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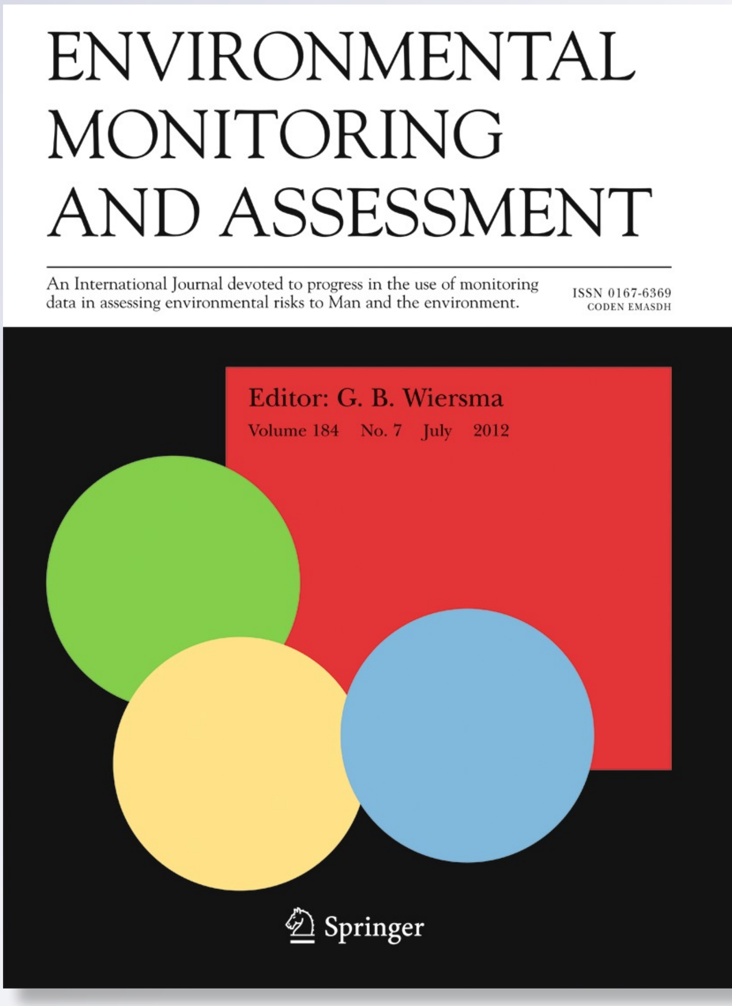

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Evaluation of hydrochemical changes due to intensive aquifer exploitation: case studies from Mexico

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Abstract The impact of intensive aquifer exploitation has been observed in numerous places around the world. Mexico is a representative example of this problem. In 2010, 101 out of the 653 aquifers recognized in the country, showed negative social, economic, and environmental effects related to intensive exploitation. The environmental effects include, among others, groundwater level decline, subsidence, attenuation, and drying up of springs, decreased river flow, and deterioration of water quality. This study aimed at determining the hydrochemical changes produced by intensive aquifer exploitation and highlighting water quality modifications, taking as example the Valle de Toluca, Salamanca, and San Luis Potosi aquifers in Mexico's highlands. There, elements such as fluoride, arsenic, iron, and manganese have been detected, resulting from the introduction of older groundwater with longer residence times and distinctive chemical composition (regional flows). High concentrations of other elements such as chloride, sulfate, nitrate, and vanadium, as well as pathogens, all related to anthropogenic pollution sources (wastewater infiltration, irrigation return flow, and atmospheric pollutants, among others) were also observed. Some of these elements (nitrate, fluoride, arsenic, iron, and manganese) have shown concentrations above Mexican and World Health Organization drinking water standards.

Keywords Intensive exploitation · Aquifer contamination · As · F · Mexico

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Introduction

Groundwater is of special importance in Mexico as it supplies 37% (29,500 Mm^3 $year^{-1}$) of the country's total water use (79,800 Mm^3 $year^{-1}$). Groundwater is mainly used for agriculture (20,500 Mm^3 $year^{-1}$); it is used for crop irrigation in up to one third of the country's total irrigated area (about 20 million hectares). Also, some 75 million people (55 million in urban areas and 20 million in rural areas) rely on this source for water supply (7,000 Mm^3 $year^{-1}$). In addition, 50% of self-supplied industrial facilities (which take water directly from rivers, streams, or aquifers) use groundwater in their processes (1,900 Mm^3 $year^{-1}$; CNA 2010).

Based on water balance estimates, the National Water Commission (CNA, for its Spanish acronym) identifies under the negative connotation of "over-exploited aquifers" those where exploitation exceeds the average annual recharge and long-term continuation of this condition is likely to produce of negative environmental impacts. The number of overexploited aquifers has increased from 32 in 1975 to 36 in 1981, 80 in 1985, 97 in 2001, and 101 in 2008 (CNA 2010). They are located in central, north, and northwest Mexico, a semi-arid and arid region which holds 31% of the country's total available water but concentrates 77% of Mexico's total population, including the main population centers. From a management viewpoint, the historical increase in aquifers classified as overexploited is a clear indication of the pressure on groundwater in Mexico, due to increases in population, industrial activity, and irrigated land.

In this review however, the expression "over-exploited aquifer" will not be applied. Instead, the term "intensive groundwater extraction" will be used to describe aquifers meeting two conditions. Firstly, a historical concentration of production wells in areas occupying less than 30–40% of the total aquifer area, around main population, or agricultural centers. And secondly, aquifers producing one or more of the following undesirable effects: desiccation of wetlands, disappearance of springs, base flow reduction, subsidence, and deterioration of groundwater quality. Social and economic problems also arise due to intensive water extraction (Simmers et al. 1992; Llamas and Custodio 2003; Vrba 2003). A synthetic description of these impacts in Mexico was presented recently by Carrillo-Rivera et al. (2008).

In the specific case of water quality deterioration related to hydrochemical changes, intensive groundwater extraction causes processes such as seawater intrusion (Re et al. 2011), mixing of surface water with groundwater (La Vigna et al. 2010), migration of contaminated and/or highly mineralized groundwater from underlying or overlying aquifers or confining layers (Flores-Márquez et al. 2006), lateral spread of contaminant plumes (Vrba 2003), and contaminant input from surface point sources through fractures or faults caused by subsidence (Mejía et al. 2007).

This paper presents the results of an extensive literature review with a particular focus on the hydrochemical changes produced by intensive groundwater extraction, highlighting water quality modifications related to the drawdown of water levels in wells. These changes are related to alterations in the circulation flow path due to large-scale water extraction in the last 30–40 years, as well as to the impact of point and diffuse sources of contaminants.

Hydrochemical changes in groundwater extracted from production water supply wells are defined here as the progressive change (most often degradation) in one or various chemical, physical, or microbiological water quality parameters with respect to pumping time in aquifers with an intensive extraction regime.

The research considers three case studies of key aquifers in Mexico: (1) Valle de Toluca, (2) Salamanca, and (3) San Luis Potosi. The selection of aquifers was made considering not only data on likely side effects produced by intensive groundwater extraction, but also the availability of peer-reviewed papers, to ensure the use of validated information. The aquifers have several distinctive hydrogeological features (they are heterogeneous, composed of detritus and fractured rock, with a thickness in excess of 500 m) which make them comparable with similar aquifers, not only in Mexico but around the world.

Methods

The study of hydrochemical changes produced by intensive groundwater extraction in aquifers was based on a comparative analysis of data obtained from different campaigns, combined with the historical compilation and appraisal of chemical analyses carried out by academic and government institutions. Complete descriptions of field and laboratory methods are presented in the original papers reviewed for every case study; however, a brief description of methods is presented below.

