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M. A. Armienta[a]; R. Rodríguez[a]; A. Queré[b]; F. Juárez[a]; N. Ceniceros[a]; A. Aguayo[a]
[a] Instituto de Geofísica, UNAM, México D. F., México [b] Facultad de Química, UNAM, México D. F., México

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GROUNDWATER POLLUTION WITH CHROMIUM IN LEON VALLEY, MEXICO

M. A. ARMIENTA*, R. RODRÍGUEZ*, A. QUERÉ†, F. JUÁREZ*, N. CENICEROS* and A. AGUAYO*

Instituto de Geofísica, UNAM. México D. F., México
†Facultad de Química, UNAM. México D. F., México

Groundwater contamination by chromium has been detected in the Leon valley central Mexico. In order to determine the contaminant concentration levels and to find its source, a sampling and analysis program was developed. The analytical determinations of chromium and physico-chemical parameters, in a known hydrogeological framework, allowed the identification of three sources of chromium, two of them anthropogenic and one natural. The anthropogenic sources are: the inadequate solid wastes disposal by a chromate factory, which produces high localized concentrations (up to 50mg/l) in groundwaters to the southwest of the valley; and residual ashes produced in brick manufacturing which generates much lower concentrations (lower than 0.05 mg/l of hexavalent chromium) over a much wider area (about 180 km^2) south of Leon city. The natural source is weathering of ultramafic rocks which produces detectable amounts (between 0.004 and 0.015 mg/l) of Cr (VI) in groundwaters to the Northeast of the valley. Although the city of Leon is one of the main shoe-manufacturing centers of the country, surprisingly tanneries did not add much chromium to groundwaters.

KEY WORDS: Chromium, groundwater, tannery wastewater, heavy metals, pollution sources.

INTRODUCTION

Groundwater contamination by heavy metals is the result of the combination of industrial development and insufficient measures of environmental protection. Chromium is one of the heavy metals considered as an indicator of anthropogenic groundwater pollution. High concentrations of chromium in groundwaters have been detected in various locations in the United States and Mexico[1,2,3,4]. The presence of chromium in groundwater may be the result of infiltration of the wastewaters discharged by industries producing such products as cement, dyes, chromates, or wastes from tanneries, plating and metallurgical plants. Industrial solid wastes, through lixiviation, may also be responsible for the presence of high concentrations of chromium in aquifer systems.

Chromium in groundwater is present in oxidation states of (VI) and (III). Cr(VI) is toxic to plants, animals and man, while Cr(III) is necessary for glucose metabolism in humans[5,6,7,8]. High levels of hexavalent chromium produce gastro-intestinal and liver diseases. Lung

cancer has been reported as a result of breathing air with high chromium levels. Besides, various studies have shown that this element, mainly Cr(VI), has mutagenic properties[9,10,11].

In addition to the different toxic properties of the two oxidation states of chromium, their chemical behavior in water is distinct. Cr(VI) is highly soluble and exists in groundwater mainly as bichromate ($HCrO_4^-$) and chromate CrO_4^{2-}. Cr(III) has very low solubility, and at the pH values (6–10) encountered in groundwater, it precipitates forming $Cr(OH)_3$ or $Cr_xFe_{1-x}(OH)_3$[12,13]. The chromium oxidation state may change through redox processes involving other species commonly present in groundwater. Fe(II), organic matter, and sulfur species are capable of reducing Cr(VI)[14,15,16]. MnO_2, one of the principal species present in aquifers is particularly capable of oxidizing Cr(III) to Cr(VI)[17]. Both Cr(III) and Cr(VI) may adsorb onto minerals such as clays, and also onto Fe (III), Mn (III, IV) and Al(III) oxides and hydroxides[18,19,20,21]. In spite of its low solubility, Cr(III) may become soluble by complex formation with diverse organic substances common in groundwaters, such as humic and fulvic acids[22].

Leon, a city in the state of Guanajuato, central Mexico, is one of the important urban centers of the country (Figure 1). Its economy depends mainly on the tanning and shoe-making industries. Nearly 85% (480) of the tanneries use chromium as a tanning agent for leather and dispose of the wastewaters without treatment directly into the Leon river through the sewage system. These wastewaters have high concentrations of Cr(III), total dissolved solids, chloride, and high values of chemical and biological oxygen demands[23].

Nearly 91% of the urban water supply comes from groundwater. Since 1975, amounts higher than 0.05 mg/l of hexavalent chromium have been observed in some of the city wells. The presence of chromium was associated with the tannery discharges.

In 1987 a research project was undertaken to evaluate the levels of chromium, its distribution in groundwater, and the pollution sources in the Leon-Guanajuato valley.

