# 16 Water Quality in the State of Aguascalientes and its Effects on the Population's Health

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## 16.1 Introduction

Aguascalientes is a state located in Central Mexico, with a surface area of 5,589 km<sup>2</sup> (0.3 per cent of Mexican territory; CONAGUA, 2000). Most of the state of Aguascalientes (87 per cent) has a semi-dry climate, with annual average precipitation of 600 mm (rainy season in the summer) and an annual average temperature of 18°C. Some locations in Aguascalientes (13 per cent) have a warm sub-humid climate, with an annual average precipitation of 700 mm, and an annual average temperature of 16°C. The annual average precipitation in the state is 552 mm, with rainfall (80 per cent) predominant between June and September (CONAGUA, 2004).

The total population of the state of Aguascalientes is more than one million. Seventy per cent of the population lives in the capital city and the remaining 30 per cent in ten municipalities. The city of Aguascalientes is a metropolitan area with a population of nearly one million. The main economic activity is in the tertiary sector, commerce, and services, which employ 49 per cent of the *economically active population* (EAP). The second most important economic sector is industry, including textiles, clothing, and automotive and electronic industries, employing 34 per cent of the EAP. The primary sector employs 15 per cent of the EAP (Avelar, 2003a; CONAGUA, 2004).

Aguascalientes has quintupled its population during the last five decades. This population growth has put stress on the demand for natural resources, resulting in non-sustainable growth. Water is the most limited resource in the state of Aguascalientes. Available surface water satisfies only about 20 per cent of the total demand throughout the state. Eighty per cent of the water demand is satisfied from groundwater resources. Water resources to feed the entire population and the industrial and services sectors are then obtained from aquifers. This results in over-exploitation of aquifers, the contamination of surface water bodies by wastewater, and detriment to the quality of groundwater (SARH, 1987; Rodriguez et al., 1997; Avelar, 2003a; Castillo, 2003).

Wastewater is produced at a rate of  $103.3 \text{ Mm}^3$ / year in the state of Aguascalientes. The municipal, industrial, and other sectors (services, farming and domestic) contribute 95 per cent, 4 per cent and 1 per cent, respectively, of the total wastewater generated in the state. Although the industrial sector generates only 4 per cent of the volume, it contributes nearly 20 per cent to the biochemical oxygen demand (BOD, CONAGUA, 2003).

The basin of the river San Pedro is the most important hydrological system of the state of Aguascalientes. It is confined to the hydrological region Lerma-Santiago. The San Pedro River has an annual discharge of 208 million m<sup>3</sup>. This river runs through the state from north to south in a straight line, with a length of 90 km and a drainage surface of 2820.6 km<sup>2</sup>. This river is also the main collector of rainfall, wastewater, and treated water. Fifty-six communities are based along the San Pedro River, including six principal municipalities as well as the city of Aguascalientes. Altogether, about 80 per cent of the inhabitants live in these communities. Historically, domestic, industrial, and farming wastes have been discharged into this river basin. For the last 20 years, wastewaters have been treated before they are discharged; however, the installed treatment systems do not remove the stubborn xenobiotics. The river does not have a flow baseline and about 96 per cent (nearly 120 million annual m<sup>3</sup>) of treated and un-treated waste waters flow directly to the river. Therefore, the contamination of the San Pedro River constitutes a risk to

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the public health of the communities bordering it, and is a potential source of contamination to the aquifer of the Aguascalientes valley (CONAGUA, 2007). State authorities have set the knowledge of the current degree of environmental quality of this river and its planned remediation as a high priority (SEDUE, 1999; SEMARNAP, 1999; CONAGUA, 2004; CONA-GUA, 2005, INAGUA, 2005).

The state of Aguascalientes has five aquifers: the valley of Aguascalientes, the valley of Chicalote, the valley of Calvillo, the valley of Venadero, and El Llano. The valley of Aguascalientes is by far the most important aquifer. The last two aquifers are the least important as far as potential and exploitation are concerned (INEGI, 1993). Groundwater is extracted from 2,846 wells with a total extraction of 556 Mm<sup>3</sup>. Extracted groundwater is used in the following activities: 70.1 per cent (390.0 Mm<sup>3</sup>) for agriculture, 3.6 per cent (19.8 Mm<sup>3</sup>) for cattle, 22.3 per cent (124.0 Mm<sup>3</sup>) for urban public use, 2.4 per cent (13.4 Mm<sup>3</sup>) for industry and services, and 1.6 per cent (8.8 Mm<sup>3</sup>) for other industries (CONAGUA, 2000, 2003).

Following the trajectory of the main trench of the river San Pedro, the aquifer of the Aguascalientes vallev is the main source of potable water for the state. This semi-confined aquifer occupies a surface area of 1250 km<sup>2</sup>. It provides nearly 80 per cent of the water resources and satisfies 65 per cent of the farming demand and almost 100 per cent of urban and industrial consumption (Avelar, 2003a). During the last three decades, the aquifer of the Aguascalientes valley has been completely over-exploited. The average abatement of the static levels is greater than 2 m annually and exceeds 4 m annually in the city of Aguascalientes (Castillo, 2003). This over-exploitation has created a change in the direction of the water flow and a cracking caused by subsidence, increasing the possibility of infiltration of contaminants into the aquifer (SEDUE, 1999). For the last two decades the sustainable use and protection of water sources has been clearly recognized as a vital priority in guaranteeing the development of the state in the long term (SARH, 1987).

