ARSENIC SOURCE AND FATE IN A VILLAGE DRINKING WATER SUPPLY, MÉXICO

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Abstract. Inhabitants of the village of Tlamacazapa display toxic health effects related to arsenic and other metal exposures from shallow well water. Arsenic is present in the dissolved phase up to a concentration of 37 µg/L, exceeding the World Health Organization guideline of 10 µg/L. Stable isotope analyses (^{2}Hwater & ^{18}Owater) indicate precipitation is recharging the wells through the soil and groundwater zones. Soil and rock analyses show that arsenic is present at concentrations up to 56 mg/kg and 26 mg/kg, respectively. High concentrations of Cl, K, Na, NO_3 and SO_4 suggest sewage or manure contamination in the well water via surface runoff into the unprotected wells or through the thin soil and shallow groundwater. Lack of sanitation facilities and free-roaming animals are the sources of this contamination. Arsenic and sewage contaminant concentrations are strongly correlated and the presence of sewage apparently promotes the release of arsenic from aquifer materials. It is likely that arsenic mobilization is the result of arsenate-phosphate competition for ion sorption sites.

Keywords: arsenic, heavy metals, drinking water, sewage contamination

INTRODUCTION

Health personnel working in a rural village in central Mexico recognize symptoms of low level, chronic metal toxicity in an undernourished, inadequately hydrated, and poor population. Observed symptymology include skin pigmentation changes (hyperpigmentation), neurological disorders and abdominal pain. Hair and nail arsenic concentrations reach 23 and 290 mg/kg by dry weight, respectively, when tested on symptomatic persons admitted to hospital. A multi-disciplinary research programme was initiated to study the environmental sources of arsenic and other metals. As part of this programme, this study's objectives are (1) to geochemically characterize the local hydrological system, (2) to investigate the source(s) of arsenic in the groundwater and (3) to assess geochemical controls on arsenic mobility in the aqueous environment.

SITE DESCRIPTION

Tlamacazapa is located in the Sierra Madre del Sur of the state of Guerrero, roughly 160 km southwest of Mexico, D.F. and 10 km east of the historical silver-mining town of Taxco de Alarcón. It has a population of approximately 9000 people, living in high-density housing (a mixture of concrete building and simple cornstalk/cedar branch structures) extending up the steep incline of a mountainside. Sanitation is a critical problem due to a lack of infrastructure, with most households using open-air excretion methods as opposed to proper sanitary facilities.

Hydrothermal sulphide veins host Ag-Au-Pb-Zn deposits in metamorphic basement, Mesozoic marine sequences, and to a lesser extent in Tertiary intrusives. Documented ore mineralogy includes source minerals for arsenic such as pyrite and arsenopyrite as well as other metal-bearing sulphides (Salas, 1991). Thin (<1 m), poorly developed soils contain abundant unweathered rock fragments. Arsenic is present in both soil and rock analyses at concentrations sufficient to contaminate ground water (Table 1).

Precipitation in Tlamacazapa occurs seasonally, with arid conditions prevailing roughly from December to May. Drinking water supply is provided by up to eight (depending on the season) shallow wells excavated into existing fractures in the limestone (Figure 2). Low concrete walls surrounding the wells limit direct surface runoff, with stairs providing access for water fetching by hand. An alternate source of drinking water – Los Sabinos – is located five kilometres northeast of Tlama. Water from a shallow (< 1m) aquifer is pumped to Tlama and distributed in pipes by gravity.

	As	Pb	Cu	Al	Fe	Mn	Sr
Limestone	2	0.8	11	0.01	0.03	35	92
Granodiorite intrusion	9	4.6	6	0.73	2.21	245	13
Mineralized veins	26	1	16	0.02	0.11	30	109
Soil	17	20	n/a	25,000	18,200	279	36

***Table 1**: Bulk metal analyses (mg/kg) from different rock units (1 sample each) and average soil composition (53 samples) (CJ, unpublished data).*

METHODOLOGY

In total, eight local, ten regional, and four surface water samples (Fig. 2) were collected at the end of both the wet (December 2002) and dry (May 2003) seasons for determination of field parameters (Temperature, pH, Eh, DO, EC), and analyses of major ions, trace metals and environmental isotopes ($^{2}H_{water}$, $^{18}O_{water}$, $^{13}C_{DIC}$, $^{34}S_{SO4}$). Trace metal samples were collected for total dissolved and total recoverable analysis, with filtered (0.45 micron) and raw water preserved with spec-pure nitric acid to a pH below 2. Arsenic analyses were done by ICP-MS (Perkin Elmer 6001).