Sampling was performed in 90 wells distributed throughout the valley. The following physico-chemical parameters were determined in the samples: pH, conductivity, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, Total Dissolved Solids, NO_3^-, total Fe, Chemical Oxygen Demand, NH_3, Cr(VI) and Cr_{total}. The analysis of the data, together with the hydrogeological and geological framework, clarified the chromium contamination problem in this valley.

EXPERIMENTAL

Sampling was done during five periods from June 1988 to March 1990. The first three included wells located in different zones of the valley covering a total area of around 500 km^2. The preliminary results allowed a tentative zonation of the pollution. The two subsequent groundwater monitoring campaigns were done in the detected area with higher chromium levels.

The 90 wells sampled were selected from a total of 250 wells on the basis of the following criteria: most of them should be distributed throughout the valley, and some should be situated near potential pollution sources, the availability of geological information suitable for the determination of the aquifer layer providing the water of each well, was also sought.

In situ Cr(VI) detections were also used for increasing the sampling points in the areas with detectable chromium concentrations.

In order to obtain a representative groundwater sample, strict care was paid to the sampling procedure[24,25,26]. In each case an aliquot of 1 liter of water in a plastic polyethylene (PE) bottle was taken for the determination of alkalinity, total dissolved solids, Cl^-, and SO_4^{2-}. A volume of 500 ml with the addition of 1 ml of concentrated HNO_3 in a plastic PE bottle was used for the analysis of metals. A 500 ml aliquot in a glass (borosilicate) bottle was taken for chromium determination. A 250 ml aliquot in a borosilicate bottle preserved with 10mg of $HgCl_2$ was used for determining NO_3^- and NH_3. A 125 ml aliquot in a borosilicate bottle added with 5 drops of concentrated H_2SO_4 was taken for the determination of Chemical Oxygen Demand. All the bottles were refrigerated immediately after the sampling of each well.

Field measurements included pH, conductivity, temperature, Eh, alkalinity and Cr(VI).

pH was measured potentiometrically, the pHmeter calibration was checked before pH measurement for each well. Buffer solutions were submerged in the water coming out from the well and allowed to equilibrate with the water temperature. Conductivity was determined with a conductimeter Conductronic C18, calibration was made once every 5 samples with a solution containing 1000mg NaCl/l.

Semi-quantitative determination of Cr(VI) was made *in situ* colorimetrically, by means of its reaction with diphenyl-carbazide and visual comparison. The determination was performed with the following procedure: an aliquot of 10ml was taken from the well, poured in a test tube and mixed with 10 drops of and acid solution of diphenyl-carbazide, 10 ml of standard solutions containing 0.01, 0.05 and 0.1 mg/l of Cr(VI) were also poured in 3 different test tubes and added with diphenyl-carbazide. After 10 min the color of the sample was visually compared with that of the standards. This procedure was adapted from APHA (1989)[25] in our laboratory.

For the alkalinity determination the procedure of APHA (1989)[25] was followed. An aliquot of 25 ml of the well water was taken and poured into an Erlenmeyer flask, phenophtalein was added as an indicator. If the color turned to pink, a solution of HCl 0.02N was used for titration, adding it with a burette until the disappearance of the color, then 4 or 5 drops of a mixture of bromocresol green and methyl red were added to the same aliquot until the color changed from greenish-blue to light pink. The volume consumed for each determination was registered and used for the alkalinity calculation.

Laboratory analytical determinations included physico-chemical parameters such as pH, conductivity, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, Total Dissolved Solids, NO_3^-, Fe, Chemical Oxygen Demand, NH_3, Cr(VI) and Cr_{total}, all those parameters were determined by the standard methods described below.

Sulfates were determined by a turbidimetric technique adapted from APHA (1989), whose modification consisted of a previous precise weighing of $BaCl_2$ in order to increase the reproducibility by means of a better control of the precipitation conditions[27].

Chloride concentration was determined with a selective electrode, adding a 5M solution of $NaNO_3$ as ionic strength adjuster. An Orion Research Potentiometer Model 407 A was used for this determination[28].

Calcium and magnesium concentrations were obtained through complexometric titration

with EDTA [25]. Sodium and Potassium were measured directly with a flame photometer (Perkin Elmer Coleman 51Ca), adding $LiNO_3$ as an internal standard [25].

