Arsenic content and groundwater geochemistry of the San Antonio-El Triunfo, Carrizal and Los Planes aquifers in southernmost Baja California, Mexico

A. Carrillo-Chávez · J.I. Drever · M. Martínez

Abstract The San Antonio-El Triunfo mining district, located at a mountainous region 45 km southeast of La Paz, Baja California, has been worked since the late 1700s. Mine waste material produced during 200 years of mineral extraction area poses a risk of local groundwater pollution and eventually, regional pollution to the Carrizal (west basin) and the Los Planes (east basin) aquifers. There are different types of deposits in the mining area. These are dominated by epithermal veins, in which arsenopyrite is an important component. Carrillo and Drever (1998a) concluded that, even though the amount of mine waste is relatively small in comparison to the large scale area, significant As in groundwater derived from the mine waste piles is found locally in the groundwater. This paper shows the results of geochemical analyses of groundwater samples from the San Antonio-El Triunfo area and the Carrizal and Los Planes aquifers during several years of monitoring (1993–1997). The highest values of total dissolved solids (TDS) and As are in the mineralized area where the mining operations occurred (~1500 ppm TDS and 0.41 ppm As). The lowest concentrations of TDS and As are, in general, away from the mineralized area (~500 ppm TDS and 0.01 ppm As). Sulfate and bicarbonate (alkalinity) are, in general, high near the mineralized area and low away from it. The arsenic concentrations vary seasonally, especially after the heavy summer thunderstorms. Geochemical modeling (MINTEQA2 and NETPATH) and analysis of the regional geochemical evolution of the groundwater from the mining area towards the aquifer of Los Planes shows that the most likely hydrochemical processes include: dilution, precipitation of calcite, and adsorption of As onto surfaces of iron oxyhydroxides (ferrihydrite). These processes act as natural controls to the extent and amount of As pollution in the Carrizal and Los Planes aquifers.

Key words Arsenic in groundwater · Baja California Peninsula · Geochemical modeling · Mine waste material

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Introduction

Aqueous discharge from mine-waste materials can have serious environmental effects on local groundwater quality (Bowell and others 1994; Maskall and others1995; Gray 1997; Rösner 1998). In semi-arid lands, where groundwater is the only source of water, mining activities can greatly affect the quality of drinking water. Effective management and remediation of polluted drainage from mining areas may be possible when the physical and chemical processes that influence the release and transport of contaminants are understood (Gray 1997; Carrillo and Drever 1998a,b; Fyfe 1998; Larocque and Rasmussen 1998). High As concentrations in surface and groundwater (above 0.05 mg/l; USEPA and WHO standard for drinking water, Gough and others 1979) are recognized to be a problem in mining areas or zones of former mining activities (Varsanyi and others 1991; Frost and others 1993; Xiangdong and Thornton 1993). It is also recognized that there are potential health consequences for the local population when exposed to drinking water with high As content (Goldman and Dacre 1991; Mass 1992; Qvarfort 1992).
The San Antonio-El Triunfo (SA-ET) area in southern Baja California peninsula has been mined for nearly 200 years (Altamirano 1971; Escandón 1983; Amado-Manri-

quez 1984, Carrillo 1996; Carrillo and Drever 1998a). This mining area is located at a mountainous region on the drainage divide between the Carrizal aquifer system to the west and the Los Planes aquifer system to the east (Fig. 1). This is the "core", of what is known as the "Cabo San Lucas Block" (CSLB). The CSLB consists dominantly of granitoids that range in composition from monzogranite to tonalite (Bates and Jackson 1987) and is of Cretaceous age (Gastil and others 1976; Frizzell and others 1984;). These plutonic rocks intrude Paleozoic (?) metasedimentary rocks and are partially covered by middle Tertiary volcanic rocks and upper Tertiary sedimentary sequences.

There are three different types of ore deposits in the SA-ET mineralized area (central part of the CSLB (Carrillo and others 1997)). These are epithermal veins containing high concentrations of sulfide associated with gold and silver (gold associated with arsenopyrite), fault-related disseminated gold deposits in igneous rocks, and one disseminated gold deposit in metamorphic rock (biotite-sillimanite schist).

There are between 800,000 and 1 million tons of mine waste materials scattered in the 350–400 km^2 area of the SA-ET region. These materials have been classified by Carrillo (1996) as: (1) oxidized tailings, (2) low-grade mineral ore, (3) cyanide heap-leached material, and (4) byproducts of old, mineral processing plants (smelters), mostly arsenic trioxide ("arsenolite", As_2O_3). The ruins of at least three old mineral-processing plants whose chambers are partially filled with arsenolite remain in the area and contain ~600 tons of arsenolite. The arsenic content in all the mine waste material ranges from >1 to 30 wt% (Carrillo 1996).

The metallurgical process for gold extraction that produced the arsenolite as a byproduct was roasting ore at the smelters (Fig. 2). The chemical reaction to produce arsenolite-rich tailings was the oxidation of arsenopyrite ores (with gold) to produce iron oxides with gold, and releasing SO_2 and As_2O_3 fumes (which further condensed in the inner chambers of the old processing plants as solid As_2O_3). Currently, the almost 1 million tons of arsenolite-rich-mine wastes potentially release high concentrations of As (>0.05 mg/l) to the local groundwater system (Carrillo 1996; Carrillo and Drever 1998a).

