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# Preliminary human health risk assessment of arsenic and fluoride in tap water from Zacatecas, México

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**Abstract** Zacatecas state is located in the central area of Mexico, where the underground water contains elevated quantities of natural arsenic and fluoride. In order to estimate health risk associated with human exposure to these pollutants, tap water samples from the southern-central region of the state were analyzed. Ninety percent of the samples exceeded the levels of arsenic established by the World Health Organization (WHO) of 0.01 mg/L and 43 % exceeded the limit established by the NOM-127-SSA1[1] of 0.025 mg/L. Forty-three percent of the samples had fluoride levels above the Mexican regulation limit of 1.5 mg/L (NOM-127-SSA1). We used WHO and EPA's health risk assessment method, we estimated 80 % of the inhabitants of sites studied could be exposed to arsenic levels higher than those recommended by EPA and the WHO, 22 % could be exposed to fluoride levels higher than those recommended by EPA, and 16 % of the local population may be in risk of suffering dental fluorosis.

**Keywords** Arsenic · Fluoride · Water · Risk assessment

## Introduction

Arsenic (As) and fluoride ($F^-$) are elements naturally found in the earth's crust, which when dissolved, by erosion of natural deposits, into bodies of water destined for human consumption may represent a health risk, depending on the quantities in which they are present (Merola et al. 2015; Huang et al. 2015). The state of Zacatecas is located in the central Mexican region, a geological zone with reported concentrations of inorganic arsenic (iAs) and $F^-$ in the granular and fluvial aquifers of the region (Ortega 2009; Vega 2002; Leal-Ascencio 2006) in concentration higher than the limits recommended by national and international organizations (0.025 mg/L (SSA 2000) and 0.01 mg/L (WHO 2011; EPA 2002) for As; 1.5 mg/L (SSA 2000; WHO 2004) and 0.7 mg/L (CDC 2015) for $F^-$.

The presence of these elements in drinking water has been recognized as a health problem worldwide. It is estimated that in Mexico 4 % of the population is exposed to high concentrations of As (McClintock et al. 2012); meanwhile, some authors report an

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exposure to fluorides in various states within the country's central zone (González-Horta et al. 2015; Grimaldo et al. 1995; Jarquín-Yañez et al. 2015; Irigoyen-Camacho et al. 2016), primarily in regions with desert and semi-desert climates and overexploited aquifers which present high probabilities of being exposed to both pollutants (González-Horta et al. 2015), this is the reason why a continued vigilance is recommended in these areas (CONAGUA[2] 2015; Armienta et al. 2013).

Many health effects have been associated to chronic exposure to As and $F^-$ in drinking water (ATSDR 2007b; ATSDR 2003a). iAs has been classified by the International Agency for Research on Cancer (IARC 2011) as a potent carcinogen. It has also been identified as a priority pollutant (EPA 2014a) associated to adverse effects in the central nervous and cardiovascular systems (Tsuji et al. 2014; Kurzius-Spencer et al. 2015; McClintock et al. 2012; Tyler & Allan 2014), as well as diabetes mellitus (Martin et al. 2015; Wang et al. 2014). In extreme cases, a chronic exposure to iAs, above to 0.5 mg/day, can induce arsenicosis (WHO 2006). On the other hand, it has been reported that $F^-$ produces effects on the male reproductive and central nervous system (Ortiz-Pérez et al. 2003; Lu et al. 2000; Rocha-Amador et al. 2007; Choi et al. 2012; Zhang et al. 2015). It has been reported that exposure to concentrations ranging from 3 to 27 mg/day of $F^-$ induces a subclinical reproductive effect (Ortiz-Pérez et al. 2003); also, individuals exposed to concentration higher than 1.5 mg/L of $F^-$ are at risk of suffering dental fluorosis and in some cases skeletal fluorosis (Rango et al. 2014). $F^-$ exposure on children has been associated with a decreased immune response and neurological effects such as a diminished intellectual quotient (Rocha-Amador et al. 2007; Lu et al. 2000). Therefore, it is important to have information based on risk evaluations that allow decision-making and optimize resources and efforts to prevent adverse effects on the population (Buchhamer et al. 2012; Jha et al. 2013). The aim of this study is to estimate the health risks due to As and $F^-$ exposure in tap water in several towns of the state of Zacatecas, Mexico.

## Materials and methods

### Study sites

Eight study sites were selected, the towns of *Guadalupe* (159,991 residents), *Jerez* (57,610 residents), *Ojocaliente* (Pop. 40,740), *Villanueva* (Pop. 29,295), *Jalpa* (Pop. 23,557), *Tabasco* (Pop. 15,656), *Huanusco* (Pop. 4306), and *El Visitador* (Pop. 532), all of them located in the state's southern-central zone. The selection of the sites was based on geological data and reports of pollutants in the state (Armienta et al. 2013; Leal-Ascencio, 2006; Bundschuh et al. 2012) (Fig. 1)

### Sampling

Purposive sampling was conducted, the chosen sites can be observed in Fig. 1. Sampling was carried out during the months of August and September 2012, to avoid the possible variations caused by differences in seasonal rainfall patterns. A total of 47 water samples were taken, directly from public access taps, mainly in elementary schools. The number of samples per site varies in relation to the conditions of each locality. Tap water was considered as a most important route for iAs and $F^-$ exposure because their contribution to total exposure is very large. Other possible routes of exposure include contaminated soil and foods such as rice (Bundschuh et al. 2012; McClintock et al. 2012).