Hexavalent chromium determinations were made by colorimetry in the laboratory. 50 ml sample aliquots were added with 2.5 ml of a solution made of diphenyl-carbazide in H_2SO_4. The absorbance measurements were made at 540nm, 15 minutes after the addition of the diphenyl-carbazide, with a spectrophotometer Carl Zeiss PM2DL. Total chromium was measured with a Perkin Elmer 2380 flame atomic absorption spectrophotometer. The samples were digested with HCl and HNO_3 and NH_4Cl was added for avoiding the chemical interference caused by Fe, Ni, Co and Mg [29]. The precision of the total chromium determination was of 0.8% as relative standard deviation, and of Cr(VI) determination was of 3%. The accuracy of the methods was determined by analyzing uncontaminated groundwater added with a known amount of Cr(VI), the differences between the true and the obtained values were less than 5%. Cr(III) was considered as the difference between Cr_{total} and Cr(VI).

Nitrates were measured colorimetrically by the phenol-disulfonic method. Total dissolved solids were quantified by gravimetry[30,25].

Chemical Oxygen Demand was determined by titrating with ferrous ammonium sulfate, after oxidizing the sample with K_2CrO_4[30].

Iron was determined by atomic absorption spectrophotometry in the sample digested with nitric acid[25].

The precision and accuracy of these methods are equivalent to those reported in APHA [25]. Results were verified by duplicate sample analysis and ionic balance. The techniques have been proven with the United States Environmental Protection Agency (USEPA) water Mineral Standard WP1185. Fifteen samples were also analyzed for chromium in the Geochemistry Laboratory at the University of Waterloo, Canada, giving a difference less than 8% between the results determined there and those obtained by us on aliquots of the same samples at the Instituto de Geofísica, UNAM.

RESULTS AND DISCUSSION

Chromium pollution

Chromium was detected in most (around 90%) of the 90 wells sampled in the valley, but the concentrations were below the potable water limit (0.05mg/l) except in one small area located to the southwest of the valley, where Cr(VI) concentrations as high as 50 mg/l were determined for the well #37 (Figure 2). These highly polluted wells are located near a chromate factory "Química Central".

The sampled wells to the east and center of the valley showed hexavalent chromium concentrations with a maximum value of 0.04 mg/l (Table 1). The presence of chromium in this area may be associated with both anthropogenic and natural sources. In this region there are many small brick factories which use leather residues as a combustible. The combustion of leather may oxidize the Cr(III) used for tanning to Cr(VI). The residual ashes are dispersed over the surrounding lands as fertilizer. Finally the action of rain and irrigation makes

Table 1 Representative results of the three sampled areas of Leon Valley.