The availability of data on field parameters such as electrical conductivity (EC), pH and temperature, measured using an inline flow cell to ensure exclusion of atmospheric contamination and improve measurement stability, was considered important for data source discrimination. Sample collection and preservation prior to laboratory analysis, in every case, followed a procedure according to the standard methods presented by American Public Health Association, American Water Works Association, Water Environment Federation (APHA, AWWA, WEF 1995). The availability of data on major and minor ions (bicarbonate, sulfate, chloride, nitrate, fluoride, calcium, magnesium, sodium, and potassium) was also considered for the selection of data sources. It was important to identify whether the analytical techniques followed regulations enforced in Mexico, which are based on the methods proposed by APHA, AWWA, WEF (1995).

The analytical techniques included determination of total alkalinity (as bicarbonate) and chloride ions by titration, sulfate by turbidimetry, nitrate by ultraviolet spectrophotometry, and cations (calcium, sodium, potassium, and magnesium) by flame atomic absorption spectrometry. Trace elements, such as arsenic, iron, and manganese, were determined by flameless atomic absorption spectrometry using a graphite furnace atomic absorption spectrophotometer. Fluoride was determined by ion selective electrode. Vanadium was analyzed by automated colorimetry. Piper and Stiff diagrams were used to define the different hydrochemical groups.

Maps were created using SURFER V.6 (Golden Software Inc. 1997) and Arc-View. A multivariate statistical analysis was performed (Davis 1986) to classify the variables (physicochemical characteristics) and observations (sampling points), and establish the relationships between them. This analysis has been used in numerous hydrogeochemical studies to discriminate groundwater flow paths and to identify processes (natural and anthropogenic) that modify the physico-chemical characteristics of water (Esteller and Andreu 2005; Kumar et al. 2006). A principal components analysis (PCA) was used to study the interdependent relationships. This technique reduces the number of variables, which is usually high in hydrochemical studies, and replaces them by new, uncorrelated, variables. These new variables are principal components arising from the linear combination of the original variables. Thus, relationships between variables and/or observations are established, and the contribution of each of them, or of each combination within the hydrochemical data structure, is estimated.

Results

Valle de Toluca aquifer

General aspects

The Valle de Toluca aquifer (Fig. 1), located in the Highlands of Mexico, has an average altitude of 2,570 m above sea level (asl) and a drainage area of about 900 km^2. The climate is temperate with dry winters, 700–1,300 mm mean annual precipitation depending on altitude, and 12–16°C mean temperatures.

The aquifer provides water for population, industrial facilities (3,438 factories), and crop irrigation (56% of land use is agricultural). Economic development sustained by groundwater has motivated an increase in population during the last five decades, which is currently estimated at 1.7 million inhabitants (INEGI 2005). The main source of surface water is the Lerma River but industrial and municipal discharges create a significant pollution load therein (Fall et al. 2007). The rise in economic activity and population has resulted in increased water demand, groundwater being the only available source of water supply. In addition to the in-basin consumption, a significant portion of water extracted from this aquifer and from the neighboring Valle de Ixtlahuaca–Atlacomulco aquifer is exported to the Mexico City metropolitan area located to the east, representing a volume of 167 Mm^3 year^{-1} (Birkle et al. 1998).

Intensive groundwater extraction has caused a significant decrease in water level, soil subsidence with a maximum rate of 10 cm year^{-1} over the 2003–2008 period (Calderhead et al. 2011), drying up of springs and lagoons, and base flow reduction (Esteller and Díaz-Delgado 2002). In addition, hydrochemical changes are evidenced by the degradation of groundwater quality, and by increased salinity, heavy metals (iron and manganese) and nutrients (nitrate; Esteller and Andreu 2005).

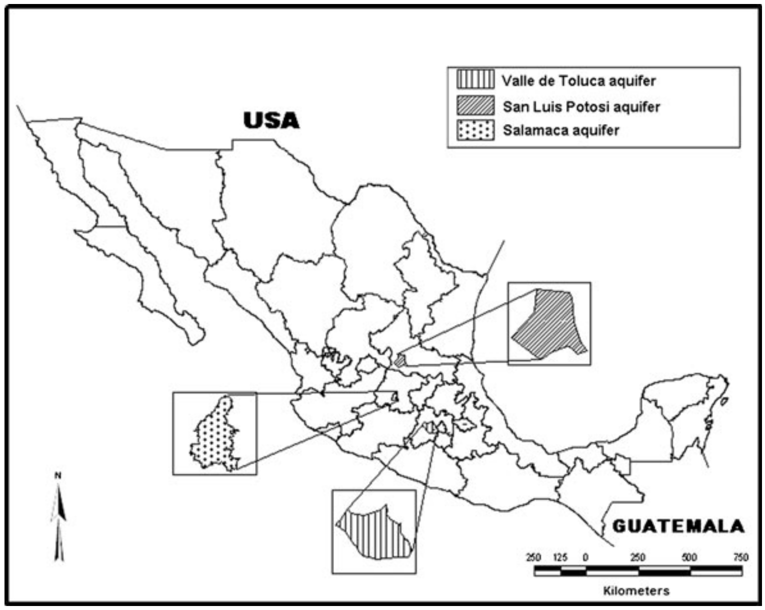

Fig. 1 Location map of the Valle de Toluca, San Luis Potosí and Salamanca aquifers, Mexico

Hydrogeology

The Valle de Toluca aquifer is located in the Trans-Mexican volcanic belt, a region constituted by outcrops of Cenozoic volcanic rocks with calc–alkaline affinity. The volcanic units are dominated by a thick sequence of andesite and rhyolite of Oligocene age, andesite of Miocene age, and Quaternary basalt and andesite. These lava flows and associated pyroclastic material and breccias produced the mountain ranges located in the high-topography portions. At lower altitudes, lacustrine and alluvial sediments are interbedded with clastic material of volcanic origin (pyroclasts, tuff, and breccia). Basin-fill materials are assigned to the late Pliocene–Quaternary age (Herrera and Sánchez 1994; CNA 2009); they have a composite thickness ranging from a few meters at the boundary with the mountains, to more than 500 m, and overlaying bedrock is constituted of rhyolite, andesite, and basalts.

The foregoing geology points to specific hydrogeological features: a heterogeneous anisotropic aquifer unit formed by both fractured rocks and granular deposits. The intensive groundwater extraction is mainly from wells tapping the porous media overlying the fractured volcanic rocks. Grain size distribution of the clastic sequence of sediments is quite heterogeneous within the basin. This heterogeneity has a definite influence on the hydraulic properties of the granular portion of the aquifer. The porous media have horizontal hydraulic conductivity values between 4 and 80 m day^{-1} and a specific yield of 0.3–0.9% (CCRECRL 1993). Local and intermediate flow systems are associated with the porous media and Quaternary volcanic rocks; regional flow systems are linked to the Oligocene–Miocene volcanic sequence. Water balance calculations for porous media consider a total input of 337 Mm^3 year^{-1} (178 Mm^3 year^{-1} from rainfall infiltration, 157 Mm^3 year^{-1} from lateral flow from the fractured portion of the aquifer, and 2 Mm^3 year^{-1} from irrigation return flow). Total output was estimated at 489 Mm^3 year^{-1}, with pumping from production wells as high as 436 Mm^3 year^{-1} (88% for urban water supply, 7% for industrial use, and 4% for farming); the remaining output corresponds to natural discharges (springs and river base flow). Additional outputs, such as evapotranspiration or lateral flow into other aquifer units, were considered absent on the basis of depth to water table and hydraulic head distribution (CNA 2009).

