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Application of water quality index to evaluate groundwater quality (temporal and spatial variation) of an intensively exploited aquifer (Puebla valley, Mexico)

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Abstract The spatial and temporal variation of water quality in the urban area of the Puebla Valley aquifer was evaluated using historical and present data obtained during this investigation. The current study assessed water quality based on the Water Quality Index developed by the Canadian Council of Ministers of the Environment (CCME-WQI), which provides a mathematical framework to evaluate the quality of water in combination with a set of conditions representing quality criteria, or limits. This index is flexible regarding the type and number of variables used by the evaluation given that the variables of interest are selected according to the characteristics and objectives of development, conservation and compliance with regulations. The CCME-WQI was calculated using several variables that assess the main use of the wells in the urban area that is public supply, according to criteria for human use and consumption established by Mexican law and international standards proposed by the World Health Organization. The assessment of the index shows a gradual deterioration in the quality of the aquifer over time, as the amount of wells with excellent quality have decreased and those with lower index values (poor quality) have increased throughout the urban area of the Puebla Valley aquifer. The parameters affecting groundwater quality are: total dissolved solids, sulfate, calcium, magnesium and total hardness.

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Introduction

While groundwater is a very widespread resource, it is hidden from view and inaccessible. Unlike surface water, changes in the quantity and quality of groundwater often occur slowly and are difficult to reverse (Foster et al. 2006). The groundwater quality is, however, being deteriorated mostly due to overexploitation, increased application of fertilizers, unsanitary conditions prevailing in rural and urban areas, inadequate water planning, etc, (Jasmin and Malikarjuna 2014). Therefore, the evaluation and periodic monitoring of the quality of this water are indispensable to the definition of strategies to protect and treat aquifers. Indices are useful instruments for this evaluation process. An index is the most effective tool to convey information about water quality to communities of users, those responsible for

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management, decision-making authorities and the general public.

To facilitate the integration and interpretation of water quality data, various water indices have been developed according to the evaluation needs and ease in handling. These indices use one or several parameters which are mostly physicochemical, and in some cases microbiological, thereby making it possible to reduce the information to a simple expression that is easily interpreted (Jasmin and Malikarjuna 2014; Nikoo et al. 2011; Boyacioglu, 2010).

According to Fernandez and Solano (2005), over 30 water quality indices are commonly used worldwide. These are based on a number of parameters ranging from 3 to 72. Horton (1965) and Liebman (1969) were pioneers who generated a unified methodology to calculate the quality index which was used and accepted by water quality monitoring agencies in the 1970s when indices were more important to the assessment of water resources (Boyacioglu, 2010; Nikoo, et al. 2011). The general water quality index was developed by Brown et al. (1970) and improved by Deininger for the United States National Academy of Sciences in 1975 (NAS, 1975). Work by the National Sanitation Foundation (NSF) in 1970 led to defining one of the most commonly used water quality indices (WQI) worldwide.

In the case study the CCME-WQI index (Canadian Council of Ministers of the Environment-Water Quality Index; CCME, 2001) was applied, which provides a mathematical framework to evaluate water quality in combination with conditions associated with water quality objectives. The CCME-WQI is flexible in terms of the type and number of water quality variables used in the analysis, the application period and the type of water body (rivers, lakes, aquifers, etc.). This is because the assessment is performed according to the type of water body, the particular use of the water resource and the number of parameters that are available. Its application provides meaningful information about a particular water body and describes trends in the results in an accessible, clear and simple manner. The index was created as an assessment tool for use by authorities, decision-makers and evaluators of water quality (CCME, 2001).

Unlike the CCME-WQI, traditional indices consider certain parameters to be more important than others and therefore assign relative weights to each variable. They use a modified weighted arithmetic average or a modified weighted sum as their calculation method. On the other hand, CCME-WQI is aimed at achieving the objective of simply comparing the values obtained to existing legislation in order to directly evaluate strategies by control agencies to improve water quality, given that changes are more noticeable when using this assessment. In addition, this methodology is among the easiest ones to adapt to the legislative requirements of a country since it does not hierarchically weight the variables and they are all equally important (CCME, 2001; Lumb et al. 2006; Boyacioglu, 2010; Nikoo et al. 2011).

To calculate the index, at least four variables are needed and a minimum of four samples is recommended. Nevertheless, there is no maximum limit on the number of variables and samples to be studied. In addition, the variables that define the quality of water in a particular region must be carefully selected in order to obtain meaningful information.

This index was applied to evaluate the quality of water in the Puebla Valley aquifer in Mexico (Fig. 1). The demand for freshwater has greatly increased in this region over recent decades due to rapid population growth and accelerated industrialization (Geotecnología 1997; Flores-Márquez et al. 2006; Garfias et al. 2010). This rapid urbanization has also affected the availability and quality of groundwater, which is the only supply source for the region, resulting in intensive exploitation of the aquifer system (CONAGUA, 2010). It is also important to mention that according to the World Health Organization (WHO, 2008) roughly 80 % of human illnesses are caused by water pollution.

Since 1982, the exploitation of two aquifer levels has been reported in the Puebla Valley. One is known as the upper aquifer and covers nearly the entire aquifer area, with the exception of the banks of the Atoyac River. The thickness ranges from 100 to 200 m and it contains good quality water with low saline contents. The second aquifer level (deep aquifer) is located below the other. The deep aquifer is thermal, with high concentrations of salts and sulphydric gas (Lesser, 1982).