This 10-year study summarizes the main results conducted by our research group on water resource issues in the state of Aguascalientes.

## 16.2 Objectives

The objectives of this chapter are twofold: a) to summarize and analyse groundwater issues in the state of Aguascalientes and bordering zones, and b) to evaluate the effects of the presence of xenobiotic compounds in the water supplies on the health of the population.

## 16.3 Methodology

An analysis of the quality of the groundwater in the states of Aguascalientes and South Zacatecas, and of surface waters, groundwater and sediments in the San Pedro river basin were conducted in this study. Procedures for the selection of sampling sites, sampling, sample preservation and the final analysis were conducted following international criteria (USEPA, 1993) and applicable Mexican official norms (NOM NMX-AA-042-1987, NOM NMX-AA-051-SCFI-2001, NOM NMX-AA-132-SCFI-2006, NOM-001-ECOL-1996, NOM-127-SSA1-1994). Risk evaluation studies were conducted according to ATSDR-USDHHS-CPEHS-OPS-OMS-UASLP (1992).

### 16.4 The San Pedro River Basin

Sampling sites were selected in collaboration with the Institute of the Environment of the State of Aguascalientes (IMAE), the Institute of Water of the State of Aguascalientes (INAGUA), the state delegation of the National Commission of Water, and the municipal operating organisms. Seventy-three sampling sites along the trench of the river San Pedro were selected, taking into account topographical, geological, and hydrological factors, besides relevant points of unloading of polluting agents to the river. In addition, 17 water wells adjacent (less than 300 m) to the trench of the river were also selected. Seven sampling stations were selected in the El Niagara dam, which is the final collector of the river. This selection was based on the morphology and size of the dam (Chapman, 1996). The geographic position of all the sampling sites was determined with a GPS (Garmin, model GPS MAP 60c). Four samplings were made: two during the time of drought (May-June) and two after the rainy season (September-November). Water samples and sediments were taken at point sampling sites on the San Pedro River. Sediment sampling was conducted by random selection at the surface and at 10 cm depth (EPA, 1993). Well water was collected in the pumping stations, after disconnecting the chlorination mechanism and bleeding the system for 15 minutes. The water samples of the El Niagara dam were taken at two depths (at one metre depth and at the mean depth).

Sampling and sample preservation procedures followed Standard Methods (Clesceri et al., 1998; APHA-AWWA-WEF, 2005).

Sediment samples were submitted to a lixiviometric treatment using the Robledo and Maldonado (1997) modified method. The sediments were dried at 50°C for 72 h, homogenized in a porcelain mortar with a wooden mallet, and screened in a 1.0 mm mesh. Five grammes of treated sample were added to 800 ml of distilled water to obtain the extracts. The mixture was stirred for 24 h and filtered. Extracts pH, COD, nutrients and organic toxics were then measured. Heavy metal determination was followed using the methods approved by EPA (1991) and the reference material RM 8704 (Buffalo River Sediments) of the U.S. *National Institute of Standards and Technology* (NIST).

The water quality of the El Niagara dam was evaluated with the *Water Quality Index* (WQI) developed by Dinius and modified by the SEDUE (Guzman, 1997). The *allowed maximum limits* (AML) published in the Mexican official norms: NOM-001-ECOL-1996, NOM-003-ECOL-1997 and NOM-127-SSA1-1994, the quality of ecological criteria of the water (CE-CCA-001-89) for agricultural use (SEMAR-NAT, 1989) and the values indicated by EPA (1977) for sediments were used as references.

#### 16.4.1 Groundwater Quality

The well water was collected in the pumping stations, after disconnecting the chlorination mechanism and bleeding the system for 15 minutes. The analytical determinations were carried out in agreement with the accepted international protocols (Clesceri et al., 1998).

#### 16.4.2 Analytical Analysis

Measurement of the pH (method 4500-H+ B), conductivity (method 2510 B) and dissolved oxygen (method 4500-O G) were conducted in the sampling sites. The analysis made of water samples included  $BOD_5$  (5210 B), COD by the closed reflux colorimetric method (5220 D), total nitrogen (N<sub>T</sub>) by micro-Kjeldahl (4500-Norg B), total phosphorus (Pt) by the ascorbic acid method (4500-P E), detergents like methylene blue active substances (MBAS, 5540 C), phenols by the 4-aminoantipirine method with chloroformic extraction (5530 C), anilines by the colorimetric method of Hess et al. (1993), and the faecal coliforms by the MPN method (9221 C). The fluorides were quantified by the electrometric method. The presence of metals in the water, soils, sediments, and urine and blood samples was quantified with an atomic absorption spectrometer (Perkin Elmer Analyst 100). Graphite furnace (3113 B) or flame (3111 B) was used to determine Al, Cd, Cr, Cu, Fe, Mn, Pb and Zn. Samples were concentrated 10 times during the digestion process to increase the method sensitivity in the flame method. Arsenic was measured using hydrides generation (3114 B), and Hg by cold steam (3112 B). Analyses were done in triplicate. A random fortified sample was used in each sample lot (between 85 and 115 per cent of recovery), as well as a random duplicated sample (variation coefficient of less than 15 per cent). Analytical methods were validated using SRM reference materials of the U.S. NIST. Organochloride pesticides were quantified by gas chromatography. All analytical techniques were conducted according to Standard Methods (Clesceri et al., 1998).

