



Water quality indices for groundwater impacted by geogenic background and anthropogenic pollution: case study in Hidalgo, Mexico

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Abstract

The studies about the quality of groundwater resources are scarce in Mexico, and often they do not consider indicators of geogenic background and anthropogenic pollution. So, we examined the quality of groundwater from five wells of the Apan aquifer (Hidalgo, Mexico). Four of these wells were taken as reference samples, while the Santa Cruz well was considered as the study site because it is locally recognized as a problem due to the geogenic presence of manganese. In all the sites, variables related to mineralization processes were analyzed, and a quality index (MWQI, from *mineralization-based water quality index*) was calculated. In the study site samples, we also determined several indicators of geogenic background (arsenic, manganese, and other heavy metals) and anthropogenic pollution (as organic matter, nutrients, and several microbial indicators), from which another quality index (GAWQI, from *geogenic background and anthropogenic pollution-based water quality index*) was calculated. The MWQI values classified the groundwater from all the sites, even that from the Santa Cruz well, as “excellent for drinking.” When the GAWQI was computed for the Santa Cruz site, this groundwater was found “unsuitable for drinking” due to its extremely high manganese content. We conclude that the GAWQI could represent a valuable communication tool to inform the population and the authorities about the quality of the groundwater resources.

Keywords Aquifer · Water resources · Drinking water · Manganese · Water governance

Introduction

Since the beginning of the Industrial Revolution, and above all after the so-called Great Acceleration, the distribution and quality of freshwater have been changing due to human decisions that have even reshaped the global hydrological

cycle (Vörösmarty et al. 2013). Among the consequences of this mismanagement of the global commons, we have that groundwater systems, a crucial resource for both socio-economic development and healthy ecosystems, are experiencing a world crisis (Foster et al. 2013). This crisis is in the first place evidenced by the depletion of aquifers, which is in itself a major issue if it is considered that almost half of all drinking water worldwide comes from underground sources (Smith et al. 2016). However, for some authors, the largest threat to these resources is pollution, as global groundwater quality is declining due to the presence of chemicals of geogenic or anthropogenic origin (Custodio 2013; Dermatas 2017). In the first case, the geochemical composition of rock and soil explains the occurrence of metalloids (i.e., arsenic in Bangladesh and India), heavy metals (as hexavalent chrome in California, Italy, and Greece), or fluorides (in India, Ethiopia, and Sri Lanka) in groundwater (Singhal and Gupta 2010; Dermatas 2017). The people affected by geogenic groundwater background, only coming from arsenic and fluorides, have been estimated at 200 million (Amini

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2011). In the case of anthropogenic pollution, it concerns the human activities that contaminate groundwater reserves with heavy metals, persistent organic compounds, petroleum hydrocarbons, pesticides, nutrients, or microorganisms. The main anthropogenic sources are industrial activities, agricultural practices, mining, and waste disposal (Singhal and Gupta 2010; Dermatas 2017). Other related aspects of the global groundwater crisis include land subsidence, saline intrusion, loss of springs, and wetland deterioration (Famiglietti 2014).

In spite of its importance and the ongoing crisis, groundwater is a barely visible resource that is monitored and managed poorly, in particular in developing countries. Mexico relies heavily on groundwater, as it accounts for almost 60% of the water used for municipal supply (CNA 2016). Further, in nearly 50% of the country, where arid or semiarid climates prevail, groundwater is the only permanent source of water. More than a hundred of aquifers are overexploited, including those supplying the population of Mexico City and its conurbation (i.e., more than 21 million of inhabitants in 2016) (CNA 2016). The quality decline is another factor that jeopardizes the sustainability of this critical resource. The geogenic background of several Mexican aquifers (mainly by arsenic and fluoride) is a well-known problem that is favored by the complex geological context of the country, as well as by its active tectonic setting (Armienta and Segovia 2008). The saline intrusion and the unintentional infiltration of wastewater are among the most reported anthropogenic impacts on aquifers (Del Campo et al. 2014; CNA 2016). However, in general, the information about the quality of groundwater in Mexico is scarce and undermines its management and governance.

Consequently, it is necessary to carry out a wide range of studies to assess the quality of the groundwater resources of Mexico and to communicate the results in an easy way to policy-makers, managers, and water users. To this end, water quality indices constitute useful tools, which express the adequacy of water for an intended use in a single value that integrates different relevant variables. Several quality indices have been proposed for groundwater, most of which are based on the variables conventionally measured in aquifers to elucidate the geochemical type of groundwater (i.e., through Piper diagrams) (Vasanthavigar et al. 2010; Sethy et al. 2017). The purpose of this work was to propose an index considering the impact of both anthropogenic pollution and geogenic background and to use it to identify quality water issues of a specific well in the Santa Cruz locality, in the Apan aquifer (Hidalgo, Central Mexico). This well was selected as the study site because it is recognized by the local population as a problem due to the geogenic presence of manganese, and it has not been included in the scarce assessment studies done in the aquifer (Huizar-Álvarez et al. 1997; Huizar et al. 1998). The proposed index was compared

against another index based on the evaluation of variables related to mineralization processes that are measured commonly in geochemical studies of groundwater.

Materials and methods

Study area

The Apan aquifer is located in the southeastern part of Hidalgo State, between north latitudes 19°35' and 19°50' and west longitudes 98°11' and 98°40', with a total drainage area of 733.2 km². The evidence suggests that it is a heterogeneous, anisotropic, and semi-confined aquifer from porous to fractured (CNA 2015). The aquifer is mostly intergranular and its bedrock is volcanic (i.e., mainly constituted by basalts and andesites) (Huizar-Álvarez et al. 1997). The mean annual temperature varies between 10 and 16 °C, and the average annual rainfall is about 610 mm (CNA 2015).

Figure 1 shows the study site (the well situated in the locality of Santa Cruz) and the four wells known as Espejel, Acopinalco, Voladores, and Loma Bonita. These four wells supply water mostly for domestic use, and they were considered as reference points. The Santa Cruz well is locally recognized as a problem due to the presence of manganese, and therefore, the water supplied is almost not used by the inhabitants of the locality. The agriculture practiced around the study site is only of seasonal type; the agricultural use is not allowed for this well (CNA 2015).

Sampling and analytical procedures

Five-monthly samplings were carried out between October 2015 and February 2016 in the Santa Cruz well. The reference sites were sampled once during the same period. Samples were collected from the five wells into HNO₃-washed plastic containers. The samples intended for metal analyses were acidified with 10% HNO₃ to prevent the formation of oxides. For the microbiological analysis, the samples of the Santa Cruz well were collected in sterile Whirl-Pak[®] bags. All the samples were maintained in ice-packed boxes, while they were transported to the laboratory and kept at 4 °C until analysis. The microbiological analyses were carried out the same day of sampling.

pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured in situ in all samples by using a multiparametric equipment (Hanna Instruments model HI 9828). Reference samples (from Espejel, Acopinalco, Voladores, and Loma Bonita wells) were analyzed ex situ only concerning the contents of the mineralization-related variables, i.e., HCO₃⁻, Cl⁻, Na⁺, K⁺, Ca²⁺, and Mg²⁺. In the Santa Cruz samples, we determined ex situ, besides the variables mentioned above, the chemical oxygen demand