Even though arsenopyrite is widely distributed in some of the epithermal veins, and the resulting arsenic enriched halo could be very large, it appears that the arsenic-rich-mine wastes have an important role in releasing As to the groundwater. Residents of San Antonio and El Triunfo and several small ranches in the area recognize the risk of drinking the water, but, in most cases, they have no alternative source of water. In this report, the results of a geochemical evaluation of the groundwater quality of the San Antonio-El Triunfo area are presented along with an assessment of the current and probable future migration of arsenic and possible effects on the groundwater quality of the Los Planes aquifer.

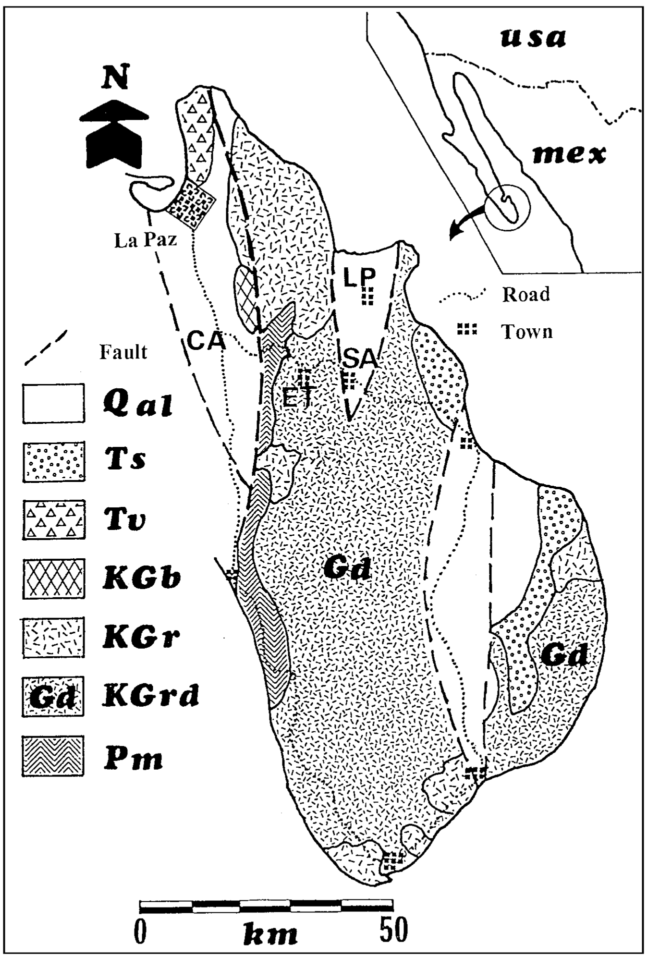


Fig. 1
General geologic map of southernmost Baja California Peninsula and the location of the San Antonio (*SA*) and El Triunfo (*ET*) mineralized area. Also shown are the Carrizal (*CA*, west basin) and Los Planes (LP) aquifers (east basin)

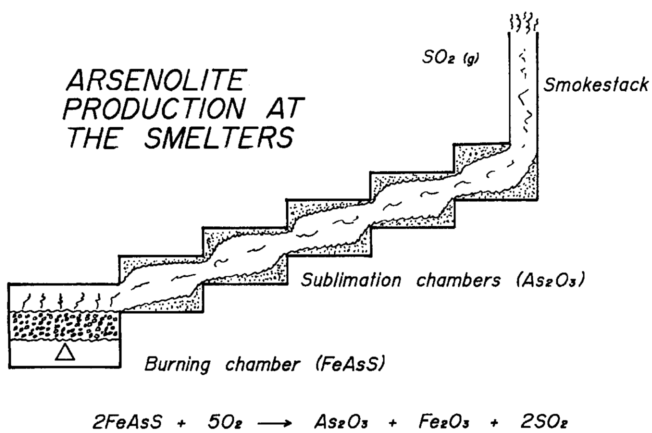


Fig. 2
Schematic diagram of the old mineral processing plants (smelters) and the generation of arsenolite inside the sublimation chambers. There are at least three of these plants in the area, with a total of almost 1000 tons of "pure" arsenolite

Site description, sampling, and methods

The average elevation of the SA-ET region is 700 m above sea level, with the highest point at 1200 m. The annual precipitation of 15 cm occurs mainly during the monsoon months of August to October, with minor rains in winter. A rough estimate indicates that ~60% of the total precipitation runs off the ground surface along rapidly flooding creeks (flash floods) that eventually infiltrate when they reach the alluvial valley. Estimates are that evapotranspiration accounts for ~30% of the total precipitation. The other ~10% of the precipitation infiltrates the subsurface into the groundwater system.

The local, shallow unconfined aquifer at the SA-ET area is mainly in highly fractured igneous rocks and in patches of alluvial material (coarse-grained sand and gravel). People in the San Antonio and El Triunfo towns and on small ranches use small pumps in wells to extract up to 50 l/min. The town of San Antonio obtains its water from a pump installed directly into a flooded old mine shaft. People who can afford it get drinking water from the town of San Pedro, 10 km northwest of El Triunfo, on the road to La Paz. The city of La Paz (~150,000 people and located on the northernmost portion of the Carrizal aquifer) gets its water from four to five wells drilled in the alluvial aquifer (~50–60 m deep). Los Planes is an agricultural town of 500 people with an irrigation area of ~25 km^2 (Fig. 3).