The volume of the water collected was a liter per sample, using amber containers (Nalgene® HDPE), certified for environmental samples, following the process established by Mexican regulation (SSA 2002). The samples were kept cold and stored at 4 °C until processed in the laboratory.

### Determination of arsenic

Five hundred milliliters of sample water were acidified with nitric acid and stored at 4 °C, shielded from light to prevent microbial activity and undesired chemical reactions. Subsequently, digestion, using a Milestone Ethos One ® microwave, was performed following EPA's 3015A method (EPA 2007), followed by a potassium iodide, 5 % ascorbic acid, and concentrated hydrochloric acid. Quantification was carried out on atomic emission optical spectroscopy equipment coupled to a source of plasma ionization ICP-OES coupled to a hydride generator based on the method 200.7-1 EPA (EPA 1994). For quality control, the reference standard NIST 1640 was used, trace elements in natural water having an arsenic concentration of ±0.0 26 mg/L to obtain a recovery of 85 %, the limits

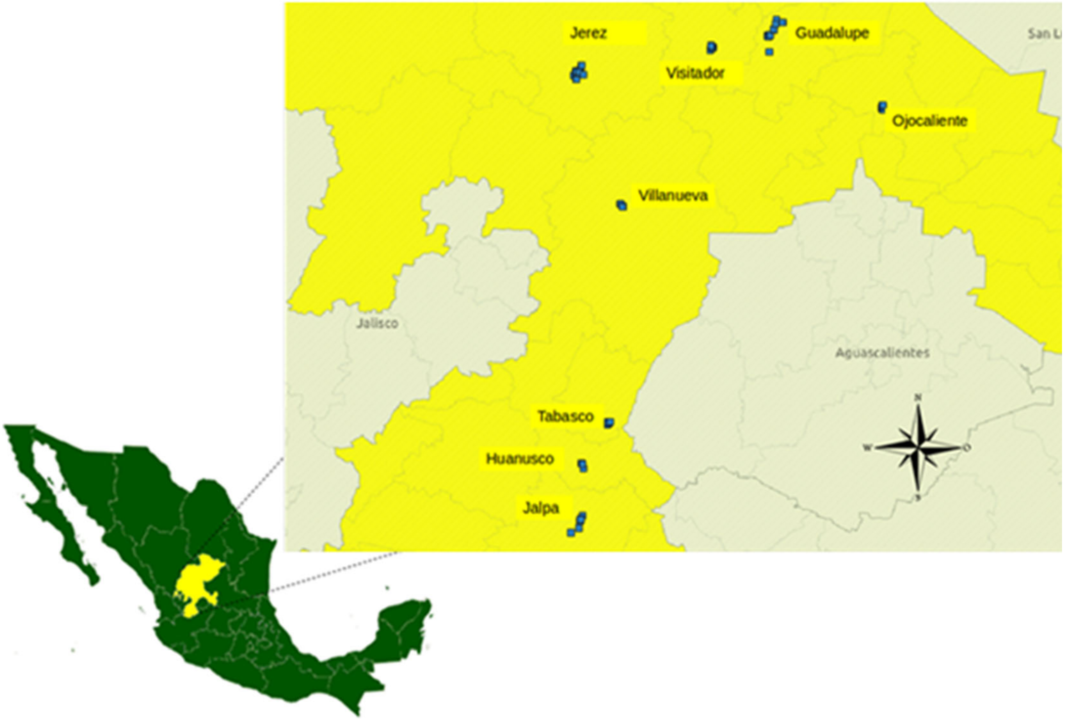

**Fig. 1** Location of the state of Zacatecas at 25° 07′ north latitude south, east 100°43′; west 104°22′ west longitude. Its climate is semi-dry with around 450 mm of precipitation per year and average annual temperatures between 20 and 15 °C (INEGI 2010). The *dots* represent the exact sites where samples were taken, all of them points of public access

of detection and quantification of the method were below the lowest concentration found in the samples.

### Determination of fluorides

Fluoride analysis was done according to Mexican regulation using the electrochemical ion-selective method described in the NMX-AA-007-SCFI-2001 (SCFI 2001). To determine exactitude, a standard NIST® 3183 water solution was used obtaining a recovery of 97 %.

### Estimation of health risk

The health risk assessment methodology proposed by Díaz Barriga (Díaz Barriga 1999) is consistent with the economic and social conditions of the study area, which coincide with most contaminated sites in Latin America for which it was adapted; this methodology is also used in conjunction with the methodology for the estimated health risk's probabilistic model proposed by EPA (EPA 2001; Ilizaliturri et al. 2009). These methods allow the estimation of health risk for non-cancer or carcinogenic, as long as the reference values for the pollutant are met within the study.