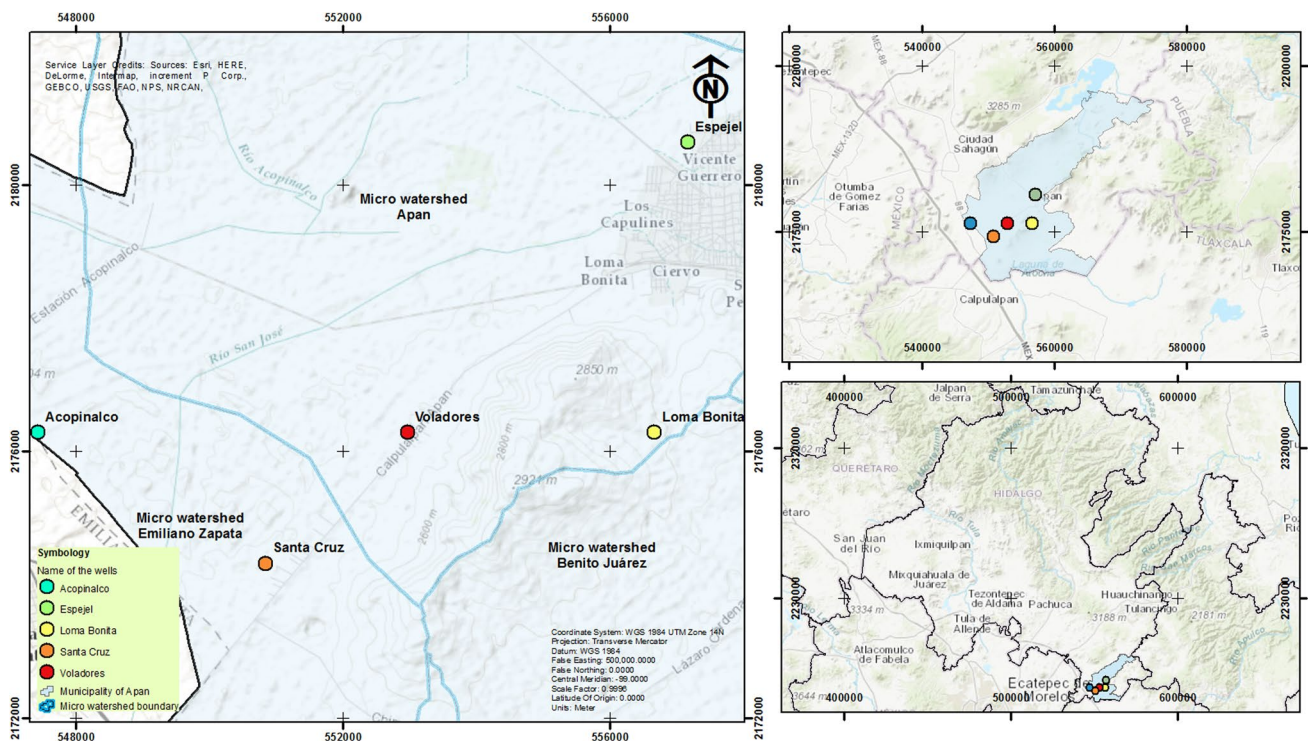


Fig. 1 Left: Location map showing the study site (Santa Cruz) and the reference sites (Espejel, Acopinalco, Voladores, and Loma Bonita) at the micro-watershed scale. Upright: Sampling points and some

near municipalities. Downright: Location of the sampling points at the scale of the Hidalgo State

(COD), and the contents of N-NH_4^+ , N-NO_2^- , N-NO_3^- , PO_4^{3-} , Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The densities of several microbial indicators—heterotrophic plate count (HPC), *Escherichia coli*, *Salmonella* sp., *Shigella* sp., *Enterobacter* sp., *Pseudomonas aeruginosa*, *Enterococcus faecalis*, *Staphylococcus* sp., *Clostridium perfringens*, and molds and yeasts (M&Y)—were also determined in the Santa Cruz samples. All the physicochemical parameters were measured in triplicate and according to the standard methods (APHA 2012), excepting the concentrations of N-NO_3^- , which were assessed by the technique of Mubarak et al. (1977). The concentrations of metals were measured by flame atomic absorption spectroscopy using a SpectrAA spectrophotometer (Varian 880, USA). For HCO_3^- and Cl^- , titrimetric methods were used, while for COD, N-NH_4^+ , N-NO_2^- , N-NO_3^- , and PO_4^{3-} , the methods were spectrophotometric.

For microbiological analyses, 100-mL aliquots of each sample were filtered through 0.45- μm nitrocellulose filters that were then cultured on non-specific solid media (Standard Plate Count Agar, Bioxon™) for the determination of the HPC or on specific solid media for the assessment of the other microbial indicators. *E. coli* was determined by culture on m-FC agar (Fluka Analytical™); *Salmonella* sp. and *Shigella* sp., on HiChrome™ ECC selective agar (Sigma-Aldrich); *Enterobacter* sp., on violet red bile agar with MUG

(BD); *P. aeruginosa*, on Pseudomonas agar (DIFCO™); *E. faecalis*, on m-Enterococcus agar (Difco™); *Staphylococcus* sp., on Staphylococcus medium 110 (BD); *C. perfringens*, on SPS medium (Merck); and finally, M&Y, on potato dextrose agar (Bioxon™). All the plates were made in triplicate and cultivated at 37 °C, excepting *E. coli* (45 °C) and M&Y (25 °C), and colonies counted after 48 h. The plates of *C. perfringens* were incubated in an anaerobic atmosphere with the BBL Gas Pack System™ (BD).

Statistical analyses

All statistical analyses were conducted using the SPSS version 21 statistical package (SPSS Inc., Chicago, USA). The results of the measurements of the mineralization-related variables were analyzed by descriptive statistics, and statistical differences were determined based on the Bonferroni correction test at the 0.025 significance level [for the samples of the study and the reference sites, and for the reference sites samples and the data reported by Huizar et al. (1998) for the same sites].

After a descriptive statistical analysis, the data collected for the study site (the Santa Cruz well) were also analyzed by multivariate techniques. Pearson correlations were calculated ($0.01 \leq p \leq 0.05$) to reveal the dependency between variables and to identify the minimal significance of the

variables, which were further used to assess the loadings of the components to be considered according to their statistical significance (Lucho-Constantino et al. 2005). Principal component analysis (PCA) and principal factorial analysis (PFA), followed by varimax rotation, were finally carried out according to the method reported by Lucho-Constantino et al. (2005).

Calculation of the water quality indices

The calculation of an index allows the reduction in different water quality data to a single number reflecting the suitability of the source for a particular use. Concerning groundwater, the common targeted use is for drinking purposes, and consequently, the water adequacy is established against several relevant quality indicators proposed in international or national drinking water guidelines. In this paper, we used a simple methodology commonly found in the bibliography to calculate weighted arithmetic groundwater quality indices (Vasanthavignar et al. 2010; Oişte 2014; Bodrud-Doza et al. 2016). Lower values of the indices indicate less deviation from the values recommended by the considered guideline and thus higher drinking water qualities.

The calculation of the water quality indices involved three steps (Sethy et al. 2017). In the first step, the variables to be taken into account were selected, and a weight (w_i) was assigned to each of them to reflect its relative importance in controlling the overall groundwater quality. Both the selection of variables and the assignment of their weights integrate expert knowledge and then are highly heuristic. Normally, practitioners choose freely the variables to be included accommodating site and treatment considerations, as well as published quality guidelines (Hurley et al. 2012). The highest weight of 5 was assigned to the variables having the major impacts on water quality; on the contrary, the minimum weight of 1 was assigned to the variables considered as having the least impacts on water quality. Intermediate weights (between 2 and 4) were allocated to the other variables depending on their perceived importance on the quality of water for human consumption.

In the second step, the relative weight (W_i) of each variable was calculated using Eq. (1):

$$W_i = \frac{w_i}{\sum_{i=0}^n w_i}, \quad (1)$$

where w_i is the assigned weight of each variable and n is the total number of considered variables.