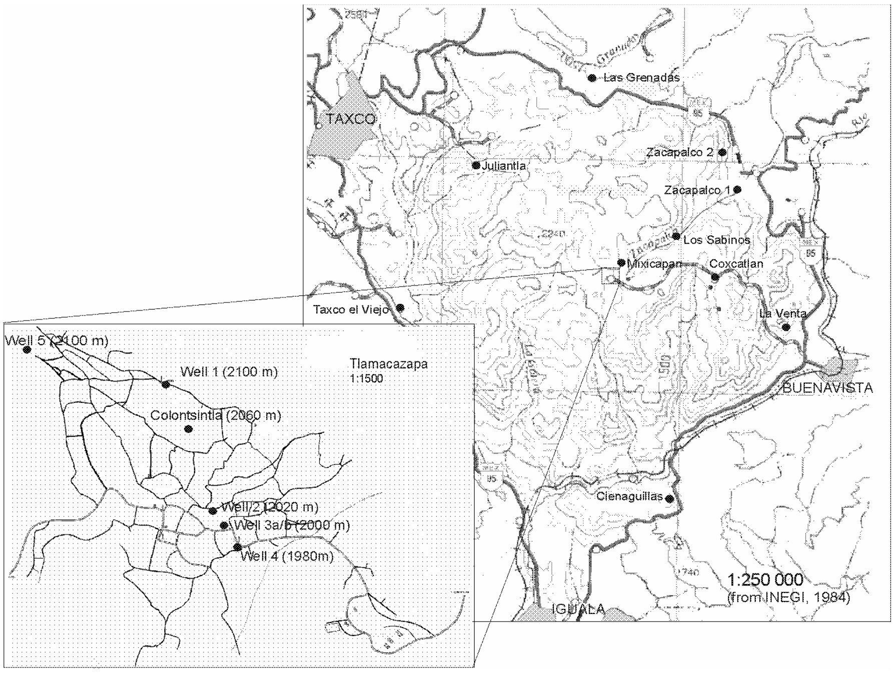

***Figure 1:** Inset shows location & elevation of wells/ in Tlamacazapa*

RESULTS & DISCUSSION

Arsenic is present in five of the nine drinking water sources of Tlama (eight wells and Los Sabinos). Four of the eight wells used for drinking water contain arsenic concentrations exceeding the WHO drinking water guideline (10 µg/L; WHO 1998) and the maximum concentration is 37 µg/L. Although concentrations are not present at levels similar to other affected areas of the world (i.e. Bangladesh, Argentina), it is believed that detrimental health effects occur at exposure to concentrations less than 50 µg/L (WHO 2001). Malnutrition and dehydration are believed to compound the adverse toxic health effects.

Ground water is near-neutral pH (6.7 to 7.7) and mildly oxidizing (Table 2). Oxidized species include nitrate, phosphate, and sulphate, and redox potential (Eh) ranges from 170 to 220 mV. Mean water temperatures reflect average annual air temperatures of 21°C. Well water geochemistry is dominated by Ca, Mg, and HCO_3, as expected for waters interacting with carbonate rocks and/or calcium-rich soils. Stable isotope results are consistent with groundwater recharge by precipitation. Tlama well water δ^2H and $\delta^{18}O$ plot closely with the local meteoric water line for Mexico City (Cortés *et al*. 1997).

	As (µg/L)	T (^{o}C)	pH	Eh (mV)	DO	EC (µS/cm)	Ca	Mg	K	Na	Cl	NO_3-N	PO_4	SO_4	HCO_3
Well 1	-[1]	21	6.7	211	3	640	74	37	1	1	3	7	0.3	30	300
Colontsintla	-	18	7.5	197	0	740	99	43	2	4	10	22	0.2	78	220
Well 2	**22**	**21**	**6.7**	**178**	**6**	**1530**	**120**	**54**	**69**	**79**	**110**	**85**	**2**	**135**	**260**
Well 3a	**32**	**21**	**7.0**	**192**	**1**	**1080**	**110**	**48**	**49**	**63**	**95**	**65**	**3**	**115**	**340**
Well 3b	**37**	**21**	**7.7**	**209**	**6**	**1040**	**110**	**47**	**51**	**49**	**98**	**51**	**0.2**	**120**	**290**
Well 4	**27**	**21**	**6.7**	**170**	**1**	**1270**	**130**	**54**	**63**	**66**	**145**	**68**	**1**	**160**	**460**
Well 5	-	17	7.3	220	4	590	69	33	0	2	2	6	1	33	250
Mixicapan	1.8	16	6.8	186	5	735	78	36	2	5	8	1	1	52	310
Los Sabinos	-	20	6.7	188	2	776	81	39	0.1	1	2	0	1	8	270
Typical Sewage Composition	--[2]	--	7.2	--	--	1336	57	17	15	112	100	2.6	11	129	241

[1]denotes results below detection limit.
[2]indicates no data available from sources.

Table 2. Dissolved arsenic, major ion concentrations and field parameters for wet season samples from Tlamacazapa drinking water wells and Los Sabinos. Typical sewage composition is included (Kim *et al*. 2002, Robertson *et al*. 1991, Crites & Tchobanoglous 1998, City of Calgary unpublished data). All values reported in mg/L unless noted. Lower elevation Tlama wells are bolded.