### Dose-response analysis

To begin estimating the health risk, it is necessary to consider the reference values established for each pollutant (Díaz Barriga, 1999). The guideline values for arsenic and $F^{-}$, proposed by the Agency for Toxic Substances and Disease Registry of the USA (ATSDR) and EPA, are summarized in Table 1 (ATSDR 2005; IRIS 1988, IRIS 1987; ATSDR 2007a; ATSDR 2003b). The guideline values used for calculating the exposure dose for each pollutant were the reference doses listed in Integrated Risk Information System(IRIS 1988; IRIS 1987). As for the guideline values to estimate the carcinogenic health risk, currently, only the carcinogenic risk for arsenic is available, while there is no guideline value available for the risk related to $F^{-}$ exposure (IRIS 1988; IRIS 1987).

**Table 1** Guideline health values for the estimation risk of exposure to As and $F^-$

| Compound | Estimated health risk | Guideline values | Definition | Value | Units | Critical effect | Organization |
|---|---|---|---|---|---|---|---|
| As | Non-carcinogenic | NOAEL | No observed adverse effect level | 0.0008 | mg/kg-day | Hyperpigmentation, keratosis and vascular complications | EPA |
| | Non-carcinogenic | LOAEL | Low observed adverse effect level | 0.014 | mg/kg-day | Hyperpigmentation, keratosis and vascular complications | EPA |
| | Non-carcinogenic | RfD | Dose reference | 0.0003 | mg/kg-day | Hyperpigmentation, keratosis and vascular complications | EPA |
| | Non-carcinogenic | MRLs | Minimal risk level | 0.0003 | mg/kg-day | Hyperpigmentation, keratosis and vascular complications | ATSDR |
| | Carcinogenic | CSF | Cancer slope factor | 1.5 | mg/kg-day | Cancer | EPA |
| $F^-$ | Non-carcinogenic | NOAEL | No observed adverse effect level | 0.06 | mg/kg-day | Dental fluorosis | EPA |
| | Non-carcinogenic | LOAEL | Low observed adverse effect level | 2 | ppm | Dental fluorosis | EPA |
| | Non-carcinogenic | RfD | Dose reference | 0.06 | mg/kg-day | Dental fluorosis | EPA |
| | Non-carcinogenic | MRLs | Minimal risk level | 0.05 | mg/kg-day | Dental fluorosis | ATSDR |
| | Carcinogenic | CSF | Cancer slope factor | NA | NA | Cancer | NA |

(ATSDR 2007a; ATSDR 2003b; ATSDR 2005; IRIS 1988; IRIS 1987)

## Exposure estimation

To estimate the daily exposure dose (ADD) the following formula was used (Díaz Barriga 1999):

$$\mathrm{ADD}\left(\frac{\frac{\mathrm{mg}}{\mathrm{kg}}}{\mathrm{day}}\right) = \left(\frac{(\text{environmental concentration} \times \text{intake rate})}{\text{body } weight}\right) \times \text{exposure factor}$$

The environmental concentration is expressed in milligrams per liter, the ingestion rate is in liters per day and the body weight in kilograms. An exposure factor (EF) of 1 is assumed, considering a permanent exposure route and maximum bioavailability of pollutant (Díaz Barriga, 1999).

The average concentration of As and $F^-$ found in the samples was used to estimate the respective exposure dose, the average value of 0.875 l/day was considered for the intake rate and the average body weight was 33.8 kg, these values correspond to the children range of 6 to 11 years old, which is the school age of elementary education in Mexico. ADD is estimated for the children because they are in a window of vulnerability by various biological and social factors such as in growth stage, their central nervous, reproductive, and immune systems are still developing; they could be exposed to higher concentrations in relation to their size and weight and accessibility to tap water in playgrounds; and in addition, using the hazard quotient (HQ) as a measure to estimate the health risk for this population, we would be estimating the most critical risk which would allow us to include the other age groups. The variable intake rate and body weight were calculated from data obtained through anthropometric measurements, and an exposure questionnaire conducted on a group of 78 children residents of the study zone, students from two schools where tap water samples were taken, these taps water were reach of children and could make use of it for consumption, with the purpose of obtaining as much information as possible about the actual conditions of the site. In Table 2, three different estimates of the rate of intake for children are summarized. As shown, the National Health and Nutrition Survey Data (Hernández et al. 2012) suggested a 0.607 l/day based in a study that includes children throughout Mexico and has a very large sample size; however, the values of 0.875 l/day obtained in the survey conducted in the study area despite having a smaller sample size could be more representative for the aims of this work; since it correspond to the local population in the sites studied, this survey was conducted in two schools where samples of tap water were taken, and information was obtained from parents of infants who are questioned about the habits of consumption tap water for their children. On the other hand, if it

**Table 2** Comparison between different intake rate for children

| Parameter | Units | *n* | Intake | Reference |
|---|---|---|---|---|
| Intake rate | l/day | 8122 | 607 (9.0) | Hernández et al. 2012 |
| | l/day | 79 | 875 (11.4) | Survey in this study |
| | l/day | – | 1 | Díaz Barriga 1999 |

Values are represented as the arithmetic mean and standard deviation

is considered that the rate of water intake suggested by the methodology of Pan American Health Organization (Díaz Barriga 1999) is 1 l/day, our estimate is an average value, in this way would be estimating the risk with a less uncertainty.

Estimation of the ADD and non-carcinogenic health risk or hazard quotients (HQ) respective for each site was conducted using measures of central tendency of each involved parameter (Díaz Barriga 1999), while for the estimation of HQ by the probabilistic method (EPA 2001), a probability distribution is assumed based on the frequency distributions of each parameter (Table 3). The Kolmogorov-Smirnov and Anderson-Darling as goodness of fit test was performed using the Crystal Ball™ program.

