

Concentration of Fluoride and Arsenic in Bottled Drinking Water in Durango City, Mexico

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ABSTRACT

Arsenic and fluoride are elements known to cause human health problems and it has been documented that both elements are found in high concentrations in the Guadiana Valley aquifer, in the state of Durango, Mexico. Since underground water is the source for potable water bottling companies commercialized in Durango City; such high concentrations reduced the quality of bottled water for human consumption according to NOM-041-SSA1-1993. Legislation establishes a maximum permissible limit (MPL) of 0.7 mg/L for fluoride and 0.025 mg/L for arsenic. In this research the main objective was to evaluate the quality of bottled water expended in Durango City with respect to the well from which water is extracted. Findings showed that the highest fluoride concentration was 5.86 mg/L (8.4 times MPL), with 100% of sampled brands exceeding the MPL (range: 1.09 to 5.86 mg/L). On the other hand, for arsenic, the highest concentration was 0.076 mg/L (threefold), with 38% exceeding the MPL (range: 0.001 to 0.076 ppm). Statistical analysis showed significant differences only for fluoride, according to Fisher LSD (Least Significant Difference) test, with an F value of 14.5 at a p value of 0.0005. According to the comparison between the quantified concentrations in bottled water and groundwater, it was found that groundwater was subjected to treatment; however, although a significant decrease in fluoride and arsenic concentration was observed, the removal processes used were not efficient to meet set standards.

Keywords: Arsenic; Bottled Water Quality; Fluoride; Guadiana Valley Aquifer; Groundwater

1. Introduction

Durango state is located in Northwest Mexico (Coordinates: 24°56'05"N 104°54'43"W) and it stands at an altitude of 1880 m. Durango City, with a population of 582,267 (2010), is the capital of Durango State and is located in the Guadiana Valley, in the southern central area of the state. Durango City is supplied with potable water from exploitation of Guadiana Valley aquifer through 1097 wells with an extraction volume of 148.31×10^6 m³/year; National Water Commission in Durango reports that 100% of water demand is covered with groundwater [1,2].

The Guadiana Valley aquifer is currently classified as

overexploited and fluoride and arsenic are present at much higher concentrations than the maximum permissible limits (MPL) established in NOM-127-SSA1-1994 [3]; however, their presence is mainly attributed to the strata geological composition [4-7].

Potable water bottling companies that are commercialized in the city extract water from groundwater wells, treat it before bottling, and must meet standards established by NOM-041-SSA1-1993 [8].

Maximum permissible limits (MPL) set by Mexican law varies depending on its use; NOM-127-SSA1-1994 [3] applies for groundwater (0.025 and 1.5 mg/L, for arsenic and fluoride, respectively), whereas NOM-041-SSA1-1993 [8] applies for bottled water (0.025 and 0.7 mg/L, for arsenic and fluoride, respectively). On the other

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hand, the World Health Organization (WHO) established 0.01 mg/L (or parts per million, ppm) for arsenic and 0.7 mg/L for fluoride in water for human use and consumption, based on the fact that both of them could pose health damage. Research has been conducted about health problems caused by arsenic and fluoride; such as bones, skin and teeth damage from high fluoride exposure and cancer in some cases for arsenic [4,6,9-20].

The objective of this research was to evaluate the quality of bottled drinking water with respect to groundwater wells of Durango City, based on arsenic and fluoride concentration.

2. Materials and Methods

2.1. Mapping and Sampling of Water Bottling Companies

All water bottling companies of Durango City were inventoried, listed assigning sequential numbers instead of brand names (confidential status), categorized by sectors (North, South, West, and East), and located in a map using AutoCAD[®]. Samples of all companies were collected twice with a time difference of six weeks. Sampling and preservation were performed according to the Standard Methods of Analysis; flasks were washed and rinsed with distilled water, for fluoride analysis; and for arsenic, flasks were washed with a 20% by volume nitric acid and hydrochloric acid solution plus the addition of concentrated nitric acid to reduce pH < 2.0 for preservation [6,8,21].

2.2. Fluoride and Arsenic Analysis

Arsenic analysis was quantified with graphite furnace atomic absorption spectroscopy (GFAAS) established by standard methods [21]; whereas fluoride was determined using SPADNS spectrophotometric method [22].

2.3. Statistical Analysis

The differences between wells and companies, with respect to fluoride and arsenic content, and sectors (North, West, South, and East) were validated with a two-factor ANOVA (wells and companies); and with the LSD (Least Significant Difference) Fisher test [6,7], to establish if the wells and companies had different contents or the same, all at an $\alpha = 0.05$ using the Statistica software version 7[®] [23].