In the third step, the quality rating of each variable (q_i) was calculated by dividing its value in water samples (V_i) by its respective standard value (S_i), according to Eq. (2):

$$q_i = \frac{V_i}{S_i} \cdot 100. \quad (2)$$

For calculating the overall water quality index, Eq. (3) was used:

$$\text{MWQI or GAWQI} = \sum_{i=0}^n W_i \cdot q_i. \quad (3)$$

Two water quality indices were calculated. One index is based only on mineralization-related variables (MWQI), and it was used to assess the quality of the reference and the study sites with a few of parameters conventionally measured in groundwater. The other index (GAWQI) was developed to include variables related to both geogenic background and anthropogenic pollution in the water quality assessment. We selected the variables and their weight after reviewing the water index bibliography and prioritizing the groundwater pollution issues of the state of Hidalgo (Gallegos et al. 1999; Armienta and Segovia 2008; Lesser-Carrillo et al. 2011). We also made sure that the Mexican guidelines for drinking water provided maximum permissible limits for the chosen variables (NOM 2000). The GAWQI was only calculated for the more comprehensive data obtained for the Santa Cruz study site. To facilitate the computation of the indices, when the variables were undetected in the samples, they were assumed to be equal to zero. Table 1 shows the assigned weights, the standard values, and the relative weights used to calculate MWQI and GAWQI. The computed values of MWQI and GAWQI were classified into five categories, as given in Table 2 (Vasanthavignar et al. 2010; Oişte 2014; Sethy et al. 2017). The concentration of *E. coli* gives no weight, as it implies to divide by zero. However, if this indicator was detected in one sample, the water was directly classified as “unsuitable for drinking” (Al-Omran et al. 2015).

Results and discussion

Water quality evaluation based on mineralization-related variables

General characteristics of groundwater from the reference and the study sites are summarized in Table 3 with mean, standard deviation (SD), and coefficient of variation (CV) values. For comparison purposes, the values of the Mexican drinking standard were also included. The CV values were lower than those reported in another studies (Jain et al. 2010; Del Campo et al. 2014), maybe because we analyzed a low number of samples ($n = 4$ for the reference sites and $n = 5$ for the study site).

The mean pH values of the reference and the study sites were 7.2 and 6.9, respectively, signaling neutral groundwater in both cases. Most of the groundwater has a pH ranging from 5.0 to 8.0 (IDNR 2002). The EC values were

Table 1 Variables, weight factors (w_i), relative weights (W_i), and standard values (S_i) considered for the calculation of the groundwater quality indices based on mineralization-related variables (MWQI) and on indicators of geogenic background and of anthropogenic pollution (GAWQI)

Variable	MWQI		GAWQI		S_i
	Weight (w_i)	Relative weight (W_i)	Weight (w_i)	Relative weight (W_i)	
pH	1	0.067	–	–	6.5–8.5
TDS (mg/L)	4	0.267	1	0.040	1000
Cl [–] (mg/L)	3	0.200	–	–	250
Na ⁺ (mg/L)	5	0.333	1	0.040	200
TH (mgCaCO ₃ /L) ^a	2	0.133	–	–	500
N–NH ₄ ⁺ (mg/L)	–	–	2	0.080	0.5
N–NO ₂ [–] (mg/L)	–	–	4	0.160	1
N–NO ₃ [–] (mg/L)	–	–	3	0.120	10
Fe (µg/L)	–	–	2	0.080	300
Mn (µg/L)	–	–	3	0.120	150
Pb (µg/L)	–	–	5	0.200	10
As (µg/L)	–	–	4	0.160	50
<i>E. coli</i> (CFU/mL) ^b	–	–	Water unsuitable		0
	Σ w_i =15	Σ W_i =1		Σ w_i =25	Σ W_i =1

^aTH total hardness, calculated from the addition of the concentrations of Ca²⁺ and Mg²⁺

^bTo avoid the division by zero, if *E. coli* is detected in one sample, it can be classified directly to be unsuitable for drinking

Table 2 Legend of the groundwater quality indices

MWQI or GAWQI	Type of water
< 50	Excellent water
50–100	Good water
101–200	Poor water
201–300	Very poor water
> 300	Unsuitable for drinking

MWQI quality index based on mineralization-related variables, GAWQI quality index considering geogenic background and anthropogenic pollution

comprised between 316 and 455 µS/cm for the reference sites and between 319 and 516 µS/cm for the study well, while the TDS values ranged from 158 to 226 mg/L and from 139 to 258 mg/L for the reference and the study sites, respectively. Values for both EC and TDS indicated low-mineralized groundwater in this area, probably due to a low residence time (IDNR 2002; Jain et al. 2010). Groundwater with a content of TDS lower than 1000 mg/L is assumed to be fresh and desirable for drinking water if it is lower than 500 ppm (Patra et al. 2016). The order of relative abundance of major cations, expressed as percentage of meq/L, was

Table 3 Mean, standard deviation (SD), and coefficient of variation (CV) of the mineralization-related variables measured at the reference and the study sites

Variable	Units	Reference sites (n=4)			Study site (n=5)			NOM ^a
		Mean	SD	CV	Mean	SD	CV	
pH	pH units	7.2	0.1	1.4	6.9	0.3	4.3	6.5–8.5
EC	µS/cm	388	57	14.7	454	71	15.6	–
TDS	mg/L	194	28	14.4	211	50	23.7	1000
HCO ₃ [–]	mg/L	193.7	27.9	14.4	154.3	26.5	17.2	–
Cl [–]	mg/L	8.0	3.9	48.8	2.6	1.0	38.5	250
Na ⁺	mg/L	29.6	11.0	37.2	20.0	10.5	52.5	200
K ⁺	mg/L	9.4	1.9	20.2	11.8	1.1	9.3	–
Ca ²⁺	mg/L	26.6	3.3	12.4	24.0	1.4	5.8	–
Mg ²⁺	mg/L	14.2	2.1	14.8	16.1	4.0	24.8	–

SD standard deviation, CV coefficient of variation

^aMexican drinking water standard (NOM 2000)

Ca^{2+} (33%) > Na^+ (32%) > Mg^{2+} (29%) > K^+ (6%) in the reference sites. In the Santa Cruz well, the relative abundance of the major cations (in meq/L) was Mg^{2+} (35.8%) > Ca^{2+} (32.5%) > Na^+ (23.5%) > K^+ (8.2%). The lack of data for other anions (particularly sulfates) rules out the full identification of the type of groundwater sampled; however, the predominance of HCO_3^- and Ca^{2+} in the reference sites suggested that the groundwater composition might be influenced by carbonate mineral dissolution (Bodrud-Doza et al. 2016). In a previous study covering the Apan–Tochac sub-basin, the $\text{Ca} + \text{Mg} + \text{HCO}_3^-$ hydrochemical facies was found to be dominant (Huizar et al. 1998). The authors of this study concluded that such chemical composition was in good agreement with a volcanic environment where calcium and magnesium were derived from plagioclase and ferromagnesian minerals, respectively.

According to the mineralization-related variables presented above, the groundwater from both the reference and the study sites complies with the Mexican water quality standards. We also evaluated the adequacy of the groundwater for irrigation purposes; for this, it is common to use the sodium adsorption ratio (SAR) and EC values. SAR is commonly calculated using Eq. (4), provided by the U. S. Department of Agriculture (Regional Salinity Laboratory 1954):

$$\text{SAR} = \frac{[\text{Na}^+]}{\sqrt{\frac{[\text{Ca}^{2+}] + [\text{Mg}^{2+}]}{2}}}. \quad (4)$$

High SAR values (> 18 meq/L) indicate a sodium hazard, because the irrigation with saline water (with high Na^+ and low Ca^{2+} contents) favors the saturation of Na^+ and the increase in the exchangeability of this cation, thereby leading to the destruction of soil structure and a diminution of its permeability (Vasanthavigar et al. 2010). The mean calculated SAR values were 1.15 and 0.77 meq/L for the reference and the study sites, respectively. Consequently, in both cases, the low Na content of the groundwater allows its use for irrigation on almost all soils without this involving the development of harmful levels of exchangeable Na (Regional Salinity Laboratory 1954). If the mean CE values are also considered (388 and 454 $\mu\text{S}/\text{cm}$ for the reference and the study sites, respectively), the irrigation with these groundwaters represents a medium salinity hazard, as in most cases plants with moderate salt tolerance could be grown (Regional Salinity Laboratory 1954).