Bayer Multistix® 10 SG Ames reactive strips were used to quantify glucose, bilirubins, ketones, proteins, erythrocytes, nitrites, leucocytes, pH, and density in urine samples. Reactive strip readings were carried out using Bayer Clinitek 50. Urinary sediments were obtained by centrifuging 10 ml of urine for 5 minutes at 7,000 rpm. Sediments were observed using a clearfield optical microscope (40X magnification). Epithelial erythrocytes, leucocytes, cells, cylinders and crystals were also determined in the sediment samples. The quality controls of the general urine examination were followed according to the criteria of Ames Bayer.

A Jaffé kinetic spectrophotometric method was used to determine urine creatinine. 100  $\mu$ l of urine diluted in distilled water in a proportion 1:50 was mixed with equal parts of a buffer solution (500  $\mu$ l) and picric acid (500  $\mu$ l). The spectrophotometer absorbance to 505 nm was recorded.

#### 16.4.3 Risk Assessment by Exposure to Fluorides

An exposed population (n = 188) was selected from the El Llano municipality, where all of the wells exceed the MPL set by NOM-127-SSAI-1994, with an average fluoride concentration of 3.76 mg/l. The control population (n = 140) was selected from the Tepezala and Asientos municipalities (<1.0 mg/l fluoride concentration in the provision of water). Socio-economic food and hygiene customs in both populations (control and exposed) were similar. The selection criteria were young minors of 14 years, born in the community and/or with a minimum time of residence of six years, with water consumption from these wells. The exclusion criteria in both populations were those children with renal and hepatic diseases antecedents. Selected individuals from the above municipalities answered a clinical questionnaire and were submitted to clinical and dental evaluations. An exposure questionnaire was also used to determine other potential sources of exposure to fluorides. Samples of the first urine in the morning were taken to determine fluorides and creatinine. The concentration of fluorides in drinking water and urine was determined using the method 8308 (ion selective electrode), recommended by NIOSH (Tolos, 1994).

#### 16.4.4 Hydroarsenicosis Study

Two regions were studied: the municipalities of Asientos, Tepezala, Cosio, San Francisco de los Romo and El Llano in the state of Aguascalientes, and Ojocaliente, Loreto, Ciudad Cuauhtemoc, Noria de los Angeles, Villa Gonzalez Ortega, Luis Moya, Villa Garcia and Pinos in the state of Zacatecas. Arsenic concentration was determined in 197 water wells in those municipalities.

In the risk assessment study three communities from the state of Zacatecas with major concentrations of As in their drinking water supplies: Ejido Hidalgo, Sauceda de Mulatos and Berriozabal (180, 140 and 94 µg/l As, respectively) were chosen as the exposed population. The control population was selected from the communities of Crisostomos and Tlacotes (with 3.9 and 6.6 µg/l arsenic in drinking water, respectively). These communities presented similar socioeconomic levels, productive activities (mainly farming), and nutritional habits. The criteria of inclusion in both populations were females and males, 20 years or older with a minimum period of residence in the community of 15 years and who used tap water as the main source of ingestion of liquids. The exclusion criteria were metabolic illnesses, hepatic and degenerative chronic diseases, and people with a work history in mining zones or labour exposure to arsenic.

Clinical and dermatological exposure surveys and evaluations were applied to both populations (Cebrian et al., 1983). The urine sample collection was followed using the ATSDR (2000) criteria. The first urine of the day was preserved with HCl and stored under refrigeration at 4°C. The creatinine determination and the general urine examination were made on the same day as the sample collection. The minimum sample size (107 people) was used following the stratified method with a proportional assignation. The real sample size was of 146 and 123 people in the exposed and control populations respectively. Comparative statistical analysis (variance analysis) between the exposed and control populations was conducted. In addition, correlation analyses were also conducted between levels of arsenic exposure, urinary excretion of metalloid, parameters of the general urine examination, and prevalence of keratosis palmoplantaris. The  $\chi^2$  test was carried out to compare the prevalence of abortions. The statistical analyses were conducted using Statistica 6.0, with 0.01 levels of significance.

#### 16.4.5 Risk Assessment by Lead Exposure

In Tepezala and Asientos, which are located in the north-west of the State of Aguascalientes, the mining industry was one of the main economic activities. For decades, great amounts of mining waste (tailings) have been accumulated in the outdoor environment, which constitute a source of water, soil, and air pollution. A risk assessment (ATSDR, 1992) in children of 8 to 12 years of age, with at least six years of residence in Tepezala and Asientos (exposed population n=139) was carried out to evaluate exposure to lead. A control population from El Llano (n=187) was selected with a similar culture and socio-economic levels to the one from the exposed population.

Lead concentration in drinking water, tailings, and soil (NMX-AA-132-SCFI-2006), and in blood (NOM-199-SSAI-2000), was quantified to evaluate the main routes and magnitude of exposure to lead. Clinical and exposure questionnaires and a clinical evaluation were conducted to determine other potential sources of lead exposure. Adverse effects were measured by means of the activity of the enzyme delta-aminolevulinic dehydratase in blood (ALA-D) and the concentration of delta-aminolevulinic acid in urine (ALA-U; ATSDR, 2000).