For the carcinogenic risk estimation or individual carcinogenic risk (ER), it was necessary to calculate the arsenic exposure dose via tap water for the adult population (Díaz Barriga, 1999; EPA, 2001), because the guideline value for the Cancer Slope Factor is based on exposure throughout life (ATSDR 2005), the details of each variable involved are shown in Table 4. This estimation was performed using the arsenic's most representative value for each site and the total distribution to estimate the exposure dose via the probabilistic method.

## Risk characterization

The ratios of non-carcinogenic and carcinogenic risks were obtained from information gathered in previous stages of this study. The non-carcinogenic risk estimated as hazard quotient was obtained through the following formula:

$$HQ = (ADD(mg/kg-day)/RfD(mg/kg-day))*EF$$

The exposure time was considered complete and with a bioavailability of 100 % so exposure factor (EF) is assumed as 1. ADD is daily exposure dose and RfD is de value of reference dose. While the carcinogenic risk ratio or theoretical risk value was calculated with the following equation:

$$ER = ADD(mg/kg-day)*CSF(mg/kg-day)$$

Díaz Barriga 1999; ATSDR 2005

ER represents the individual carcinogenic risk and CSF is cancer potency factor or slope; $F^{-}$ is not included in this estimation because the carcinogenic potency factor for this pollutant is not available. A sensibility analysis using tornado graphic provided by the Crystal Ball ® program is included, to assess the possible changes of relative importance of the variables involved in the equations used.

**Table 3** Parameter used to estimate non-carcinogenic hazard quotients (HQ)

| Parameters | Units | *n* | Distribution | Value | Reference |
|---|---|---|---|---|---|
| $F^{-}$ concentration | mg/l | 47 | Lognormal | 1.4 (0.4–3.0) | [a] |
| As concentration | mg/l | 47 | Lognormal | 0.05 (0.004–0.298) | [a] |
| Body weight | Kg | 79 | Normal | 33.8 (17.7–67.5) | [b] |
| Intake rate | l/day | 79 | Triangular | 0.87 (0.1–1.5) | [b] |
| Reference $F^{-}$ dose | mg/kg-day | – | Single value | 0.06 | (IRIS 1987) |
| Reference As dose | mg/kg-day | – | Single value | 0.0003 | (IRIS 1988) |

The distributions were assumed based on goodness of fit tests

[a, b] Information obtained in the study area

Table 4 Parameters for estimating cancer risk (ER) by exposure to arsenic in tap water

| Parameters | Units | *n* | Distribution | Value | Reference |
|---|---|---|---|---|---|
| iAs concentration | mg/l | 47 | Lognormal | 0.05 (0.004–0.298) | [a] |
| Intake rate | l/day | – | Single value | 2.0 | (Díaz Barriga 1999) |
| Body weight | Kg | – | Single value | 70 | (Díaz Barriga 1999) |
| Cancer potency factor | mg/kg-day | – | Single value | 1.5 | (Díaz Barriga 1999) |

[a] Average arsenic concentration in water from the study area

## Results

### Arsenic and $F^-$ concentrations in tap water

The concentrations of As and $F^-$ corresponding to the water samples taken from taps in the studied communities are summarized in Table 4. Ninety percent of the samples exceeded the permissible limits for As in water according to the WHO (WHO 2011), and 43 % exceeded the Mexican regulation (SSA 2000). Forty-three percent of the water samples exceeded the limits permissible by the WHO and Mexican regulation (WHO 2004; SSA 2000) to $F^-$. Only the samples taken at Villanueva were found below the permissible limits for both elements.

### Estimation of the exposure and risk characterization

Initially, a representative value of the exposure dose for each site was obtained, hence, a risk ratio value. The HQ and the ADD for each community are shown in Table 5, while the exposure dose for adults and the ER is summarized in Table 6.

The probabilistic method (EPA 2001) allows us to perform multiple iterations as from assumed probability distributions for each variable in the model, yielding a probability distribution for the estimated output variable, in this case the ADD. This probability distribution allows us to estimate the most probable ADD. As shown, the ADD obtained through the iterations of the Monte Carlo method, for both the children and adult

Table 5 As and $F^-$ concentrations in tap water and the non-carcinogenic risk ratio (HQ) estimated for each community