Statistical analysis of the mineralization-related variables

Paired difference tests were performed between the data measured in the reference and the study sites (presented in

Table 3), but also between each of them against the characteristics reported for the reference sites in a previous study (Huizar et al. 1998). On the one hand, this analysis revealed significant differences ($p \leq 0.025$) between the reference sites and the study sites concerning the mean values of pH, EC, HCO_3^- , and Cl^- . In spite of the correlation existing between EC and TDS values, no significant differences were found in the TDS measured in the reference and the study sites, nor in the contents of the major cations. On the other hand, when the characteristics measured at the reference sites were compared against those measured at the same sites but more than 19 years ago, significant differences were found only for one parameter after Bonferroni correction. In this way, the mean value of Cl^- (33.5 ± 2.7 mg/L) was significantly higher in the above-mentioned previous study (Huizar et al. 1998) than in our samples (8.0 ± 3.9 mg/L).

Assessment of the mineralization-based water quality index (MWQI)

The quality index based on mineralization variables (MWQI) was calculated from the values presented in Table 3. For the study site, we used the mean values of these parameters and then we could only obtain one value for the MWQI (i.e., 17.9), while for the reference sites we calculated the index for each site (i.e., Espejel, Acopinalco, Voladores, and Loma Bonita) separately. The MWQI ranged between 15.4 and 23.0 for the reference sites. The results are presented in Fig. 2. We used the values of the quality parameters reported in Huizar et al. (1998) to compute the MWQI of the groundwater from these reference wells (which were comprised between 24.8 and 29.7), and the resulting values are presented in Fig. 2 too. All the calculated MWQI values allow

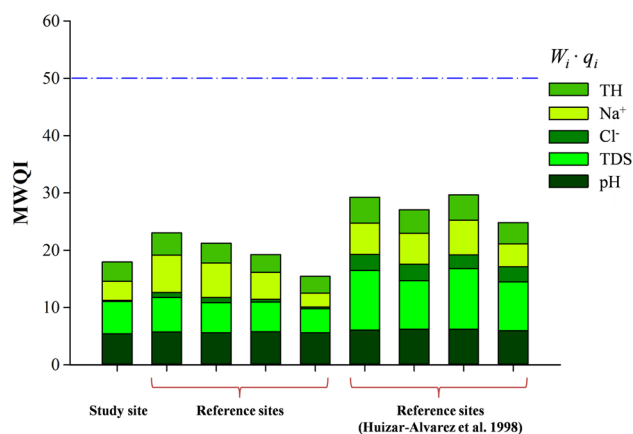


Fig. 2 Values of MWQI calculated for the mean quality values measured at the study and the reference sites. The values measured in the reference sites by Huizar et al. (1998) are also shown, as well as the upper limit value of the “excellent water” category (discontinuous line)



these groundwaters to be classified as excellent for drinking, according to Table 2.

It should be noted that the groundwater from the reference sites presented higher MWQI values in 1998, due mainly to its higher mineralization compared with the same sites nowadays. In Fig. 2, the contribution of each parameter ($W_i \cdot q_i$) to the final MWQI value is also presented. Evidently, the biggest contributions come from the most weighted parameters (i.e., from the parameters rated with the highest w_i values, as Na^+ and TDS). However, for the reference samples analyzed in 1998, the influence of the chloride concentrations (weighted with a mean value, $w_i=3$) in the final value of the MWQI is noteworthy. In fact, the mean Cl^- content reported for the reference sites in 1998 (33.5 ± 1.3 mg/L) is more than ten times higher than the Cl^- concentration that we measured in the Santa Cruz samples recently (2.6 ± 1.0 mg/L).

Water quality evaluation including indicators of geogenic background and anthropogenic pollution

The groundwater from the study site (the Santa Cruz well) was analyzed in a more comprehensive way than the reference sites, and several indicators of geogenic background and anthropogenic pollution were also determined for this particular well (Table 4). Higher CV values were obtained for these parameters (ranging from 4.2 to 200%) than for the mineralization-related variables presented above (that fluctuated between 1.4 and 52.5%; Table 3).

Concerning the geogenic indicators, their relative abundance was $\text{Mn} > \text{Fe} > \text{Al} > \text{Ni} > \text{Cr} > \text{Pb} > \text{Cd} > \text{Cu}$. Neither As nor Zn was detected in any sample, despite the fact that arsenic is a frequently reported contaminant of groundwater from several zones of Mexico, such as the region known as “Comarca Lagunera,” the Río Verde basin, the Salamanca aquifer, and Zimapán, also in Hidalgo State, among others (Armienta and Segovia 2008).

As expected, the groundwater of the Santa Cruz site presented high contents of Mn (ranging from 3718 to

Table 4 Mean, standard deviation (SD), and coefficient of variation (CV) of the indicators of geogenic background and anthropogenic pollution measured at the study site

	Variable	Units	Mean	SD	CV	NOM ^a
Geogenic indicators	Al	µg/L	253	34	13.4	200
	As	µg/L	0	0	NC	50
	Cd	µg/L	12.5	1	5.7	5
	Cr	µg/L	31	7	22.8	50
	Cu	µg/L	11	8	77.1	2000
	Fe	µg/L	395	213	53.8	300
	Mn	µg/L	5145	730	14.2	150
	Ni	µg/L	50.5	2	4.2	–
	Pb	µg/L	28	26	92.7	10
	Zn	µg/L	0	0	NC	5000
	Anthropogenic indicators	COD	mg O ₂ /L	35.2	14.2	40.3
N-NH ₄ ⁺		mg/L	0.13	0.16	122.5	0.5
N-NO ₂ ⁻		mg/L	0.02	0.03	149.1	1
N-NO ₃ ⁻		mg/L	0.48	0.93	191.9	10
PO ₄ ³⁻		mg/L	1.52	0.78	51.3	–
HPC		CFU/100 mL	178	310	174.6	–
<i>E. coli</i>		CFU/100 mL	2.5	4.4	174.4	0
<i>Salmonella</i> sp.		CFU/100 mL	0.25	0.5	200	–
<i>Shigella</i> sp.		CFU/100 mL	0.5	1	200	–
<i>Enterobacter</i> sp.		CFU/100 mL	0	0	NC	0
<i>P. aeruginosa</i>		CFU/100 mL	174	155	89.3	–
<i>E. faecalis</i>		CFU/100 mL	0	0	NC	0
<i>Staphylococcus</i> sp.		CFU/100 mL	23	24.3	105.7	–
<i>C. perfringens</i>		CFU/100 mL	120	167	139.1	–
M&Y		CFU/100 mL	79	70.7	90	–

NC non-calculated to avoid a division by zero, HPC heterotrophic plate count, M&Y molds and yeasts

^aMexican drinking water standard (NOM 2000)

5759 $\mu\text{g/L}$), which were significantly different from the Mn concentrations found in the reference sites ($p < 0.05$, comprised between 10 and 43 $\mu\text{g/L}$) and quite higher than the permissible limit of 150 $\mu\text{g/L}$ established by the Mexican guidelines (NOM 2000). High Mn concentrations restrain the water uses, because they lead to organoleptic problems, staining of surfaces and reduced water pressure and flow in distribution pipelines derived from the accumulation of Mn oxides (Homoncik et al. 2010). Besides, recent epidemiological studies report the association between Mn exposure from drinking water supplies with cognition and behavioral deficits in children and adults (Frisbie et al. 2012; Oulhote et al. 2014).