The immunological effect to Pb exposure was also studied using an analysis of components related to the humoral and cellular immune response. The control group included 15 children with blood levels of Pb of  $3.12 \pm 0.54 \mu g/dl$ . The exposed group included 14 children who presented blood concentrations of Pb of  $11.70 \pm 1.6 \mu g/dl$ . Lymphocytes CD19+, total CD2+, and sub-populations CD4+ and CD8+ were quantified. Serum immunoglobulin concentration was quantified by radial immune diffusion and electroimmunodiffusion. The activity of the complementary system, the functional capacity of the humoral and cellular response to the measles immunizing agent, and the test for intradermoreaction to PPD were determined by means of specific antibodies quantification, using the ELISA technique (Martínez, 2001). Exposed and control populations were compared using comparative statistical analysis (variance analysis).

## 16.5 Study of Indicators of Renal Damage in Populations Exposed to Cd and Pb

The young population is the most susceptible to toxic exposure. The enzymatic systems of biotransformation and detoxification in infants have not been completely developed. Furthermore, infants have enhanced absorption of metals. The groundwater in Aguascalientes has high concentrations of metals; so evidence of early renal damage in children, induced by Cd and Pb exposure in drinking water, was researched using low-cost non-invasive techniques. This study was performed within the framework of the international project: "Impact of the contamination of potable water by heavy metals: cadmium, lead, chromium and nickel in the renal function during perinatal and postnatal development" (Reyes/Poujeol, 2003).

Rural towns of Aguascalientes whose wells displayed concentrations of cadmium and lead near or slightly above the AML established by NOM-127-SSA1-1994 (0.005 mg/l and 0.01 mg/l, for Cd and Pb respectively) were selected as exposed populations. The principal municipality of Tepezala, where drinking water had a lead concentration of 0.0138 mg/l (1.38 times the AML), was selected. The town of La Luz in the municipality of El Llano was also selected, with a water concentration of cadmium of 0.0036 mg/l (72 per cent of the AML). The control population included the town of La Escondida in the municipality of San Francisco de los Romo, where the well presented lead and cadmium concentrations of 0.0054 mg/l and 0.00035 mg/l, respectively (54 per cent of the AML for Pb, and 7 per cent of the AML for Cd). The three selected communities presented similar socio-economic levels and nutritional habits.

The inclusion criteria were elementary school students between 6 and 12 years old and with a minimum time of residence in the community of two years. The number of children was: control population, n=134; population exposed to cadmium, n=86; and population exposed to lead, n=179 (Torres, 2007). Clinical and exposure questionnaires and a clinical evaluation were applied to determine other potential sources of exposure to lead and cadmium.

#### 16.5.1 Statistical Analysis

Hypothesis testing with sampling from populations that do not present the normal distribution was performed using the central limit theorem (sample magnitude >30). This test determined the significance level between the averages of the urinary excretion of cadmium and lead in the control and exposed populations.

Hypotheses:

 $H_{0:}$  The averages of the populations are equal  $(\mu 1 = \mu 2).$ 

 $H_A$ : The averages of the populations are different

$$(\mu 1 \mu 2)$$
.

$$\alpha = 0.05$$

The statistical test is:

$$Z = \frac{(\bar{x}_1 - \bar{x}_2) - (\mu_1 - \mu_2)_0}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}}$$

Decision rule: Reject  $H_0$  if the value of p obtained with the statistical test is < 0.05.

#### 16.5.2 General Urine Examination

Chi-squared  $(\chi^2)$  tests were performed using contingency tables with a level of significance ( $\alpha$ ) of 0.05 (Milton/Tsokas, 1993). These tests determined if the exposure of these three populations to lead and cadmium in drinking water had any relationship to the number of observed positive cases of the different parameters analyzed with the general urine examination. The chi-squared test is used to prove the null hypothesis  $(H_0)$ . It indicates that two criteria of the classification are independent when they are applied to the same set of organizations. In accordance with both criteria, the classification is represented by means of a table, in which the rows r represent the levels of one of the classification criteria, and the columns c represent the levels of the second criterion. This table is known as a contingency table (Milton/ Tsokas, 1993; Daniel, 1997). Both statistical analyses were carried out using Microsoft Office Excel version 2003.

## 16.6 Results

#### 16.6.1 San Pedro River Basin

Over 350 wastewater and treated water discharge points to the river were documented all along the basin of the San Pedro River and its main affluents. The majority of these discharge points were not registered and the environmental authorities did not know of their existence. Seventy-three sampling sites along the trench of the river and its main affluents were selected. Site selection was conducted based on the released volume to the river and its origin. Four field sampling campaigns were conducted: two during the dry season and two after the rainy season. Results clearly revealed that in spite of the wastewater treatment infrastructure installed in the two last decades, the organic matter, nutrients (phosphorus and nitrogen), and faecal pathogens continue to be the main contaminants of the San Pedro River (Avelar, 2009).

BOD and TSS values in 60 per cent of the water samples exceeded the *allowed maximum limit* (AML) established by NOM-001-ECOL-1996 (150 mg BOD/l and 200 mg TSS/l). Fats and oils were exceeded in 70 per cent of the samples based on the AML (25 mg/l, Avelar 2006). Almost 90 per cent of the water samples exceeded the AML for total nitrogen (40 mg N/l), and 20 per cent exceeded the AML (20 mg P/l) for total phosphorus (Avelar, 2006). Faecal contamination was observed in all the sampling points. The total and faecal coliforms were between 100 and 10,000 times greater than the AML (1000 coliforms MPN/100 ml) established by NOM-003-ECOL-1997 (Avelar, 2009).