| Element | Site | *N* | Water concentration in mg/L average (min-max) | ADD mg/kg/day | HQ |
|---|---|---|---|---|---|
| As | Jerez | 10 | 0.019 (0.008–0.062) | 5.0E-04 | 1.6 |
| | El Visitador | 4 | 0.022 (0.018–0.025) | 5.7E-04 | 1.9 |
| | Guadalupe | 8 | 0.078 (0.021–0.233) | 2.0E-03 | 6.7 |
| | Ojocaliente | 5 | 0.186 (0.125–0.298) | 4.8E-03 | 16.1 |
| | Villanueva | 3 | 0.006 (0.004–0.0074) | 2.0E-04 | 0.5 |
| | Tabasco | 4 | 0.014 (0.008–0.025) | 4.0E-04 | 1.2 |
| | Huanusco | 3 | 0.026 (0.025–0.026) | 7.0E-04 | 2.2 |
| | Jalpa | 5 | 0.019 (0.013–0.035) | 5.0E-04 | 1.7 |
| $F^-$ | Jerez | 10 | 1.8 (1.6–2.3) | 5.0E-02 | 0.8 |
| | El Visitador | 10 | 1.3 (0.8–2.4) | 3.0E-02 | 0.6 |
| | Guadalupe | 6 | 0.45 (0.4–0.5) | 1.0E-02 | 0.2 |
| | Ojocaliente | 4 | 0.7 (0.6–0.8) | 2.0E-02 | 0.3 |
| | Villanueva | 3 | 0.4 (0.3–0.6) | 1.0E-02 | 0.2 |
| | Tabasco | 5 | 1.9 (0.8–3.0) | 5.0E-02 | 0.8 |
| | Huanusco | 4 | 1.1 (0.4–1.9) | 3.0E-02 | 0.5 |

The exposure doses were calculated based on data for each site

**Table 6** Ratio of estimated cancer risk (ER) for exposure to arsenic in tap water

| Site | Population (residents) | iAs concentration mg/L average (min-max) | ADD mg/kg-day | ER (individual)[a] |
|---|---|---|---|---|
| Jerez | 57,610 | 0.019 (0.008–0.062) | 5.40E-04 | 8.10E-04 |
| El Visitador | 532 | 0.022 (0.018–0.025) | 6.30E-04 | 9.40E-04 |
| Guadalupe | 159,991 | 0.078 (0.021–0.233) | 2.20E-03 | 3.30E-03 |
| Ojocaliente | 40,740 | 0.186 (0.125–0.298) | 5.30E-03 | 8.00E-03 |
| Villanueva | 29,395 | 0.006 (0.004–0.0074) | 1.70E-04 | 2.60E-04 |
| Tabasco | 15,656 | 0.014 (0.008–0.025) | 4.00E-04 | 6.00E-04 |
| Huanusco | 4306 | 0.026 (0.025–0.026) | 7.40E-04 | 1.10E-03 |
| Jalpa | 23,557 | 0.019 (0.013–0.035) | 5.40E-04 | 8.10E-04 |

[a] Cancer risk estimated for exposure to arsenic in tapwater

population, is expressed through a cumulative frequency graph in Fig. 2, this is in order to observe the percentages 50, 90, 95, and 99, which are values considered for decision-making (WHO 2006); on the graph, it is also possible to see the attenuated zone to the left of the distribution where the percentage of the population estimated to be exposed to a dose that is considered safe appears, according to the applicable criteria, which is stated on the lower left end of each graph.

The ADD for the population living in the study area using the probabilistic risk assessment method (EPA 2001) is summarized in Table 7. Based on these exposure doses, HQ and ER were calculated.

When the risk ratios are obtained based on the model of probabilistic risk estimate, the probability of exposure to certain levels for each pollutant can be elucidated. As shown in Table 8, various dividing criteria can be used in decision-making, just as in exposure doses. Likewise