The intensive groundwater extraction has caused distortion of the original groundwater flow. Water level evolution, based on measurements conducted in wells, is displayed on the map of drawdown isopleths for 1968–2007 (Fig. 2); the average decline rate was determined as ≈1.4 m year^{-1}. In relation to this decline in water level, it has been possible to verify, in the city of Toluca, how cracks or faults in the soil have caused damage to houses and urban infrastructure (Esteller and Díaz-Delgado 2002).

Hydrochemistry

The natural baseline composition of groundwater flow in the granular portion of the aquifer indicates bicarbonate (130 mg L^{-1}), sodium (19 mg L^{-1}), and magnesium (15 mg L^{-1}) as major ions (Table 1). This average composition is mainly derived from water–mineral interaction (hydrolysis) in a noncarbonate system. Low nitrate (average value of 8 mg L^{-1}) suggests limited impact from anthropogenic inputs. Average sulfate (9 mg L^{-1}) and chloride (14 mg L^{-1}) values are low, indicating their atmospheric origin, and that they are introduced into the aquifer by rainfall recharge.

In the first stage of groundwater extraction, production wells tapping the granular portion of the aquifer extracted water from local and intermediate flows. Water was of low salinity, HCO_3–Mg type, produced from natural recharge in the piedmont areas, and/or by lateral flow from the fractured portion of the aquifer (comprising basalt and andesite). After some time, the intensive groundwater extraction caused a general drawdown of the water table. The hydraulic head decline in the upper portion of the aquifer facilitated the induction of regional flow from beneath, derived from fractured felsic volcanic rocks (Esteller and Andreu 2005), producing hydrochemical changes in the extracted groundwater. The regional flow

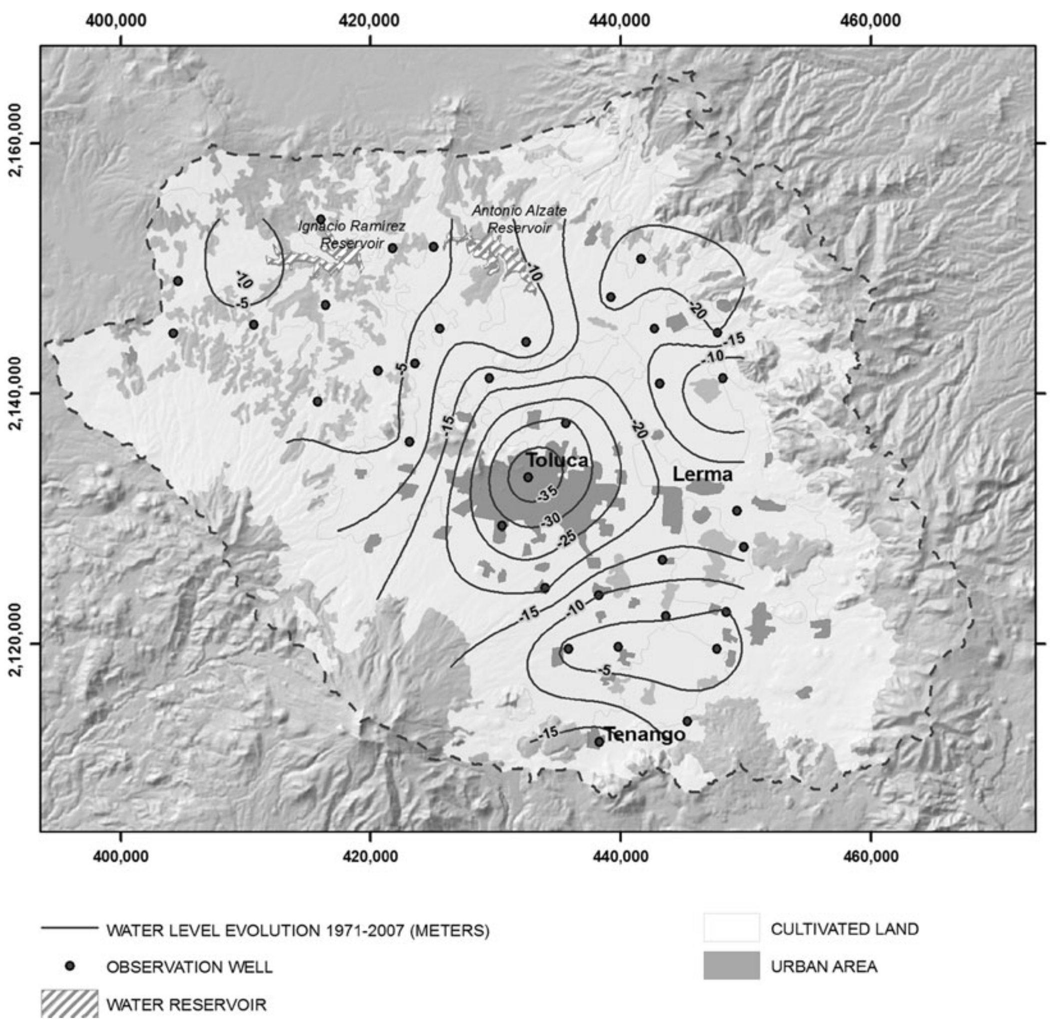

Fig. 2 Map of drawdown isopleths of the Valle de Toluca aquifer between 1971 and 2007 (in meters)

Table 1 Results of physicochemical analysis of the groundwater samples (values in mg L^{-1} except EC in µS cm^{-1}; *Nd* not detected)

	pH	EC	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	F^-	As
Mexican drinking water standards	6.5–8.5	–	–	400	250	44	–	–	200	–	1.5	0.025
Toluca aquifer												
Max	8.5	446	264	117	52	38	32	33	37	11	1.24	Nd
Min	6.6	117	63	2	6	0.4	7	4	9	2	0.04	Nd
Salamanca aquifer												
Max	8.2	1,958	472	458	115	12.2	93	67	250	25	6.5	0.072
Min	7.1	591	257	39	11	0.6	4	0.9	102	5	Nd	0.006
San Luis Potosí (shallow aquifer unit)[a]												
Max	8.1	3,190	554	1,534	435	1,918	598	49	278	122	1.7	0.135
Min	5.9	615	92	69	5	1.6	50	4.6	11	16	0.02	0.002
San Luis Potosí (deep aquifer unit)[b]												
Max	7.8	889	246	96	129	52	86	10	58	22	4.3	0.026
Min	6.2	93	53	2	7	4.4	12	0.1	7	4	0.2	0.002

[a] Cardona et al. (2008)

[b] Cardona et al. (2009)

has HCO_3–Na water type with high K^+ (11 mg L^{-1}), and higher EC (978 µS cm^{-1}) and temperature (23°C), as compared with temperature (18°C) and EC (233 µS cm^{-1}) in the granular media. In addition to the regional flow input, induced recharge from the surface has produced an increase in nitrate (up to 38 mg L^{-1}) and sulfate (up to 117 mg L^{-1}). The source of these ions seems related to the use of fertilizers, confirming the impact of agricultural activities.

Iron (2.52 mg L^{-1}), manganese (0.22 mg L^{-1}), and fluoride (1.24 mg L^{-1}) concentrations in the regional flow are usually very close to or above Mexican drinking water standards (0.30 mg L^{-1} iron, 0.15 mg L^{-1} manganese, 1.5 mg L^{-1} fluoride).