3. Results and Discussion

Thirty water bottling companies established in Durango City were inventoried; however, 6 run out of business, then only twenty-four were sampled twice: North (4), South (5), East (7), and West (8) [6].

3.1. Quantification of Fluoride and Arsenic

Calibration curves were developed for arsenic and fluoride. Concentration values were averaged with data gathered of the two samplings, by company and by sector. Results were evaluated comparing them to the maximum permissible limits (MPL) in drinking water according to the Mexican regulation (0.7 and 0.025 ppm, for fluoride and arsenic, respectively).

3.2. Quality of Bottled Drinking Water

The consumption of purified bottled water is a very common practice nowadays everywhere. In Durango City, many consumers buy bottled potable water because quality of water provided by municipal services is not trusted. In most cases companies offer containers of 20 liters (refillable) and only a minority offers bottles of less than or equal to 1 liter (non-refillable).

Results showed that the overall average concentration for fluoride was 2.67 mg/L with a range from 1.12 to 5.15 ppm. According to geographical location, it was found that the western sector (**Figure 1**) presented a greater incidence of fluoride, with an average of 3.29 ppm exceeding the MPL of 0.7 ppm by almost fivefold. None of the average values in all four sectors were below the MPL, implying that 100% of the samples analyzed did not meet quality issues according to NOM-041-SSA1-1993 with respect to the fluoride concentration. However, it is important to mention that fluoride concentration in bottled drinking water was statistically different from groundwater wells concentration; efficiency ranged from 20% to 70% by its decrease in concentration and from 75% to 87% with respect to the MPL (0.7 ppm), concentration was reduced in all cases except for one company (**Table 1**). **Figure 1** shows average concentration

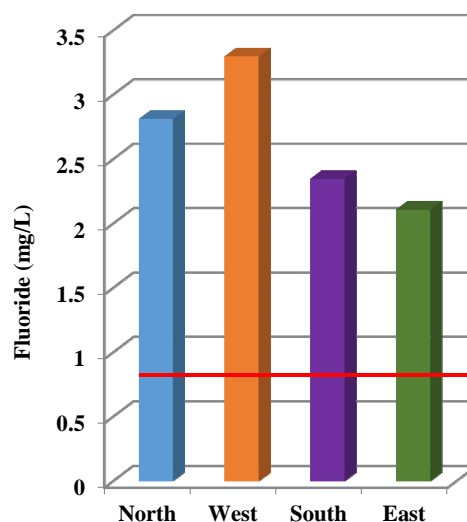


Figure 1. Average concentration of fluoride in water bottling companies by sector. Red line represents the MPL.

Table 1. Fluoride and arsenic concentration in water bottling companies and well from which water is extracted.

No. (Sector)	Fluoride Concentration (mg/L)		Arsenic Concentration (mg/L)		No. (Sector)	Fluoride Concentration (mg/L)		Arsenic Concentration (mg/L)	
	Water Bottling Company	Groundwater Well	Water Bottling Company	Groundwater Well		Water Bottling Company	Groundwater Well	Water Bottling Company	Groundwater Well
7 (N)	4.131	****	0.073	****	5 (S)	1.661	5.459	0.017	0.026
13 (N)	3.026	3.766	0.025	0.009	10 (S)	2.187	4.902	0.060	0.037
14 (N)	2.053	2.809	0.012	0.034	11 (S)	2.536	3.741	0.008	0.047
30 (N)	2.028	2.809	0.003	0.034	12 (S)	3.493	4.902	0.001	0.038
20 (W)	2.754	5.888	0.032	0.037	15 (S)	1.854	3.741	0.007	0.046
21 (W)	2.726	6.209	0.012	0.051	1 (E)	2.620	3.366	0.055	0.025
22 (W)	1.264	2.640	0.004	0.044	2 (E)	1.918	2.107	0.016	0.024
23 (W)	2.370	3.463	0.003	0.035	4 (E)	2.760	3.233	0.002	0.029
24 (W)	1.936	3.463	0.005	0.035	6 (E)	1.276	****	0.003	****
25 (W)	5.724	3.589	0.054	0.049	9 (E)	2.312	4.684	0.076	0.021
26 (W)	4.440	5.375	0.070	0.034	18 (E)	2.741	3.069	0.034	0.072
27 (W)	5.151	5.375	0.042	0.034	19 (E)	1.119	4.752	0.001	0.011

N = North; S = South; W = West; E = East; MPL for Fluoride = 0.7 mg/L; MPL for Arsenic = 0.025 mg/L; **** Private well, not sampled.

tions by sector and **Table 1** resumes concentrations for all water bottling companies and groundwater city wells.