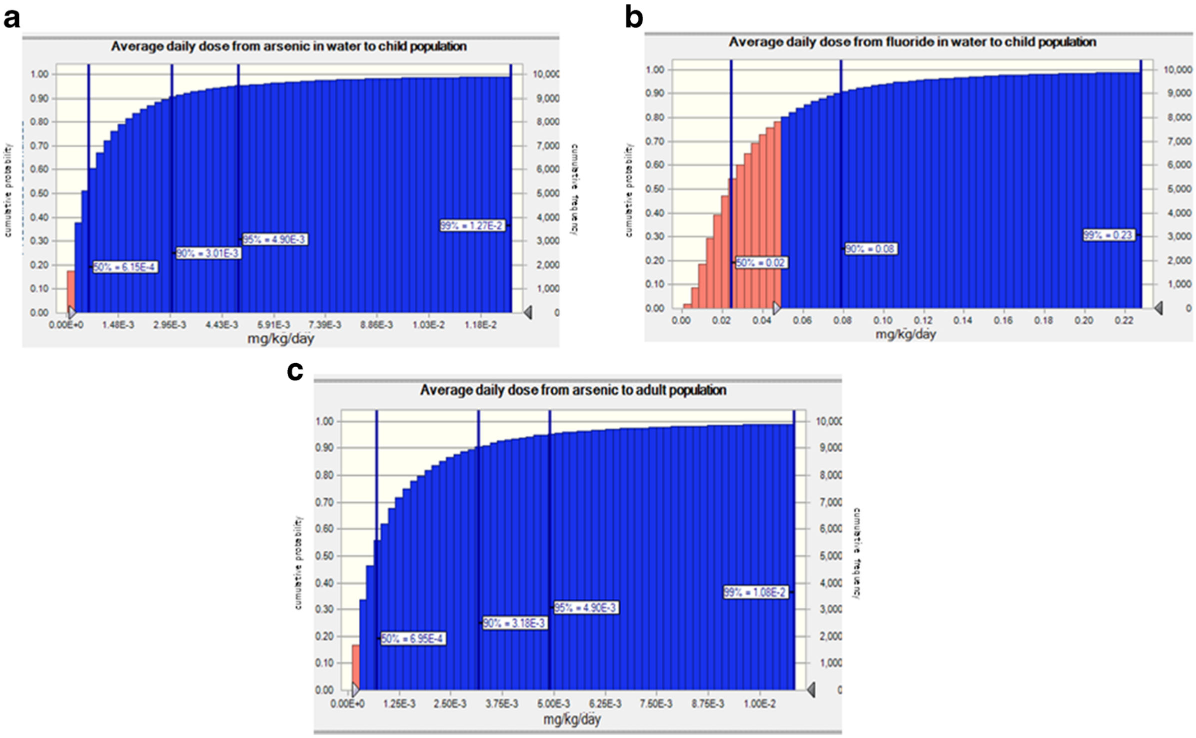

**Fig. 2** Accumulative frequency distribution for the ADD. **a** ADD to iAs calculated for child consumption. **b** ADD to $F^-$calculated for child consumption. **c** ADD to As calculated for adult consumption (dose of exposure throughout a life time, used to calculate the ER for As). The *white area* represents the percentage of the local population estimated to be exposed to a dose lower than that of the suggested health criteria by EPA (RfD) for each pollutant

Table 7 Estimation of exposure doses to As and $F^-$ in the water using probabilistic risk assessment method

| Pollutant | Population | ADD (mg/kg/day) | | | | Safety criteria | | | % above the safety level |
|---|---|---|---|---|---|---|---|---|---|
| | | Percent | | | | | | | |
| | | 50 | 90 | 95 | 99 | Name | mg/kg/day | Ref. | |
| $F^-$ | Children | 0.02 | 0.08 | 0.11 | 0.23 | RfD | 0.05 | EPA[a] | 22 |
| As | Children | 6.2E-04 | 2.9E-03 | 4.6E-03 | 1.2E-02 | RfD | 3.0E-04 | EPA[a] | 73 |
| As | Adults | 7.0E-04 | 3.1E-03 | 4.8E-03 | 1.1E-02 | RfD | 3.0E-04 | EPA[a] | 80 |

[a] RfD non-carcinogenic risk (EPA 2002)

in Table 8, the safety criteria suggested by EPA is included, both for carcinogenic and non-carcinogenic risk. In Fig. 3, these results are shown.

In addition, the percentage of the population that may be at risk was estimated using the criteria HQ > 1 and the value of 1.0E-04 for ER, this information is included in Table 8.

## Discussion

The state of Zacatecas, for the most part, has soil that is rich in minerals such as arsenopyrite, fluorite, and fluorapatite; to the south of the state, there have been reports of geothermal activity. The climate is predominantly semi-desert and most of its aquifers are considered to be overexploited (Mojarro-Davila et al. 2013); the water destined for public consumption is 113 million $m^3$/year (Herrera-Toledo 2012). In addition to this, the regulation and control of pollutants in the water provided for human consumption is one of the challenges to overcome at present and in the coming years (Vega 2002).

There is limited information available about environmental concentration of As and $F^-$ in water in Zacatecas state, data referent to city of Guadalupe is summarized in Table 9. These results are consistent with our data, there is not a great variability in the As concentration reported in previous years; on the other hand, we found slightly lower $F^-$ values than reported in the past. Padilla and colleagues estimated that the children younger than 12 years old and women residing in the area were in high health risk associated to As and $F^-$ (Padilla-reyes et al. 2012). For the rest of the sites, no available information was found so as to compare the seasonal variability of the environmental concentrations.

Chronic exposure to As and $F^-$ is mainly due to the consumption of contaminated water; in addition, it is permanently available for the inhabitants of the site (Armienta et al, 2013; Huang et al. 2015; Bundschuh et al. 2012; McClintock et al. 2012). Neither ADD $F^-$ estimated for each community nor the corresponding HQ exceeds the health criteria suggested by the WHO (WHO 2006); however, when estimating the population risk, 22 % of the population may be exposed to a dose higher than considered safe and 16 % could be at risk of suffering dental fluorosis, according to the criteria

Table 8 Estimation of health risk for As and F- in water

| Pollutant | Population | Risk | Estimated theoretical risk | | | | Safety criteria | Ref. | % above the safety level |
|---|---|---|---|---|---|---|---|---|---|
| | | | Percent | | | | | | |
| | | | 50 | 90 | 95 | 99 | | | |
| $F^-$ | Children | Non-carcinogenic (HQ) | 0.4 | 1.4 | 1.9 | 3.9 | 1 | EPA | 16 |
| As | Children | Non-carcinogenic (HQ) | 2.0 | 10.6 | 16.3 | 41.5 | 1 | EPA | 74 |
| As | Adults | Carcinogenic (ER) | 1.0E-03 | 4.5E-03 | 7.4E-03 | 1.7E-02 | 1.0E-04 | EPA | 95 |

(EPA 2001; ODEQ 1999; EPA 2014a)