The hydrochemical changes were also identified by statistical analysis with 54 sampling points, considering major ions as well as trace and minor elements. A PCA was carried out to ascertain the relationships between chemical variables. The two principal axes of the PCA explained 55% of the sampling variance. Component I (35% of total variance) discriminated ions linked to local flow (sulfate, chloride, calcium, and magnesium), including the effect of contamination by nitrate (Fig. 3a). Component II (20% of total variance) revealed important associations between sodium, bicarbonate, iron, manganese, and fluoride, linked with regional flow. These two components (Fig. 3b) displayed a spatial grouping which clearly separated samples that characterize regional flow (in the upper quadrant) from samples that represent local flow (in the lower quadrant).

Salamanca aquifer

General aspects

The city of Salamanca, located in the state of Guanajuato (Fig. 1), within the Trans-Mexican volcanic belt, has strong industrial development and intensive farming production. The dry semi-arid climate with rainy season occurring in summer has a mean annual temperature and precipitation of 19°C and 590 mm, respectively (INEGI 1999).

The hydrogeological unit supporting water supply is the Salamanca aquifer. Groundwater constitutes the only source of water supply for 400,000 inhabitants in the urban and rural areas of Salamanca. There are no alternative sources. Surface water from the Lerma River, which passes through the city of Salamanca, is heavily polluted by discharges of untreated municipal and industrial wastewater, not only from the basin itself, but also from upper basins such as the Valle de Toluca (Fall et al. 2007).

Groundwater extraction (from about 1,600 production wells) is ≈380 Mm^3 $year^{-1}$ (GUYSA 1998): ≈46 Mm^3 $year^{-1}$ for water supply, extracted from

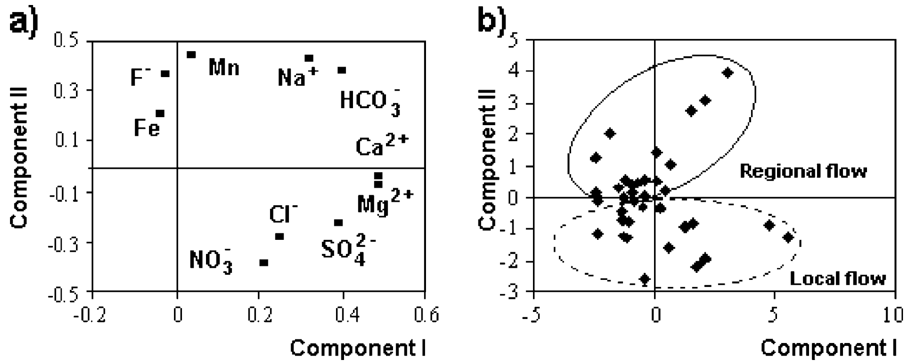

Fig. 3 Scatter plots of the first two components for the PCA, for the chemical parameters (**a**) and sampling wells (**b**), Valle de Toluca aquifer

33 municipal wells operated by the Salamanca Municipal Committee for Drinking Water and Sewage Systems (CMAPAS, for its Spanish acronym), ≈312 Mm^3 $year^{-1}$ for agriculture, and ≈22 Mm^3 $year^{-1}$ for industrial use (mostly oil refining and electric power generation). The estimated annual natural recharge (≈36 Mm^3 $year^{-1}$) accounts for less than 10% of total extraction. Leaking pipes and mains from water supply and sewage networks constitute sources of induced recharge (≈4 Mm^3 $year^{-1}$). Irrigation return flow is an additional source of induced recharge; however since potential evapotranspiration is high and efficient, irrigation systems are quite common in the area, it has been estimated at ≈5 Mm^3 $year^{-1}$ (Rodríguez et al. 2001a).

Hydrogeology

The sedimentary environment and regional geologic framework help define two geologic environments: the north and south portions, separated by the Lerma River running approximately westwards. In the northern portion, borehole logging indicates a heterogeneous and anisotropic sequence, including clayey sand; local variations of sandy clay; and intercalations of clay, sand, and gravel, with a composite thickness of about 100 m. The coarse material with sedimentary lenticular structure is derived from Quaternary fluvial processes, probably linked to paleochannels with a random distribution in the subsurface. This sequence overlies fractured volcanic rocks, mainly Pleistocene and Miocene andesitic and basaltic rocks with a composite thickness in excess of 200 m. In the Southern portion, Quaternary lava flows at shallow depth restrict basin fill thickness; in this portion, basin fill includes grain size ranging from clay to sand in variable proportions (Rosales 2003).

Data on depth to water level and hydrogeochemical distribution (major and trace elements, as well as temperature) discriminate between a number of production units and groundwater flow systems within the heterogeneous aquifer system (Rodríguez et al. 2001b). In the northern portion, the shallow production unit (locally called shallow aquifer) corresponds to granular alluvial sediments (50–80 m thick) and a local flow system. Depth to water table level is about 18–19 m. Water in this aquifer is polluted by point and diffuse surface sources, restricting water use without previous treatment. The intermediate production unit (200–300 m thickness) supports about 90% of total water extraction from intermediate and regional flow systems. It is a heterogeneous sedimentary deposit with coarse-to-medium particles and discontinuous clay layers overlying fractured volcanic rocks. Depth to water level varies from 40 to 60 m. The deep production unit (500–700 m deep), with regional flow systems, consists of fractured Pleistocene and Miocene volcanic rocks, and has a depth to water level of 70–75 m (Mejía et al. 2001). There are no pumping test data to evaluate the hydraulic properties of these production units, although in situ measurements (constant head permeameter) suggest horizontal hydraulic conductivity values of 86.4–0.2 m day^{-1} for the shallow production unit and 129.6–2.2 m day^{-1} for the intermediate production unit (Rodríguez et al. 2001a). In the southern portion, the aquifer includes two production units: an intermediate unit, consisting of fractured volcanic rocks, ashes and volcanic debris, and a deep unit, consisting of basaltic volcanic rocks with intercalations of fine sand and clay between lava flows (Rodríguez et al. 2001a).

Intensive groundwater extraction in the last 40 years has produced significant changes in the original groundwater flow distribution. In the northern portion, the average drawdown rate identified for the intermediate unit is 2.0 m year^{-1}, with a drawdown cone in the central part of the Salamanca urban zone (Fig. 4); whereas in the Southern portion, it is 1.6 m year^{-1}. The shallow unit has maintained the same water level in the last 6 years, with a minor increase produced by rainfall infiltration through faults and fractures associated with land subsidence. The presence of clay layers interbedded in the aquifer system of the northern portion, combined with the intensive groundwater extraction, has caused subsidence at an estimated rate of 6 cm year^{-1}. The main fault, generated by land subsidence, crosses the Salamanca urban area in a NE–SW direction (Fig. 4) and is more than 6 km long (Mejía et al. 2007).

Hydrochemistry

Groundwater chemical data from the intermediate unit of the Salamanca aquifer system indicate alkaline pH values. The major ions are bicarbonate and sulfate (anions) and sodium (cation; Table 1). Minor and trace elements such as fluoride, arsenic, and lead (0.009–0.075 mg L^{-1}), are usually in concentrations above Mexican drinking water standards (1.5 mg L^{-1} fluoride, 0.025 mg L^{-1} arsenic, 0.01 mg L^{-1} lead; Rodríguez et al. 2005). Vanadium in groundwater shows maximum values of 0.08 mg L^{-1}. Fortunately, there is still no convincing evidence of health effects in Salamanca's population due to water consumption (Rodríguez et al. 2002).