In a joint study with the company Geotecnologia in 1997, the Potable Water System of the City of Puebla (SOAPAP, Spanish acronym) reported the degradation of the quality of the water in the aquifer. In this study were performed chemical analyses of water samples from 51 wells. The results showed evolving changes in the water quality of the upper aquifer, with slow and gradual changes in total hardness and total dissolved contents. The study found that total dissolved solids exceeded 500 mg/L in 14 of the wells and 1000 mg/L in three others (Geotecnología, 1997). Chemical
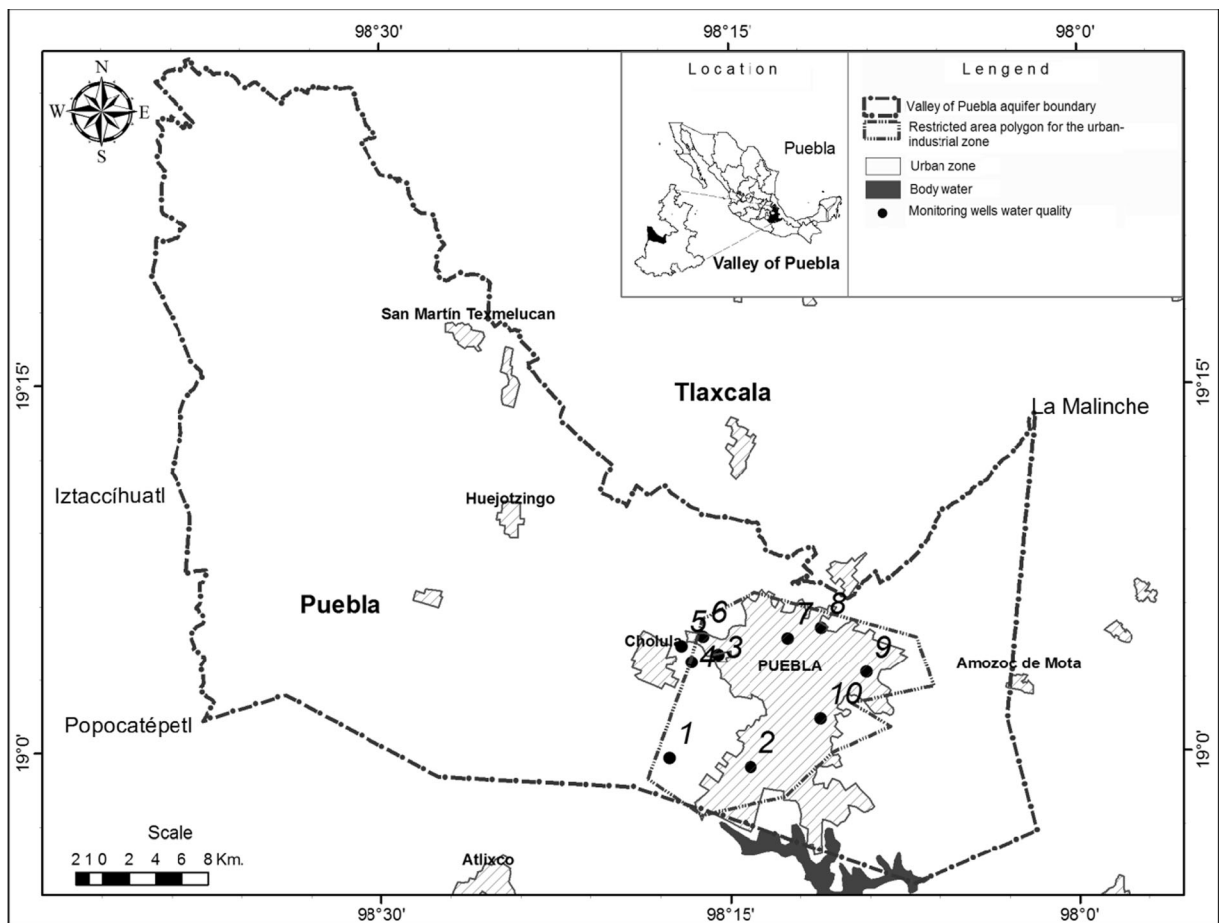
Fig. 1 Location of the study area and the polygon representing the urban-industrial restriction zone in the Puebla Valley aquifer region. Wells sampled in 2011 are identified

analysis showed evidence of the presence of sulphydric acid and carbon dioxide associated with the moderate heating of groundwater in the deep aquifer.

According to Jimenez-Suarez (2005) and Garfias et al. (2010), intensive use of groundwater in the Puebla Valley, and primarily in the City of Puebla itself, has negatively affected the equilibrium of the aquifer. One of the effects is a decrease in the piezometric level, which has resulted in decreased water volume in the valley's springs and surface flows. The most significant effect is the degradation in the quality of freshwater in the upper aquifer due to mixing with sulphydric water which rises from the deep aquifer. This mineralized water contains concentrations of sulfates and sulfurs above the WHO's quality standards for potable water (250 and 0.05 mg/L, respectively).

In addition, a study performed in 2009 (Brenes et al. 2011) reported the existence of pollution from nitrates in

the groundwater. Data obtained over one year from 16 wells in 8 municipalities located in the Puebla Valley aquifer region showed changes in the nitrate concentrations in 56 % of the wells, seeming to have a direct relationship with rainfall. An average nitrate concentration of 10.75 mg $N-NO_3/L$ and a maximum of 48 mg $N-NO_3/L$ were also determined and 44 % of the wells exceeded the concentration limits (10 mg $N-NO_3/L$ o 44.3 mg NO_3^-/L) for water for human use and consumption established by Mexican norms. These nitrate levels can present a risk to the health of the population that consumes water from these wells.

Given the importance of the quality of the water in the Puebla Valley aquifer and its deterioration, the objective of the present investigation was to spatially and temporally evaluate the water quality using the CCME-WQI quality index, since no systematic evaluation has

been conducted to-date of the spatial or temporal variations in water quality.

In addition, while this index is usually applied to surface water, the present work was enabled evaluating its use for groundwater.

Study area

The Puebla Valley is located in the central portion of the Trans-Mexican Volcanic Belt. This valley extends from the capital of the state of Puebla in the east to the Sierra Nevada, bordered by three powerful volcanoes: Malinche, Iztaccíhuatl and Popocatépetl (Fig. 1). The region is located between the parallels 18°54′ and 19°30′ and meridians 98°00′ and 98°40′ west of Greenwich. The average altitude is 2160 m above sea level (masl). The main rivers running through the Puebla Valley are the Atoyac, Zahuapan and Alseseca. The region of the Puebla Valley aquifer covers two states–Tlaxcala and Puebla—and its area is approximately 4060 km^2 (of which 2151 km^2 is located in the state of Puebla and 1909 km^2 in the state of Tlaxcala).

The climate is temperate and precipitation is moderate during summer. The annual mean temperature is 16.6 °C, with a maximum of 21.3 °C in May and a minimum of 10.8 °C in February. Annual mean precipitation in the basin ranges from 650 to 900 mm, with maximums of 1000 mm in volcanic zones in the eastern and western portions of the basin (Gárfias et al. 2010).

The City of Puebla has a population of 1.4 million inhabitants, and 2.2 million in the metropolitan area (INEGI 2010) where 85 % of the state's industry is located. The main industries are basic metal, light chemicals and electronics, while the textile, metallurgy and automobile industries are also important (INAFED 2009). Industry grew 60 % over the past 20 years primarily because of its proximity to Mexico City, where increasing environmental problems have required the decentralization of industry (Gárfias et al. 2010). Thirty-six percent of the economically active population works in the primary sector (agriculture, livestock, hunting and fishing), 24 % in the secondary sector (construction) and 35.1 % in the tertiary sector (financial services, public administration, restaurants and hotels and community, social, professional and technical services, among others) (INAFED 2009).

