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CASE REPORT

Correlates of Arsenic Mobilization into the Groundwater in El Paso, Texas

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Abstract: This paper addresses the contamination of groundwater by arsenic, a naturally occurring phenomenon that has caused serious cases of arsenic poisoning around the world. While a number of chemical processes are known to be capable of mobilizing arsenic, the extent to which different processes are active in actual geological settings is much less clear. In this work, the El Paso, Texas region is analyzed as a case study to better understand the factors associated with high arsenic levels in groundwater. This study includes two basins that supply drinking water to approximately 2.5 million people. The average arsenic was 8.5 ppb, which is below the current American and WHO Maximum Contaminant Level of 10 ppb. However, arsenic concentrations reached approximately 80 ppb in three different locations. Governmental archival information was combined with field water sampling, and with leaching and analysis of solid phase materials from well cuttings (sediments of the aquifers). The study identifies evidence for both competitive desorption and reductive dissolution operating to mobilize arsenic, with the importance of different mechanisms likely varying throughout the aquifers. A mean of 21% of the solid arsenic content was leached out to solution at pH 9, and mean solid phase arsenic concentration was 4.3 ppm, solid phase iron 7000 ppm, and solid carbon 0.6%, consistent with arsenic desorption out of sediments into the aqueous phase. A potential role of geothermal waters was also identified at a southern hot spot. This information is important to better understand the basic science of the arsenic geochemical cycle and may also provide a rough guide as to where low arsenic waters may be found: groundwater with high potentiometric head and short flow paths, groundwater under the influence of surface water, and lower pH groundwater.

Keywords: arsenic, groundwater, correlates, desorption, reductive dissolution

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Introduction

High arsenic concentrations in drinking water have been linked to diverse types of cancer and to other serious diseases.[1,2] To reduce this potential health risk, in 2001 the United States Environmental Protection Agency (USEPA) lowered the maximum level of arsenic permitted in drinking water from 50 micrograms per liter (µg/l) to 10 µg/l or parts per billion (ppb). Concentrations of arsenic in groundwater naturally occur in a very large range of values, from <0.5 to 5000ppb[3].

While a number of chemical processes are known to be capable of mobilizing arsenic, the extent to which different processes are active in actual geological settings is much less clear. This situation creates a need for case studies to identify the processes mobilizing arsenic in particular geochemical settings. In this work, the El Paso region of Texas in which approximately 20% of the groundwater (analyzed from 1984 to 2003) exceed the arsenic drinking water standard of 10 ppb,[4] is analyzed as a case study to better understand the factors associated with high arsenic levels in groundwater. The groundwater flows throughout two basins (the Hueco and the Mesilla), and parts of both are studied here. This study combined governmental groundwater databases with experimental results for the statistical analyses and conclusions. The El Paso Water Utilities archival database used here provided information about well numbers, locations and hydrological conditions such as confinement, artesian wells and depth of wells as well as of water chemistry.

The study was initiated by calculating the correlations among water constituents involved in arsenic mobilization. These correlations may serve as first indicators while comparing them with the necessary associations expected when specific geochemical processes occur. The data suggested the occurrence of arsenic desorption and experiments performed tested this possibility by analyses of solid phase, aqueous phase and leaching arsenic. The study concludes that there is evidence for both competitive desorption and reductive dissolution operating to mobilize arsenic, with the importance of different mechanisms likely varying throughout the aquifers. Geothermal waters associated with high arsenic were identified at a southeastern spot as well.

Location and Hydrology

The Paso Del Norte Region is an urbanized region of the Rio Grande Valley located at the intersection of the states of Texas and New Mexico in the United States, and the Mexican state of Chihuahua. The region includes the cities of El Paso, Texas, USA, and Ciudad Juarez, Mexico. The entire region is inhabited by more than 2.5 million people. The area studied is approximately 350 square miles. The geographical coordinates of El Paso city are 31.8 ° North, 106.4 ° West, with an elevation of 3943 ft. It is located in the northern Chihuahuan Desert and has a subtropical arid climate with mean annual precipitation of about 20 cm.[5]

The Franklin Mountains divide the two basins that underlie the region (see Fig. 1). The basins supply approximately 50% of El Paso's drinking water, and the Rio Grande River supplies the other 50% (with percentages varying seasonally). The Hueco Bolson (Hueco basin) is located east of the Franklin Mountains and the Mesilla Bolson (Mesilla basin) is northwest of them. These basins are not hydraulically connected, and both partially drain to the Rio Grande River (which defines the US-Mexico border).

Arsenic Geochemistry

Arsenic is commonly found in one of two oxidations states in natural waters. Under oxidizing conditions, arsenic(V) or arsenate (AsH_3O_4) is the predominant form. Arsenate exists as an oxyanion at neutral pH. Under reducing conditions arsenic(III) or arsenite (AsH_3O_3) may be found. Arsenite is neutrally charged at pH 7.0.

Aqueous phase arsenic concentrations are controlled by a number of geochemical processes that govern interactions between aqueous and solid phase aquifer materials.[6–9] Stollenwerk (2003) found that the solubility of arsenic-bearing minerals is much higher than the aqueous concentrations of these minerals typically found in ground water.[9] This indicates that adsorption and desorption of arsenic from the solid-phase surfaces of the aquifer is the predominant control on dissolved arsenic concentrations in many ground water systems, rather than precipitation-dissolution reactions.