A high vulnerability to surface sources of contamination has been determined by DRASTIC and SINTACS methodologies in some specific areas (Mejía 2007). These areas, in addition to the faults and fractures created by subsidence in the northern portion, have facilitated the migration of vanadium and arsenic from surface industrial emissions to shallow groundwater. A deposition model of industrial aerosol emitted mainly by the power plant (Rodríguez 2002), in conjunction with chemical analyses of soil and groundwater, confirm that both vanadium and a fraction of the total arsenic come from air pollution deposited in highly vulnerable areas (Mata 2006; Mejía et al. 2007). Spatial and temporal variations in arsenic concentrations also confirm these results (Figs. 4 and 5; Rodríguez et al. 2005). However, it is also possible that faults are increasing surface water inflow, oxidizing arsenic bearing minerals, thus increasing arsenic concentration in groundwater. A similar condition has been documented in Zimapan, Mexico (Rodríguez et al. 2003). Contrary to some Asian countries where arsenic increase in groundwater has been associated with intensive exploitation (Singh and Singh 2002), there is still no evidence of such process in the Salamanca aquifer.

These contamination problems highlight the fact that intensive groundwater extraction has caused subsidence, land fracture, and consequently, increased vulnerability of the aquifer unit to contaminants from point and diffuse sources.

An additional contaminant source in the shallow production unit was the spill of hydrocarbons (containing vanadium and arsenic) produced by the neighboring refinery (northern portion). The leak was produced by pipe failure caused by land subsidence. In addition, the fault created a preferential pathway for free-phase hydrocarbons, allowing direct mass transport from the shallow into the intermediate production unit (tapped for water supply to the population; Rodríguez et al. 2000). Several organic compounds such as chloroform and chlorobenzene have been identified in both production units, resulting from this incident. Some sections of the sewage system collapsed due to displacement along faults and cracks, and resulted in the mixing of drinking water (with chlorine added for microorganism control) and wastewater (containing organic matter), creating an alternative source of chloroform and chlorobenzene in the shallow production unit.

San Luis Potosi aquifer

General aspects

The prevailing climatic conditions are characteristic of semi-arid environments, with an average annual rainfall of 400 mm. Average annual temperature is 17.6°C, with an annual potential evaporation of about 2,000 mm (Cardona 2007). Surface water available for water supply, from the San Jose Dam located in the vicinity of the urban region, is very limited (less than 5% of total groundwater extraction ≈133 Mm^3 year^{-1}).

Two aquifer units have been identified in the San Luis Potosi drainage basin (Fig. 1). These aquifers are informally named, according to their depth, the shallow aquifer and the deep aquifer. The latter is

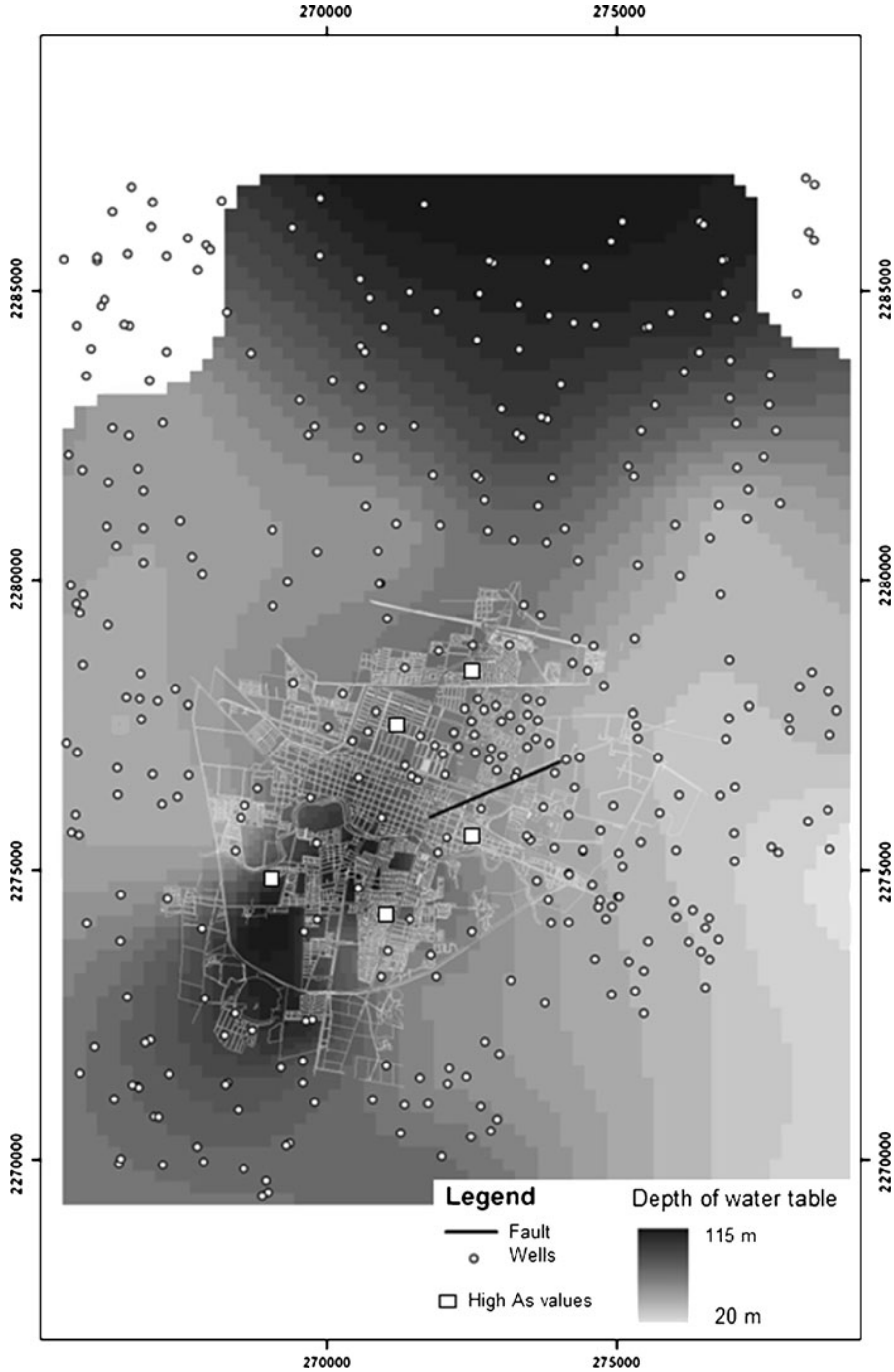

Fig. 4 Contours of equal depth of groundwater table, subsidence faulting and location of the wells, Salamanca aquifer

recognized as the San Luis Potosi aquifer (ASLP, for its Spanish acronym). Fractured volcanic rocks comprise the deep aquifer unit, which has a regional extension beyond the surface drainage basin boundaries; however, for administrative purposes, the CNA has set boundaries delineating an area of 1,980 km^2.