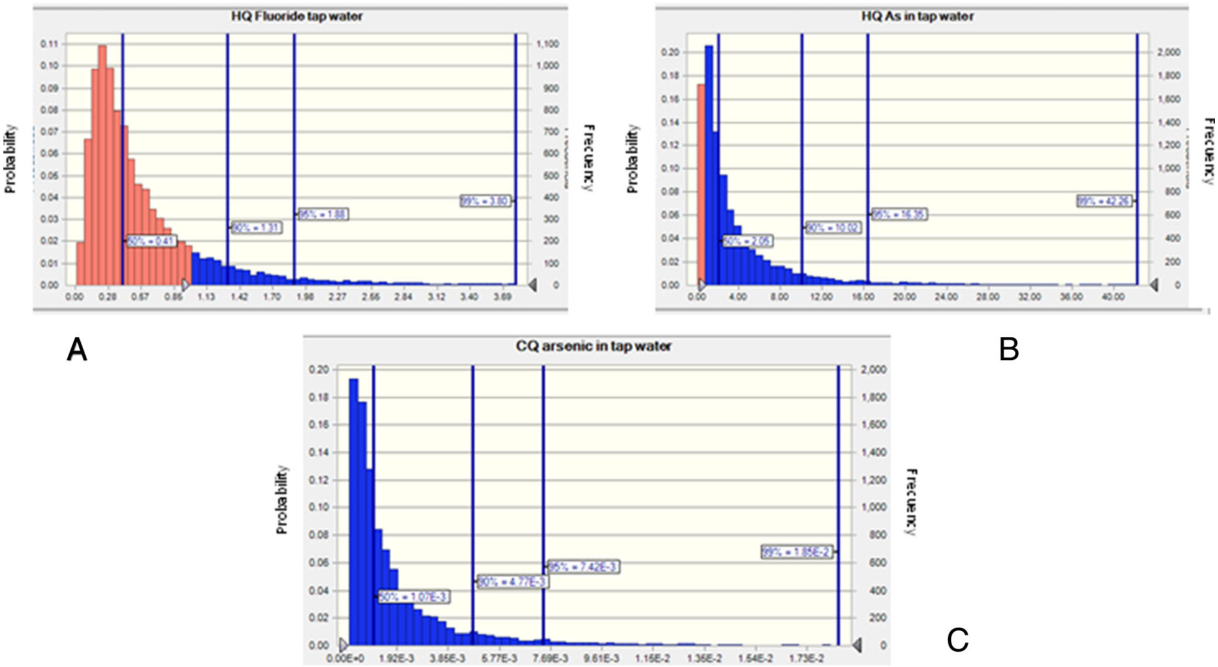

**Fig. 3** HQ obtained through the Monte Carlo method. **a** HQ for $F^-$ in water estimated for child consumption. **b** Non-carcinogenic risk ratio for arsenic in water estimated for child consumption. **c** ER show as CQ for arsenic in water. The *lines* correspond to the level of estimated risk for percentiles 50, 90, 95, and 99

established by EPA (EPA 2014b). An intervention action in the zone is recommended to mitigate the risk.

It has been reported that children exposed to fluoride concentrations in tap water lower to 0.7 mg/L have a low occurrence of moderate or severe fluorosis, while concentrations of 1.6 mg/L cause moderate or severe dental fluorosis (Irigoyen-Camacho et al. 2016). In this study, two communities, Guadalupe and Villanueva, were found to have average concentrations of fluoride lower than 0.7 mg/L. Zacatecas has reported a community fluorosis index (CFI) above 1 similar to neighboring states such as Durango, San Luis Potosi, and Aguascalientes with naturally occurring fluoride in water (Betancourt-Lineares et al. 2013); it is known that dental fluorosis is closely related to the presence of $F^-$ in drinking water (Mariño 2013).

RfD and MRL to As suggested by EPA and the ATSDR (IRIS 1988; ATSDR 2007b) is at 0.0003 mg/kg/day. Only As ADD for the community of Villanueva is lower than these safety doses, the

**Table 9** Background on the concentration of iAs and $F^-$ in Guadalupe, Zacatecas

| Locality | Pollutant | Results | Reference |
|---|---|---|---|
| Guadalupe, Zacatecas | As | 80 % wells above 0.025 mg/L | (Leal-Ascencio 2006) |
| | $F^-$ | 40 % of wells above 1.5 mg/L | |
| | As | 0.04–0.27 mg/L | (González-Dávila 2011) |
| | $F^-$ | 1.28–2.85 mg/L | |
| | As | 0.016–0.3 mg/L | (Padilla-reyes et al. 2012) |
| | $F^-$ | 1.28–3.2 mg/L | |
| | As | 0.021–0.233 mg/L | (Data from this work) |
| | $F^-$ | 0.4–0.5 mg/L | |

Studies conducted in the zone of San Ramón-Ojo de Agua, which are included in this work. The values correspond to the percentage of wells that exceeded Mexico's existing environmental guide in the years of publication, as well as the concentration range for the water samples from wells used to supply water for human consumption, respectively population of the rest of the communities has a higher probability of being exposed to doses of above the safety level as show in Table 5. Similarly, the HQ estimated to As exceed the unit, with the exception of Villanueva. The RfD and MRL to As were calculated taking into account hyperkeratosis and possible vascular alterations. The state of Hidalgo, Mexico, has reported various health effects related to the presence of As in the water; Smeester and colleagues reported epigenetic changes related to various diseases associated to arsenicosis in populations chronically exposed to As in drinking water (Smeester et al. 2011). Del Razo and colleagues found a relation between As exposure and the prevalence of diabetes (Del Razo et al. 2011); furthermore, there are reports of skin injuries whose severity is altered by individual susceptibility factors (Valenzuela et al. 2009). The probability that these trends will present themselves in Zacatecas is high, since, according to our estimation, 74 % of the local children and 99 % of the local adult may be exposed to elevated doses of this pollutant. The 90, 95, and 99 % of the HQ estimated for the local population exceed the unit above the acceptable risk level criteria. In the case of $F^{-}$, we estimated 16 % of local resident children were above the criteria safety. This estimation justifies an intervention in the zone (ODEQ 1999; EPA2014b).