Adsorption-desorption processes

Aquifers typically contain a variety of solid phase materials capable of adsorbing arsenic from solution, including iron, manganese, and aluminum hydroxides.[3,7,9] At the alkaline pH values typical of many groundwaters, iron hydroxide would have greater affinity for the arsenate anion than manganese

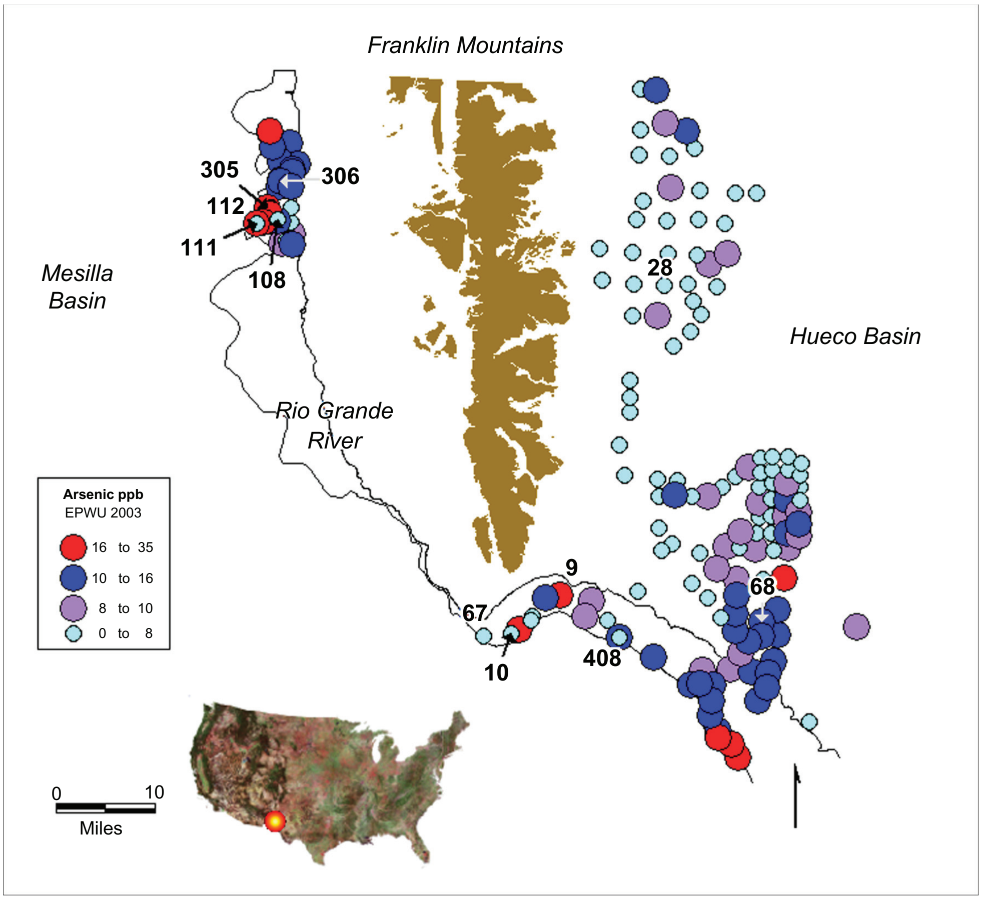

Figure 1. Average arsenic concentrations in El Paso wells from 1984 to 2003 (EPWU 2003). Numbers show the well# of cuttings analyzed and leached.

and aluminum hydroxides, and adsorption to ferric hydroxide is a major control on aqueous arsenic concentration.[10] A variety of anions compete with arsenate for adsorption sites on the solid phase of ferric hydroxides (≡FeOH). The molecules that usually occur in groundwater and compete with arsenic oxide are: CO_3^{2-} , SiO_2, PO_4^{3-}, OH^-.

Reductive dissolution and geothermal inflow processes

When iron or manganese are reduced they become more soluble and may release arsenic ions adsorbed to them. In addition, as arsenate is reduced to arsenite, it will bind less strongly to the hydroxide solids (at neutral and near neutral pH values), as shown by the following summary reactions which increase the concentrations of both Fe and As in solution:

Fe(III) less soluble → Fe(II) more soluble
As(V) more adsorbed → As(III) less strongly adsorbed

This mechanism is referred to as reductive dissolution in this paper. Reduced environments generally occur deep in the aquifer or when microorganisms promote reduction. Expected dissolved oxygen (DO) would be very low or absent as would the concentrations of oxidized species of almost all molecules.[8]

The upwelling of waters from deeper portions of the basins may influence arsenic concentrations. This upwelling may occur from geothermal inflow or excessive pumping. The waters coming from deeper strata in general will be older, warmer, and more mineralized as these waters have had many opportunities to dissolve both trace ions and major ions.[11] As mineralized waters will have high alkalinity and high pH, they will likely promote arsenic mobilization via the competitive desorption mechanism.