High concentrations of Cl, K, Na, NO_3-N, and SO_4, and high electrical conductivity (EC) values (Table 2) indicate sewage contamination in four lowest-elevation Tlama wells. The composition of the most contaminated wells is comparable to or more concentrated than typical sewage compositions (Table 2). This is likely due to the lack of dilution by grey water (toilet flushing and wash water). Nitrate values exceed the World Health Organization (WHO) drinking water guideline (11.3 mg/L NO_3-N; WHO 1998) in the four topographically lowest wells in Tlama, while the higher elevation wells have concentrations below the guideline. The occurrence of sewage impact in lower elevation wells suggests inadequate sewage management in Tlama is the source of the contamination.

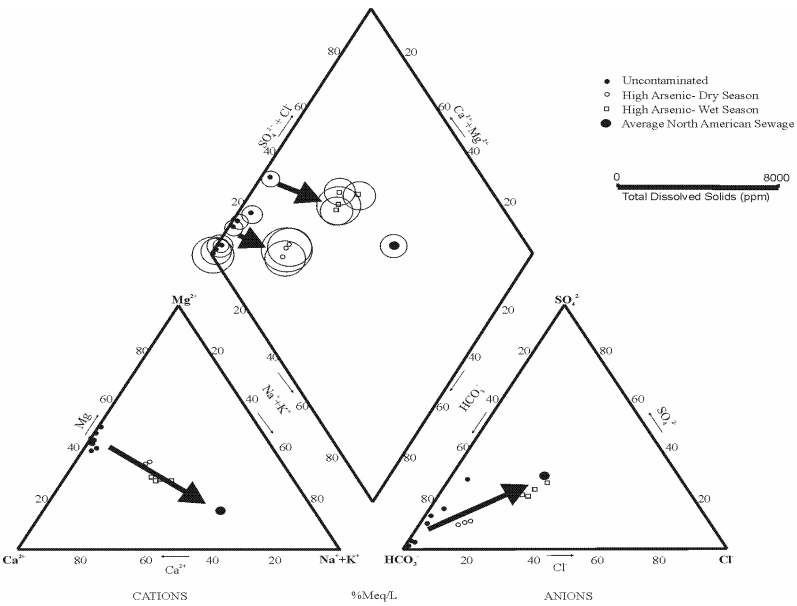

Figure 2. Piper plot of Tlama wells and typical sewage concentrations (Kim *et al*. 2002, Robertson *et al*. 1991, Crites & Tchobanoglous 1998, City of Calgary unpublished data). Circle diameter of central diamond indicates total dissolved solids. High arsenic locations indicate concentrations > 10 µg/L.

A mixing line between uncontaminated (higher elevation) wells and sewage impacted wells is evident by increasing Na+K, Cl, and SO_4 concentrations and relatively high estimated total dissolved solids (Figure 2). Wet season samples are more concentrated than dry season samples in all sewage-related parameters, with the cluster of most contaminated wells. Elevated wet season concentrations are likely related to increased recharge, with sewage transport to the wells through the thin soil and shallow groundwater.

Total and dissolved arsenic results correlate closely (R^2=0.997) suggesting that arsenic is present in the dissolved phase. Arsenic concentrations are also correlated to sewage contamination (Figure 2), with positive correlations including Cl^- (R^2=0.6), NO_3-N_2 (R^2=0.5), K (R^2=0.6), and HCO_3^- (R^2=0.7). These correlations are stronger during the wet season, which is consistent with increased sewage impact during the period of higher ground water recharge.

Of the sewage-related anions introduced into the Tlama wells, PO_4, SO_4, Cl and NO_3 compete with arsenic for sorption sites (Manning and Goldberg, 1996) with a relative affinity for Fe(III)-oxide surfaces being $PO_4 > SO_4 > Cl \approx NO_3$ (Rau *et al.*, 2003). It is likely that phosphate is sorbed and arsenic desorbed during the infiltration of phosphate-rich sewage impacted recharge through soil and shallow groundwater. This would attribute for this decrease in aqueous phosphate concentrations with respect to other sewage contaminants.

CONCLUSIONS

Arsenic is present in the ground water of Tlamacazapa at levels above the WHO guidelines (10 µg/L; WHO, 1998). Average arsenic concentrations from the bedrock-hosted well waters are 13 µg/L with a maximum concentration of 37 µg/L. Elevated levels of arsenic in the bedrock and soil suggest that the source of arsenic contamination to the well water is geologic.

Sewage contamination, resulting from a lack of proper sanitation facilities, is indicated by elevated levels of Cl, Na, K, NO_3, SO_4, and EC with respect to other wells in the village. Wells located at the lowest elevation are the most contaminated, being comparable to raw sewage (Table 2). Sewage transport to wells through thin soil and shallow groundwater is increased during periods of active recharge.

A positive correlation between arsenic and sewage contamination indicates that the arsenic release mechanism is anthropogenic. It is likely that ions introduced to well water in sewage are competing with arsenic for sorption sites, most notably phosphate.

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