The area of the Puebla aquifer encompasses two states Tlaxcala and Puebla and covers a surface area of

approximately 4060 km^2, of which 2151 km^2 are in Puebla and 1909 km^2 are in Tlaxcala. Mooser et al. (1996) reported in the area three important structures (Fig. 2). The Iztaccíhuatl-Malinche graben (E–W), which is bordered to the north by the Tlaxcala normal fault (a) and the Tetlatlahuca normal fault to the south (b). A second structure is the Malinche fault (c), NE–SW that begins in the volcanic edifice of that name and crosses Puebla; and finally, the NW–SE Valsequillo fracture (d) that also crosses the urban zone. The NE–SW orientation Fosa Atlixco is a graben with a, that extends southwest from Puebla to Atlixco (Fig. 2).

The Puebla Valley aquifer is made up of three hydrogeological units called the upper, middle and deep aquifers (Salcedo et al. 2013; Flores-Márquez et al. 2006). The upper and deep aquifers are of interest because of their levels of exploitation. The upper aquifer (free, semi-confined) is composed of granular sedimentary and fractured rock formations consisting of lava flows from different volcanic cones that created the mountains. This aquifer basically functions as a free aquifer and has high hydraulic conductivities. The water quality is good for use as a supply source. This upper aquifer lies above Pliocene lacustrine deposits, which have very low permeability, functioning as an aquitard between the upper and middle aquifers.

The middle aquifer (semi-confined) is made up of andesites, basalts, igneous tuffs and Balsas Group conglomerates. Since these are fractured material, this aquifer has secondary permeability. This middle aquifer in turn rests on another aquitard made up of a folded sea formation called Mezcala, from the Upper Cretaceous. This is composed of marls, limestone and shales and is therefore considered to be practically impermeable, although some areas have a high degree of fracturing.

The deep aquifer lies below this level and is composed of formations identified as Tecomasuchil and Atzompa which contain limestone, sandstone and shales, in addition to the Tecocoyunca Group with sandstone, shales with gypsum and siltstone. These Cretaceous deposits are affected by dissolution and tectonic fracturing processes resulting in secondary permeability and consists of a sequence of early Cretaceous Limestones with variable amounts of gypsum and anhydrites (Flores-Márquez et al. 2006). High concentrations of sulfates and sulfurs have been found in this hydrogeological unit (Garfias et al. 2010).

The valley's demand for water for human and industrial use is almost entirely met by groundwater from the
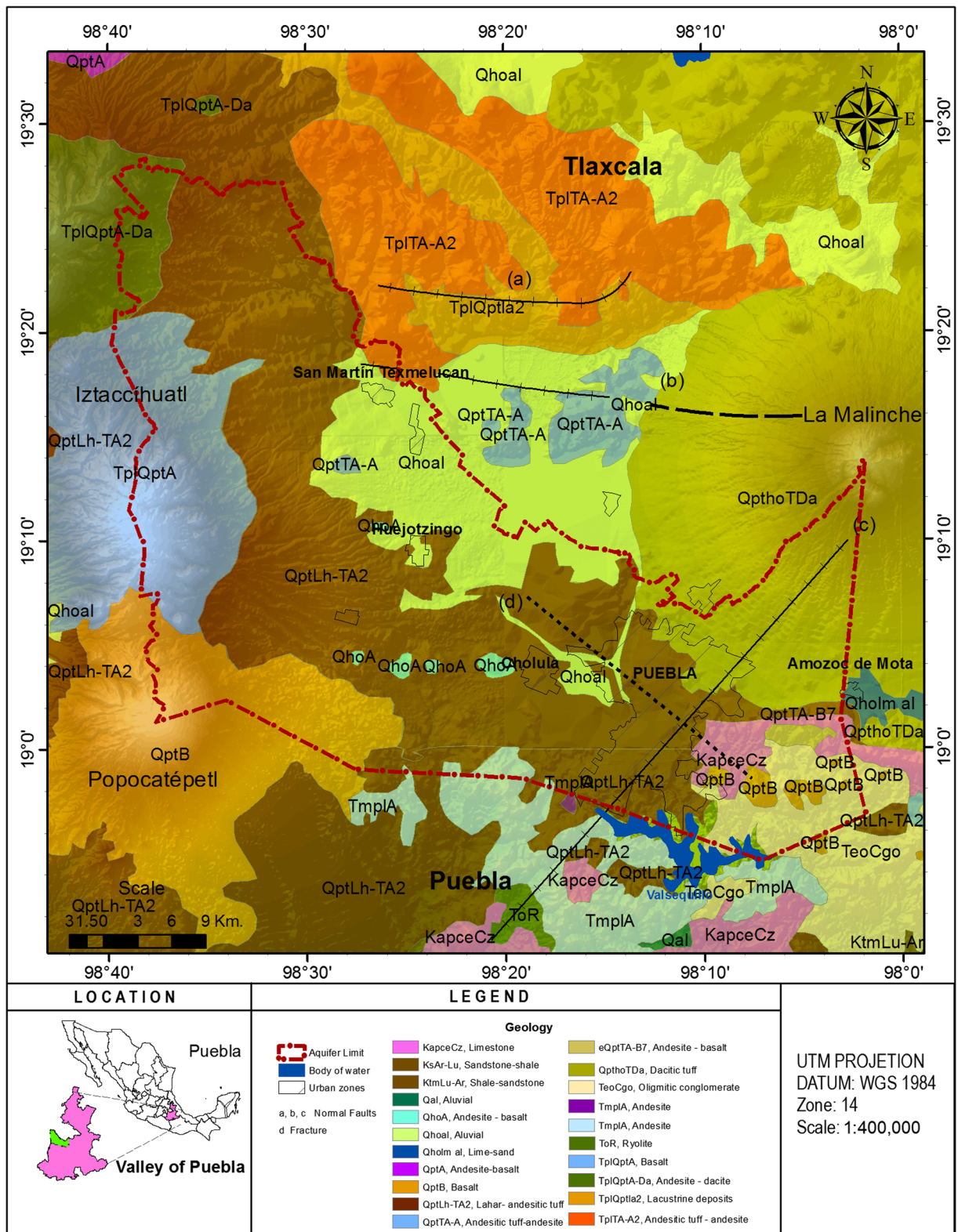
Fig. 2 Geology of the study area and the main faults

upper aquifer. This has resulted in its intensive exploitation, which has increased over the years. This phenomenon has been caused a continual decrease in the piezometric level of the upper aquifer (at an average rate of 2 m/year); the appearance of an 80-m drawdown cone with an amplitude of 5 km and a water deficit in the aquifer estimated at 700 l/s (Garfías et al. 2010; Flores-Márquez et al. 2006; Arroyo 2005; Geotecnología, 1997).