Materials and Methods

Archival information

The archival information used in this work included 6000 records of El Paso Water Utilities groundwater database.[4] These data comprise information on the concentrations of 14 major ions, pH, dissolved arsenic and dissolved iron in 287 drinking and non-drinking water wells, collected between 1927 and 2003. The dissolved arsenic, iron and the arsenic speciation analyses were performed between the years 1980 to 2003 by EPWU with high precision EPA methods for trace levels of concentrations in water.

Correlation analysis

The first method was to statistically identify the strong associations among water constituents and match them with known geochemical mechanisms when possible. Different mechanisms produce different associations and therefore significant correlation coefficients from archival information may be used as "indicators" of geochemical processes which are probably mobilizing arsenic. When the associations are weak or are not significant, then we cannot tell if a specific mechanism is significantly supported (P-values of 0.05 or less).

In every well, each of the chemical components was averaged giving a mean value per well per component, the correlations were performed with the mean values for the wells studied (229 in the Hueco basin or 58 in the Mesilla basin). In this way, the total dissolved arsenic, dissolved iron, and arsenic speciation analyses studied here, consider averages of the last 20 years, and common constituents are averages of 84 years.

Spearman's (non-parametric) correlation coefficients were used to identify associations between variables to avoid the need to make assumptions about the distribution of the variables. Statistical analyses were performed with SPSS package (IBM Chicago, IL), and the map prepared with GIS software ArcView (Esri, Redlands, CA).

Sample collection

Additional information from a subsample of nine wells was collected for this work in the Hueco basin at Ciudad Juarez, Mexico.

The water samples were collected when the wells were operating and were drawn at the wellhead, before chlorination. The water was allowed to flow for about three minutes before sample collection. Samples were collected in 200 ml plastic containers, which were thoroughly rinsed and filled without headspace. The pH, temperature, electrical conductivity, and salinity were measured in the field. Water was analyzed for arsenic within 10 days of the collection date by the New Mexico State University Soil and Water (NMSU SWAT) laboratory (Las Cruces NM) using ICP method EPA 200.8.

Analysis of solid phase aquifer materials

Additional solid phase aquifer materials (cuttings) experiments were then performed with sediments of the basins, strengthening the indications of desorption and reductive mobilization.

The cuttings used here were obtained when El Paso Water Utilities drilled in the basins establishing the wells, make a total of 15 samples. In Figure 1, the numbers refer to these well cuttings.

Well cutting samples of 1.5 g material from each of the 15 wells were analyzed for arsenic and iron levels. Eleven of these samples were from wells of higher dissolved arsenic content (11 to 16 ppb arsenic) while 4 were from lower arsenic wells ($<$6 ppb arsenic). Total organic carbon (TOC) was analyzed in 11 cuttings. Each 1.5 g sample was thoroughly sieved to 75 microns particle size (standard sieve # 200) before analysis. Additionally, for each one of the 15 cuttings approximately 5 g of the original loose sediments were leached at pH 9. Each solution was made of 15 ml of deionized water adjusted with NaOH to the desired pH. The total set of 30 sand samples was leached for 48 hours while being shaken mechanically, then centrifuged at 3500–4500 rpm, for 15–25 min, filtered and analyzed for dissolved arsenic in the NMSU-SWAT laboratory (EPA 200.8 method for dissolved arsenic in water).

Results and Discussion

The mean average arsenic concentration in raw groundwater in El Paso region was 8.5 ppb,[4] with individual observations ranging from 0 to 95 ppb. However, since 2006 no more than 7.8 ppb of arsenic are present in the drinking water supply, due to the presence of treatment plants which treat 30 million gallons per day.[12]

The map in Figure 1 shows the region studied, color circles representing the average arsenic concentrations over approximately 20 years per well. The wells identified by number are the wells used in the cuttings and leaching experiments here (numbers by EPWU). The extent of the Hueco basin studied here is very large. From Figure 1, at the East side of well #67 are the wells in the Hueco basin including 229 out of the 287 wells (extended in about 95% of the area studied). The Northwestern cluster of circles in Figure 1 includes all the Mesilla basin wells considered here. The Mesilla basin is composed of three horizontally piled semi-confined aquifers, named in the EPWU database as "shallow", "intermediate" and "deep". The "shallow" aquifer yields water from wells between 40 ft and 150 feet, the "intermediate" between 145 ft and 600 ft, and the "deep" wells between 250 ft and 1200 ft depth, however the "intermediate" aquifer includes regions down to 1000 ft deep.[4]

Table 1. Descriptive statistics in the Mesilla and Hueco Basins from EPWU(a) archieves. Units of As, Fe, and Mn are ppb (mg/1), units of the other components are in ppm (mg/1).