To the best of our knowledge, the Mn concentration measured at the Santa Cruz site is the highest value reported for groundwater from Mexican sources. Lower Mn contents were reported for the Apan–Tochac sub-basin (0–188 $\mu\text{g/L}$; Huizar et al. 1998) and for other near aquifers of Hidalgo State, as the Tecocomulco sub-basin (0.1–133 $\mu\text{g/L}$; Huizar-Álvarez et al. 2001), the Río de las Avenidas sub-basin (1–1068 $\mu\text{g/L}$; Huizar-Álvarez 1997), and the Mezquital Valley (0.3–150 $\mu\text{g/L}$; Lesser-Carrillo et al. 2011). For groundwater from the Mexico basin, the measured Mn concentrations ranged between 3 and 960 $\mu\text{g/L}$ (Domínguez-Mariani et al. 2015). In this same basin, the groundwater from individual wells of the Peñón-Textcoco site has peaked at 4610 $\mu\text{g/L}$, but the overall mixture of the water from 15 wells yields a mean concentration of 1520 $\mu\text{g/L}$ (Piña and Ramírez 2003). The values reported for groundwater from other Mexican sources are also lower than those obtained in our study, such as wells supplying the cities of Guaymas, Son. (100–1500 $\mu\text{g/L}$), Navojoa, Son. (1300 $\mu\text{g/L}$), and Veracruz, Ver. (390–540 $\mu\text{g/L}$) (Piña and Ramírez 2003).

The presence of Mn in groundwater is controlled by such factors as rock geochemistry, water composition, and microbial activity. The weathering of Mn-bearing rocks (i.e., shale, graywacke, limestone, or ultramafic rocks) can result in elevated concentrations of this metal in soils and sediments. In the aquifer, groundwater dissolves these materials, which release Mn to the water. The groundwater characteristics, such as pH, redox potential, dissolved oxygen, and dissolved organic matter, control the resulting concentration and speciation of Mn. The most likely species is Mn^{2+} at $\text{pH} < 7$ and at a redox potential as high as 800 mV (Homoncik et al. 2010), as it occurs in the Santa Cruz site, where redox potentials of around -4 and 133 mV were measured (data not shown). Finally, the microbial activity has a significant role enhancing the Mn oxidation as well as its reduction.

As all the mechanisms mentioned above act similarly on Mn and Fe, these metals are often found concurrently in groundwater, with Fe being present at higher levels than Mn (Homoncik et al. 2010). However, this was not the case

for the Santa Cruz site. The mean concentration of Fe found in the Santa Cruz groundwater (395 ± 213 $\mu\text{g/L}$) was not significantly different from the average content of this metal measured in the reference sites (318 ± 126 $\mu\text{g/L}$; $p < 0.05$; data not shown). However, the content of this metal in the Santa Cruz well exceeded the Mexican guideline value (300 $\mu\text{g/L}$) in 83% of the samples. The mean contents of Al (253 ± 34 $\mu\text{g/L}$), Cd (12.5 ± 1 $\mu\text{g/L}$), and Pb (28 ± 26 $\mu\text{g/L}$) also surpassed the permissible limits of the Mexican guidelines (200, 5, and 10 $\mu\text{g/L}$, respectively). In the cases of the concentrations of Al and Cd, the permissible limits were surpassed in 100% of the samples, while for the content of Pb, it exceeded the limit in 60% of the samples. The concentrations measured for Cu (ranging from 5 to 17 $\mu\text{g/L}$) and Cr (varying from 26 and 36 $\mu\text{g/L}$) did not exceed the guideline values (of 2000 and 50 $\mu\text{g/L}$, respectively).

Concerning the eventual anthropogenic pollution of the study site, we assessed the contents of organic matter, nutrients, and the densities of several microbial indicators in the groundwater. The results are summarized in Table 4. Although COD is rarely determined in groundwater, it is used as an indicator of aquifer pollution by wastewater. The mean concentration of COD measured in our samples was 35.2 ± 14.2 mgO_2/L , which is quite similar to the value determined (31.3 ± 18.7 mgO_2/L) for an aquifer affected by excessive withdrawal and maybe by sewage intrusion (Domínguez-Mariani et al. 2015). Ammonium is another indicator of sewage pollution, even though it is also associated with the intrusion of leachates from landfill sites or agricultural activities into aquifers (Böhlke et al. 2006). For these cases, concentrations of N-NH_4^+ of the order of 10–100 mg/L have been reported (Böhlke et al. 2006), which are quite higher than the contents determined in our samples (0.13 ± 0.16 mg/L). Our values were always lower than the Mexican permissible limit (0.5 $\text{mg N-NH}_4^+/\text{L}$).

By far, nitrate is the most ubiquitous anthropogenic pollutant in groundwater (Spalding and Exner 1993; Montiel-Palma et al. 2014). Its primary source is the excessive use of nitrogenous fertilizers in agricultural zones, followed by farming activities and sewage intrusions. Nitrate is linked to harmful health effects, mainly in children, and consequently, its presence in drinking water is a matter of public concern (Spalding and Exner 1993). Unexpectedly, taking into consideration that the study site is entirely dedicated to agricultural activities, the measured concentrations of this pollutant in our samples were not significant (0.48 ± 0.93 $\text{mg N-NO}_3^-/\text{L}$) and always lower than the Mexican guideline value (10 $\text{mg N-NO}_3^-/\text{L}$). Our results contrast with several studies made in Mexican agricultural zones, where nitrate is present at unsafe concentrations. For instance, in wells of the Comarca Lagunera region and of the Mezquital Valley (Hidalgo State), mean concentrations of 23.4 $\text{mg N-NO}_3^-/\text{L}$ (Medina and Cano 2001) and

13.46 ± 4.25 mg N-NO₃⁻/L (Gallegos et al. 1999) have been measured, respectively. In the case of the Mezquital Valley study, the difference in the contents of nitrates can be attributed to the irrigation with raw wastewater made in the zone, while at the Santa Cruz site the agriculture is of rain-fed type. Likewise, the nitrite concentrations determined in our samples (0.02 ± 0.03 mg N-NO₂⁻/L) were always lower than the Mexican guideline value (1 mg N-NO₂⁻/L). The measured content of orthophosphates in the Santa Cruz well ranged between 0.93 and 2.74 mg/L. These contents can be considered as high, because they are in the same order of magnitude as the concentrations assessed in the groundwater from the Mezquital Valley (< 0.01–3.08 mg/L; Gallegos et al. 1999). Phosphates are not considered by the Mexican drinking water guidelines (NOM 2000).

Groundwater is a recognized source of potentially hazardous pathogens. The primary cause of the microbial groundwater pollution is the intrusion of sewage, municipal wastes, leachates from farming sites, and even surface water, into aquifers (Murphy et al. 2017). Usually, the degree of microbial pollution is assessed by the concentration of fecal coliforms, which is the main indicator of the microbial quality of drinking water. However, in a recent review, a total of 17 pathogens belonging to several groups and families were found responsible for the latest groundwater-related outbreaks. Among these pathogens, *E. coli* was the seventh most common outbreak cause, and coming after norovirus, *Campylobacter*, *Shigella*, the Hepatitis A virus, *Giardia*, and *Salmonella* (Murphy et al. 2017).

The densities of the microbial indicators analyzed are presented in Table 4. The most abundant indicator was the heterotrophic bacteria group (HPC), followed by *P. aeruginosa*, *C. perfringens*, and M&Y. These indicators were found with the highest frequency too (in 100% of the samples). *Staphylococcus* sp. (detected in 75% of the samples), *E. coli* (50%), *Salmonella* sp. (20%), and *Shigella* sp. (20%) were also found but in lower quantities (they are listed in descending order of abundance). Neither *Enterobacter* sp. nor *E. faecalis* was detected in any sample. Consequently, the Santa Cruz groundwater did not comply with the Mexican regulations for drinking water, which establish that *E. coli*, as well as fecal coliforms and thermotolerant microorganisms (term including *Enterobacter* sp. and *Enterococcus* sp.), must be absent in drinking water samples (NOM 2000). The mean concentration of *E. coli* found in our samples (2.5 ± 4.4 CFU/100 mL) is of the same order of magnitude as the majority of the values reported for wells of the Mezquital Valley (< 3 CFU/100 mL). However, very high concentrations of this indicator ($> 2.4 \cdot 10^3$ CFU/100 mL) were measured in some of these wells (Gallegos et al. 1999). For groundwater from the Mexico basin, mean concentrations of *E. coli* of 0.27 ± 0.97 CFU/100 mL have been reported (Mazari-Hiriart et al. 2005). These authors state that *E. coli*,

Enterococcus sp., and *P. aeruginosa* were the most prevalent microorganisms throughout a year. In our samples, the most ubiquitous and most abundant microbial indicator was *P. aeruginosa*.