Vegetation cover and land use in Puebla Valley aquifer is varied, 73 % of the area is of agricultural type, 13 % urban, 8.5 % is forest area, where the main recharge takes place, and 5.5 % is pasture area (Fig. 3). The urban area of Puebla City has been increasing due to the rapid population growth; this area has expanded to neighboring municipalities to form the metropolitan area. This situation was intensified by the establishment of an industrial zone at north of the city

and the construction of infrastructure like road, producing the urban expansion towards the west. The declaration of the vegetation cover and land use for Angelópolis in 1993, worsened the situation, consolidating a new node of services between Puebla, San Pedro Cholula and San Andres Cholula (Ayuntamiento de Puebla, 2014). This evolution is evident in the urban growth of the municipality of Puebla, it went from a land area of 22.83 km^2 in 1970 to 223.94 km^2 in 2010 (Table 1). This situation is accompanied by population growth and more demand of natural resources like groundwater. In the same reference period, population went from 532,000 to 1,539,819 inhabitants (Table 1). The present investigation is conducted in Puebla City and neighbor municipalities (urban area), because in this part of the aquifer, the effects of the intensive use of groundwater has been negatively evidenced in a drawdown cone of 0.5 m per year and water quality changes.
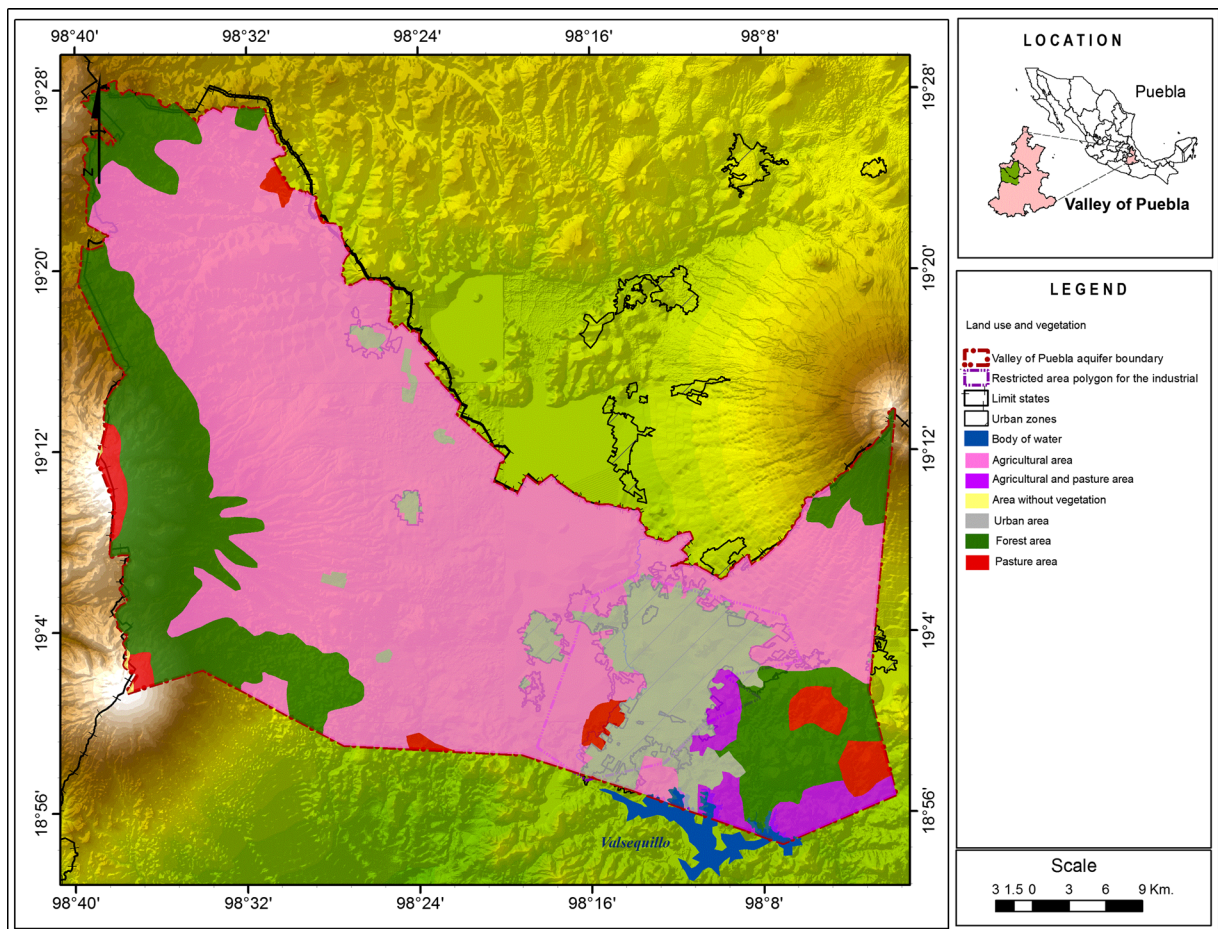
Fig. 3 Land use and vegetation cover in the Puebla Valley aquifer

Table 1 Territorial growth of the city of Puebla in a period between 1930 and 2010

Year	Territorial growth area (km^2)	Population (Inhabitants)
1930	10.6	114,793
1950	14.6	234,603
1970	22.83	532,744
1975	60.94	684,251
1990	108.40	1 007,170
2000	171.07	1 346,176
2005	204.32	1 485,941
2010	223.94	1 539,819

Table 2 Quantified parameters and analytical techniques applied to water samples collected during the sampling campaign conducted in the year 2011

	Parameters	Technique / equipment
Anions	CO_3^{2-}, F^-, Cl^-, NO_3^-, Br^-, PO_4^{2-}, HCO_3^- and SO_4^{2-}	High performance liquid chromatography (HPLC). Equipment: Dionex ICS-2500 HPLC/IC.
Cations	Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sr, Ti and Zn	Inductively coupled plasma with optical emission spectrometry (ICP-OES). Equipment: Thermo iCAP 6500 Duo View.
	Total hardness	EDTA Tritation

Materials and methods

Compiling of information

This study compares the values compiled from physio-chemical analyses for different time periods and from different institutions. The data corresponding to the year 1997 were reported in a study conducted by the company Geotecnologia for the City of Puebla Potable Water System (SOAPAP). The data from the years 2000, 2002, 2005 and 2013 were obtained from information generated by the SOAPAP.