Mesilla	**As***	**pH***	**Depth (m)**	**Fe**	**Mn**	**SiO_2**	**Ca^{2+}**	**Ca^{2+}%**
Mean	12.4	8.4	99	247	148	31	42	19
Std. Dev.	5.2	0.45	72	277	202	6	33	8
Minimum	3.5	7.6	13	18	2	18	3	4
Maximum	27.8	10	290	940	769	43	139	37
Hueco	**As**	**pH**	**Depth (m)**	**Fe**	**Mn**	**SiO_2**	**Ca^{2+}**	**Ca^{2+}%**
Mean	7.56	8.0	168	388	86	31	47	24
Std. Dev.	3.64	0.22	38	991	290	3	27	9
Minimum	1.15	7.1	45	6	1	16	17	11
Maximum	19.5	8.8	259	8756	2700	42	180	68
Mesilla	**Na^+**	**Na^+%**	**Mg^{2+}**	**Mg^{2+}%**	**Cl^-**	**Cl^-%**	**HCO_3^-**	**HCO_3^-%**
Mean	167	77	7	5	123	35	132	23
Std. Dev.	74	11	7	4	80	8	73	7
Minimum	84	53	0.2	0	33	17	34	7
Maximum	455	95	29	16	467	57	347	48
Hueco	**Na^+**	**Na^+%**	**Mg^{2+}***	**Mg^{2+}%**	**Cl^-***	**Cl^-%**	**HCO_3^-**	**HCO_3^-%**
Mean	152	64	15	13	207	52	147	29
Std. Dev.	78	16	21	14	148	18	38	14
Minimum	4	2	3	3	25	14	0	0
Maximum	486	83	212	87	923	91	271	66
Mesilla	**SO_4^{2-}***	**SO_4^{2-}%**	**PO_4^{3-}**	**TDS (b)**	**Hardness**	**Ec (μS/cm)**	**F^-**	**NO_3^-**
Mean	195	42	0.21	652	130	1013	0.68	2
Std. Dev.	104	4	0.29	322	107	471	0.25	2
Minimum	51	29	0.02	249	10	407	0.14	0
Maximum	495	48	1.2	1530	461	2320	1.48	8
Hueco	**SO_4^{2-}**	**SO_4^{2-}%**	**PO_4^{3-}**	**TDS (b)**	**Hardness**	**Ec (μS/cm)**	**F^-**	**NO_3^- ***
Mean	90	19	0	640	167	1072	0.76	6
Std. Dev.	44	7	1	269	88	497	0.26	5
Minimum	31	7	0	241	63	1	0.23	0
Maximum	288	38	6	2004	584	3677	2.73	43
Mesilla	**K^+**	**CO_3^{2-}***	**Num_wells**					
Mean	4	6	58					
Std. Dev.	2	11						
Maximum	10	55						
Hueco	**K^+***	**CO_3^{2-}**	**Num_wells**					
Mean	9	0.89	229					
Std. Dev.	3	1.16						
Maximum	22	10						

(a) EPWU: E1 Paso Water Utilities. (b) TDS: Total Dissolved Solids.

• Concentrations that differ significantly between the two basins at 0.05 significance level.

Table 2. Spearman's correlation coefficients of dissolved arsenic with selected constituents, in well water in the Hueco (sub-regions) and the Mesilla basins.

Region	**pH**	**Fe**	**Mn**	**SiO_2**	**Ca^{2+}**	**Ca^{2+}%**	**Na^{+}**	**Na^{+}%**
Mesilla	0.395**	–0.281	–0.627**	–0.086	–0.482**	–0.399**	–0.453**	0.488**
Hueco	0.410**	–0.027	–0.076	–0.057	–0.044	–0.447**	0.486**	0.609**
Hueco High potentiometric level	0.253	0.156	0.205	0.425*	0.095	–0.306	0.441*	0.534**
Hueco Low potentiometric level	0.711**	0.170	–0.335	0.13	–0.596**	–0.672**	0.216	0.738**
Region	**Mg^{2+}**	**Mg%**	**Cl^{-}**	**Cl^{-}%**	**HCO_3^{-}**	**HCO_3^{-}%**	**SO_4^{2-}**	**SO_4^{2-}%**
Mesilla	–0.55**	–0.54**	–0.435**	0.156	–0.450**	–0.053	–0.478**	–0.203
Hueco	–0.30**	–0.64**	0.360**	0.334**	–0.373**	–0.421**	0.277**	–0.029
Hueco High potentiometric level	–0.438*	–0.63**	0.487**	0.464**	–0.674**	–0.634**	0.277	0.132
Hueco Low potentiometric level	–0.71**	–0.73**	–0.022	0.162	–0.46**	–0.146	–0.316	–0.162
Region	**Depth**	**NO_3^{-}**	**PO_4^{3-}**	**TDS**	**K^{+}**	**EC**	**F^{-}**	**CO_3^{2-}**
Mesilla	0.532**	0.071	–0.253	–0.47**	–0.357*	–0.411**	0.082	0.301
Hueco	–0.34**	–0.43**	0.125	0.346**	–0.046	0.338**	–0.170*	0.191*
Hueco High potentiometric level	–0.083	0.073	0.185	0.367*	0.424*	0.369*	–0.679**	–0.001
Hueco Low potentiometric level	–0.115	–0.104	–0.227	–0.137	–0.561**	–0.079	0.321	0.56**

Notes: TDS: Total Dissolved Solids in ppm (mg/l). *Correlation significant at 0.05 level; **Correlation significant at 0.01 level.