Multivariate statistical analysis of the geogenic and anthropogenic pollution indicators

The correlation matrix indicates how well the variance of each variable can be explained by relationships with each other of the remaining variables (Bodrud-Doza et al. 2016). The Pearson correlation coefficients of the water quality variables measured in the Santa Cruz site are presented in Table 5. Strong ($p < 0.01$) and significant ($p < 0.05$) correlations were found, which reveal the influence of several processes on the groundwater composition.

On the one hand, the geochemistry showed an impact on the indicators of both the mineralization and the geogenic pollution of water. Accordingly, a strong and positive correlation ($r = 0.966$) was found between the Mn content and the EC. As signaled before, the most likely manganous species at the Santa Cruz site is Mn²⁺, which certainly contributes to the water conductivity. The pH presented a significant and positive correlation with Cl⁻ ($r = 0.851$), while it showed a significant but negative correlation with K⁺ ($r = -0.881$). Bodrud-Doza et al. (2016) also found a negative correlation between pH and K⁺, which was attributed to geogenic processes in rocks altered by the acidification of the groundwater.

On the other hand, certain correlations highlight the anthropic entries of pollutants, mainly concerning nutrients. N-NO₂⁻ was found to be strong and positively correlated with PO₄³⁻ ($r = 0.996$), as well as N-NO₃⁻ with Cr ($r = 0.994$) and Ni ($r = 0.994$). This correlation suggests a common origin of these macro- and micronutrients, maybe the application of fertilizers. Significant and positive correlations were also detected between N-NH₄⁺ and Cr ($r = 0.902$), Ni ($r = 0.902$), and N-NO₃⁻ ($r = 0.894$). Although the microbial indicators are often correlated positively with nutrients, in our study, we only found significant and positive correlations of HPC with N-NO₂⁻ ($r = 0.815$) and with PO₄³⁻ ($r = 0.812$).

Both PCA and PFA are multivariate techniques used to derive a small number of relevant factors from a broad data set. Hereafter, we only present the results of the PFA, because this analysis confirmed the relationships between the study variables found preliminarily by the PCA. Table 6 shows the orthogonally rotated matrix with the loadings of 18 quality variables measured in the groundwater of the Santa Cruz site. Two factors were extracted (F1 and F2) (Fig. 3), which together explained 100% of the total variance in the original dataset. Each factor loading designates the correlation between the variable and the new factor.



Table 5 Pearson correlation matrix for 18 variables measured at the study site

	K ⁺	Cl ⁻	N-NH ₄ ⁺	N-NO ₂ ⁻	PO ₄ ³⁻	HPC	Cu	Cr	Cd
K ⁺	1								
Cl ⁻	-0.582	1							
N-NH ₄ ⁺	-0.170	0.138	1						
N-NO ₂ ⁻	0.232	-0.433	-0.272	1					
PO ₄ ³⁻	0.190	-0.445	-0.286	0.996**	1				
HPC	-0.030	-0.492	0.047	0.815*	0.812*	1			
Cu	0.226	0.000	-0.902*	0.000	-0.014	-0.218	1		
Cr	-0.226	0.000	0.902*	0.000	0.014	0.218	-1.000**	1	
Cd	0.226	0.000	-0.902*	0.000	-0.014	-0.218	1.000**	-1.000**	1
Ni	-0.226	0.000	0.902*	0.000	0.014	0.218	-1.000**	1.000**	-1.00**
Fe	-0.251	0.577	0.671	-0.855	-0.868	-0.720	-0.419	0.419	-0.419
Mn	0.678	-0.691	0.206	-0.247	-0.250	-0.169	-0.127	0.127	-0.127
N-NO ₃ ⁻	-0.288	-0.002	0.894*	-0.055	-0.035	0.195	-0.994**	0.994**	-0.994**
COD	-0.033	0.001	0.241	0.246	0.290	-0.039	-0.574	0.574	-0.574
M&Y	0.499	0.799	-0.746	-0.628	-0.695	-0.688	0.863	-0.863	0.863
pH	-0.881*	0.851*	0.230	-0.446	-0.417	-0.358	-0.229	0.229	-0.229
EC	0.522	-0.746	0.155	-0.243	-0.226	-0.110	-0.139	0.139	-0.139
<i>P. aeruginosa</i>	-0.212	0.309	-0.928	-0.678	-0.708	-0.340	0.884	-0.884	0.884
	Ni	Fe	Mn	N-NO ₃ ⁻	COD	Y&M	pH	EC	<i>P. aeruginosa</i>
K ⁺									
Cl ⁻									
N-NH ₄ ⁺									
N-NO ₂ ⁻									
PO ₄ ³⁻									
HPC									
Cu									
Cr									
Cd									
Ni	1								
Fe	0.419	1							
Mn	0.127	0.146	1						
N-NO ₃ ⁻	0.994**	0.432	0.135	1					
COD	0.574	0.071	-0.021	0.557	1				
M&Y	-0.863	0.671	0.665	-0.885	-0.550	1			
pH	0.229	0.531	-0.662	0.270	0.186	-0.023	1		
EC	0.139	0.062	0.966**	0.169	0.010	-0.162	-0.587	1	
<i>P. aeruginosa</i>	-0.884	0.765	0.565	-0.791	-0.886	0.635	0.136	0.374	1

HPC heterotrophic plate count; M&Y molds and yeasts

*Correlation is significant at the 0.05 level (two-tailed)

**Correlation is significant at the 0.01 level (two-tailed)

In Table 6, the loading factors higher than 0.812 are highlighted in bold characters. This threshold value corresponded to the minimum Pearson correlation value calculated with $p < 0.05$ (Table 5) and allowed the strong correlations between the original variables and the new factors (F1 or F2) to be identified. F1 explained 65.72% of the total variance of the original data. F1 was positively loaded by organic

matter (COD), macronutrients (N-NH₄⁺ and N-NO₃⁻), and some micronutrients (Cr and Ni). At the same time, F1 was negatively contributed to by metals (Cu, Cd, and K⁺), as well as the contents of *P. aeruginosa* and M&Y (Fig. 3). In this way, F1 seems to be related to the anthropogenic pollution and geogenic background of the Santa Cruz site, probably due to the convergence of several sources, i.e., the intrusion

Table 6 Loadings of 18 variables measured at the study site on two significant principal factors (F1 and F2)

	F1	F2
K ⁺	-0.861	-0.509
Cl ⁻	-0.496	0.868
N-NH ₄ ⁺	0.983	-0.181
N-NO ₂ ⁻	0.277	-0.961
PO ₄ ³⁻	0.362	-0.932
HPC	0.293	-0.956
Cu	-0.971	0.241
Cr	0.971	-0.241
Cd	-0.971	0.241
Ni	0.971	-0.241
Mn	-0.277	0.961
N-NO ₃ ⁻	0.992	-0.126
Fe	-0.277	0.961
COD	0.998	0.058
<i>P. aeruginosa</i>	-0.831	0.557
pH	0.451	0.892
EC	0.527	0.850
M&Y	-0.898	0.439