Some samples of the groundwater were taken during summer 1993. The main sampling season was carried out during the summer of 1994, when 43 samples were collected within the SA-ET area and another 17 water samples were collected from the Carrizal and Los Planes aquifers. Further sampling was carried out during 1996 and 1997. Table 1 indicates the location of all the samples.

All water samples were collected in acid-washed, deionized water-rinsed (3×) polypropylene bottles. Samples were stored in the dark at 4 °C for 2 weeks prior to analysis for cations and anions. Alkalinity was determined by Gran titration to pH 3.5. Major and minor cations (Ca, Mg, Na, K, Si, Al, Fe, As, Zn, Pb, Cu) were measured in acidified samples by inductively coupled plasma-emission spectrophotometry (ICP-ES). Anions (Cl^-, SO_4^{2-}, NO_3^-) were measured by anion chromatography (AC). The alkalinity, and cations and anions from the 1993 and 1994 samples were analyzed at the Hydrogeochemistry Laboratory of the University of Wyoming. Arsenic analyses of the 1996 and 1997 samples were analyzed at the Hydrogeochemistry Laboratory of the Geophysics Institute of the National University of Mexico (UNAM) by a colorimetric method and reaction with diphenyl-carbazide. The geochemical modeling computer codes MINTEQA2 (Allison and Brown 1991) and NETPATH2 (Plummer and others 1994) were used to calculate the saturation index (SI) of minerals in the groundwater and the possible geochemical evolution path of the groundwater.

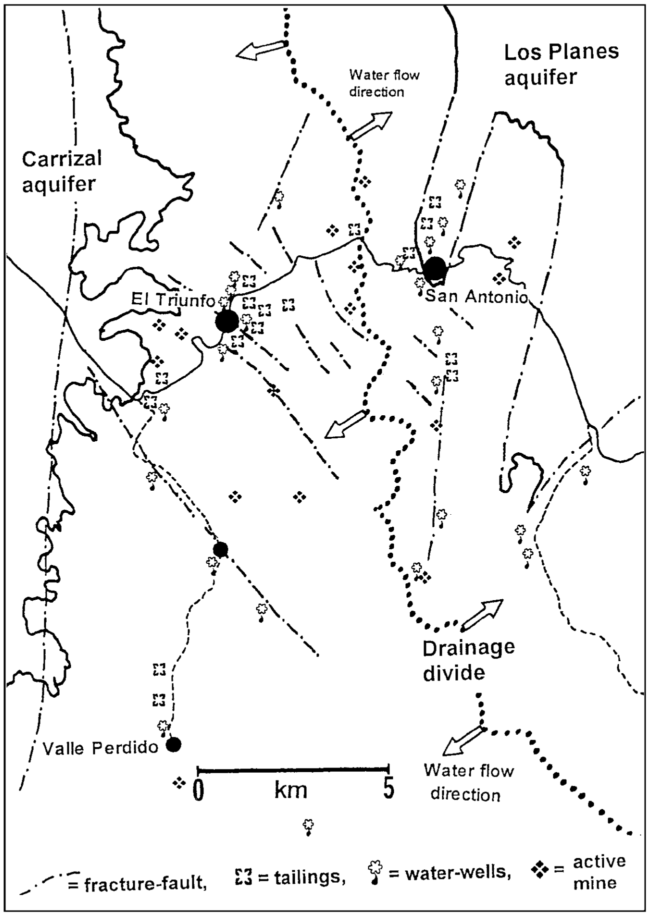


Fig. 3
Detail of the San Antonio and El Triunfo mineralized area, and the location of some fractures, tailing piles, water wells (see Table 1 for exact location), and active mine sites

Results

Based on the analytical results of all the water samples and their location, 11 groundwater subareas were defined. Four to 12 samples were taken from each subarea. These subareas had different amounts of total dissolved solids (TDS) and different concentrations of As. Figure 4 shows a general map of the Carrizal and Los Planes aquifers, the SA-ET mining area (box) and the 11 subareas – seven of which are within the limits of the SA-ET area, two are in the Carrizal aquifer, one is in the Los Planes aquifer, and one (# 10) is within a region with no influence of mining tailings (topographically above any mine waste pile and in a sub-basin with no waste pile within it). The circles and numbers in Fig. 3 indicate the relative amounts of average TDS in the groundwater of each region (1 = highest TDS, 10 = lowest TDS).

Table 2 shows the general average groundwater chemical composition in each of the 11 subareas. Because of the scatter of the data points, it is not possible to draw boundaries to the subareas. The El Triunfo (ET), San An-

Table 1
Location of groundwater samples in the SA-ET area and the Carrizal and Los Planes aquifers