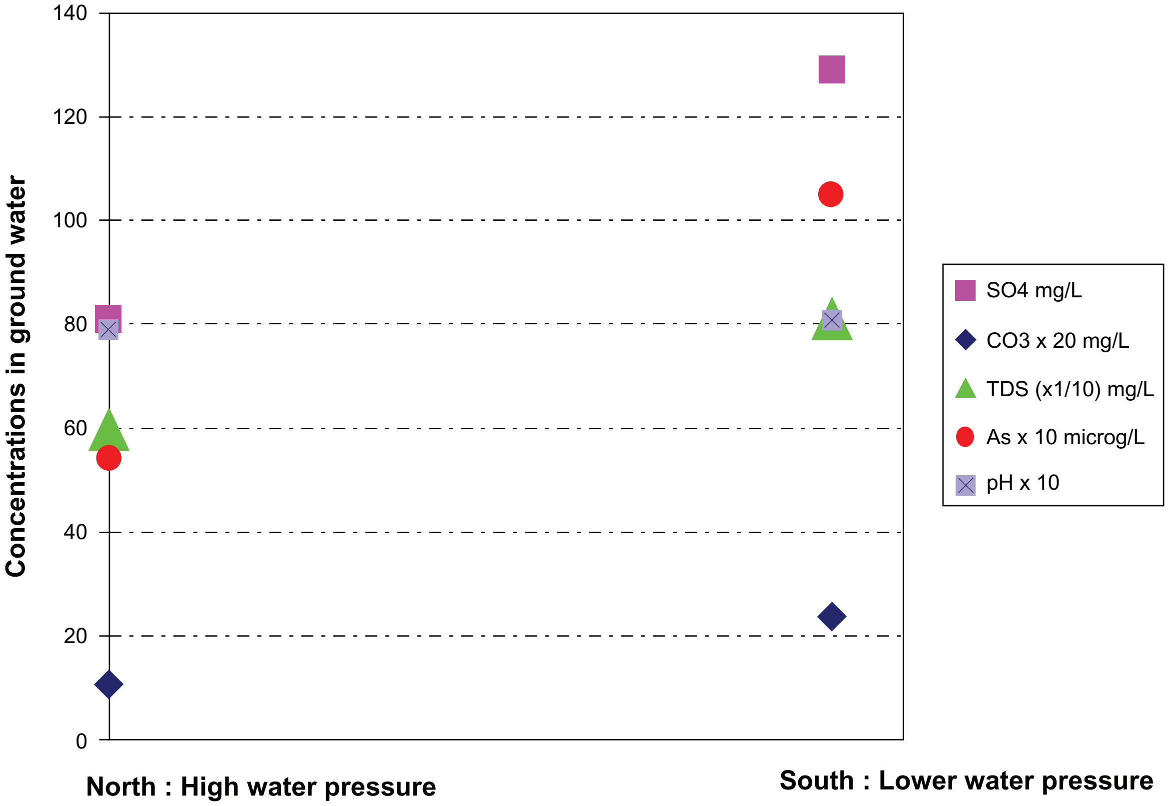

Figure 2. Schematic showing changes in the average concentration of arsenic, some ions, and pH, while the water flows from higher to lower headwater regions through the Hueco basin.

Water chemistry in both basins

Table 1 summarizes water quality values for the Mesilla and Hueco basins. Tables 1 and 2, and Figure 2 show means of the means for each variable.

The water in the Mesilla is alkaline (mean pH 8.4, ranging from 7.6 to 10), high in arsenic (mean 12.4 ppb), sulfate (probably from gypsum dissolution), and sodium.[13,14] The high alkalinity of the environment in the Mesilla ground water would be expected to increase the potential for mobilization of arsenic(V) by desorption.

In the Mesilla the most significant positive correlations with arsenic found were for pH and depth; the most significant negative correlations with arsenic were Cl^-, total dissolved solids (TDS), Mn, Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-} and electroconductivity (EC) (Table 2). The proportional association of arsenic with depth and pH but negative association with TDS, reflect the influence of the Rio Grande River on shallow wells in the Mesilla basin. The river water is generally low in arsenic concentration, alkalinity, and pH, but high in dissolved solids. The low arsenic concentrations are common for aerobic surface waters where arsenic is present in the oxidized form arsenic(V), which can be readily removed from the aqueous phase by sorption to a variety of minerals, such as iron and aluminum oxides. Thus, the positive correlation between arsenic and pH may simply reflect that the deeper wells have both higher alkalinity and pH than the shallow wells under the influence of river water. However, it may also result at least in part from the higher pH causing desorption of arsenic from hydroxide solids.[15]