Phenols and chlorinated organic compounds (endrin, aldrin, dieldrin and hexachlorobenzene) were not measured in significant concentrations in all samples. By contrast, concentrations of detergents (MBAS) and aniline greater than 20 mg/l were measured in 80 per cent of the water samples. This is considered as a toxic level (Avelar, 2009).

With respect to the heavy metal concentrations, 5 per cent of the water samples had levels of mercury and chromium greater than the AML set by NOM-001-ECOL-1996 (0.02 mg Hg/l and 0.1 mg Cr/l). More than 90 per cent of the samples presented concentrations of aluminium greater than the typical values reported by Metcalf & Eddy (2000) for wastewater (0.1 mg Al/l), and almost 15 per cent exceeded 4 mg Al/l. 13 per cent of the samples exceeded the typical values of manganese (0.2 mg/l) for wastewater. Copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), and lead (Pb) concentrations did not have significantly high levels in the water samples analyzed (Avelar, 2006).

More than 96 per cent of these samples presented acute toxicity for *Daphnia magna* and *Lecane quadridentata* (Ramirez et al., 2007; Avelar, 2009; Rico-Martínez et al., 2000), which is consistent with the high concentrations of organic pollutants and metals observed.

Heavy metals such as Hg, As, Zn, and Cu were the main contaminants in soil and sediments of the trench of the river San Pedro and its main affluents. More than 50 per cent of the samples had concentrations higher than the maximum values as recommended by USEPA (1997) and OMEE (1992). In decreasing order of importance of pollution magnitude, it was found that Pb was the most significant (16 per cent), followed by Cr (9 per cent), Mn (6 per cent), Cd (6 per cent), and Fe (3 per cent). With respect to the organic polluting agents and the nutrients in soil and sediments, generally they were consistent with the results obtained in the water samples (Avelar, 2009).

Although no significant correlation was observed between the contaminant concentrations in the water samples and sediments, the levels of organic matter, inorganic nutrients, and organic xenobiotics were high in both matrices. It is probable that the high content of organic matter and detergents observed in the sediments contribute to the adsorption of heavy metals, increasing the concentration of these xenobiotics in the sediments (Seoanez, 1999), and consequently diminishing their content in the water samples. On the other hand, to a great extent the pH controls the mobility of heavy metals. Values of pH were above 7.0 in all the sediments. As reported in Petrovich et al. (1999), values of pH > 6.0 and high levels of organic matter and detergents, similar to this study, are combined with the argillaceous texture of the soil. They keep the activity of metallic ions in water low, thus remaining almost totally adsorbed, fixed, and precipitated in sediments.

The high concentrations of arsenic in the trench sediments and wells suggest that this metal is mainly of geogenic origin (Gutierrez et al., 2007). This agrees with the high concentrations of arsenic observed in wells located in the north zone of the state (Martínez, 2006).

The water quality of the El Niagara dam, which is the final collector of the river, clearly shows the overall quality of the San Pedro River and the efficiency of the main wastewater treatment plants that discharge to the river. The overall *Water Quality Index* (WQI) of El Niagara puts this water body in the category of 'contaminated' to 'very contaminated' water sources. The highest heavy metal concentrations were Al and Fe. This agrees with the concentrations observed in the samples of water and sediments from the trench. The concentrations of these metals did not exceed the AML established by CE-CCA-00I-89 for agricultural irrigation. Even though the water of El Niagara is used for irrigation in the bordering zones and areas of cultivation located downstream, its pollution level means it is not useful because of its content of microorganisms of faecal origin.

There was no evidence of groundwater contamination of anthropogenic origin. Nevertheless, due to the high degree of contamination of the San Pedro River, it represents without a doubt a permanent risk of contamination of the aquifer, the main potable water source in the state of Aguascalientes (Avelar, 2009).

#### 16.6.2 Groundwater Quality

The first reports on groundwater quality in Aguascalientes are somewhat contradictory. Rodriguez et al. (1997) reported high concentrations of lead, phosphates and fats and oils, this last being an indicator of the anthropogenic origin of pollution. By contrast, Hansen et al. (1997) reported high levels of fluorides, phosphates and ammoniac nitrogen.

A study conducted by our group, in which groundwater was assessed in 60 wells from 10 municipalities in the state, found that groundwater had fluoride, arsenic, mercury, chromium, iron, manganese, and lead concentrations higher than the AML set by NOM-127-SSAI-1994. These findings differ from the results of previous studies. In our study, high concentrations of fluorides were found in the municipalities of Calvillo, Cosio, Jesus Maria, Rincon de Romos, San Jose de Gracia, and El Llano. A significant number of wells with high concentration of arsenic were also noted in the municipalities of Asientos, Cosio, and Tepezala, located in the north of the state. These arsenic concentrations were at or above the AML set by the NOM. Elevated levels of salinity and low values of pH (< 6.5) were also very frequent in wells in all parts of the state (Avelar/Llamas, 2000).

