

ARSENIC'S ASSOCIATION WITH SOLID PHASE OF THE NAZAS RIVER SEDIMENT

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ABSTRACT

In order to reduce the effects of intensive exploitation in the aquifer of the region named "La Comarca Lagunera" in North of Mexico, artificial recharge of the aquifer has been proposed. Unfortunately, "La Comarca Lagunera" aquifer is an area of endemic arsenic, threatening the 2 million people living there. Studies have been performed to understand the geochemical behavior of arsenic in the groundwater. However, the studies made to date are based on the analysis of arsenic concentrations in the groundwater themselves, and do not provide any information on the geochemistry of the aquifer sediments. The aim of this study was to determine if the Nazas river sediment is a source of arsenic and arsenic's association with solid phase of the sediment. The results could be extended to the whole aquifer, as the Nazas river, deposited sediments throughout the area. Four samples of subsurface alluvial sediments were taken along the path of the Nazas River, covering a distance of 60 km. Samples were submitted to a seven-step sequential extraction protocol to evaluate arsenic fractionation and mobilization potential. The mineralogical fractions in which the arsenic is associated are: Soluble, Exchangeable; Associated with carbonates, Specifically adsorbed, Associated with iron and manganese oxides and Residual.

Keywords: Arsenic, River sediment, México, Arsenic fractionation, Groundwater

INTRODUCTION

Since the early 1960s, the health institutions of Mexico reported health problems in humans and animals, in the Laguna Region, in Northcentral Mexico, due to consumption of groundwater with high arsenic concentrations. Groundwater is the main source for drinking, agricultural and industrial use. Studies (CINVESTAV, 1986 [1]; IMTA, 1992[2]) have outlined extensive areas of the La Laguna where arsenic levels are above 25 µg/L, the maximum level adopted in Mexico. The high arsenic concentrations are a threat to the 2 million people living in the area.

Hydrochemical and isotopic studies (SICYGSA, 2000 [3]; Molina, 2004 [4], Ortega, 2003[5]) have been performed to understand the geochemical behavior of arsenic and other components in the groundwater. Molina believes that high arsenic levels in the groundwater are produced by a combination of dissolution of Fe oxides and desorption of arsenic due to elevated pH values. SICYGSA suggests that arsenic desorption depending on the pH of the groundwater is a process of mobilization, given that found relationship between arsenic and pH. Ortega's research, conducted in the lagoon of Viesca, found low values of arsenic in the carbonate aquifer and high values in the clay aquitard. However, the studies made to date are based on the analysis of arsenic concentrations in the groundwater themselves, and

do not provide any information on the geochemistry of the aquifer sediments.

This paper examines both the geochemistry of the sediments and the groundwater, in order to establish the relationship between the aqueous and solid phase and understand the trends of arsenic concentrations in the groundwater.

STUDY AREA

The study area is located in the North central part of Mexico and occupies southwestern portions of Coahuila and northeastern of Durango (Fig. 1). This area is located in the region named "La Comarca Lagunera" in Mexico. It is bounded on the west and south by the Sierra Madre Oriental and the east and north by isolated mountains.