Wells	$CrVI$ mg/l	$Cr Total$ mg/l	Cl^- mg/l	Na^+ mg/l	NO_3^- mg/l	Mg^{2+} mg/l	Ca^{2+} mg/l	HCO_3^- mg/l	Total Dissolved Solids (TDS) mg/l
Eastern area									
84	0.007 ± .0002	n.d.	3.6 ± .07	18.45 ± .92	6.64 ± .73	33.16 ± 1.66	42.17 ± 2.1	299.1 ± 11.96	396.6 ± 23.79
78	0.008 ± .0002	n.d.	4.2 ± .08	19.12 ± .96	8.86 ± .97	34.90 ± 3.84	45.08 ± 2.25	317.8 ± 12.71	353.8 ± 21.22
165	0.013 ± .0004	n.d.	4.3 ± .09	45.04 ± 2.25	3.54 ± .39	11.70 ± .59	32.76 ± 1.64	238.4 ± 9.54	356.2 ± 21.37
338	n.d.	n.d.	5.2 ± .10	24.55 ± 1.23	6.20 ± .68	19.63 ± .98	42.90 ± 2.14	282.8 ± 11.31	534.8 ± 32.09
La Loza	n.d.	n.d.	4.7 ± .09	15.50 ± .31	4.43 ± .49	17.45 ± .87	47.26 ± 2.36	226.7 ± 9.07	415.8 ± 24.95
171	0.006 ± .0002	n.d.	4.3 ± .09	17.40 ± .35	7.92 ± .87	34.60 ± 1.73	46.80 ± 2.34	329.5 ± 13.18	600.0 ± 36.00
Central area									
521	0.033 ± .001	n.d.	114.0 ± 2.28	28.98 ± .58	17.80 ± 1.96	39.36 ± 1.97	116.00 ± 5.80	368.4 ± 14.74	653.4 ± 39.20
408	0.009 ± .0003	n.d.	27.0 ± .54	25.97 ± 1.29	16.60 ± 1.83	27.60 ± 1.38	65.20 ± 3.26	322.1 ± 12.88	344.6 ± 20.68
413	0.041 ± .0012	n.d.	2.6 ± .05	20.96 ± 1.05	6.99 ± .77	21.36 ± 2.35	41.60 ± 2.08	287.92 ± 11.52	303.4 ± 18.20
548	0.011 ± .0003	n.d.	2.9 ± .06	34.49 ± 1.72	4.60 ± .51	8.40 ± 0.42	32.00 ± 1.60	222.0 ± 8.88	360.0 ± 21.60
424	0.010 ± .0003	n.d.	2.6 ± .05	18.45 ± .37	5.80 ± .64	23.28 ± 1.16	40.80 ± 2.04	292.8 ± 11.71	321.4 ± 19.28
535	n.d.	n.d.	430.0 ± 8.60	113.70 ± 2.27	35.80 ± 3.94	26.66 ± 1.33	282.80 ± 14.14	384.3 ± 15.37	1648.6 ± 98.92
Western area									
791	n.d.	n.d.	191.0 ± 3.8	73.40 ± 3.67	8.61 ± .95	48.48 ± 2.42	145.50 ± 7.27	269.0 ± 10.77	1182.6 ± 70.96
499	n.d.	n.d.	450.0 ± 22.5	124.30 ± 6.22	39.34 ± 4.33	54.54 ± 2.73	311.11 ± 15.55	433.7 ± 17.35	1903.4 ± 114.20
699	0.006 ± .0002	n.d.	4.0 ± .08	35.27 ± 1.76	3.90 ± .43	48.98 ± 2.45	58.99 ± 2.95	340.4 ± 13.62	572.0 ± 34.32
P. Blanca	n.d.	n.d.	510.0 ± 10.2	169.60 ± 8.48	9.54 ± 1.05	27.87 ± 1.39	292.90 ± 14.65	428.2 ± 17.13	1690.0 ± 101.40
S. Roque	n.d.	n.d.	45.0 ± 0.9	73.40 ± 3.67	1.98 ± .22	8.16 ± 0.41	72.00 ± 3.60	431.8 ± 17.27	628.4 ± 37.70
645	0.007 ± .0002	n.d.	4.4 ± .09	25.88 ± 1.29	7.12 ± .78	23.75 ± 1.19	67.07 ± 3.35	373.3 ± 14.93	551.6 ± 33.09
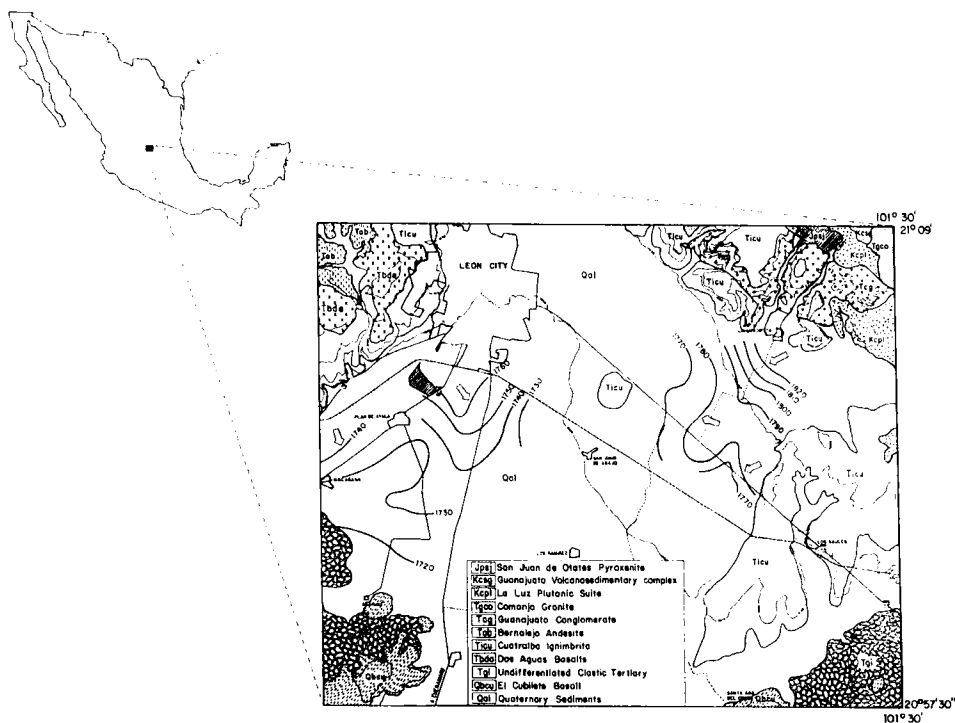
Figure 1 Localization and regional geology of Leon valley. Pyroxenite, Jpsj, outcrop is shown. The arrows represent groundwater flow direction, perpendicular to isolines of piezometric head.
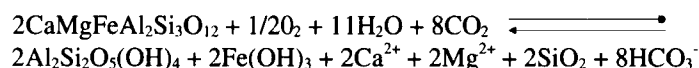
chromium leaching possible in the soil and subsoil and consequently results in aquifer contamination.