Correlates supporting arsenic desorption in the Hueco basin

In the Hueco the most significant positive correlations of arsenic are with: pH, CO_3^{2-}, SO_4^{2-}, Cl^-, TDS, Na^+, and electrical conductivity (EC), the most significant negative correlations were with Mg^{2+}, NO_3^-, and Ca^{2+} (Table 2). The positive significant correlations with pH, Cl^-, SO_4^{2-}, and CO_3^{2-} support competitive desorption of arsenic, as high concentrations of these competing anions may be driving the desorption of arsenic from the aquifer solid surfaces into the groundwater (see equations 1 and 2). Observing the substitution of AsO_4^{3-} by CO_3^{2-} molecules in the hydroxide mineral (≡FeOH) the equations according to Montoya and Gurian (2004)[15] are:

$$\equiv FeOH + AsO_4^{3-} + 3H^+ = \equiv FeH_2AsO_4 + H_2O \quad (1)$$

$$\equiv FeOH + CO_3^{2-} + 2H^+ = \equiv FeH\,CO_3 + H_2O \quad (2)$$

When carbonate increases in equation 2, the reaction shifts toward the right and the hydroxide ≡FeOH concentration diminishes. Then the reaction in equation 1 shifts toward the left side, releasing arsenic into the water (from the solid $\equiv FeH_2AsO_4$ surfaces). Thus high carbonate concentrations produce high arsenic concentrations in solution, which imply a positive correlation coefficient between the arsenic and the carbonate molecules. The positive correlation with sodium and negative correlation with magnesium suggest that more cation-exchanged waters have higher arsenic concentrations. More cation-exchanged waters would be expected have been exposed to more minerals, longer flow paths, and have had more opportunities to encounter arsenic-bearing minerals.

The pH dependence of adsorption/desorption reactions is different for the two species of arsenic. Because arsenic(III) is neutrally charged at near neutral pH values, its sorption reactions are not highly pH dependent. In contrast, the negatively charged arsenic(V) desorbs from metal hydroxide surfaces as the surfaces become negatively charged at high pH.[8,9] Montoya and Gurian (2003, 2004) found this pH-arsenic(V) association becomes clearer for pH values above 8.[10,15]

Short and long flow paths in the Hueco basin also support desorption

In El Paso, the groundwater naturally flows from North to South.[14] In this paper northern regions will be considered as having higher water pressure or higher 'potentiometric' values, analogously southern regions in the Hueco will be called 'low potentiometric' regions. The statistical analysis suggested that arsenic accumulates after the groundwater has flowed longer. The concentrations and the correlations were analyzed in two sub-regions in the Hueco basin, northern and southern (Fig. 2).

Previous research suggests that arsenic may be associated with older groundwater that has had more opportunities to encounter arsenic deposits after longer flow paths.[7] In this study, El Paso Southern wells (with lower potentiometric heads) clearly have higher arsenic than Northern wells where groundwater has traveled shorter distances. The high arsenic wells also have higher pH, TDS, and a bigger proportion of monovalent cations compared to divalent cations (magnesium and calcium) than northern wells with shorter flow-paths. All of this is consistent with longer flow paths allowing water to have more opportunity to encounter arsenic deposits, to dissolve aquifer solids, and become more cation exchanged. Also the level of significance of the association between arsenic and pH varies between the two regions (Table 2). The positive correlation between arsenic and pH is 0.25 (P-value > 0.05) at the northern wells close to the Franklin Mountains where some recharge occurs[13] but this correlation rises up to 0.71 for the longer flow paths (P-value < 0.001). For shorter flow paths, arsenic concentrations may relate less to water chemistry and more to the presence or absence of localized arsenic deposits. Over longer flow paths two factors may change this: 1) exposure to localized arsenic deposits will tend to average out and have less impact on arsenic variability, and 2) as levels of both arsenic and competing anions increase, competition for available adsorption sites will become a more important factor. Hence the correlation with water chemistry parameters such as pH may be more pronounced over longer flow paths. Figure 2 shows a subgroup of wells including those with shorter flow paths (Northern) and longer paths (Southern). Many of the southern wells were also artesian wells with high arsenic concentrations as registered in the EPWU archives.[4]

Arsenic speciation in the Mesilla-indications of reductive dissolution

Data on the species of arsenic present is available from a study in the Mesilla basin conducted by the EPWU (speciation data was not available for the Hueco basin). In the Mesilla basin, arsenic is present as both arsenic(III) and arsenic(V) but with at least half and usually closer to two-thirds of the arsenic present as arsenic(V). The presence of arsenic(III) (from 3.9% to 63%) indicates that conditions are at least moderately reductive in the wells with higher average arsenic, and reductive dissolution may be occurring. However, the predominance of arsenic(V) indicates that either reductive dissolution is not the sole mechanism mobilizing arsenic, or that substantial re-oxidation occurs subsequent to mobilization. The lack of a correlation between aqueous iron and arsenic (Table 2) is puzzling. It may be that reduction is sufficient to convert arsenic(V) to the less strongly adsorbed arsenic(III) but not to mobilize substantial amounts of iron.

Solid phase digestion and leaching experiments

Solid phase arsenic found in the well cuttings ranged from a concentration of approximately 0 to 10 ppm (Table 3a); the average for the Earth's crust is approximately 2 ppm.[3] The mean solid-phase concentrations obtained from the analysis of the well cuttings are shown in Table 3a, and their correlations in Table 3b. A positive, significant correlation was found between solid-phase iron and aqueous arsenic (r = 0.66, P-value = 0.05). A positive correlation was also observed between solid iron and the percentage of arsenic leached at pH 9 (r = 0.52, P-value = 0.56). The association between solid iron (Fe cuttings) and aqueous arsenic (r = 0.66) is stronger than among solid iron and solid arsenic (As cuttings) (r = 0.43) suggesting that not all of the arsenic in the solids is readily exchanged with the aqueous phase. It may be that this readily exchangeable arsenic is associated with iron in the solids, while less accessible forms of arsenic are not as strongly associated with iron. This is consistent

Table 3a. Results summary of the well cuttings and leachates analyses.