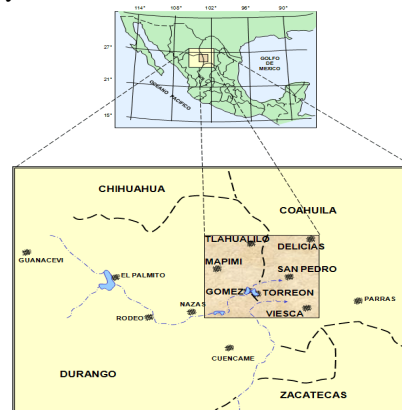


Fig. 1. Study area

The geological formations cover a period of time from the Paleozoic to the recent Quaternary alluvium (Álvarez, 1961[6]; Tamayo, 1982[7]). The basin is composed of both sedimentary deposits (limestone, dolomite, gypsum, sandy clays and conglomerates) and igneous rocks (granite and volcanic deposits). The geological succession (INEGI, 1988[8]) includes: (1) The Jurassic formation, "Minas Viejas", with gypsum, shale and limestone, (2) The Cretaceous formation: "Aurora" with limestones and dolomites, "Indura" composed of shales, limestones and siltstones (Tardy, 1974[9]) and "Caracol" with shales, clays and sands, (3) The tertiary formation: "Ahuichila" composed of limestones and conglomerates and "Santa Ines" also formed of limestones and conglomerates with a matrix of impermeable clay, and (4) The Quaternary Alluvium, which forms the aquifer of the region (fig. 2).

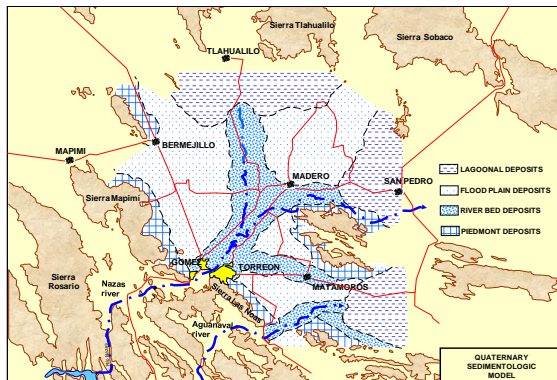


Fig. 2. Quaternary sedimentologic model

The Laguna Region is an endorheic basin fed by rivers Nazas and Aguanaval: (1) The Nazas, with 220 km of length, drains the western with a 60,000 km² basin covering the states of Coahuila and Durango. The annual average flow is 1.1×10^9 m³ and is regulated by dams Lazaro Cardenas and Francisco Zarco (PIFSV-SARH, 1991[10]), (2) Aguanaval River, 305 km of length, drains the southeastern with a 25 500 km² basin. The annual average flow is 1.6×10^8 m³ (PIFSV-SARH, 1991[10]). The rainy season covers four months, from June to September, with an annual average rainfall of 200-300 mm. The annual average temperature is 20.6 °C.

In the eastern part of the region is located a vast plain of alluvial lacustrine deposits, where in the past the Nazas and Aguanaval rivers discharged their water, forming both ephemeral and perennial lakes. Part of the water infiltrated to form an aquifer in granular materials.

The groundwater circulation is characterized by a general flow eastwards, from the Sierra towards the depression. Figure 3 presents water table elevation under natural conditions (Escolero et al., 1992 [11]). At present there are several areas of water table

depression due to pumping, but essentially flow trend continues.

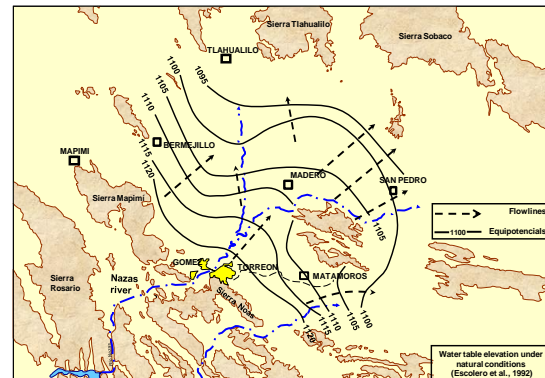


Fig. 3. Natural groundwater flow (Escolero et al., 1992)

METHODOLOGY

Geochemistry of the sediment

Four samples of subsurface alluvial sediments were taken along the Nazas river path (Fig. 4). Sampling was carried out following the direction of the river channel and selecting those sites containing representative samples of alluvial deposition.