Also, in the eastern part of the valley there is an outcrop of ultramafic rocks, San Juan de Otates pyroxenites (Jpsj, Figure 1) which generally have a high chromium content[31]. A chemical characteristic of these types of rocks is their high concentration of magnesium (26.4% for samples of Leon pyroxenites). The alteration of these kinds of rocks which is produced by the action of water at high temperatures (although not greater than 500°C) produces their serpentinization[32]. This process has been observed in this area[33]. Soils derived from serpentines are the highest in chromium, with an average concentration of 2000–3500ppm[31].

Chromium was determined in samples of the rocks obtaining an average value of 1525 mg/kg of chromium, wells adjacent to the outcrop were also sampled and major ions and chromium were determined.

In view of the fact that pyroxenites give chromium and magnesium as weathering products, a correlation between these species in the groundwaters of the area near the outcrop was expected. The correlation index between these elements and also between saturation indices of minerals containing magnesium (dolomite and magnesite), as indicators of high magnesium levels and chromium concentration was determined for 13 wells located to the

east of the valley near the outcrop (in a radius around 12 km) and also for 20 wells located far from it. Representative analytical results of wells are presented in Table 1. A correlation index of 0.93 was obtained between chromium and dolomite and of 0.82 between chromium and magnesite for wells located near the outcrop having high magnesium levels (>30mg/l) and of 0.19 for chromium and dolomite and -0.14 for chromium and magnesite for all the other wells. Those correlations may be considered an indication of the origin of chromium in this area, since the weathering of pyroxenites produces magnesium, calcium and bicarbonate as products according to the following reaction[34]:

$$2CaMgFeAl_2Si_3O_{12} + 1/2O_2 + 11H_2O + 8CO_2 \rightleftharpoons$$
$$2Al_2Si_2O_5(OH)_4 + 2Fe(OH)_3 + 2Ca^{2+} + 2Mg^{2+} + 2SiO_2 + 8HCO_3^-$$

These results allow us to infer that the presence of chromium in this area is associated with the ultramafic rocks. We also take into account the fact that during weathering Cr(III) tends to oxidize easily to Cr(VI)[31]. This together with the fact that there are no anthropogenic sources nearby, and the groundwater in this zone flows down from the mountains, where the pyroxenites are located, to the valley (Figure 1) leads us to this conclusion.

The higher hexavalent chromium values obtained from the wells located to the southwest of the valley about 13.5km from Leon are associated with the operation of a chromate factory, "Química Central" (QC). In this area of around 5 km^2, five highly contaminated wells were detected (Figure 2). The maximum value of 50 mg/l of Cr(VI) was obtained for the well "La Hulera" (#37, Figure 2). The well "La Cartonera" (#34, Figure 2) had 10.75 mg/l, and the well "La Laminadora" (#40, Figure 2), had 2.3 mg/l. These three wells are used only for industrial processes. Another well which had been used until March 1992 for human consumption had a concentration of 0.74 mg/l (#44, Figure 2). The potable water source of the small community "Buenavista" (#32, Figure 2), showed chromium concentration (0.23 mg/l of hexavalent chromium) which is almost one order of magnitude higher than that of the potable limit (0.05 mg/l). As a result of the chromium level, this well was closed by local authorities.

The localization of the contaminated wells did not follow an evident horizontal concentration gradient; wells with high chromium concentration (10.75 mg/l) were very near (about 50 m) to wells with much lower concentrations (0.23 mg/l). The contaminated plume is traveling through shallow high permeability layers (gravels and sands). The wells placed in deeper aquifers (more than 50 m depth) partially confined by clayey formations have relatively low Cr(VI) concentrations (#39, 26, 27, Table 2). The well #31 (Figure 2) does not show detectable amounts of chromium because is exploiting a deeper confined aquifer unit (around 100m deep).

In the area around "Química Central" (QC) there are various possible contamination sources of chromium in the groundwater: the solid wastes located in a pile in the factory yards and in a landfill about 500m to the southwest of QC; the discharge from two tanneries; the water infiltration of the San German Dam; the sewage of QC; and the irrigation using water from the San German Dam. The results of total Cr and Cr(VI) in the water samples from these possible sources are presented in Table 2.

The analysis of the tannery effluents from a factory located at the northeast of QC at a

Table 2   Analytical Results of Wells and Superficial Waters Around "Química Central".