For the purpose of the present investigation, 10 potable water supply wells distributed throughout the urban area of the City of Puebla were sampled in October, 2011 (Fig. 1). In order to determine field parameters, water was collected in plastic containers which were appropriately washed in the laboratory. Different Hanna 9828 CB-29,586 multi-parametric electrode probes were inserted to read water temperature, pH, total dissolved solids (TDS), electrical conductivity and oxidation-reduction potential. The water samples were collected according to existing protocols detailed in Boulding (1995), as well as procedures presented in norm NOM-230-SSA1–2002 (DOF, 2003) which conformed to APHA, AWW and WEF guidelines (2005). Two water samples were taken, one to analyze anions and the other major cations and minor elements; the latter sample was preserved with nitric acid until reaching a pH less than or equal to 2. All the samples were stored in refrigeration (4 °C) until analyzed. The data presented in Table 2 were determined in the laboratory.

Information processing

The spatial and temporal evaluation of the groundwater quality was performed using historical water quality data from supply wells in the City of Puebla for the years 1997, 2000, 2002, 2005, and 2013, as well as the results from the 2011 sampling. To complement this information, the existence and conditions of the wells were verified based on the databases containing the historical data.

It is important to mention that the information shown in the present article relates to the results from the chemical analyses of water from wells administered by the city's potable water operating entity and differences were identified in the number of the wells sampled and their correspondence. Another important consideration is that in the year 2011 it was not possible to sample several of the wells that were sampled in previous years because of different problems related to closures, operations and accessibility to the responsible authorities. The reliability of the historical data was evaluated by the authorities at the potable water operating entity (years 1997, 2000, 2002, 2005 and 2013) and the authors of the work published in 2010.

The first step to process the information was to apply descriptive statistical techniques to determine the maximum, minimum, mean, standard deviation and coefficient of variation of each parameter for each year studied.

Total dissolved solids (TDS) was the parameter chosen to analyze the evolution of the water quality in the aquifer's urban area, since this parameter is associated with material dissolved in water. It is also a

representative parameter since its value specifically measures total filterable residue (salts and organic residue) (Huízar-Álvarez, et al. 2001). The TDS data was spatially interpolated to create isocontour maps of the concentrations (iso-contents map). The interpolation process to create the isocontour maps consisted of creating a georeferenced database in Arc-View (version 9.3) with the application of interpolation or the Kriging spatial prediction method. This method is based on geostatistics and estimates the variability and spatial correlation of the study phenomenon. Therefore, its application involves a previous analysis of the information in order define or extract the initial information to generate a model that represents the spatial continuity (Bohling, 2005). The use of this method with other applications– such as the interpolation of hydrogeological data, chemical parameters of soil and climate data– has been demonstrated to be highly applicable and has contributed to improving the precision of the results obtained (Richard, 1982; Goovaerts, 2000; Vicente-Serrano et al. 2003).

In addition, a structural analysis of TDS was performed by calculating the experimental semivariogram and the fit to a known theoretic model. The variogram is a mathematical function that measures variability, that is, the dissimilarity of a variable, when its values are seen at points separated by a concrete distance. The variogram of the TDS parameter was constructed for each range of locations and serves as an instrument to determine the concrete shape of the spatial autocorrelation of the concentration: that is, its spatial structure (Meyers et al. 1982).

Calculation of the CCME-WQI index for human use and consumption

Water quality was evaluated according to criteria established for human consumption by the World Health Organization (WHO, 2008) and criteria established for human use and consumption by Mexican norm NOM-127-SSA1–1994, "Environmental Health. Water for Human Use and Consumption. Permissible Quality Limits and Treatment Required for its Potabilization," modified in the year 2000 (DOF, 2004).

The methodology to evaluate the index involves defining the time period to be considered, the variables and the desirable quality objectives. The calculation consists of determining three factors which are the components of the index: F1, F2 and F3. The calculation of F1 and F2 is relatively simple while F3 requires some additional steps (CCME 2001).

F1 represents the number of variables (parameters) that do not meet the objective (the limit or desirable level defined as the criterion for the particular water usage) at least once during the time period considered:

$$F1 = \left(\frac{\text{Number of failed variables}}{\text{Total number of variables}}\right) * 100 \quad (1)$$

F2 represents the percentage of individual tests (water samples from wells) that do not meet the objective with respect to the total number of tests performed during the time period considered:

$$F2 = \left(\frac{\text{Number of failed tests}}{\text{Total number of tests}}\right) * 100 \quad (2)$$

F3 represents the amount by which the values of the individual tests deviated from the objectives. This factor is calculated using three steps:

(i) Calculating the number of times by which an individual concentration is greater than or less than the objective, where this objective is a desirable value. The value obtained represents the anomalous deviation ("excursion"), or nse_i (normalized sum of excursions), and is expressed in two ways:

When the test value must not exceed the value of the objective:

$$nse_i = \left(\frac{\text{Number of failed tests}}{\text{Objective}_j}\right) - 1 \quad (3)$$

When the test value must not fall below the objective:

$$nse_i = \left(\frac{\text{Objective}_j}{\text{Number of failed test}}\right) - 1 \quad (4)$$

(ii) Calculating the variable nse, which represents the amount (amplitude) by which the water quality deviates from the objectives or quality criteria. This is calculated by dividing the sum of the

amplitudes of each of the excursions from the objective by the total number of tests:

$$nse = \frac{\sum_{i=1}^{n} \text{excursions}_i}{\text{Total number of tests}} \quad (5)$$

(iii)   And lastly, F3 is calculated using an asymptotic function of normalized scales and taking the sum of the excursions from the objective (*nse*) to obtain a value with a range between 0 and 100:

$$F3 = \left(\frac{nse}{0.01\,nse + 0.01} \right) \quad (6)$$

After obtaining the factors, the index itself is calculated by summing the three factors as though they were vectors. The sum of the squares of each factor is thus equal to the square of the index, as expressed by the following equation:

$$CCMEWQI = 100 - \sqrt{\frac{F_1^2 + F_2^2 + F_3^2}{1.732}} \quad (7)$$

This approach treats the index as a variable in a three-dimensional space defined by each one of the factors along an axis. With this model, the index of changes is proportional to the three factors.

After the value of the index is calculated, the water quality can be classified as:

- Excellent (WQI between 95 and 100);
- Good (WQI between 80 and 94);
- Fair (WQI between 65 and 79) (fair water quality represents conditions which require treatment for its use);
- Polluted (WQI between 45 and 64);
- Very polluted (WQI between 0 and 44).

The evaluation was based on six parameters defined by the NOM-127-SSA1–1994 (SSA, 2004) and nine defined by WHO criteria. These parameters represent the objectives, or quality criteria, used to evaluate the index, as shown in Table 3.