For arsenic, the concentration ranged from detection limit (0.001) to 0.076 ppm; the overall average concentration was 0.0256 and the highest value found in bottled water in the city was 0.076 ppm (eastern sector) 3 times the MPL. The resulting average concentrations by sector were slightly (6% to 13%) above the MPL (0.025 mg/L) for North, West and East sector and below MPL for South sector, and only 38% of the companies exceeded the MPL, see **Table 1** and **Figure 2** for results. As already mentioned, for arsenic, concentration in bottled drinking water was much lower than groundwater well; efficiency ranged from 14% to 97% by the reduction in its concentration and from 4% to 65% with respect to the MPL (0.025 ppm), concentrations in 5 companies were higher than groundwater well. If WHO standard (0.01 ppm) were considered, then 59% of the companies would not meet the MPL. In order to support information, random samples were sent for analysis to a certified laboratory and results were comparable to the ones obtained in this research.

3.3. Isoconcentration Maps

Surfer[®] software was used to elaborate isoconcentration maps with lines of equal concentration. It helps visualize the behavior of the concentration of fluoride and arsenic, of wells from which water is extracted by bottling companies. **Figure 3** shows an isoconcentration map for fluoride in groundwater wells and location of companies. No isoconcentration map for arsenic is included because there were no significant differences between sectors, water bottling companies, and groundwater wells.

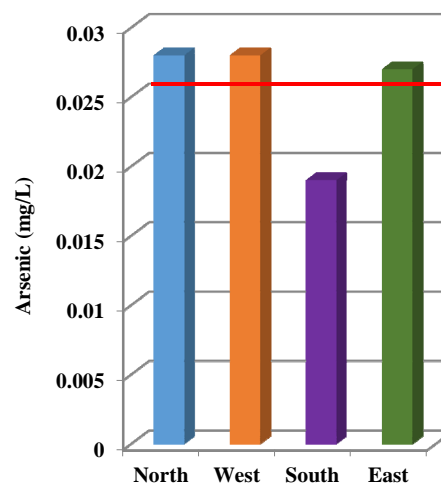


Figure 2. Average concentration of arsenic in water bottling companies by sector. Red line represents the MPL.

3.4. Statistical Analysis: Water Quality Based on Fluoride and Arsenic Concentration

Data of fluoride and arsenic concentrations gathered in this research was subjected to a statistical evaluation [6, 7] and was compared to concentration in Durango City groundwater wells, from which water is extracted prior to treatment and bottling process [4,7].

The ANOVA analysis showed significant differences for fluoride concentrations among bottling water companies (C) and groundwater wells (GW) with an F value of 14.5 at a p value of 0.0005; the mean fluoride concentration in GW was 4.1 mg/L versus 2.7 mg/L for C; however, MPL was not met in any case. On the other hand, for arsenic, there were no significant differences between bottled water and groundwater wells. **Figure 4** shows the

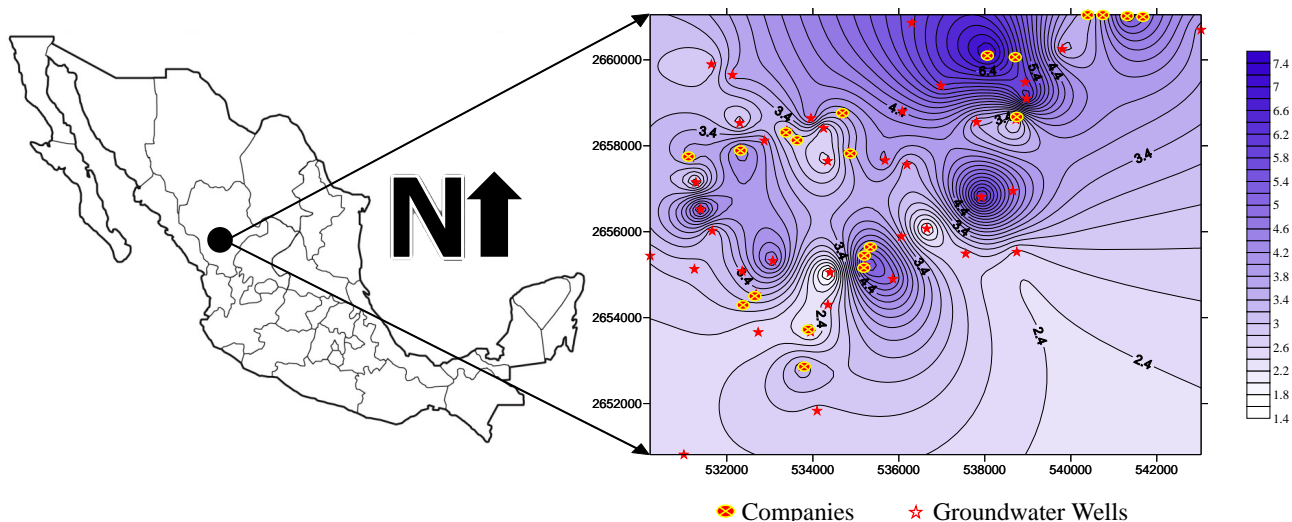


Figure 3. Fluoride isoconcentration (mg/L) map for groundwater wells in Durango City, Mexico.