	Sample	Cr(VI) mg/l	Cr Total mg/l	NO$_3^-$ mg/l	Total Dissolved Solids (TDS) mg/l	Cl mg/l	Chemical Oxygen Demand (COD) mg/l
Wells	32	0.23 ± .007	0.30 ± .0024	0.8 ± .09	434.4 ± 26.06	7.4 ± .15	19.23 ± 2.11
	34	10.75 ± .322	11.45 ± .092	13.46 ± 1.48	587.8 ± 35.27	33.0 ± .66	n.d.
	37	50.00 ± 1.50	—	—	—	—	—
	40	2.30 ± .069	3.00 ± .024	9.12 ± 1.00	655.0 ± 39.30	103.0 ± 2.1	n.d.
	44	0.74 ± .022	1.01 ± .008	23.03 ± 2.53	561.9 ± 33.71	48.5 ± .97	11.90 ± 1.31
	27	n.d.	n.d.	6.56 ± .722	397.0 ± 23.82	3.9 ± .08	7.72 ± .85
	26	n.d.	n.d.	4.64 ± .51	433.6 ± 26.02	14.0 ± .28	—
	22	n.d.	n.d.	3.00 ± .33	1965.8 ± 117.95	480.0 ± 9.6	—
	42	0.76 ± .023	0.85 ± .007	2.0 ± .22	1393.2 ± 83.59	255.0 ± 5.1	28.00 ± 3.08
	39	0.05 ± .001	0.07 ± .001	0.86 ± .95	448.4 ± 26.90	54.0 ± 1.1	9.95 ± 1.09
	20b	n.d.	n.d.	26.96 ± 2.97	2063.8 ± 123.83	450.0 ± 9.0	46.98 ± 5.17
	21	n.d.	n.d.	35.2 ± 3.87	1833.4 ± 110.00	400.0 ± 8.0	n.d.
Superficial waters	Tannery Effluent	n.d.	73.2 ± .59	2.21 ± .24	1334.8 ± 80.08	210.0 ± 4.2	964.22 ± 106.10
	Irrigation Canal	0.006 ± .0002	0.88 ± .007	—	2049.6 ± 122.98	680.1 ± 13.6	—
	"San German" Dam	0.10 ± .003	0.144 ± .0011	1.51 ± .166	2315.0 ± 138.9	700.2 ± 14.0	472.79 ± 52.01
	"Química Central" Sewage	n.d.	0.17 ± .001	14.6 ± 1.46	525.4 ± 31.52	800.0 ± 16.0	89.56 ± 9.85

Cr(VI) Detection Limit = 0.004 mg/l
Cr Total Detection Limit = 0.05 mg/l
COD Detection Limit = 1.0 mg/l
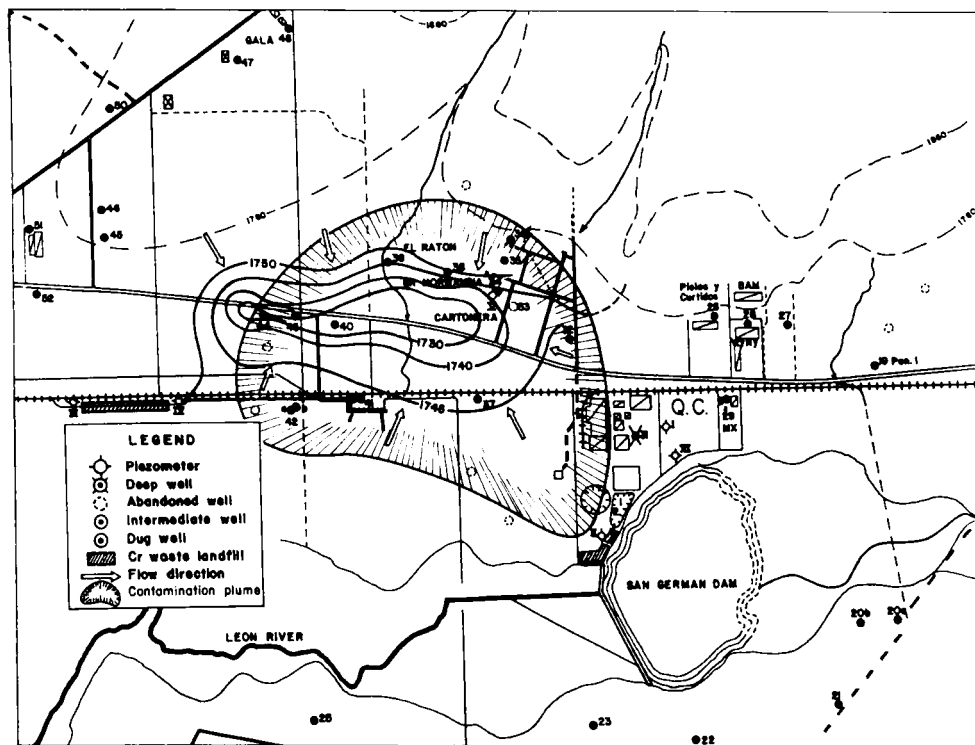
Figure 2 Area around "Química Central" (Q.C.). The contamination plume and the groundwater flow direction are shown.