Based on the ER suggested by EPA (see Table 1), we estimated that the As ER, with the exception of Villanueva, exceeds the risk criteria of $1 \times 10^{-05}$; the 90, 95, and 99 % surpass the safety criteria for environmental health of $1 \times 10^{-04}$, $1 \times 10^{-05}$, and $1 \times 10^{-06}$, respectively, suggested as safety criterion by various international organizations (Cotruvo 1988; Paul R. Hunter & Fewtrell 2001; WHO 2006). We estimated that 99 % of the population resident in the sites study has a high probability of being exposed to a non-safe As dose (see Fig. 3 and Table 8). In this sense, the state of Zacatecas have reported an incidence in skin cancer, a type of cancer associated to arsenic (ATSDR 2007b; McClintock et al. 2012), of 20 cases per every 100,000 inhabitants and estimated that it will increase by 10.5 % annually (Pinedo-Vega et al. 2014).

The estimation for exposure risk for both pollutants, despite sharing the same route of exposure, presents different methodological challenges; the reference dose for arsenic and fluoride is calculated based on different effects, hyperkeratosis and dental fluorosis, respectively, making it impossible to simply assume an additive risk. Although it is known that both, As and $F^{-}$, show associated effects on the central nervous system, which actually does not exist a reference dose for this effects, nonetheless, we must consider that evidence is being accumulated on the health risks assessment that could present themselves in the children exposed to this mixture when consuming tap water (Choi et al, 2012; Lu et al. 2000; Wang et al. 2007; Rocha-Amador et al. 2007). Should be considered, not currently exist a carcinogenic risk factor for $F^{-}$, regulatory agencies do not have sufficient evidence to develop criteria, making not possible to estimate the risk by methodology used in this study.

By not considering the contributions of other possible routes of exposure for the studied pollutants such as dust, bottled water, milk and food prepared using tap water, and in the specific case of fluoride, the use of fluoride salt and tooth paste, the exposure doses may be underestimated, factors that must be taken into account when designing an intervention in the area. Childhood malnutrition is another source of uncertainty which must be considered at the moment of intervention, since the body's defense mechanism may not be up to par due to a lack of nutrients, for example, in the case of arsenic; it is know that a folate deficient diet decreases the metabolization of As (Ghose et al. 2014). Likewise, dental fluorosis incidence is higher in states that present malnutrition in its population (Irigoyen-Camacho et al. 2016) which may increase the vulnerability of the exposed population.

However, we believe that the exposure doses, in addition to the risk ratio estimates, together with the epidemiological history found in the literary sources in zones where the environmental levels of arsenic and fluoride in water, are similar to the ones in our study area are enough to justify actions for diminishing the environmental exposure to these pollutants, in comparison to the health and economic cost if they are not carried out. Notably, people who have lived for generations in the study zone may be exposed from an early age and at crucial stages from maternal exposure, during pregnancy (Rager et al. 2014), to childhood, adolescence, and continuing on into adulthood, which could increase the risk of severe health effects associated to As and $F^{-}$ (Smeester et al. 2011), as well as other natural pollutants from a mineral rich soil, characteristic of our study zone such as mercury and lead, which are known to affect the central nervous system, which could cause synergism. Likewise, the presence of other carcinogenic agents in the environment such as ultraviolent radiation (Pinedo-Vega et al. 2014) could aggravate health effects associated to chronic exposure to As and F⁻.

The results obtained from the health risk estimation represent a quick and cheap decision-making tool related to environmental health problems. The use of probabilistic methodology helps to diminish uncertainties when performing iterations that simulate different possible scenarios. The children population was considered for the non-carcinogenic risk estimation because they are in a window of vulnerability due to physiological characteristics of their particular phase of development and play habits (Ilizaliturri et al. 2009), also to include the population most at risk when planning and intervention in this zone. Therefore, the implementation of environmental health programs and risk communication to diminish the exposure to As and F⁻present in tap water should focus mainly on children, because if this particularly vulnerable sector of the population can be protected, the rest of the population will benefit from it.

## Conclusions

Base on the results obtained in this study, it is clear that the children have a higher risk of presenting health effects caused by the consumption of water with a high As and F⁻content. For this reason, it is imperative to take action towards providing these communities with clean drinking water by installing public treatment plants either through campaigns or risk communication, as well as maintaining epidemiological surveillance aimed at mitigating the risks associated to contaminated water exposure. The main contribution of this study is to provide information for decision-making based on risks and to protect the health of the population that resides in the zones with natural contamination in the state of Zacatecas.

## Endnotes

[1] For its acronym in Spanish Norma Mexicana (Mexican Regulation).

[2] For its acronym in Spanish *Comisión Nacional del Agua* (National Water Commission)

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