Sample	Location	Subarea
1	San Juanes old processing plant (12 km south of SA)	SA
2	1.2 km south of SA	SA
3	Santa Cruz flood	SA
4	San Antonio gas station	SA
5	2 km north of SA	SA
6	2 km north of SA	SA
7	El Cantil Ranch (3 km north of SA)	SA-spring
8	200 m west of El Cantil Ranch	SA-spring
9	150 m west of El Cantil Ranch	SA-spring
10	Marroñera Rach (2 km south of ET)	ET
11	El Triunfo	ET
12	2 km east of ET	ET
13	Ranch 5–6 km east of ET	ET
14	Rach of the highest part of the old road ET-SA	ET
15	Las Parritas well (old road ET-SA)	ET
16	100 m west of ”big“ chimney of ET	ET
17	500 m north of ET (next to highway)	ET
18	Last house on east side of ET	ET
19	Baseball field of ET	ET
20	400 m east of sample 19	ET
21	60 m south of sample 20	ET
22	Los Cuates well, 500 m south of ET	ET
23	Well on creek, 200 m north of ET	ET
24	”Tienda“ of ET	ET
25	Well in old house next to ”big“ chimney of ET	ET
26	100 m north-west of El Palmar of SA	SA-spring
27	El Palmar of SA	SA-spring
28	Spring of El Palmar-SA	SA-spring
29	Las Flores Ranch, 6.5 km on the road SA-Testera	Testera
30	Testera mine	Testera
31	Fundicion Ranch, old road Testera-SA de la Sierra	Fundicion
32	Ancon de Guayabos, 1 km upstream from Fundicion	Fundicion
33	Agua Caliente Ranch, road to SA de la Sierra	Fundicion
34	El Tule mineral processing plant	Tule
35	El Aguajito Ranch, road to Rosario	Tule
36	El Rosario 1	R-VP
37	El Rosario 2	R-VP
38	El Rosario 3	R-VP
39	Valle Perdido 1	R-VP
40	La Junta spring, 6 km south-east of VP	R-VP
41	Valle Perdido 1	R-VP
42	El Salto Dam	Salto
43	San Blas-La trinchera	Salto
44	Los Divisaderos	Salto
45	Tamales Ranch 1 (mid-way on the road La Paz-Planes)	Salto
46	Tamales Ranch 2	Salto
47	Los Planes 1 (west side of town)	Los Planes
48	Los Planes 2 (well at high-school)	Los Planes
49	Los Planes 3 (well for potable water)	Los Planes
50	La Paz 1 (Bledales well)	La Paz
51	San Pedro	Carrizal
52	El Carrizal	Carrizal
53	La Mojonera Ranch, 11.5 km on the road to Todos S.	Carrizal
54	La Paz 2 (drinking water)	La Paz
55	La Paz 3 (potable water)	La Paz
56	San Patricio Ranch (just south of La Paz)	La Paz
57	La Paz 4, university well	La Paz
58	La Paz 5, university public faucet	La Paz
59	Arroyo Hondo Ranch (between La Paz and ET)	Carrizal
60	Ponderosa Ranch (between ET and VP)	R-VP

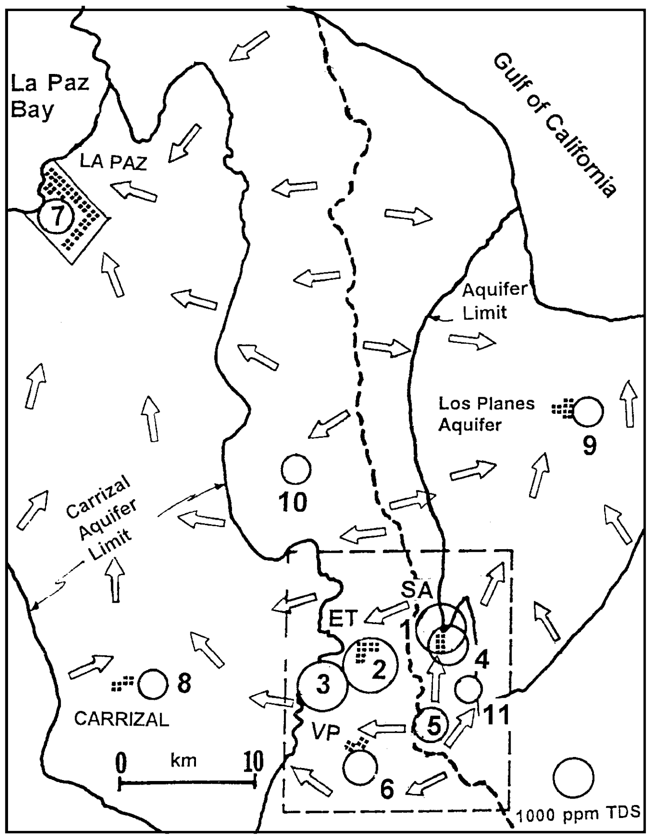


Fig. 4
General geohydrological map of the SA-ET area and the Carizal and the Los Planes alluvial aquifers. *Arrows* indicate the general groundwater direction flow. The inbox indicates the San Antonio (*SA*) – El Triunfo (*ET*) mineralized area. *Circles* with numbers indicate the subareas (see text for the criteria for the subdivision). Diameter of circles indicates the relative amount of TDS. *1* San Antonio spring (SA-spring); *2* El Triunfo (ET); *3* Tule; *4* San Antonio, *5* Testera, *6* Rosario-Valle Perdido, *7* La Paz, *8* Carrizal, *9* Los Planes, *10* Salto, *11* Fundicion. Diameter of circle in the lower right corner is for scale only and indicates 1000 ppm TDS

Table 2
Average groundwater chemical composition for the 11 subareas. These data were used for construction of the Piper and Stiff diagrams. The sampling was only done at a few closely related points, and it is not possible to draw boundaries to subareas. The "subareas" concept reflects the chemical variations of the different points within the Carrizal and Los Planes aquifers. All concentrations are given in mg/l, except for the Sum (+) and Sum (−), which are given in meq/l