distance of about 300 m, showed a non detectable amount (less than 0.004 mg/l) of Cr(VI) and 73.2 mg/l of total chromium. The chromium present in this waste water may be considered as Cr(III) coming from the tanning process which uses trivalent chromium compounds. The tannery effluents contain many organic compounds, such as amminoacids and fatty acids, capable of complexing Cr(III). In this case, at the pH of the water (6.18), the high concentration of Cr(III) in solution could be attributed to the formation of soluble complexes since based only on the solubility product value (10^{-30}) of Cr(OH)$_3$, the maximum amount of dissolved Cr(III) would have been only 0.015 mg/l. The same rationale may be applied to the San German Dam waters and to the canal waters that are used for irrigation. These waters have also high values of chemical oxygen demand.

Although the solid wastes disposed off by QC are the more probable sources for the presence of chromium in the groundwaters of this area, there are various types of solid waste deposits that could be the origin of this pollution. Those waste deposits are two solid waste landfills (one in QC yards and one about 300m to the southwest of QC) (Figure 2) and two solid waste piles above the ground that do not have landfill characteristics within QC yards.

The two landfills were discarded as pollution sources in view of the results obtained with a vertical sampling carried out in a piezometer system installed on their flanks[23,35].

The solid waste deposits above the ground were analyzed by us for chromium and water content. Cr(VI) was determined by leaching the sample with water and analyzing by colorimetry through the reaction with diphenyl-carbazide; total chromium was determined by dissolving the sample with a mixture of HNO_3 and HCl, and analyzing it by atomic absorption spectroscopy, the humidity was determined by gravimetry. One of the solid waste deposits above the ground which contains about 54000 tons with 0.137% of Cr(VI), and 2.26% of total chromium was placed over a plastic sheet and covered with clay; these characteristics together with the water content of the material (7%) and the absence of surficial evidence of leaching (collapses, lost of volume) indicate that it is not an important pollution source. The other deposit with about 14700 tons of material was formed by piling plastic bags containing alumina. The analysis of the alumina gave 6.12% of Cr(VI), 15.55% of total chromium, and a water content of 55.3%. The plastic bags used to store the alumina can support the weight produced by a pile 5m high, however, the pile is now about 8m high. As a result the bags broke and the residue came out; in this way the soluble hexavalent chromium might have been leached by the action of rainfall and infiltrated to the aquifer, surficial evidence of this process was observed by the formation of pools with high concentrations of Cr(VI) within the deposit. This hypothesis is confirmed by the high Cr(VI) concentrations (80 mg/l) obtained for piezometer II (Figure 2)[23,35].

The tannery waste water as a pollution source

High levels of nitrates and dissolved solids together with a high chemical oxygen demand may be indicative of aquifer contamination resulting from infiltration of sewage waters. In this case, before this study was performed, the authorities and Leon citizens considered that the groundwater pollution by chromium was originated from the infiltration of the tannery discharges, that are disposed off to the municipal sewage and after mixing with household sewage are used for irrigation. In view of the chemical characteristics of the sewage waters, a correlation between concentrations of dissolved solids and nitrates with that of chromium was sought.

High concentrations of nitrates and of total dissolved solids were observed approximately in the same area as shown in Figure 3. Both parameters showed higher values to the southwest of Leon city. In this area waste waters are discharged from the municipal sewage to an oxidation pond and then through canals to the nearby lands for irrigation. There is also an increase of nitrates and dissolved solids near the San German Dam, where the dam's water is used for irrigation. Although tannery waste waters with high concentrations of Cr(III) are discharged and mixed without any treatment with urban sewage, Cr(VI) was not detected in the wells located in this area, indicating the retention of chromium as Cr(III) by the soil due to the adverse conditions for its oxidation to Cr(VI) in this reductor medium with high quantities of organic matter. Nevertheless these waste waters contain high concentrations of sodium and chloride that could affect the suitability of the land for agriculture.
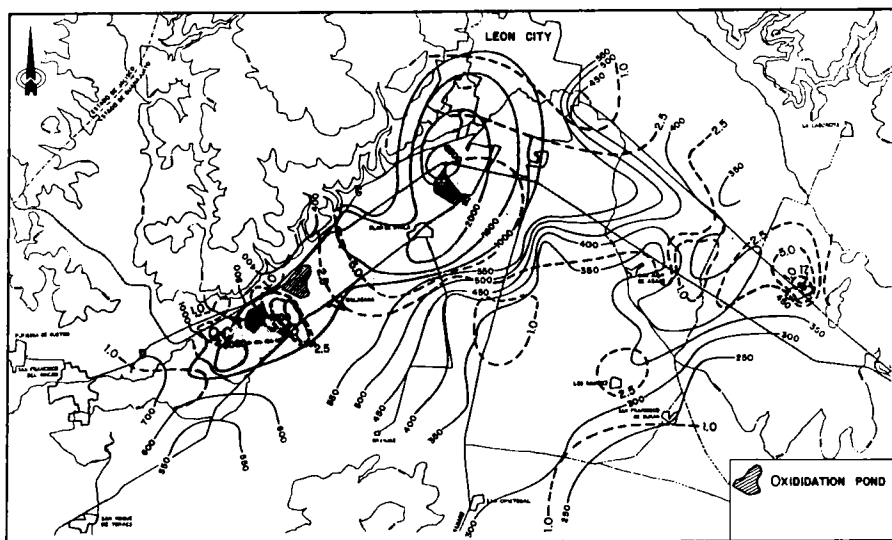
Figure 3 Concentration of Nitrates (dotted lines) and Total Dissolved Solids (TDS) (Continuous lines) in groundwater. Concentrations in mg/l. The shaded area corresponds to TDS values over 1000 mg/l. The star situates "Química Central" (Q.C.).