One hundred and seventy-eight wells provide water to the population in the municipality of Aguascalientes. A systematic monitoring (31 parameters by well, twice a year) was conducted between 1995 and 2001. The problem in the aquifer of the Aguas-

calientes valley (Castillo, 2003) was found to be high concentrations of fluorides, mercury, phenols, lead, and ammoniac nitrogen (exceeding the AML set by NOM-127-SSA1-1994). The high concentration of fluorides in the water of the aquifer of the Aguascalientes valley was the most important issue. Forty-two per cent of wells in the municipality of Aguascalientes had concentrations of fluorides greater than 2.0 mg/l (the AML set by the NOM is 1.5 mg/l), which implies that an approximate population of 360,000 inhabitants is exposed to non-recommendable levels of this substance. The highest concentration of fluorides was 7 mg/l (Castillo, 2003). Mercury concentrations higher than the AML set by the NOM (0.001 mg/l) were observed in 26.7 per cent of the wells in the municipality of Aguascalientes. Only 0.6 per cent of the wells presented concentrations equal to or greater than 0.002 mg/l, that is, double the AML. In accordance with these results, more than 200,000 inhabitants would be exposed to mercury levels near the AML set by the NOM, and approximately 5,000 inhabitants would be exposed to concentrations twice as high as this AML. With respect to lead, 37 per cent of wells presented concentrations greater than the AML set by the NOM (0.01 mg/l). Approximately 294,000 inhabitants could be exposed to non-recommended levels of lead (Castillo, 2003).

16.8 per cent of the wells in the municipality of Aguascalientes had concentrations of phenols greater than the AML set by the NOM (0.001 mg/l), which implies an approximate population of 145,000 inhabitants exposed to non-recommended phenol levels. 8.5 per cent of the wells in the municipality of Aguascalientes showed levels of ammoniac nitrogen higher than the AML set by the NOM (0.50 mg/l). Since the ammoniac nitrogen present in the water of the aquifers is normally produced by microbial degradation of organic matter, these last results evidence a probable contamination of the aquifer by organic matter, which would imply an interaction between the aquifer and superficial wastewaters (Castillo, 2003).

Important problems of groundwater quality in relation to physico-chemical parameters such as pH, conductivity, hardness, alkalinity, and temperature were observed. Generally, the water of the aquifer tends to present low values of pH. 5.42 per cent of wells presented pH below 6.5 units (the minimum allowed by the NOM). High concentrations of dissolved salts in the aquifers are reflected by high values of conductivity. 46.9 per cent of the wells registered values greater than  $600 \,\mu$ Siemens/cm of conductivity. Hardness and alkalinity were usually located between

moderate and high levels. Finally, high temperatures were registered frequently. In general, groundwater showed several problems of quality because of a combination of low pH, high conductivity and elevated hardness, high temperature, and the presence of fluorides (Castillo, 2003).

This study also reflected an alarming depression of the aquifer. Between December 1998 and June 2001 an average depression in the static levels of 11.9 m was observed; which means a rate of depression of approximately 40 cm monthly; that is, an annual loss of almost five metres. A previous study indicated an average annual depression of 2 to 4 m. This result implies a substantial increase in the rate of depression of the aquifer during the last few years (Castillo, 2003).

Statistical analysis (almost 30,000 items of data) showed evidence of a correlation between the level of depression of the aquifer and alterations in the groundwater quality. The concentrations of arsenic and manganese, as well as the temperature, showed an increasing tendency in relation to the depression of the aquifer. Groundwater quality in the municipality of Aguascalientes is affected due to the accelerated over-exploitation of the aquifer. Parameters of quality representing significant problems, such as the fluorides, mercury, phenols, and lead, could be exacerbated in the near future (Castillo, 2003).

#### 16.6.3 Risk Assessment by Exposure to Fluorides

Fifty-one per cent of the wells that provide potable water to the population in the state of Aguascalientes had a concentration of fluorides higher than the allowed maximum levels (AML) established by NOM (1.5 mg/l). This problem is especially important in the municipality of El Llano, in which all the wells exceeded the AML set by the NOM (the average concentration was 3.8 mg/l). The exposed population (n=188) included children with a minimum time of residence of 6 years in the municipality of El Llano. The control population (n=140), also children with a minimum time of residence of 6 years, was selected from the municipalities of Tepezala and Asientos, which had a concentration of fluorides in the water supplies lower than 1.0 mg/l. The prevalence of dental fluorosis in the exposed and control populations were more than 60 per cent and less than 20 per cent, respectively. Thus, the high fluoride concentration in the water supplies constitutes the main factor determining the greater incidence of dental fluorosis in the exposed population. The high frequency of caries found in both populations (37 per cent) is explained by the lack of oral hygiene practices (Perez, 2004).

#### 16.6.4 Hydroarsenicosis Study

The study included 197 water wells from the border zone of the inter-state limit between Aguascalientes and Zacatecas. Forty-two communities were found to be exposed to high arsenic concentrations in drinking water, at arsenic concentrations between 2 and 7 times greater than the AML set by the NOM ( $25 \mu g/l$ ). These communities included four principal municipalities: Cosio and Tepezala in Aguascalientes, and Ojocaliente and Luis Moya in Zacatecas. The exposed communities represent a population of 95,000 people. In southern Zacatecas, 28 out of the 86 wells analysed had arsenic concentrations higher than the AML established by the NOM.

