Geochemistry*, *24*, 2061–2071.
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, *17*, 517–568.
- SSA, Secretaría de Salubridad y Asistencia (2000). Modificación Norma Oficial Mexicana NOM-127-SSA1-1994. Salud ambiental. agua para uso y consumo humano-límites permisibles de calidad y tratamiento a que debe someterse el agua para su potabilización. In: *Diario Oficial de la Federación CVIII* 13, México.
- Vinson, D. S., McIntosh, J. C., Dwyer, G. S., & Vengosh, A. (2011). Arsenic and other oxyanion-forming trace elements in an alluvial basin aquifer: evaluating sources and mobilization by isotopic tracers (Sr, B, S, O, H, Ra). *Applied Geochemistry*, *26*, 1364–1376.
- Wang, Y., Shvartsev, S. L., & Su, C. (2009). Genesis of arsenic/fluoride-enriched soda water: a case study at Datong, northern China. *Applied Geochemistry*, *24*, 641–649.
- Westerhoff, P., Esparza-Soto, M., Caballero Mata, P., Parry, W. T., Johnson, W. P. (2004). Drinking water quality in the US–Mexico Border Region. Project Number: W-03-19. Final Report, 2004. p. 72. http://scerpfiler.org/cont_mgt/doc_files/W-03-19-final.pdf.