The metropolitan areas of San Luis Potosi and Soledad de Graciano Sanchez (SLP–SGS) are located close to the geographic center of the basin. The SLP–SGS conurbation has become the most influential socioeconomic and policy factor, determining the use and reuse of groundwater extracted from the ASLP, as

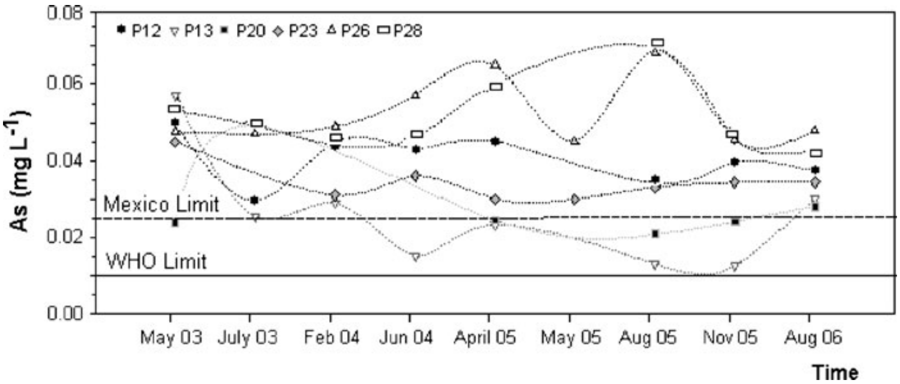

Fig. 5 Temporal variations of arsenic concentration from selected wells of the Salamanca aquifer (May 2003 to August 2006)

well as the locations of new wells for municipal water supply (COTAS-ASLP 2006). Approximately 65–70% of total water extraction from the ASLP is destined to supply the population. Currently, water supply comes from approximately 120 production wells (≈90 Mm^3 $year^{-1}$). In addition, when surface water is available in the San Jose Dam, ≈3–5 Mm^3 $year^{-1}$ are incorporated to the distribution mains. About 8 Mm^3 $year^{-1}$ are extracted for industrial use, and 35 Mm^3 $year^{-1}$ are extracted for agricultural purposes. The economic development of the SLP–SGS conurbation, supported by groundwater extraction, has resulted in population growth in the last decades, in such a way that two of the three municipalities which are supplied by the ASLP had the highest population growth in the state, in the second half of the twentieth century (COTAS-ASLP 2006).

Hydrogeology

The hydrogeology of the ASLP has been described in detail by Carrillo-Rivera et al. (1996, 2002). The closed drainage basin occupies a horst and graben structure developed during the Oligocene. A thick (>1,000 m) sequence of extrusive volcanic (Tertiary ignimbrites, lava flows, and tuffs) and alluvial materials were deposited, covering Cretaceous limestone and calcareous mudstone outcroppings in the eastern portion, with folded NW–SE structures and the presence of a post-Mesozoic granodiorite intrusion. The volcanic rocks are felsic to intermediate (ranging from rhyolite to latite), although a minor component of mafic (andesite) rocks is also present. A clastic sequence of debris flow sediments containing volcanic material from the surrounding volcanic rocks, interbedded with calcareous sediments from carbonate rocks in the adjacent hills, fills the graben structure forming the basin fill, identified here as tertiary granular undifferentiated (TGU) material. Using geological and geophysical well-logs, Cardona (2007) identified a transition from alluvial fan deposits near high-topography regions to playa sediments in the lowest portion of the graben structure. Prevailing arid conditions produced fine silty–clayey (loess-like) sediments of aeolian origin and silty–clayey flood plain deposits with subordinate amounts of very fine sand, resulting in a 50–50 m thick bed of compact and fine-grained layer, fully enclosed in the TGU. This layer is found under most of the study area except the TGU margin, and has an extent of about 300 km^2. Depth to bedrock beneath the basin-fill sediments is about 250–300 m on average, with the deepest portions located in the northeastern area of the SLP–SGS at about 450–500 m.

The shallow and deep aquifers are vertically separated by the compact fine silty–clayey layer. The shallow aquifer unit comprises local groundwater flows in the Quaternary alluvial material (sand and silt with erratic amounts of clay), with a maximum thickness of approximately 50 m. It is unconfined and perched over a fine silty–clayey layer, with a water table elevation ranging between 1,810 and 1,930 m asl, and a general flow direction from west and southwest to east and northeast (depth to water table between 5 and 35 m). The ASLP is confined under the fine silty–clayey layer and unconfined elsewhere outside the layer. It is heterogeneous and anisotropic, including TGU (intermediate flow) and fractured volcanic (regional flow) geological units. Some wells (350–450 m deep) located within the SLP–SGS conurbation penetrate the upper 100–300 m of fractured volcanic rocks below the basin fill. Moreover, in the last years, drilling of deep production wells up to 700 m deep, in rhyolite outcrops in the western region of the SLP–SGS conurbation, has become frequent.

Intensive groundwater extraction from the ASLP has produced two drawdown cones, one located in the SLP urban area, and the other one to the southeast, in the vicinity of the industrial park (Fig. 6). In the deep aquifer, depth to water level in 2007 ranged between 100 m in the northern and southern portions, with lower well densities, and 170 m below the SLP–SGS, with a mean depth of 133 m. Mean annual (1970–2007) drawdown was calculated at approximately 1.4 m year^{-1} (Cardona 2007). A low hydraulic conductivity, derived from fine-grained basin fill below the SLP–SGS and concentrated water extraction by water supply wells, has resulted in a maximum accumulated local drawdown of about 70 m in the last 30 years. The subsidence phenomenon, linked to

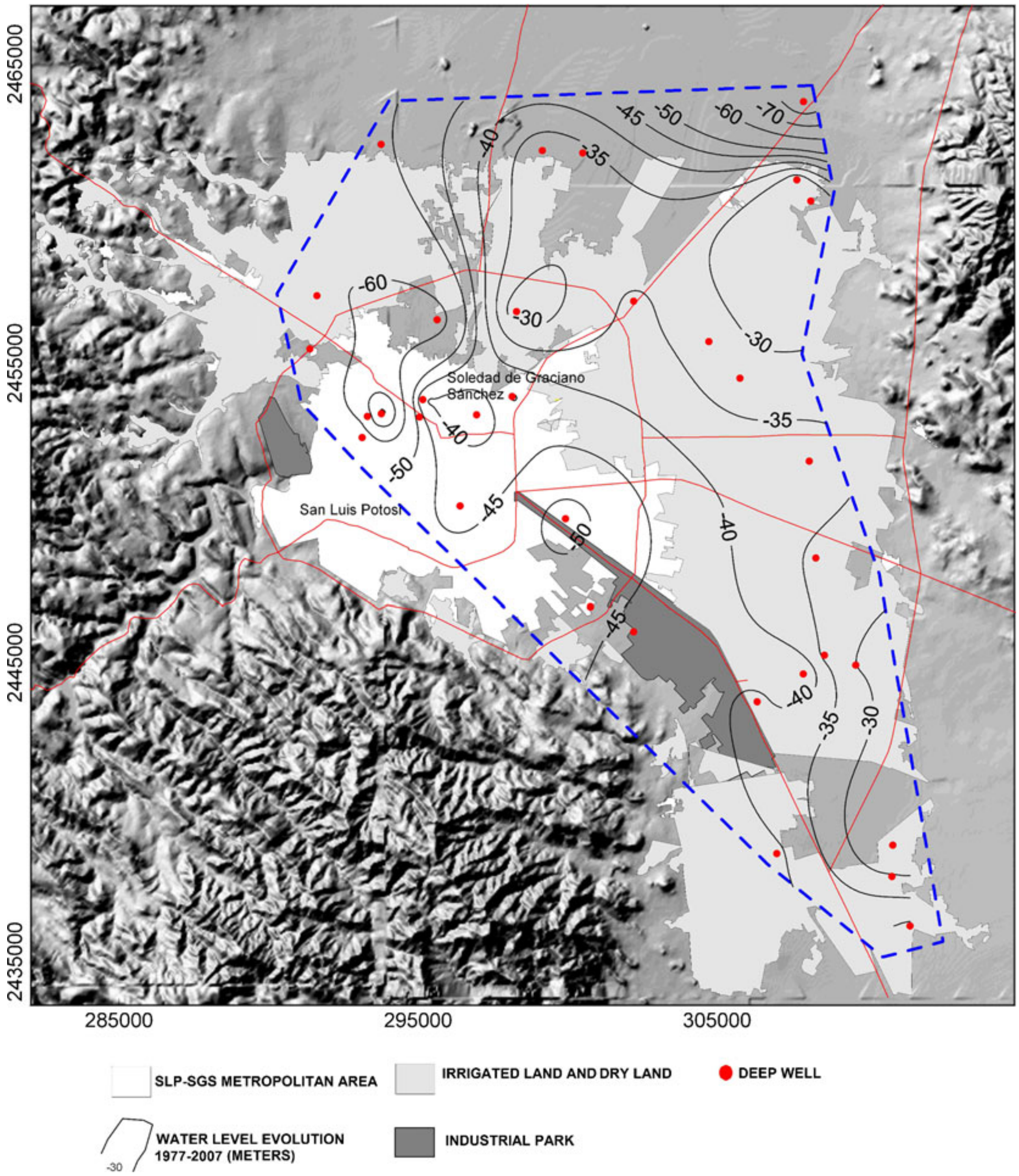

Fig. 6 Map of drawdown isopleths of the deep unit of the San Luis Potosi aquifer between 1977 and 2007 (in meters)