In northern Aguascalientes, 14 out of the 111 water wells analysed had arsenic concentrations higher than the AML set by the NOM. In the municipality of Cosio, 83 per cent of the water wells studied had high concentrations of this metalloid (Avelar, 2003b; Martínez, 2006). Arsenic pollution in these water wells is more important if the concentrations found are compared with the maximum arsenic concentration in drinking water recommended by the WHO (10 µg/l). Forty-five out of the 111 (40.5 per cent) water wells in northern Aguascalientes exceeded the maximum arsenic concentration recommended by the WHO. Affected municipalities included Cosio, Tepezala, Asientos, and San Francisco de los Romo (Tchounwou et al., 1999; ATSDR, 2000; Avelar, 2003b; Martínez, 2006).

Table 16.1 shows data from the study of arsenic exposure in the control and exposed populations (Berriozabal, Sauceda de Mulatos and Ejido Hidalgo). The daily ingestion of arsenic from drinking water in the exposed communities was 1.5 and 3.5 times higher than the tolerable maximum value recommended by the WHO ( $2 \mu g/kg$ , Tchounwou et al., 1999). A statistical correlation of arsenic concentrations ( $r^2 = 0.989$ ) in urine and drinking water was observed to be significant. Also highly significant were the differences between the urinary arsenic concentrations in the exposed population (n=146) with respect to the control population (n=123). It is concluded that the main human exposure to arsenic is through drinking water.

Twelve per cent of the exposed individuals (over 20 years of age and with a minimum residence in the community of 15 years) showed an incidence of cutaneous injuries related to arsenical keratosis (palmoplantaris). In addition, a statistically significant corre-

Community	Arsenic in drinking water (µg As/l)	Daily ingestion of arsenic (µg As/Kg)	Urinary excretion of arsenic (mg As/mg creatinine)	Population with keratosis palmoplantaris (%)
Control (n = 123)	5	0.2	$0.24 \pm 0.11$	3.2
Berriozabal (n = 55)	94	3.4	2.25 ± 1.3	10.9
Sauceda de Mulatos (n = 20)	140	5.2	$3.63 \pm 2.0$	15.0
Ejido Hidalgo (n = 71)	180	7.5	$5.04 \pm 2.6$	18.3

 Table 16.1: Exposure to arsenic and adverse effects in control and exposed populations.
 Source: Authors' research results.

lation ( $r^2 = 0.987$ ) was found between the incidence of arsenical keratosis and the level of exposure to arsenic. According to these results, high arsenic levels in drinking water are causing adverse effects on health for a significant percentage of the population chronically exposed (Avelar, 2003b; Flores 2006).

Even though not conclusive, it is speculated that the frequency of abortions was positively correlated with the daily intake of arsenic in drinking water. There was a statistically significant difference between the control population (38 per cent) and the Ejido Hidalgo sample (57 per cent) using a p < 0.05. It is an urgent priority that the Health Services Agency should take care of this problem. There was no statistically significant evidence linking the consumption of water contaminated with arsenic and alterations in the parameters determined in the general urine examination.

#### 16.6.5 Risk Assessment by Lead Exposure

Levels of Pb in blood showed a different distribution in the two populations. Highest concentrations of lead were observed in the exposed population, and fourteen samples displayed values between 10 and 16  $\mu$ g/dl of Pb in blood. With respect to the injury biomarkers, in 139 samples of the exposed population, which presented an overage Pb concentration in blood of 9.35 ± 1.3  $\mu$ g/dl, a greater urine excretion of ALA-U (amino levulinic acid) and a smaller activity of ALA-D (amino delta levulinic dehydratase) were observed with respect to the control population. The statistical differences in both biomarkers were statistically significant for p < 0.05 (Martínez, 2001).

The absolute number of lymphocytes CD19+, CD2+, and CD8+, and the concentrations of immunoglobulins G, M and A, did not show significant differences between the two groups (exposed and control populations). The antigenic challenge with the measles virus did either show significant differences between the two groups, in relation to the levels of specific immunoglobulins M and G. Estimation of the capacity of the cellular response, through the cutaneous test of the PPD (*purified protein derivative*), was also similar in both populations. On the other hand, significant differences (p < 0.05) were observed between both groups in the absolute number of lymphocytes CD2+/CD4+ (Martínez, 2001).

#### 16.6.6 Study of Indicators of Renal Damage in Populations Exposed to Cd and Pb

Children exposed to cadmium in La Luz presented an average urinary excretion of Cd four times greater than the control population. This represents a statistically significant difference (p=0.0009) between the two populations. The average urinary excretion of cadmium in the control population (0.31 µg of Cd/g of creatinine) was similar to values typically reported (0.1 to 0.6 µg of Cd/g of creatinine; Jarüp, 2006). In contrast, the exposed population presented an average urinary excretion of cadmium of 1.16 µg of Cd/g of creatinine. With this level of exposure, statistically significant differences were observed (with a level of significance of I per cent) in the percentage of positive cases of proteinuria (10.6 per cent), bilirubins (8.23 per cent) and ketones (11.76 per cent) in the exposed population, with respect to the values observed in the control population (0.8 per cent, 0 per cent and o per cent for proteinuria, bilirubins and ketones, respectively; Torres, 2007). Early renal effects, like tubular proteinuria, have been reported with urinary cadmium excretions from 2 to 4 µg of Cd/g of creatinine. A three times greater risk of proteinuria was observed in people with cadmium urinary excretion of 1  $\mu$ g of Cd/g of creatinine (Jarüp, 2006).