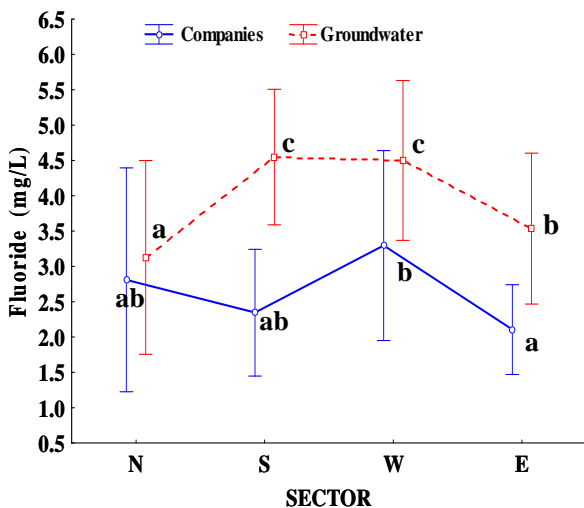


Figure 4. Fisher LSD test. Statistical analysis for fluoride concentration in water bottling companies versus groundwater wells, in Durango City, Mexico, from which water is extracted prior to treatment. Same letters meaning no differences between groups ($\alpha = 0.05$).

results for the statistical analysis for fluoride; which refers to the significant differences for fluoride concentration by sector (N, S, W and E) and source (C and GW) according to Fisher LSD (Least Significant Difference) test. Fisher’s LSD is one of the existing methods for comparing treatment group means after the ANOVA null hypothesis of equal means has been rejected using the ANOVA F-test. Same letters equals to no differences between groups ($\alpha = 0.05$).

4. Conclusions

Results gathered in this research revealed deficiency in treatment, low removal efficiency and bad quality of potable bottled water, with respect to fluoride and arsenic

content. Water source for water bottling companies established in Durango City comes from underground of Guadiana Valley aquifer. This aquifer is classified as overexploited and with high content of fluoride and arsenic due to its strata geological composition. All companies that commercialized bottled water in Durango City were tested to quantify fluoride and arsenic concentrations and compared to those concentrations present in groundwater wells.

For fluoride, 100% of the bottled water companies presented lower fluoride concentration compared to the groundwater wells. Comparing one of the cases, the well with the highest content had 5.46 ppm, whereas the concentration of bottled water extracted from the same well was 1.66 ppm. Efficiency ranged from 20% to 70% (decrease in concentration) and 75% to 87% with respect to the MPL (0.7 ppm); only one company presented a higher concentration than the source, however, none of them met the MPL established (0.7 ppm).

For arsenic, 68% of the companies had a lower arsenic concentration compared to the underground water. In this case, the well with the highest arsenic concentration had 0.072 ppm and the concentration found in the samples of the water bottling company, extracted from the same well, was 0.034 ppm. When determining efficiency, based on reduction in its concentration, range was from 14% to 97% and with respect to the MPL (0.025 ppm) ranged from 4% to 65%. Fifteen companies (62.5%) met MPL; nine (37.5%) did not meet MPL, where seven of them (26%) presented a higher concentration than the source.

It is very clear that not all removal treatments used by water bottling companies were effective. In the case of fluoride, even though concentrations decreased substantially, none of the companies met the MPL. For arsenic removal treatments, 62.5% of the removal treatments used achieved the MPL.

Statistical analysis showed significant differences only for fluoride, according to Fisher LSD test, with an F value of 14.5 at a p value of 0.0005.

It is important to point out that the regulatory Agency of Water Resources, in Durango City, has made several attempts to solve this problem, to promote decrease concentration of fluoride and arsenic. Resources were allocated to the acquisition of small treatment plants for the removal of these compounds and were assigned to high concentration areas, without success due to lack of training in the handling of equipment and appropriately following the former proposal. A high percentage of the wells did not comply with standards representing latent health risk for adverse effects conferred by fluoride and arsenic. Action must be taken because chronic or acute health problems will manifest in the short or medium term, which represents high spending in the health sector.

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