pore-pressure reduction due to drawdown in the deep aquifer, has produced substantial damage to buildings of historical significance within the SLP–SGS conurbation (López-Doncel et al. 2006). The combination of underlying normal faults, associated with the development of the graben structure and the geotechnical properties of the basin fill, has produced differential sinking and cracking of the land mass, resulting in a series of fractures with patterns following major Tertiary geological structures (Labarthe et al. 2005). Since the water table in the shallow aquifer has not experienced drawdown, attenuation and redistribution of strengths and deformations due to subsidence have been produced, and so until now the effects, although conspicuous and widespread in SLP (Mata-Segura et al. 2004), are not as important as those identified in other Mexican cities (such as Toluca and Salamanca).

Hydrochemistry

Shallow aquifer unit Geochemical and microbiological results indicate that the baseline water quality of local shallow groundwater flow (Table 1) is heavily affected by return flow from the reuse of raw wastewater for crop irrigation (Cardona et al. 2008). The historical socioeconomic conditions and the original design of the sewage system in the SLP–SGS area, dating from the early 1900s, have determined the use of up to 2 m^3 s^{-1} of raw wastewater for crop irrigation (CNA 1996). A negative impact on shallow groundwater quality has been identified more than 45 years ago (Stretta and Del Arenal 1960). More recently, considering high nitrate, nitrite and pathogen concentrations above Mexican drinking water standards and microbiological indicators, Cardona (2007) and Cardona et al. (2008) evaluated the historical evolution and extension of areas affected by diffuse contamination (Fig. 7). In addition, elevated concentrations of other major ions such as bicarbonate, chloride and sulfate, were identified in specific regions of the industrial park, where former liquid waste disposal practices (prior to sewage system installation) included direct injection into the aquifer using shallow wells. Shallow depth to water table, hydraulic properties, and the widespread distribution of point (dumps) and diffuse contaminant sources (crop fields, leaking sewage systems, unlined channels for sewage distribution, lagoons for wastewater collection), have produced a direct relationship between shallow groundwater contamination and land use (Martínez Revilla et al. 2006). Thus, an increase in major ions was detected in the urban land area, with higher average concentrations for sodium (103 mg L^{-1}), calcium (118 mg L^{-1}), chloride (87 mg L^{-1}), bicarbonate (277 mg L^{-1}), and sulfate (148 mg L^{-1}) in shallow groundwater. In the case of trace elements, vanadium (6 μg L^{-1}), and arsenic (22 μg L^{-1}) showed higher average concentrations in the urban land area; the highest concentrations of manganese (533 μg L^{-1}), cadmium (5.4 μg L^{-1}), and lead (4.2 μg L^{-1}) were observed in the industrial park area, and zinc (45.4 μg L^{-1}) and uranium (48.3 μg L^{-1}) in the cultivated land area.

Deep aquifer unit Chemical composition and temperature for the regional flow system showed a baseline geochemistry resulting from water-fractured volcanic rock interaction, producing devitrification of the glassy matrix and dissolution of topaz, with average values for temperature (36.3°C), sodium (53.2 mg L^{-1}) and lithium (0.19 mg L^{-1}), indicating a deep circulation path (up to 1,000 m). The baseline geochemistry for the intermediate flow system associated with the basin fill is very different: water interaction with basin fill sediments is restricted mainly to diagenesis of clay minerals and dissolution of carbonates (Cardona and Carrillo-Rivera 2006); a limited vertical circulation (up to 400 m) produces contrasting average values for temperature (25.1°C), sodium (14.6 mg L^{-1}) and lithium (0.01 mg L^{-1}) compared to the regional flow. Regarding the concentrations of minor and trace elements relevant to the environment and/or health, the combination of long residence time (estimated from 1,000 to 4,000 years, Cardona 2007) and temperature in the deepest portion of the regional flow circulation path (about 60–80°C, Carrillo-Rivera et al. 1996), results in high fluoride and arsenic concentrations (Table 1).

Most wells extracting groundwater with temperatures over 30°C are located in areas adjacent to normal faulting related to the graben structure (Carrillo-Rivera et al. 1996). Intensive groundwater extraction from the deep aquifer has produced a mixture of the regional and intermediate flow systems, whereby wells linked to faults and cracks identified in the volcanic rocks, extract mixed water with a higher percentage of water coming from the