Table 3 Objectives in the assessment using the water quality index (CCME-WQI)

	Objective (parameter evaluated)	Units	Mexican standards (NOM-127-SSA1–1994)	WHO (2008)
1	pH	pH unit	6.5–8.5	7–8
2	TDS	mg/L	1000	1000
3	Total hardness	mg/L CaCO$_3$	500	100
4	Sulfate (SO$_4^{2-}$)	mg/L	400	250
5	Chloride (Cl$^-$)	mg/L	250	250
6	Calcium (Ca^{2+})	mg/L	-	75
7	Magnesium (Mg^{2+})	mg/L	-	30
8	Sodium (Na$^+$)	mg/L	-	200
9	Nitrate (NO$_3^-$)	mg/L	44.3	50

Results

General characteristics

The results from applying the descriptive statistical study to the compiled hydrochemical data are shown in Table 4. When evaluating these data based on the Mexican standard, the maximum pH was found to be within the interval (6.5–8.5) for nearly all the years studied, while the minimum was slightly below for several years (except 1997). Total dissolved solids (TDS) ranged from 107.5 to 3796 mg/L, while maximum values for all years exceeded the limits of 1000 mg/L established by Mexican norms.

The concentration of sulfates detected ranged from 1.9 mg/L to 1300 mg/L, and the maximum value was always above the limit of 400 mg/L. The concentrations of chlorides varied and the maximum concentrations of this anion were above the limits defined by both the Mexican standard and the WHO only for the years 2002 (610.0 mg/L) (Table 4). The maximum concentrations of nitrates were below the limit of Mexican norm of 44.3 mg NO$_3^-$/L (42.5 mg/L in 2011 and 11.2 mg/L in 2013), except the year 1997 (52.8 mg/L, Table 4). The zone with the highest concentrations of NO$_3^-$ corresponds to the urban area, and it can be associated with wastewater.

With respect to cations, a limit has been established by the WHO but not by Mexican norms. For all the years except 1997 (274.2 mg/L), maximum sodium concentrations were below the 200 mg/L established by the WHO. Maximum concentrations of calcium and magnesium exceeded WHO criteria for all the years

Table 4 Minimum, maximum and statistical parameters of physical and chemical characteristics of groundwater samples (TH: total hardness, TDS: total dissolved solids, SD standard deviation, Nd: not determined, VC: Variance Coefficient)

Limits	pH	EC (μS/cm)	TH CaCO$_3$ (mg/L)	TDS (mg/L)	NO$_3^-$ (mg/L)	SO$_4^{2-}$ (mg/L)	Cl$^-$ (mg/L)	Na^{2+} (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)
Mexican standards	6.5–8.5	-	500	1000	44.3	400	250		-	-
WHO	7–8	-	100	1000	50	250	250	200	30	75
1997 (*n* = 75)										
Max	8.3	2980.0	1436.0	2553.3	52.8	754.0	100.0	274.2	88.5	428.8
Min	6.9	152.0	32.0	156.0	0.9	1.9	2.10	3.8	3.9	6.4
Median	7.3	462.1	169.4	433.3	8.4	29.1	11.8	31.8	18.9	36.5
SD	0.14	403.8	210.4	393.4	8.9	96.0	17.5	37.7	15.6	61.4
VC (%)	5.4	93.9	123.3	90.1	106.0	327.1	147.1	117.7	81.9	167.6
2000 (*n* = 97)										
Max	8.3	3800.0	2200.0	3796.9	Nd	1300.0	134.0	Nd	308.8	600.0
Min	6.2	190.0	16.0	194.3	Nd	4.8	1.5	Nd	3.8	15.2
Median	7.4	944.5	410.1	856.1	Nd	102.4	25.1	Nd	39.2	104.5
SD	0.5	737.7	370.3	700.5	Nd	177.1	24.2	Nd	46.9	92.6
VC (%)	7.0	77.6	89.8	81.4	Nd	172.0	95.9	Nd	119.1	88.1
2002 (*n* = 47)										
Max	8.2	4430.0	1669.9	2260.0	Nd	810.5	610.0	Nd	621.2	1048.6
Min	5.4	172.7	70.3	107.5	Nd	Nd	3.6	Nd	19.4	38.8
Median	7.5	715.8	257.0	407.7	Nd	81.2	45.3	Nd	89.2	170.1
SD	0.5	903.4	295.1	436.9	Nd	171.1	120.1	Nd	122.5	198.1
VC (%)	7.0	124.8	113.6	106.9	Nd	208.2	262.3	Nd	135.8	115.2
2005 (*n* = 179)										
Max	8.1	2221.0	1380.0	1628.0	1.3	417.4	82.5	Nd	504.9	1020.0
Min	6.2	189.4	79.2	120.0	0.1	2.2	1.9	Nd	5.7	9.9
Median	7.2	831.9	333.6	580.7	0.5	63.2	20.4	Nd	136.0	188.3
SD	0.4	587.9	243.5	415.1	0.3	77.6	17.1	Nd	105.7	175.3
VC (%)	6.0	70.5	72.8	71.3	72.4	122.5	83.3	Nd	77.5	92.8
2011 (*n* = 10)										
Max	8.6	3072.0	1718.0	1998.0	42.5	1018.0	134.4	141.3	120.6	489.2
Min	6.4	240.0	62.0	156.0	0.1	13.0	4.9	12.2	6.5	32.9
Median	7.0	1362.5	571.9	886.1	10.3	176.7	44.9	87.4	61.0	153.0
SD	0.7	851.6	498.5	553.6	13.3	300.1	34.3	50.9	41.9	129.9
VC (%)	9.9	59.2	55.2	59.2	82.7	161.1	72.5	80.5	65.1	122.2
2013 (n = 179)										
Max	8.0	2763.0	1473.2	2000.0	11.2	541.9	93.0	148.1	661.2	818.1
Min	6.5	199.3	37.4	154.0	0.1	2.9	0.4	6.8	2.1	10.3
Median	7.3	813.1	367.0	585.9	2.7	62.8	23.2	33.9	134.0	232.2
SD	0.4	565.0	296.2	389.2	2.7	81.1	19.7	37.4	146.2	174.7
VC (%)	5.4	69.3	80.5	66.2	99.4	128.8	84.8	109.4	108.8	75.0

studied. These high calcium and magnesium concentrations (with maximums of 1048.6 in 2001 and 661 mg/L in 2013, respectively) were in turn reflected in the total hardness, whose maximum value for all years studied

exceeded the 500 mg/L limit established by Mexican standard (Table 4).

As has already been mentioned, parameters other than those presented in Table 4 were analyzed during the sampling campaign performed in the year 2011 (Table 2). The value of those parameters were determined to be below the permissible limits for water for human consumption, except for boron which exceeded the concentration of 0.5 mg/L defined by the WHO. Table 4 also shows a large spread between the data for some of the parameters, such as sulfates, calcium and total hardness. The coefficient of variation was therefore often greater than 100 %. In all cases, a large spread of the data can be seen for the highest values (above the median) and atypical data (anomalies or extremes) that are distinct from the majority of the data are also shown, especially for ranges representing the highest concentration values.