Cuttings	Aqueous As archives µg/l	Fe cuttings mg/l	As cuttings mg/l	Leached at pH 9 %	Organic carbon cuttings %
Mean	10.4	7254	4.3	21.0	0.6
Std. Dv	7.1	5643	2.3	11.9	0.4
Min	<0.4	1820	<0.2	4.0	0.1
Max	26.8	19700	10.0	38.0	1.4

Table 3b. Spearman's correlations of well cutting and leaching results for both Basins.

	As aqueous	As cuttings	Fe cuttings	As leached
As cuttings	0.305			
Fe cuttings	**0.658***	0.431		
As leached at pH 9	**0.612***	**0.663****	0.520$^+$	
Organic carbon	**0.738***	0.182	0.559	0.183

Notes: *Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level; $^+$Correlation is significant at the 0.056 level.

with there being a layer of adsorbed arsenic on the surface of iron hydroxide solids (ie, the fraction readily exchanged with solution as pH changes). Additional solid-phase arsenic may be present, but not in an adsorbed state where it can be readily mobilized. Arsenic leached at pH 9 is correlated with both aqueous arsenic (r = 0.61) and solid phase arsenic (r = 0.66) suggesting that such competitive desorption at high pH may play a role in mobilizing arsenic. These correlations are all consistent with arsenic being often associated with iron in the solid phase.

These results are in agreement with a previous study where aqueous arsenic concentrations were found to be controlled largely by sorption-desorption reactions with iron hydroxides.[7]

The strong correlation between organic carbon and aqueous arsenic (r = 0.74, *P*-value = 0.056) is consistent with a role for reductive processes in mobilizing arsenic (Table 3b). The decomposition of organic matter can deplete oxygen, leading to reductive conditions, which mobilize arsenic into the groundwater.[3]

Geothermal inflow and reductive processes: Lower Valley water samples

As the archival database did not include any samples from the Mexican portion of the Hueco basin, this work augmented the archival database with sampling and analysis of water from wells in the Juarez (Mexican) part of the Hueco basin (around 31.4 ° North, 106.1 ° West and at 3630 ft elevation). The wells sampled at Juarez are South of El Paso, all belong to the Hueco basin and yield water that has traveled throughout longer flow paths. The second and third highest arsenic observations for the entire Hueco basin are from two of these wells (70 and 87 ppb). These highest arsenic wells also tap a confined aquifer. Further hydrologic study is required to determine if confinement and length of the flow path in the aquifers have consistent roles in mobilizing arsenic. Very strong correlations were found, indicating geothermal and reductive mechanisms associated with arsenic levels. The pH, dissolved oxygen, and temperature were strongly correlated with arsenic (r = 0.99, r = –0.57, and r = 0.94, respectively). The two highest arsenic observations were measured in the lowest DO wells, and the odor of sulfide in one of those is an additional indication of the role of reducing conditions as a mobilization mechanism. The high and significant correlation of arsenic with pH (r = 0.99, $P\text{-value} < 0.001$) supports competitive desorption as a mobilization mechanism. The correlation of arsenic with temperature suggests a possible geothermal influence in arsenic concentrations. Geothermal waters would be expected to have high temperature, be reduced, and have high concentrations of competing anions. Thus the different mobilization mechanisms need not act independently but may work in concert with each other.

Conclusions

This work provides information about a basin-wide groundwater arsenic levels in El Paso TX (approximately 350 square miles). The study supports the occurrence of arsenic desorption and reductive dissolution processes that mobilize arsenic into the groundwater. In geothermal waters reductive processes were linked to high arsenic levels (in the southern Mexican sub-region in the Hueco basin). The different mobilization mechanisms suggest arsenic has a local origin; these mechanisms need not act independently but may work in concert with each other.

The mean level of 8.5 ppb dissolved arsenic in the entire region, is lower than the 10 ppb maximum contaminant level (MCL), but a couple of individual observations reached between 75 and 95 ppb, and despite the very low average values, relevant statistical correlations were significant at least at the $P = 0.05$ level.

Dissolved arsenic is higher in semi-confined wells deeper than 150 ft in the Mesilla basin (Mesilla basin mean arsenic level of 12.4 ppb), where the reduced arsenite species is estimated to be 32% of the total dissolved arsenic. The presence of reduced arsenite together with a clear association between dissolved arsenic and leached arsenic, solid arsenic, and solid organic carbon, suggest that both processes, desorption and reductive dissolution, are mobilizing arsenic in the Mesilla basin. The superficial (shallow) wells, influenced by the river water, contain lower amounts of arsenic ions, and have a lower pH and higher TDS than deeper wells in the Mesilla.