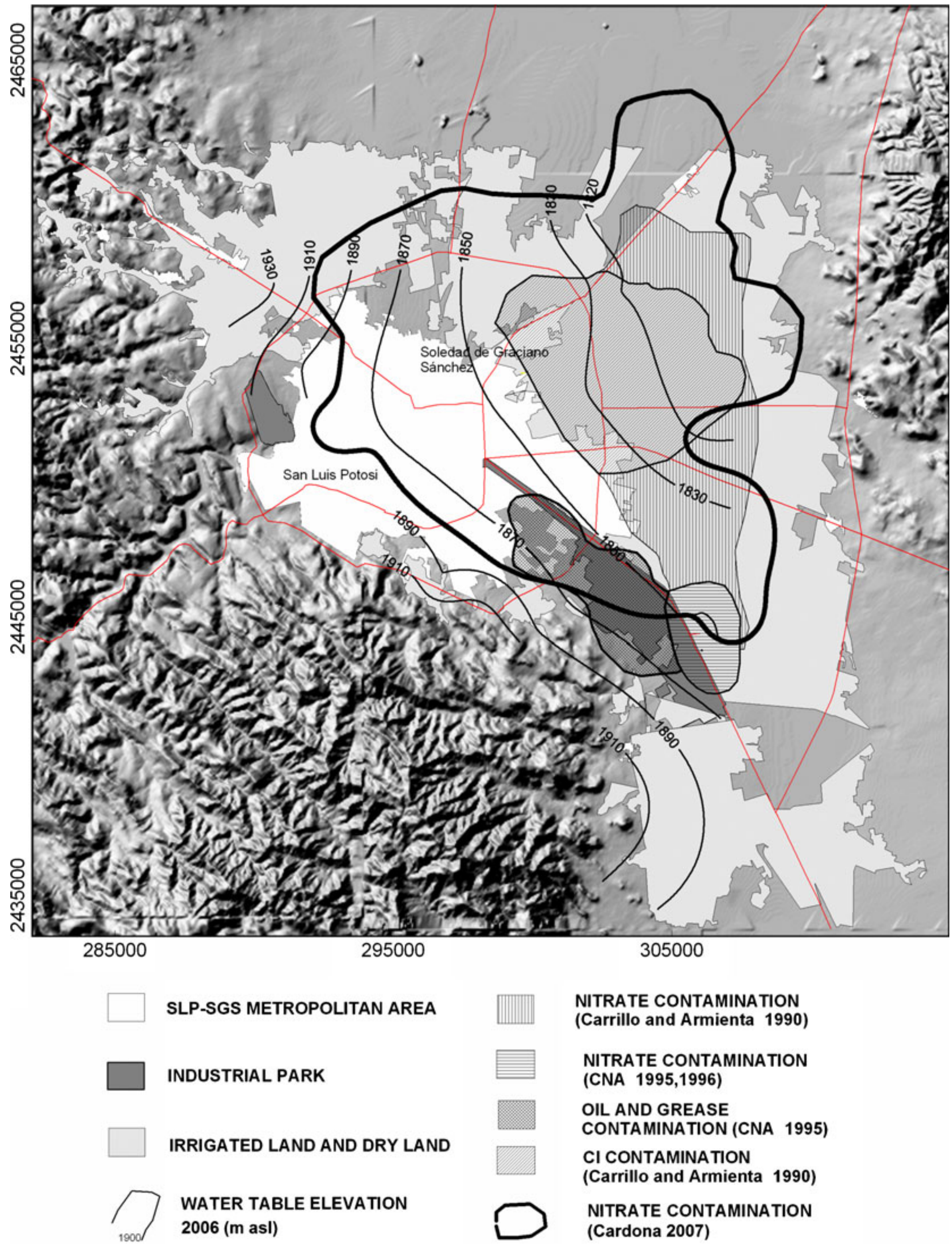

Fig. 7 Groundwater areas contaminated by wastewater irrigation, land use, and elevation of the groundwater table of the shallow unit of the San Luis Potosi aquifer (after Martínez Revilla et al. 2006; Cardona 2007)

regional flow. Currently, 60% of the total of wells destined for urban water supply extracts water from this regional flow system (Landín-Rodríguez 2006). The interception of fractured and faulted zones associated with the graben structure is a common practice to increase water production. Yields of up to

50–60 L s^{-1} are common for wells tapping fractured zones, in contrast with an average yield of 20–30 L s^{-1} for wells tapping basin fill sediments, and so intensive groundwater extraction is biased towards the regional flow. The total flow rate of fluoride and arsenic-rich groundwater for urban water supply is currently about 3.3 m^3 s^{-1} (Cardona 2007).

Two sets of observations have been adduced toward a strategy to reduce fluoride concentration, for wells tapping both the basin fill and fractured volcanic rocks. Firstly, groundwater temperature and fluoride concentration seem linearly related. Secondly, the change in mix proportions over pumping time is produced by the variable conservative mixing between end-members, in this case corresponding to regional and intermediate flow systems (Carrillo-Rivera et al. 2002). The strategy would be as follows: Maintaining the water temperature between 28°C and 30°C by means of operation time and/or changing flow rate during extraction would produce groundwater with a fluoride concentration of ≈1.5 mg L^{-1}. Solubility controls related to minerals such as fluorite and calcite may also be used to reduce fluoride concentrations, especially when it is feasible to use the well's construction, design, and operation to regulate groundwater flow conditions in the influence area of the cone of depression (Carrillo-Rivera et al. 2002).

Discussion

The noticeable hydrochemical changes associated with intensive groundwater extraction, generally include the presence of two types of inputs: (1) the induction of older groundwater with longer residence times and a distinctive chemical composition into the production zone; and (2) the incorporation of shallow and younger waters that may include anthropogenic components.

These inputs can come from several sources. For example, they can be located above the groundwater flow system (irrigation return flow, wastewater infiltration, industrial aerosol infiltration, etc.) or beneath (deep saline or trace element-rich thermal groundwater). This diversity in input location enhances water quality stratification. In specific hydrogeological settings, inputs such as contaminants from buried waste disposal sites can produce lateral changes in water quality.

Considering the information provided in the case studies, input from beneath is represented by the induction of high iron, manganese, fluoride, and arsenic concentrations from regional groundwater flow into partially penetrating production wells (i.e. deep unit of the San Luis Potosi aquifer, the Valle de Toluca aquifer). The natural geogenic environment of the regional system produces a wide range of concentrations derived from water-rock interaction, residence time, pH-Eh, and temperature conditions, promoting the mobility of minor or trace elements that have a significant impact on the environment and/or health. Residence time can also promote increased sodium concentration in groundwater flowing through felsic volcanic rocks. Exchange reactions with calcium and magnesium are restricted, and the absence of solubility controls allows for an increase in sodium along the flow path.

The conditions for intensive groundwater extraction are still at work: water demand from population centers is mounting, arguably requiring the number of wells tapping the upper portions of thick aquifer units to rise. New wells, drilled to replace those with a noticeable decline in yield and/or water level, are constructed deeper (more than 500 m deep) and with a larger diameter. The increase in screen length sometimes allows these wells to be more productive than older wells. These deeper wells, used for urban supply, can extract water of different ages and/or quality, disturbing the natural hydrogeological conditions and producing a mixture of at least two end members. Therefore, water quality in these wells depends not only on pumping time, but also on: (1) baseline chemistry of end members, (2) screen length and location with respect to production units, (3) flow rate and pumping conditions, (4) hydraulic properties, anisotropy, and thickness of productive lithological units, and (5) additional water–rock interaction during and after mixing.

The information reviewed here indicates that other hydrochemical changes can be produced by inputs from the upper portion of groundwater flow systems. These inputs are dependent on socioeconomic conditions and implemented wastewater management strategies. Shallow groundwater systems, particularly in semi-arid and arid regions with low natural recharge rates, are usually more vulnerable to point and diffuse contaminant sources than deep aquifers. Leaking sewage systems and irrigation return can produce increased concentrations of nitrate, chloride, and sulfate (Valle de

Toluca aquifer, shallow unit of San Luis Potosi aquifer), and higher occurrence of pathogenic microorganisms in groundwater. Under specific socioeconomic conditions, the infiltration of toxic trace elements (vanadium, arsenic) from industry emissions can also constitute a source of deterioration of natural baseline quality (Salamanca aquifer).

Conclusions

The data and analyses presented here helped establish the consequences of intensive groundwater extraction on groundwater quality in different aquifers in Mexico. The groundwater quality problems are diverse but they can be divided into three types:

1. Salinization processes caused by extensive and prolonged wastewater and groundwater irrigation (sodium, chloride, and sulfate).
2. Anthropogenic pollution caused by inadequate protection of vulnerable aquifers against discharges and/or leachates from urban and industrial activities and intensive agriculture (pathogens, nitrate, chloride, sulfate, heavy metals, and hydrocarbons).
3. Naturally occurring contamination related to the pH–Eh evolution of groundwater and dissolution of minerals from rocks. This problem can be aggravated by: intensive exploitation, induction of thermal or paleo-saline groundwater, and upconing from regional and intermediate groundwater flow systems.

The evidence provided suggests that chemical changes in intensively extracted groundwater can be associated to: (1) induction of regional flow systems with a natural baseline including elements at concentrations above drinking water standards, (2) alterations in the natural baseline of local flow systems via induction of irrigation and sewage pollutants, and (3) introduction of contaminants from the surface through faults created by subsidence.

If in the future, intensive exploitation in these aquifers were to continue, the water table would not be restored and groundwater quality would become inadequate for many uses. This excessive groundwater exploitation would irreversibly deteriorate the aquifers.

To improve groundwater management programs in these aquifers, it is fundamental to gain more knowledge on their performance. This has been acknowledged for all the studied aquifers, for which there are plans to conduct further in-depth research.

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