Given that the TDS parameter indicates higher saline contents in water, its spatial variation is presented for the years studied. To this end, a geostatistical analysis of total dissolved solids (TDS) for the years 2000, 2005 and 2103 was first conducted (Fig. 4). This consisted of analyzing the variables and obtaining the experimental variogram and its fit to a spherical variogram. In the directional variograms a specific trend was not detected, therefore the omnidirectional variogram was applied for the fitting process. The spherical variogram obtained for the year 2000 presented a nugget effect of 45,000 with a variance of 180,000 and a scope or range of 4500 m. For the data from the year 2005, the values fit a spherical variogram with a nugget effect of 15,000 and variance parameters of 2.20×10^5 and range 12,000 m. Finally, for the year 2013 the resulting spherical variogram has a nugget effect of 15,000 and a range of 13,000 with a variance of 1.95×10^5. For the years 2002 and 2011 with few sample populations, linear interpolated variograms were applied for the corresponding year (Fig. 5).

These maps of the spatial distribution of TDS contents show a change over the years studied in the areas where the maximum values were observed. Although a constant behavior is seen in which the highest TDS values fall within the urban area of the City of Puebla (Fig. 4).

Water quality index

Table 5, Figs. 6 and 7, present the results from the calculation of the water quality index. According to Mexican standard, the water quality in the wells was basically excellent for the years 1997, 2000, 2002, 2005 and 2013

since the percentages of wells with this classification were 63.16 %, 65.63 %, 77.08 %, 61.3 % and 71.7 %, respectively (Fig. 6 and Table 6). For the WHO criteria indicated a higher percentage of wells with good water quality in 1997 (47.37 % of the wells) and 2000 (40.63 % of the wells); on the other hand, a higher percentage of the wells was classified as polluted for the year 2002 (52.08 %) and very polluted for the years 2005 (28.4 % polluted and 17 % very polluted) and 2013 (35 % polluted and 15.25 % very polluted) (Fig. 7 and Table 6).

In 2011 for the 10 sampled wells, the water was classified as good by Mexican standard (80 % of the wells evaluated) and as fair or polluted by the WHO criteria (40 % and 30 %, respectively) (Figs. 6 and 7, Table 6).

In general, the index calculated with the World Health Organization criteria can be considered stricter than with Mexican norms (NOM-127-SSA1–1994). This is because WHO establishes lower limits for sulfates and hardness and also includes other parameters which are not included in the Mexican norms, such as calcium and magnesium (Table 2).

The evaluation of the index based on WHO criteria shows a gradual deterioration in the water quality of the aquifer over time, given that the percentage of wells with excellent quality decreased while those with the lowest index values (very polluted, polluted and fair) increased. The quality was excellent in 34 % of the wells in 1997, decreasing to 10 % of the wells in 2002, 3.4 % of the wells in 2005 and none of the wells in 2011 (Tables 5 and 6). But, for the year 2013 the quality was excellent for 8 % of the wells.

Figures 8 and 9 present the spatial distribution of the index values based on Mexican norms and WHO criteria, respectively. The highest index values can be seen inside the urban area of the City of Puebla, and to a greater extent in the year 2002. In addition, the index values calculated with WHO criteria show a larger decrease in the water quality.