Children exposed to lead in Tepezala presented an average urinary excretion of lead 2.5 times greater than in the control population, giving a statistically significant difference (p=0.0000). The average urinary lead excretion in the control population was 10.5 µg of Pb/g of creatinine. By contrast, the exposed population showed a lead excretion of  $26 \,\mu g$  of Pb/g of creatinine. With this level of exposure, statistically significant differences were observed (with a level of significance of I per cent) in the percentage of positive cases of proteinuria (8.4 per cent), bilirubins (3.4 per cent) and ketones (6.2 per cent) in the exposed population, in contrast with the values observed in the control population (0.8 per cent, 0 per cent and 0 per cent for proteinuria, bilirubins and ketones, respectively; Torres 2007). These results agree with a previous study done by Fels (1998) that observed a urinary excretion of Pb twice as great as the control population, and the presence of indicators of renal damage.

In this study, carried out in infant populations exposed to metals in drinking water, a statistically significant correlation was observed between the levels of exposure to cadmium and lead and the incidence of indicators of renal dysfunction. The cadmium and lead concentrations in the water supplies slightly exceeded the AML set by the World Health Organization (0.003 mg/l and 0.01 mg/l for cadmium and lead respectively; WHO, 1995). The cadmium concentration in the exposed population was lower than the AML (0.005 mg/l) set by NOM-127-SSA1-1994 (Torres, 2007). It is of the greatest importance to follow up the communities studied in order to better establish the risks of exposure to heavy metals in drinking water, even in concentrations considered to be safe.

## 16.7 Conclusions

The San Pedro River is heavily contaminated with the discharge of domestic and industrial effluents with high concentrations of organic matter, nutrients (total phosphorus and total nitrogen), organic xenobiotics and faecal matter. The sediments reflected the anthropogenic impact on the trench, which has been used as a reservoir of a multitude of residues for decades. The sediments showed high volumes of organic xenobiotics (anilines and detergents), and levels of pollution by Cu and Zn. Besides the anthropogenic impact, an

important contamination of natural origin by arsenic was observed. The physico-chemical characteristics observed in the sediments suggest a high capacity for immobilizing metals and organic xenobiotics. The capacity for auto-purification of the San Pedro River is reduced and its contamination constitutes a risk to public health and to its ecological surroundings. The water quality of the Niagara dam is not suitable for irrigation. Evidence of the contamination of the aquifer by the surface water from the San Pedro River was not conclusive.

The main problem of groundwater quality is the high concentrations of fluorides, arsenic, mercury, chromium, iron, manganese, and lead. In the municipality of Aguascalientes, groundwater supplies contaminated with phenols and ammoniac nitrogen were also observed; these results suggest the infiltration of polluting agents into the aquifer of the Aguascalientes valley. Other issues deal with high concentration of salts, low pH and high temperature. There are water wells that frequently combine low pH, elevated conductivity and hardness, high temperature, and fluoride concentrations above the AML. An important increase in the abatement rate of the aquifer of the Aguascalientes valley was observed, reaching 5 m annually. A correlation between the level of abatement of the aquifer and alterations in the quality of the groundwater was observed. Groundwater in the municipality of Aguascalientes is affected by the accelerated over-exploitation of the aquifer. High concentrations of fluorides were found throughout the state of Aguascalientes. High concentrations of arsenic were found in the municipalities of the north near the state of Zacatecas.

The presence of high concentrations of fluorides in the drinking water supply constitutes the main factor determining the greater incidence of dental fluorosis in the exposed populations.

In the municipalities of northern Aguascalientes and southern Zacatecas, 42 communities were found to be exposed to high concentrations of arsenic in drinking water. The evidence suggests that the intake of polluted water constitutes the main exposure pathway of this metalloid. High levels of arsenic in drinking water are having adverse chronic effects on the health of a significant percentage of the exposed population.

In the municipalities of Tepezala and Asientos, high lead concentrations in blood were observed (above to 10  $\mu$ g/dl). With respect to injury markers, a greater excretion of ALA-U and a smaller activity of ALA-D were observed for the control population. The

differences in both biomarkers were statistically significant.

The infant populations that were exposed to metals in drinking water showed a statistically significant correlation among the levels of exposure to cadmium and lead, and the incidence of indicators of renal dysfunction (proteinuria, bilirubins and ketones). The cadmium and lead concentrations in the water supplies were slightly higher than the AML set by the World Health Organization (0.003 mg/l and 0.01 mg/l for cadmium and lead respectively; WHO, 1995). The cadmium concentration in the exposed population was lower than the AML (0.005 mg/l) set by NOM-127-SSA1-1994 (Torres, 2007). A follow-up of the communities studied is of the utmost importance to better establish the risks of exposure to heavy metals in drinking water, even in concentrations considered safe. Further research is needed to determine the effects of xenobiotics in drinking water on the health of the population.

It is very important to be in continuous communication with the appropriate State agencies concerning the health risks of the populations exposed to raised concentrations of xenobiotics and other contaminants in surface water. The effective and immediate intervention of the State authorities is also urgently required, to clean up the polluted surface water bodies and to reduce the consumption of contaminated water, as well as to upgrade the quality of drinking water to acceptable levels. The sustainable use of water resources is the most fundamental challenge facing the state of Aguascalientes. Methods to promote sustainable consumption of water resources include actions such as combating water spills, eliminating subsidies in the price of water supplies (particularly in wealthy colonies), and the use of state-of-the-art technology in the irrigation system of parcels of agricultural land.

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