Area	As	Fe	Al	Zn	Na	K	Ca	Mg	HCO_3	SO_4	Cl	NO_3	Si	TDS	Sum (+)	Sum (−)	Error (%)
SA	0.41	0.01	0.02	0.07	95.45	7.03	107.01	46.30	360.51	270.42	95.72	8.06	14.44	1005.45	13.49	14.37	−3.16
ET	0.21	0.14	0.08	0.08	119.83	13.27	121.04	76.80	383.69	555.73	119.83	33.48	13.80	1437.98	17.9	21.79	−9.80
SAs	0.26	0.04	0.03	0.04	145.82	12.49	101.00	91.39	421.51	457.74	184.35	31.00	20.63	1466.30	19.23	22.14	−7.03
Tes	0.08	2.48	1.60	0.04	68.54	8.98	93.98	36.58	328.79	157.06	59.21	112.23	19.67	889.24	10.91	12.14	−5.34
Fun	0.02	0.06	0.10	0.02	63.48	2.73	49.70	15.92	290.36	37.46	34.39	0.00	16.74	510.98	6.61	6.51	0.76
Tule	0.02	0.02	0.06	0.17	153.64	11.71	145.68	53.11	431.27	178.20	209.88	169.27	14.41	1367.44	18.62	19.43	−2.13
R-V	0.04	0.04	0.09	0.06	80.96	5.46	99.59	34.88	409.31	89.82	110.97	21.08	15.89	868.19	11.5	12.05	−2.34
Sal	0.01	1.47	0.22	0.06	69.46	3.90	52.30	16.53	293.41	6.72	58.85	16.12	27.44	546.50	7.09	6.87	1.58
Pl	0.01	0.15	0.20	0.24	120.98	3.90	56.31	21.63	135.42	24.98	215.91	22.32	9.74	611.79	9.95	9.19	3.97
Ca	0.02	0.08	0.64	0.11	97.52	6.24	57.51	24.18	221.43	88.86	124.08	22.94	31.03	674.66	9.26	9.35	−0.48
LP	0.01	0.17	0.20	0.12	75.21	7.42	94.78	37.31	226.31	102.31	185.42	37.20	36.58	803.04	11.25	11.67	−1.83

tonio (SA), San Antonio spring (SA-spri), Tule, Testera and El Rosario-Valle Perdido (Ros-VP) subareas are directly within the mineralized area and the sampled wells are near mine waste piles. These subareas have the highest concentrations of TDS (900–1500 ppm), and also present the highest As concentrations (0.04–0.41 ppm; locally up to 2 ppm). The Testera subarea is located 10 km to the south (upstream) of San Antonio. In this subarea there is one of the few active mines in the region that still is extracting some Au ore. This subarea has the highest Fe concentration (2.48 ppm). The Ros-VP area is located 10 km from any mine waste pile, but still within the mineralized district. It has an average content of 0.01 ppm As. The lowest As contents are in the La Paz and Los Planea subareas (≤ 0.01 ppm).

The Salto and Fundicion subareas are located in the high part of the mountainous region, above the elevation of the mineralized area. Both areas have the lowest TDS content (546 and 511 ppm) and low As content (0.01 and 0.02 ppm, respectively). The western catchment area of the Salto subarea is mafic igneous rock. The Fundicion subarea is entirely located on granitic igneous rocks.

Figure 5 shows Stiff and Piper diagrams for the different subareas. The Piper diagram indicates no dominant type of water in any of the subareas (sulfate type, bicarbonate type or chloride type; Freeze and Cherry 1979). The Stiff diagram indicates that sulfate and bicarbonate are the principal anions in the subareas close to the mineralized areas (i.e., SA, SA-spring and ET); bicarbonate and chloride are the principal anions in most of the rest of the subareas. Results from the computer code MINTEQA2 (geochemical equilibrium speciation model capable of computing equilibrium among the dissolved phases in an environmental setting; Allison and others 1991) show that groundwater from all the subareas except Los Planes is supersaturated with respect to calcite (SI of Los Planes = −0.43; in the other subareas SI ranges from 0.07 to 0.83). Ferrihydrite is supersaturated in all the subareas (SI varies from 1.22 to 3.77) and gypsum is undersaturated in all the subareas. Because both the aquifer in fractured rock (SA-ET area) and the alluvial aquifers (Carrizal and Los Planes) are unconfined and relatively shallow, it was assumed that the redox conditions represent equilibrium with atmospheric oxygen.

Hydrogeochemical evolution

The general geochemical evolution of the groundwater can be defined using TDS data. In general, TDS decreases with increasing distance from the SA-ET area towards La Paz and Los Planes (the general direction of groundwater flow). Figure 6 shows the relationship between distance from the SA-ET area and TDS, and concentrations of particular ions. Sulfate and bicarbonate (alkalinity) show a general decrease with increasing distance. Arsenic concentration decreases with increasing distance, and Zn content shows a great deal of variation but no significant pattern along the path. The concentration of iron in the groundwater remains almost constant along the whole path. Some possible explanations for these relationships between concentration in the groundwater and distance from the mining area are dilution, mixing, As adsorption, and the travel time for the groundwater from the SA-ET area to Carrizal and Los Planes areas (discussed below).