In the wells around the factory "Química Central", no correlation was observed between concentrations of chromium, nitrates, and total dissolved solids. The wells with higher chromium content showed NO_3^-, TDS and chemical oxygen demand values similar to those of the other wells within this area that did not have chromium. (Table 2).

Some of the wells that contained high nitrate and low solid levels were polluted by point sources, for example, cattle raising.

CONCLUSIONS

Three chromium groundwater pollution sources were identified: two anthropogenic (brick production and chromate factory) and one natural (ultramafic rocks). Their respective areas of influence which are independent from each other are shown in Figure 4.

Although the factory produces the highest chromium concentration levels, the residual ashes from brick manufacturing deliver chromium to most of the valley groundwaters.

In this study, due to the fact that chromium may exist in two oxidation states in groundwater, it has been possible to determine and localize the main sources of the presence of this element in the groundwater of Leon valley.

The QC surroundings and the pyroxenites zones of influence are not hydrodynamically connected. A piezometric depression to the west of QC, together with the hydraulic head produced by the San German Dam and the Leon River hinder also the hydrodynamic communication between the areas A and B (Figure 4).
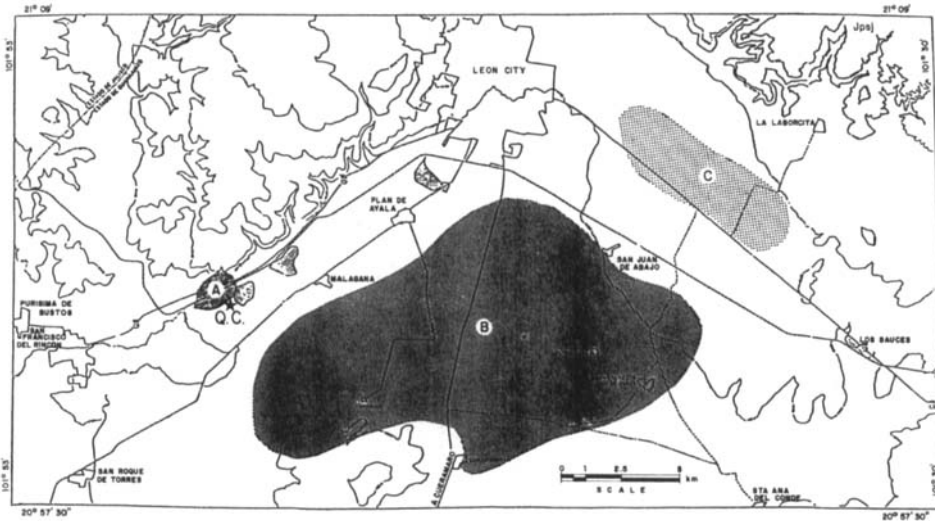
Figure 4 Areas corresponding to different sources of chromium in Leon Valley. A) Chromate factory, B) Brick manufacturing C) Pyroxenites weathering.

Contrary to expectations, tannery wastewaters do not represent at the moment, an important source of hexavalent chromium in the groundwater because they contain the element as Cr(III) and the reducing environment maintains it in this oxidation state.

The high chloride content, up to 2000 mg/l, and the absence of chromium in the groundwater of the agriculture area using urban waste-waters for irrigation, indicates that Cr(III) remains in the canal sediments and irrigated soils.

Leon-Guanajuato Valley seems to be a unique case of simultaneous pollution by man and nature by a multivalent element.

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