HPC heterotrophic plate count, M&Y molds and yeasts

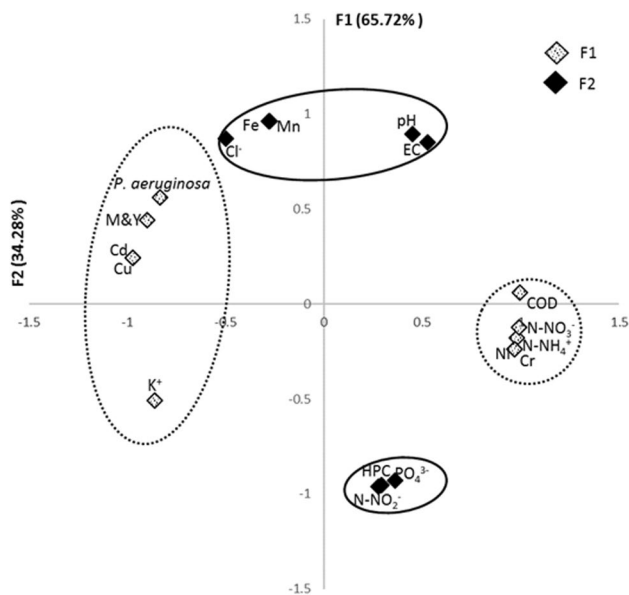


Fig. 3 Loading plot of 18 variables measured at the study site on two significant factors, F1 (in discontinuous lines) and F2 (in continuous lines)

of wastewater or the infiltration of agricultural wastes or inputs (such as fertilizers). F2 accounted for 34.28% of the total variance in the dataset and showed a positive correlation between the pH, the EC and the contents of Mn, Fe, and Cl⁻. F2 might be thus associated with mineralization

and geogenic processes modifying the composition of the groundwater. It is worth to note that F2 revealed a strong correlation of both Mn and Fe, as it is often signaled in the bibliography (Homoncik et al. 2010). F2 also consisted of a negative loading of nutrients (N-NO₃⁻ and PO₄³⁻) and HPC (Fig. 3).

Assessment of the groundwater quality index including geogenic and anthropogenic pollution indicators (GAWQI)

We proposed an index that considers mineralization processes, as well as geogenic background and anthropogenic pollution, in the groundwater quality for drinking purposes. The GAWQI values calculated for the individual samples taken from the study site are presented in Fig. 4, as well as the contribution of each indicator considered. The breakdown of the GAWQI calculated for the samples 3 and 4 is also presented even though both samples were classed as unsuitable for drinking only due to the detection of *E. coli*.

The GAWQI values ranged from 451.1 to 560.3, which indicate that the groundwater from the Santa Cruz site is unsuitable for drinking (Table 2). The contributions of some of the indicators (i.e., Na⁺ and the nitrogenous pollutants) to the total GAWQI value are not discernible in Fig. 4 because they are too small. In the case of As, a metalloid undetected in our samples, its contribution is null. However, due to its historical importance in the groundwater resources in Mexico and to its high toxicity, we think that it is important to include As in the GAWQI calculation for further uses of the index. Figure 4 shows that the poor quality of the groundwater is due, by far, to its excessive Mn concentration (more than 35-fold higher than the maximum permissible value established by the Mexican guideline). In some samples, the second largest contribution to the GAWQI value comes

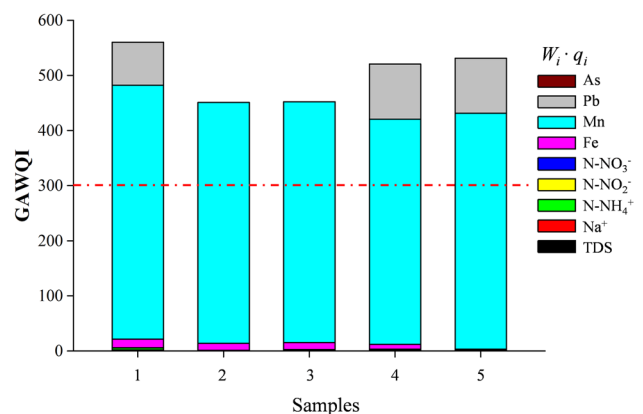


Fig. 4 Values of GAWQI calculated for the study site. The discontinuous line indicates the upper limit of GAWQI values for drinking water

from Pb, because it was the most weighted parameter for the GAWQI calculation due to its high toxicity. Finally, Fe represents the third contribution to the GAWQI value, even though this is not considered a toxic metal as Pb but rather a micronutrient. Altogether with Mn, Fe oxidizes when the groundwater enters in contact with atmospheric air, and the resulting deposits are considered a nuisance in water supply systems (Piña and Ramírez 2003).

As the GAWQI values indicate, the groundwater quality of the Santa Cruz site is unsuitable for drinking due to combined geogenic and anthropogenic sources. Therefore, the monitoring of a range of parameters wider than the usual is necessary for a proper assessment of the groundwater quality. Such assessment can provide options for water treatment systems able to deliver safe water to the inhabitants of the study zone and to enhance the governance of their water resources.

Conclusion

We analyzed the quality of groundwater of the Apan region (Hidalgo State, Mexico), coming from one well in the study site (Santa Cruz) and four reference wells. When only conventional variables related to mineralization processes were assessed (i.e., pH, TDS, Na⁺, Ca²⁺, Mg²⁺, and Cl⁻), as is often done in groundwater studies, all the samples complied with the Mexican standard for drinking water. Besides, the SAR values calculated for all the samples indicated that the use of these groundwaters for irrigation is allowed. The values of the index calculated from these mineralization-related variables (MWQI) showed that the groundwater qualities of these wells were well suited for drinking; actually, they were classified as “excellent.”

The groundwater from the Santa Cruz site was further analyzed regarding several indicators of geogenic background and anthropogenic pollution. We confirmed that the groundwater of the study site presents a significant problem due to the concentration of Mn, which is probably the highest reported value for Mexican groundwater sources. The groundwater of the study comply with the Mexican guidelines established for nitrogenous pollutants, arsenic, and some heavy metals (such as Cu, Cr, and Zn), but all the samples exceeded the limits concerning Al, Cd, and obviously Mn. Due to seasonal differences in the groundwater quality, some of the samples also exceeded the permissible limits of Pb and *E. coli*. According to the GAWQI values, the groundwater of the study site was found largely unsuitable for drinking. This should be a major concern for the

local water managers and users, leading to the search for adequate treatment options.

Our results support the need for the continuous monitoring of the groundwater quality, and the usefulness of a comprehensive water quality index. The main advantage of the proposed index is that it embraces a range of indicators of mineralization and anthropogenic pollution, as well as of a geogenic background common in Mexican aquifers. Although undoubtedly the index proposed herein is perfectible, it is our view that it could represent a valuable communication tool to inform the population and the authorities about the quality of the local water bodies. This accessible information is necessary for the scientifically sound management of groundwater resources, which is a crucial aspect of the development of a semiarid country as Mexico.

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References

- Al-Omran A, Al-Barakah F, Altuquq A, Aly A, Nadeem M (2015) Drinking water quality assessment and water quality index of Riyadh, Saudi Arabia. *Water Qual Res J* 50(3):287–296
- Amini M (2011) Putting geogenic contamination on the map. *Eawag News* 71:6–9
- APHA (2012) Standard methods for the examination of water and wastewater, 22nd edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington
- Armienta MA, Segovia N (2008) Arsenic and fluoride in the groundwater of Mexico. *Environ Geochem Health* 30(4):345–353
- Bodrud-Doza M, Islam AT, Ahmed F, Das S, Saha N, Rahman MS (2016) Characterization of groundwater quality using water evaluation indices, multivariate statistics and geostatistics in central Bangladesh. *Water Sci* 30(1):19–40
- Böhlke JK, Smith RL, Miller DN (2006) Ammonium transport and reaction in contaminated groundwater: application of isotope tracers and isotope fractionation studies. *Water Resour Res* 42(5):W05411
- CNA (2015) Actualización de la disponibilidad media anual de agua en el acuífero Apan (1320), Estado de Hidalgo (in Spanish). Comisión Nacional del Agua, Mexico. https://www.gob.mx/cms/uploads/attachment/file/103069/DR_1320.pdf. Accessed 6 July 2017
- CNA (2016) Estadísticas del Agua en México (in Spanish). Comisión Nacional del Agua, Mexico