The possible geochemical evolution of the groundwater along its path from the mining area to the alluvial valleys of La Paz and Los Planes was modeled using NETPATH2. NETPATH2 is an interactive Fortan 77 computer program used to interpret net geochemical mass-balance reactions between the initial and final water along a hydrologic flow path (Plummer and others 1994). Results from NETPATH2 indicate that it is plausible to have dilution along the path between the Tule and La Paz subareas with a dilution factor (d.f.) that ranges between 1.5 and ~ 3.1 and precipitation of calcite along the path. It would also be possible to have dilution (d.f. ~ 10–15) and no calcite precipitation (Tables 3–6). Considering that the Carrizal and Los Planes aquifers are alluvial unconfined aquifers with recharge along all the surface alluvial valley,

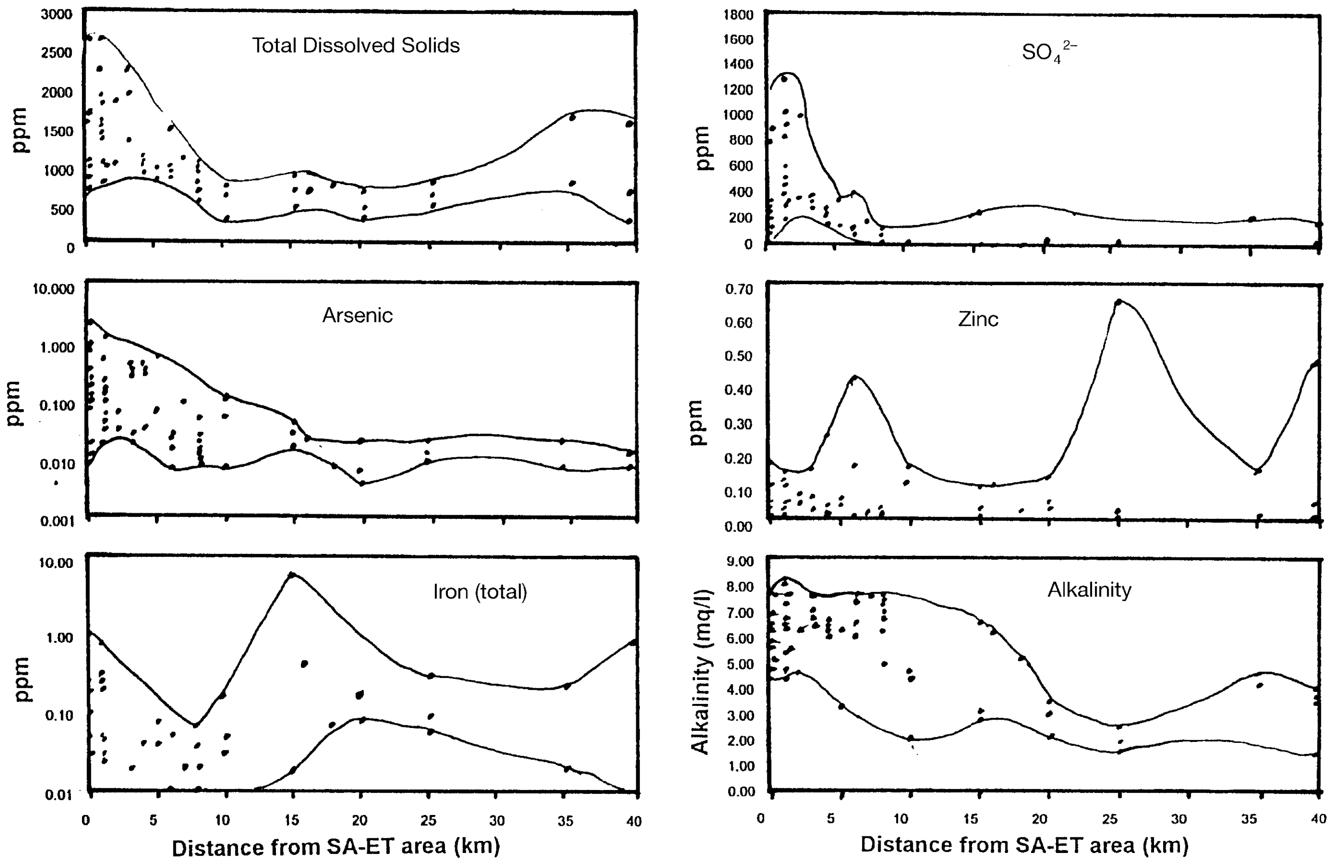


Fig. 5
Piper and Stiff diagrams of the different subareas

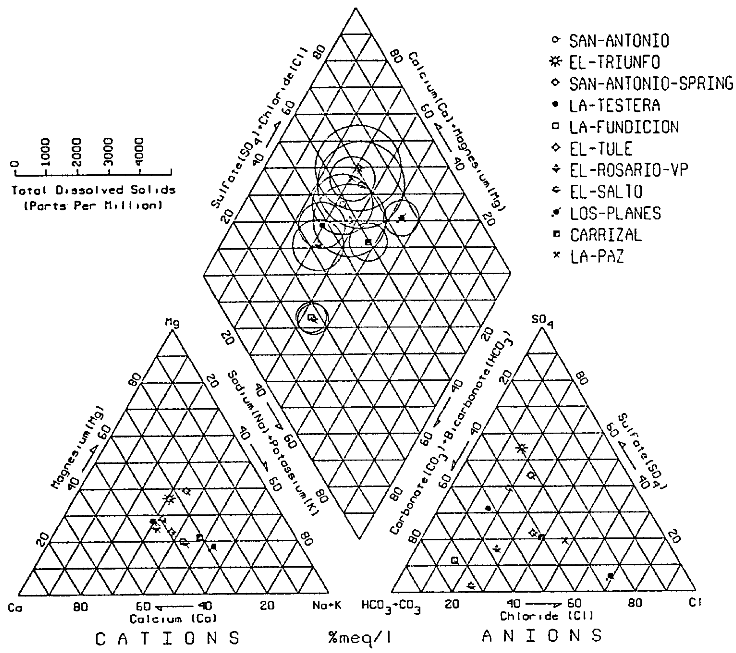
these NETPATH2 dilution and calcite precipitation models are very plausible. The mixing models generated for different subareas were not compatible with the undersaturation of gypsum, and were thus not plausible (some models indicated precipitation of gypsum, but water is undersaturated with respect to gypsum).