In the Hueco basin, competitive desorption and reductive dissolution are compatible with the concentrations and the associations from the archival and laboratory information, however no speciation data was available there. In the Mexican part of the Hueco basin, a thermal spring showed very significant associations of dissolved arsenic with dissolved oxygen supporting arsenic reductive processes (P-values < 0.01).

Southern wells in the Hueco basin generally have longer flow paths and higher concentrations of arsenic and some ions than the northern wells, suggesting that arsenic accumulates in the aqueous phase as ground water flows throughout the aquifers from higher to lower potentiometric head regions.

Solid content in the cuttings from both basins showed amounts of arsenic and iron compatible with a desorption model, presuming that part of the arsenic is adsorbed to iron hydroxides on the surfaces of the sediments in the aquifers. Also, organic carbon content was present and was significantly associated with dissolved arsenic, suggesting that reductive dissolution contributes to arsenic mobilization. Organic carbon decomposition depletes oxygen and thus contributes to reductive processes.

Leaching experiments showed 21% of arsenic being leached out of the solids at pH 9. The leached arsenic was significantly associated with solid phase arsenic, dissolved arsenic, and with solid phase iron. As pH increases, the numbers of adsorption sites on the iron hydroxide solids decreases, then the previously adsorbed arsenic (arsenicV) ions are presumably leached out of the solids into the groundwater.

The study found support for arsenic desorption, reduction and geothermal inflow to cause arsenic pollution in the groundwater with high statistical significance (P-values < 0.05). Therefore a first guidance for where to find lower arsenic levels, advises in waters where pH is low, located in the northern zones of the Hueco basin (farther from the river), and in waters with no geothermal inflow, the reductive dissolution and desorption mechanisms may operate together or separately, and their relative importance may vary throughout the aquifers and the basins.

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Disclosure

This manuscript has been read and approved by all authors. This paper is unique and is not under consideration by any other publication and has not been published elsewhere. The authors and peer reviewers of this paper report no conflicts of interest. The authors confirm that they have permission to reproduce any copyrighted material.

References

1. Berg M, et al. Arsenic contamination of groundwater and drinking water in Vietnam: a Human health threat: *Environment Sc and Tech*. 2001;35(13).
2. Siegel FR. *Environmental Geochemistry of Potentially toxic Metals*: Springer Verlag. 2002.
3. Smedley PL, Kinniburgh DG. A review of the source, behavior and distribution of arsenic in natural waters*: Applied Geochemistry*. 2002;17(517).
4. El Paso Water Utilities EPWU, Common water chemistry database 1927 to 2002, extended with some Trace elements and speciation data. Personal sharing. 2003.
5. Fisher RS, Mullican WF. *Integration of ground-water and vadose-zone geochemistry to investigate hydrochemical evolution: a case study in arid lands of the northern Chihuahuan Desert*, *Trans-Pecos Texas*: Bureau of Economic Geology, University of Texas at Austin. TX. 1990.
6. Heinrichs G, Udluft P. Natural Arsenic in Triassic rocks: a source of drinking water contamination in Bavaria: *Germany Hydrogeology Journal*. 1999;7(468).
7. Robertson FN. *Arsenic in ground water under oxidizing conditions, south west United States. Environmental Geochemistry and Health*: US Geological Survey, Tucson, AZ, 1989;11:171–86.

8. Sracek O, et al. Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments: *Applied Geochemistry*. 2004; 19(169).
9. Stollenwerk KG. *Geochemical Processes Controlling Transport of Arsenic in Groundwater: A Review of Adsorption*: US Geological Survey, Denver CO. 2003. In Welch AH, Stollenwerk KG. *Arsenic in Ground Water:* Klumer Academic Publishers Boston, Dordrecht, London; 2003:475.
10. Montoya T, Gurian PL. Numerical Solution of a Chemical Equilibrium Model of Arsenic Sorption to Ferric Hydroxide. Proceedings of the *Modeling and Simulation Workshop of the International Test and Evaluation Association*, Las Cruces, NM. 2003.
11. Bexfield LM. *Occurrence and sources of arsenic in ground water of the middle Rio Grande basin, central New Mexico*: M.S. Thesis, Hydrology, New Mexico Institute of Mining and Technology, Socorro, NM; 2001:183.
12. El Paso Water Utilities EPWU, 2006. *Hueco Bolson report*: on line at http://www.epwu.org/water/hueco_bolson.htmlwww.epwu.org/water/pdf/dwr2006.pdf.
13. Anderholm SK, Heywood CE. *Chemistry and age of ground water in the southwestern Hueco Bolson, New Mexico and Texas*: US Geological Survey, Water-Resources Investigations Report 02-4237, 2003:16.
14. EPA; and WRRI, (Environmental Protection Agency and Water Resources Research Institute), *Transboundary Aquifers of the El Paso Ciudad Juarez Las Cruces Region*: Final Report. Prepared by Texas Water Development Board New Mexico Water Resources Research Institute for EPA Region VI, Las Cruces, NM. 1997.
15. Montoya T, Gurian PL. Modeling Arsenic Removal by Coagulation with Ferric Salts: Effects of pH and Dosage. Proceedings of the *Texas Water 2004 Conference*, Arlington; TX; 2004.