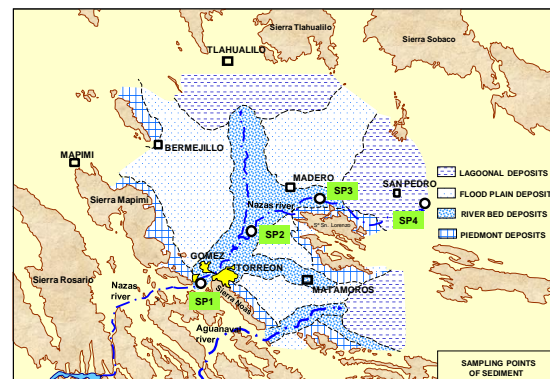


Fig. 4. Sampling points of sediment

Samples were dried at 35 °C for 48h, then were homogenized, quartered and sieved to 60 mesh (dp <250µm).

Samples were submitted to a seven-step sequential extraction protocol (SEP) to evaluate As fractionation and mobilization potential. We used the protocol proposed by Briones-Gallardo et al., 2009[12], with modifications of the protocols of Keon et al., 2001[13] and Tessier et al., 1979 [14]. This method distinguishes the following mineralogical fractions in which may be associated the arsenic to seven mineralogical fractions: soluble fraction (SOL); Non-Specific adsorption fraction. Loosely adsorbed arsenic (NSA); fraction associated with carbonates (CAR); Specific adsorption fraction. Arsenic strongly adsorbed (SA); fraction associated with iron and manganese oxyhydroxides

(IMO); fraction associated with organic matter and sulfides (OMS) and the residual fraction (RES).

Once prepared the sample, 0.5 g was placed in a conical vial to start SEP using the following procedure: for **SOL** fraction, the sample is contacted during 20-min with deionized water at pH 5.5. The supernatant is centrifuged and analyzed; the **NSA** comprises three sequential extractions with 0.5 M solutions of NaNO_3 , $\text{Mg}(\text{NO}_3)_2$ and MgCl_2 over the sediment recovered from the soluble fraction. Contact times for each extraction are 20 min. The supernatant from each extraction is centrifuged and analyzed. The report of this fraction is the sum of the concentration obtained with each extracting agent; for **CAR** sediment recovered from the previous fraction is contacted for 5 h with a solution of CH_3COONa (1 M) to pH adjusted to 5.0 with concentrated CH_3COOH . The supernatant is centrifuged and analyzed; at **SA** sediment recovered from the previous fraction is contacted with NaH_2PO_4 solution (1 M) for two cycles of 24 h, centrifuging the supernatant and analyzing between each extraction cycle; for determining the **IMO** sediment recovered from the previous fraction is contacted 20 min with a solution of $\text{NH}_2\text{OH} \cdot \text{HCl}$ (0.04 M) graduated with CH_3COOH at 25% v/v. This step is performed in a water bath for 6 hours at 96 °C in a semiclosed reflux system. The supernatant is centrifuged and analyzed; for **OMS** sediment recovered from the previous fraction is contacted with H_2O_2 at 30% at pH 2.0 for two cycles, the first of two hours and the second of three hours, both at 85 °C, then adding a solution of ammonium acetate with HNO_3 at 20% and stirred for 20 min. The supernatant is centrifuged and analyzed; finally for the **RES** sediment recovered from the previous fraction is digested with acid in a microwave system using a solution of HNO_3/HCl with a ratio of 3:2 vol/vol.

Geochemistry of the groundwater

Water samples were taken from wells located in the study area. The parameters measured in the field were: water temperature and ambient (T), the potential of hydrogen (pH), electrical conductivity, dissolved oxygen and redox potential.

Groundwater samples were filtered through 0.45 μm in-line filter by pumping water from the sampler probe using a peristaltic pump. The filtered samples were then acidified to pH ~2 by addition of ultra-pure HNO_3 to determine metals. The samples to determine anions were preserved only at 4 °C. All samples were collected in pre-cleaned HDPE bottles. Trace element concentrations were determined by ICP-MS.

RESULTS AND DISCUSSION

The total concentration of arsenic is presented in Fig. 5, defined from the sum of the fractions determined in the sequential extraction. The arsenic content is increased from 11 mg/kg to 36 mg/kg.