The possibility of a long travel time (>200 years, which is the time that the SA-ET area has been mined) for the groundwater from SA-ET mines towards La Paz and Los Planes subareas was explored using a rough calculation for the velocity of groundwater. This calculation could be improved with field transmissivity data for different wells, but these data are currently not available. Table 7 shows estimates for the groundwater travel time considering different hydraulic conductivities (K), and typical porosity (n) values (Freeze and Cherry 1979) for the fractured igneous rock in the SA-ET area and the sand-gravel alluvial material in the valley. Because the lowest and highest values of K and n used in the calculation are the extreme cases, a good estimate for the total time for the groundwater to reach the Los Planes area would be in the range of 50 to several hundred years.

The possibility of As being adsorbed onto mineral surfaces (mainly iron oxyhydroxides) was considered based on the relation between the SI of ferrihydrite (MINTEQA2 results) and the As concentrations in the different subareas. As mentioned before, ferrihydrite SI remains positive (supersaturation) along the whole path, whereas As concentrations decrease with increasing distance from the mining area. This suggests that there are favorable conditions for adsorption of As (Fuller and others 1993; Bowell 1994; Manceau 1995). Carrillo and Drever (1998b) explored, in detail, the possibility of arsenic adsorption by natural aquifer material. They concluded that both experimental and modeled adsorption suggest that As is being adsorbed mostly by iron oxyhydroxide surfaces in the natural environment. This process produces a significant retardation of the arsenic plumes.

Seasonal changes in As concentration within the Los Planes aquifer

To further test the existence of an As contamination plume leaching from the San Antonio mining area towards the Los Planes aquifer the authors selected seven water wells for sampling and monitoring As concentration (Table 8). These wells are roughly aligned in a south-north direction, which is the general direction of groundwater flow from the mineralized area towards the Los Planes aquifer. These wells were sampled during the peak of the dry season (June), the beginning of the rainy season (August), and the peak of the rainy season (September) of the same year (1997). Table 8 shows the results from the chemical analyses. From Table 8 it is clear that



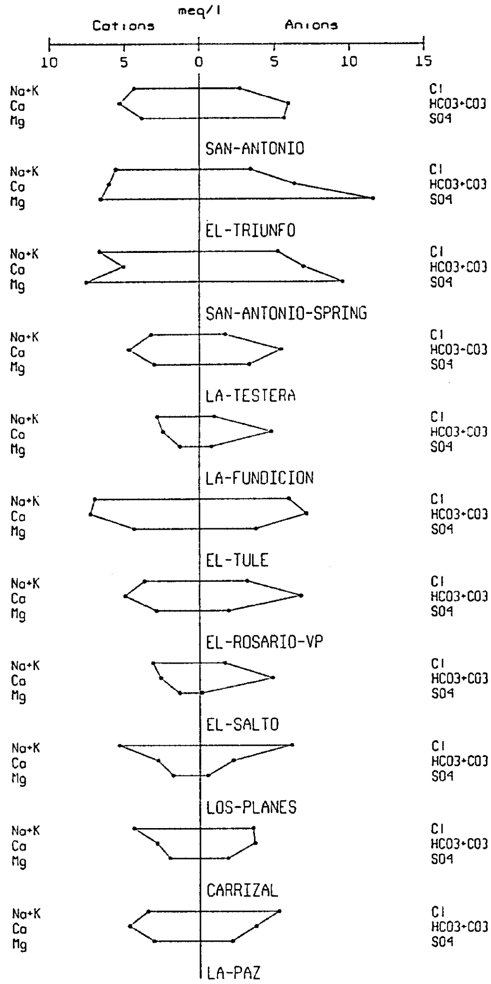


Fig. 6
Relation between concentration of different ions in the groundwater and distance from the San Antonio-El Triunfo mining area ($n = 73$)

the As content varies seasonally. Along this line of samples (M1–M8) there are two different sources of arsenic (arsenic-rich mine waste piles). The first (in the upstream direction) is located next to well M-1, the second is located between wells M-4 and M-5. During the peak of the dry season, the highest As concentrations are near the As sources (M1–M2 and M4–M5). This indicates two possible moving and dispersing As plumes. Immediately after the first thunderstorms, the As concentration increased near the As source. This may indicate the flux of newly leached As into the groundwater with minimal dispersion. At the peak of the rainy season (September) the highest As concentration had decreased in wells M1 and

Table 3
NETPATH results for the modeled geochemical path between different subareas. Constraints are the species in solution used for mass balance calculations. Different models indicate phases that would be precipitated (negative numbers) or dissolve (positive numbers) in the mass balance calculations. Exchange is between Ca-Mg. All numbers are in mmol/l (M)

Constraints	Initial	Final
Initial area: Tule, final area: La Paz		
HCO_3	7.42	3.88
SO_4	1.86	1.06
Ca	3.63	2.36
Mg	2.19	1.53