- Custodio E (2013) Trends in groundwater pollution: loss of groundwater quality and related services. Groundwater governance: a global framework for country action. *GEF* 10(3726):1–76. http://www.groundwatergovernance.org/fileadmin/user_upload/groundwatergovernance/docs/Themat. Accessed 31 May 2017
- Del Campo MM, Esteller MV, Expósito JL, Hirata R (2014) Impacts of urbanization on groundwater hydrodynamics and hydrochemistry of the Toluca Valley aquifer (Mexico). *Environ Monit Assess* 186(5):2979–2999
- Dermatas D (2017) Waste management and research and the sustainable development goals: focus on soil and groundwater pollution. *Waste Manag Res* 35(5):453–455
- Domínguez-Mariani E, Vargas-Cabrera C, Martínez-Mijangos F, Gómez-Reyes E, Monroy-Hermosillo O (2015) Determinación de los procesos hidrogeoquímicos participantes en la composición del agua de las fuentes de abastecimiento a pobladores de la delegación Iztapalapa, DF, México (in Spanish). *Bol Soc Geol Mex* 67(2):299–313
- Famiglietti JS (2014) The global groundwater crisis. *Nat Clim Change* 4(11):945–948
- Foster S, Chilton J, Nijsten GJ, Richts A (2013) Groundwater—a global focus on the ‘local resource’. *Curr Opin Environ Sustain* 5(6):685–695
- Frisbie SH, Mitchell EJ, Dustin H, Maynard DM, Sarkar B (2012) World Health Organization discontinues its drinking-water guideline for manganese. *Environ Health Perspect* 120(6):775–778
- Gallegos E, Warren A, Robles E, Campoy E, Calderón A, Sainz MG, Bonilla P, Escolero O (1999) The effects of wastewater irrigation on groundwater quality in Mexico. *Water Sci Technol* 40(2):45–52
- Homoncik SC, MacDonald AM, Heal KV, Dochartaigh BÉÓ, Ngwenya BT (2010) Manganese concentrations in Scottish groundwater. *Sci Total Environ* 408(12):2467–2473
- Huizar AR, Méndez GT, Madrid RR (1998) Patterns of groundwater hydrochemistry in Apan-Tochac sub-basin, Mexico. *Hydrol Sci J* 43(5):669–685
- Huizar-Álvarez R (1997) Hydrochemistry of the aquifers in the Rio las Avenidas basin, Pachuca, Hidalgo, Mexico. *Water Air Soil Pollut* 96(1–4):185–201
- Huizar-Álvarez R, Campos-Enríquez JO, Lerma-Samaniego J, Delgado-Rodríguez O, Huidobro-González A (1997) Geophysical and hydrogeological characterization of the sub-basins of Apan and Tochac (Mexico basin). *Geofis Int* 36(4):217–234
- Huizar-Álvarez R, Campos-Enríquez O, Mitre-Salazar LM, Alatríste-Vilchis D, Méndez-García T, Juárez-Sánchez F (2001) Evaluación hidrogeológica de la subcuenca de Tecocomulco, Estados de Hidalgo, Puebla y Tlaxcala, México (in Spanish). *Rev Mex Cien Geol* 18(1):55–73
- Hurley T, Sadiq R, Mazumder A (2012) Adaptation and evaluation of the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) for use as an effective tool to characterize drinking source water quality. *Water Res* 46(11):3544–3552
- IDNR (2002) Ground-water quality. In ground-water resources in the White and West Fork White River Basin, Indiana. Indiana Department of Natural Resources, Indianapolis. http://www.in.gov/dnr/water/files/WFWR_web.pdf. Accessed 6 July 2017
- Jain CK, Bandyopadhyay A, Bhadra A (2010) Assessment of ground water quality for drinking purpose, District Nainital, Uttarakhand, India. *Environ Monit Assess* 166(1):663–676
- Lesser-Carrillo LE, Lesser-Illades JM, Arellano-Islas S, González-Posadas D (2011) Balance hídrico y calidad del agua subterránea en el acuífero del Valle del Mezquital, México central (in Spanish). *Rev Mex Cien Geol* 28(3):323–336
- Lucho-Constantino CA, Poggi-Varaldo HM, Beltrán-Hernández RI, Prieto-García F, Álvarez-Suárez M (2005) A multivariate analysis of the accumulation and fractionation of selected cations and heavy metals in agricultural soils in Hidalgo State, Mexico irrigated with raw wastewater. *Environ Int* 31:313–323
- Mazari-Hiriart M, López-Vidal Y, Ponce-de-León S, Calva JJ, Rojo-Callejas F, Castillo-Rojas G (2005) Longitudinal study of microbial diversity and seasonality in the Mexico City metropolitan area water supply system. *Appl Environ Microbiol* 71(9):5129–5137
- Medina MC, Cano PR (2001) Contaminación por nitratos en agua, suelo y cultivos de la Comarca Lagunera (in Spanish). *Rev Chapingo Serie Zonas Áridas* 2(1):9–14
- Montiel-Palma S, Armenta-Hernández MA, Rodríguez-Castillo R, Domínguez-Mariani E (2014) Identificación de zonas de contaminación por nitratos en el agua subterránea de la zona sur de la Cuenca de México (in Spanish). *Rev Int Contam Amb* 30(2):149–165
- Mubarak A, Howald RA, Woodriff R (1977) Elimination of chloride interferences with mercuric ions in the determination of nitrates by the phenol disulfonic acid method. *Anal Chem* 49(6):857–860
- Murphy HM, Prioleau MD, Borchardt MA, Hynds PD (2017) Epidemiological evidence of groundwater contribution to global enteric disease, 1948–2015. *Hydrogeol J* 25(4):981–1001
- NOM (2000) Modificación a la Norma Oficial Mexicana NOM-127-SSA1-1994, Salud ambiental. Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización. Modified guidelines for drinking water and treatments to be applied (in Spanish). Secretaría de Salud, Mexico
- Oişte AM (2014) Groundwater quality assessment in urban environment. *Int J Environ Sci Technol* 11(7):2095–2102
- Oulhote Y, Mergler D, Barbeau B, Bellinger DC, Bouffard T, Brodeur ME, Saint-Amour D, Legrand M, Sauvé S, Bouchard MF (2014) Neurobehavioral function in school-age children exposed to manganese in drinking water. *Environ Health Perspect* 122:1343–1350
- Patra HP, Adhikari SK, Kumar S (eds) (2016) Groundwater quality and contamination. Groundwater prospecting and management. Springer, Singapore, pp 183–195
- Piña M, Ramírez A (2003) Remoción de Hierro y Manganese en Fuentes de Agua Subterránea para Abastecimiento Público (in Spanish). In Agua potable para comunidades rurales, reuso y tratamientos avanzados de aguas residuales domésticas, Red Iberoamericana de Potabilización y Depuración del Agua. <http://tierra.rediris.es/hidrored/ebooks/ripda/index.html#>. Accessed 6 July 2017
- Regional Salinity Laboratory (1954) Diagnosis and improvement of saline and alkali soils. United States Department of Agriculture, Washington
- Sethy SN, Syed TH, Kumar A (2017) Evaluation of groundwater quality in parts of the Southern Gangetic Plain using water quality indices. *Environ Earth Sci* 76(3):116
- Singhal BBS, Gupta RP (eds) (2010) Groundwater contamination. Applied hydrogeology of fractured rocks. Springer, Dordrecht, pp 221–236
- Smith M, Cross K, Paden M, Laban P (2016) Spring—managing groundwater sustainability. IUCN, Gland
- Spalding RF, Exner ME (1993) Occurrence of nitrate in groundwater—a review. *J Environ Qual* 22(3):392–402



- Vasanthavigar M, Srinivasamoorthy K, Vijayaragavan K, Ganthi RR, Chidambaram S, Anandhan P, Manivannan R, Vasudevan S (2010) Application of water quality index for groundwater quality assessment: Thirumanimuttar sub-basin, Tamilnadu, India. *Environ Monit Assess* 171(1–4):595–609
- Vörösmarty CJ, Pahl-Wostl C, Bunn SE, Lawford R (2013) Global water, the Anthropocene and the transformation of a science. *Curr Opin Environ Sustain* 5(6):539–550