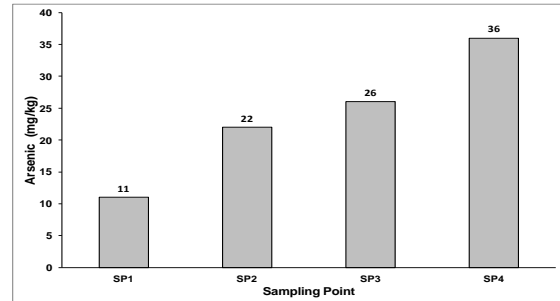


Fig. 5. Concentration of arsenic in the sediment

Figure 6 shows the variation of arsenic fractionation in the longitudinal sampling (S1 to S4), dominating downstream a higher percentage of arsenic in the Loosely Adsorbed Fraction (NSA), which ranges from 0% (SP1) to 44% (SP4). The percentages of arsenic potentially available comprise 47% to 85%. The same figure also shows arsenic in fractions associated with iron oxides in all cases, in significant percentages.

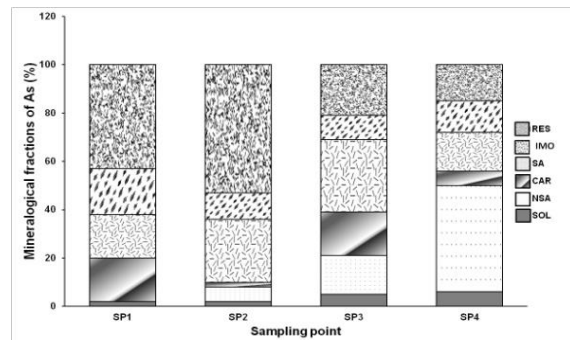


Fig. 6. Mineralogical fractions of Arsenic

Arsenic values versus pH are displayed in Fig. 7. It is noted that the water samples having a pH lower than 8.1 have a low arsenic content. However, when the pH is greater than 8.1 the values of arsenic increases considerably.

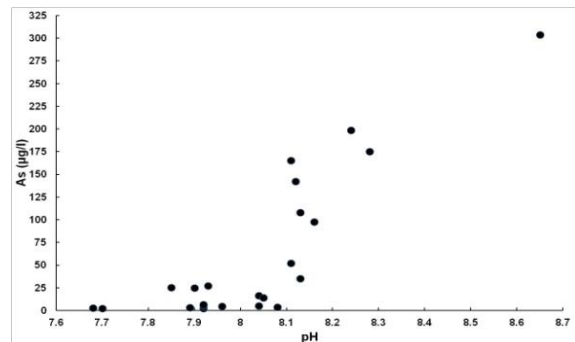
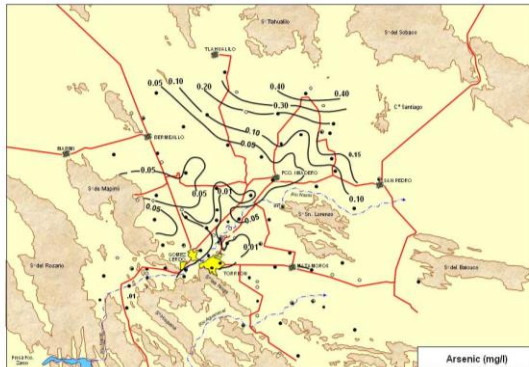


Fig. 7. Arsenic versus pH

When the pH values are higher than 8, the net charge of the iron oxides surface becomes negative, and repels negatively charged ions, such as arsenic. Because part of the arsenic is adsorbed to iron oxides (Fig. 6), this is desorbed when the pH is greater than 8.1.

Isolines of arsenic concentrations are shown in Fig. 8. It is noted that the concentration increases in the direction of flow, which coincides with the Loosely Adsorbed Fraction, which also increases downstream (Fig. 6). It is possible that the anions present in the groundwater compete with arsenic for adsorption sites.



[13] Keon N.E., Swartz C.H., Brabander D.J., Harvey C. and Hemond H.F. (2001) Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environmental Science & Technology* 35, 2778-2784.

[14] Tessier, A., Campbell, P.G.C. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry* 51, 844-851.