Table 4
NETPATH results for the modeled geochemical path between Tule and La Paz subareas (continued from Table 3). Constraints are the species in solution used for mass balance calculations. Different models indicate phases that would be precipitated (negative numbers) or dissolve (positive numbers) in the mass balance calculations. Exchange is between Ca-Mg. All numbers are in mmol/l (M)

	Model 1	Model 2	Model 3	Model 4
Initial area: Tule, final area: La Paz				
Calcite	−1.64	−0.38	−0.01	−1.9
Dolomite	0.49	2.9	0.49	
Gypsum		1.69		0.34
CO_2 gas exchange	−1.63		−0.16	−1.97
Dilution factor	1.75	3.31	1.75	1.42

Table 5
NETPATH results for the modeled geochemical path between SA and Los Planes subareas. Constraints are the species in solution used for mass balance calculations. Different models indicate phases that would be precipitated (negative numbers) or dissolve (positive numbers) in the mass balance calculations. Exchange is between Ca-Mg. All numbers are in mmol/l (M)

Constraints	Initial	Final
Initial area: SA, final area: Los Planes		
HCO_3	6.22	2.31
SO_4	2.81	0.26
Ca	2.66	1.40
Mg	1.90	0.89

Table 6
NETPATH results for the modeled geochemical path between SA and Los Planes subareas (continued from Table 5). Constraints are the species in solution used for mass balance calculations. Different models indicate phases that would be precipitated (negative numbers) or dissolve (positive numbers) in the mass balance calculations. Exchange is between Ca-Mg. All numbers are in mmol/l (M)

	Model 1	Model 2	Model 3
Initial area: SA, final area: Los Planes			
Calcite	3.36	6.06	4.79
Dolomite	7.73	12.23	7.73
Gypsum		1.31	
CO_2 gas exchange	−1.42		−1.42
Dilution factor	10.83	15.81	1.75

Table 7
Estimated travel time for the groundwater from the San Antonio mineralized area towards Los Planes aquifer. *K* Hydraulic conductivity; *dh/ds* hydraulic head gradient; *n (%)* percent porosity

SA area dh/ds=0.02			Alluvial Valley dh/ds=0.01			
K (m/s)	n (%)	Time (years)	K (m/s)	n (%)	Time (years)	Total time (years)
1e-08	2	27,000	1e-06	15	20,000	47,000
1e-06	4	550	1e-04	25	330	880
1e-04	6	15	1e-02	45	5	20

Table 8
Seasonalvariations (June, August and September 1997) on the arsenic concentration within seven water wells selected along groundwater flow from the San Antonio mineralized area towards Los Planes alluvial aquifer (see Fig 6 for location of the wells). All concentrations are given in mg/l

Well #	Location	As concentration (June/1997)	As concentration (August/1997)	As concentration (September/1997)
M-1	2.2 km south of SA	0.38	1.29	0.29
M-2	1.2 km south of SA	0.52	0.80	0.70
M-3	Santa Cruz (SA)	0.06	0.10	0.10
M-4	SA-spring (SA)	0.52	0.41	Not sampled
M-5	0.3 km north of SA	0.43	0.64	0.44
M-6	1.0 km north of SA	0.33	0.36	0.41
M-8	2.3 km north of SA	0.29	0.27	0.20

M2 . Dilution had probably taken place at the wells next to the source points after the heavy thunderstorms, and the As concentrations at well M1 had decreased considerably. For wells M4 and M5, it is possible that dilution had dispersed the As content. Even though few data are available, it is clear that the As content in groundwater is affected by rainfall.

This work represents the first attempt to assess the groundwater arsenic content in the mineralized area and its influence on the regional alluvial aquifers. The seasonal fluctuations of As in groundwater in wells near mine waste indicates that, at least locally, the anthropogenic sources of As have a significant influence on water quality. Is it concluded that the possibility of high arsenic concentrations (>0.05 mg/l) in groundwater of La Paz and Los Planes areas is very low because of retardation caused by adsorption and long groundwater travel times. However, it is of great importance to continue groundwater sampling and monitoring. Improved hydraulic data from the fractured and alluvial aquifers would permit better constrained modeling and better delineation of the possible As plumes.

Recently, the local authorities of San Antonio have installed a water processing plant (reverse osmosis) to provide drinking water to the local population. Regretfully, farm animals (which are, of course, a food source for humans) continue to drink from the local arsenic-contaminated water. It also would be very interesting to determine As concentrations in humans and animals in the area.

Conclusions

- Based on groundwater compositions, the SA-ET area and the aquifers of La Paz and Los Planes were divided into 11 different subareas.
- Total dissolved solids in the groundwater varied from ~500 to ~1500 ppm, and were highest in the SA spring subarea and lowest in the Fundicion subarea.
- The arsenic concentration in the groundwater varied from 0.01 to 0.41 ppm. The highest concentration was in the San Antonio subarea, the lowest was at the La Paz, Los Planes and Salto subareas.
- The general trend of the groundwater is for decreasing TDS and As concentrations with increasing distance from the mineralized area.
- Analysis and modeling of the geochemical evolution of the groundwater indicates that, along the path from the mineralized area towards the aquifers of Carrizal and Los Planes, the most likely processes are dilution of groundwater, adsorption of As onto iron-hydroxides surfaces and precipitation of calcite.
- Seasonal monitoring of seven wells during spring and summer of 1997 shows seasonally related variations.
- The people from San Antonio have recently been able to obtain their drinking water from a processing plant (reverse osmosis), but farm animals continue to drink from the local arsenic-contaminated water.

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