Discussion

The use of the index facilitated the management and interpretation of the data obtained, making it possible to conduct a simple evaluation of the spatial and temporal trends in water quality for the Puebla Valley aquifer. A certain degree of deterioration in the water quality over the years was demonstrated, which was more significant within the urban area
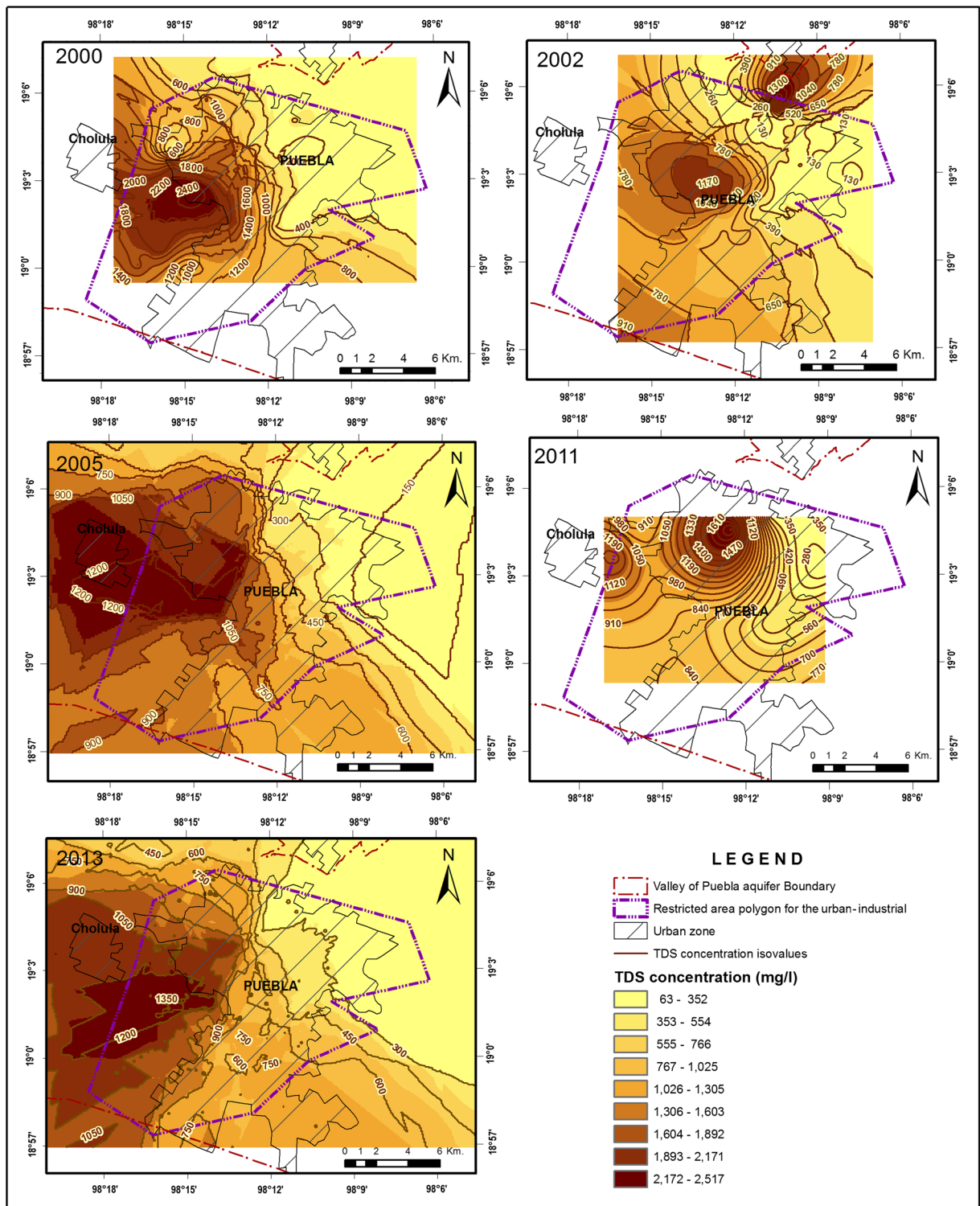
Fig. 4 Spatial distribution of the concentration of TDS (mg/L) for the years 2000, 2002, 2005 and 2011, in the urban region of the Puebla Valley aquifer
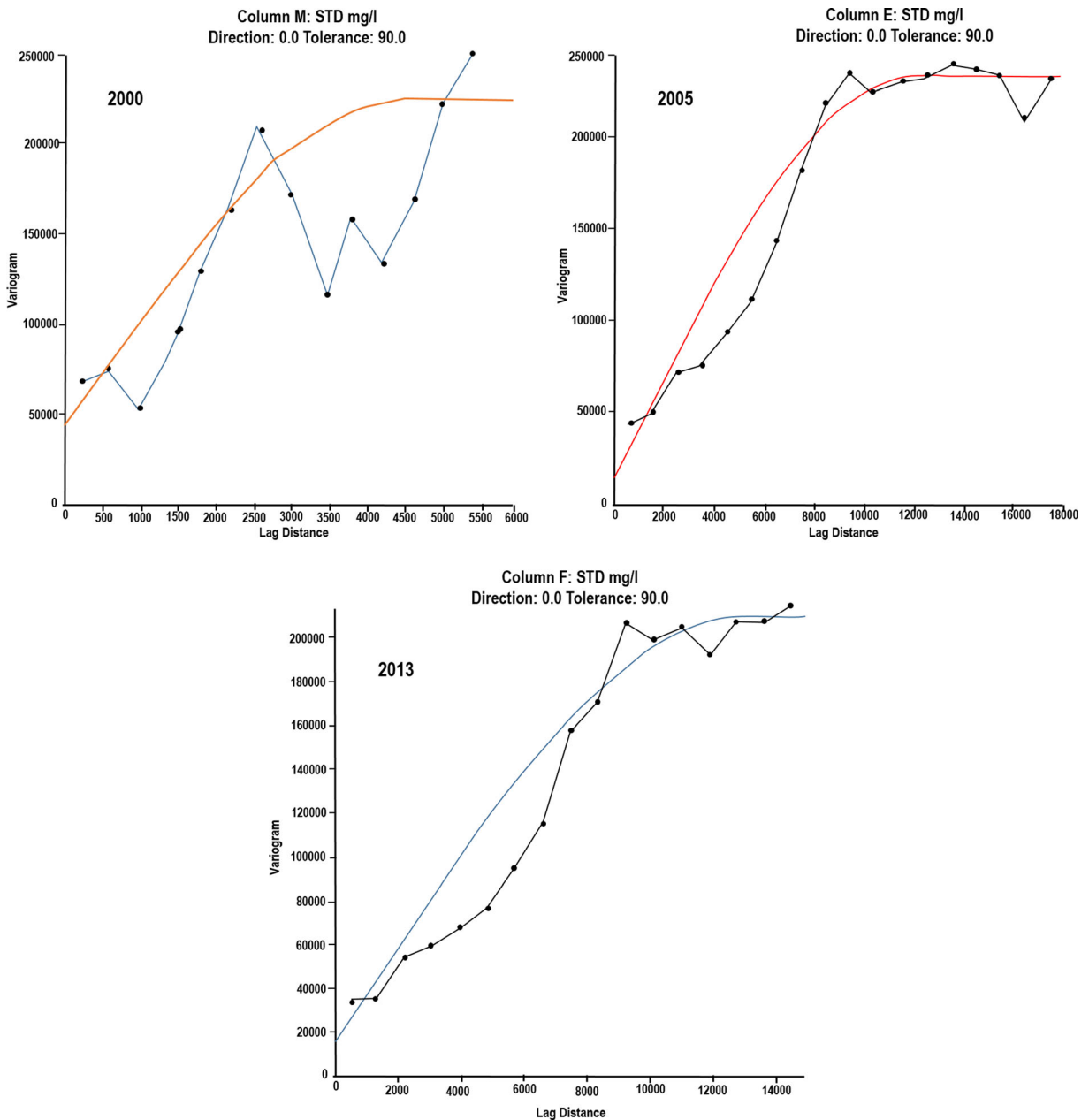
Fig. 5 Experimental TDS variograms for the years 2000, 2005 and 2013

of the City of Puebla. The use of the index also identified the parameters that most often affected the water quality: total hardness, total dissolved solids, sulfates, calcium and magnesium (Table 6).

The information obtained in this study, corroborate the data presented by different authors (Flores-Márquez et al. 2006, Jiménez-Suárez, 2005, Garfias et al. 2010) who reported that the water quality of the urban zone of Puebla Valley aquifer is negatively affected by upwelling mineralized water. This phenomenon has been caused by the depletion of the upper aquifer, which is reflected in a decrease in piezometric levels,

Table 5 Values of the water quality index (WQI)

	1997		2000		2002		2005		2011		2013	
	n = 77		n = 97		n = 48		n = 179		n = 10		n = 179	
	WHO	NOM*	WHO	NOM	WHO	NOM	WHO	NOM	WHO	NOM	WHO	NOM
Very polluted	2.63	0.00	31.25	3.13	14.58	4.17	17.05	0	10.00	0.0	15.25	0
Polluted	2.63	3.95	8.38	12.50	52.08	6.25	28.41	2.3	30.00	0.00	35.03	2.3
Fair	9.21	7.89	11.46	16.67	22.92	6.25	34.0	8.7	40.00	20.00	24.29	14.7
Good	22.37	25.00	40.63	2.08	0.00	6.25	17.05	27.7	20.00	80.00	17.51	11.3
Excellent	34.21	63.16	8.33	65.63	10.42	77.08	3.41	61.3	0.00	0.00	7.91	71.8

*Mexican Standards (NOM-127-SSA)

n = number of samples

contributing to water from the deep aquifer rising up and mixing into the upper aquifer.

Several processes contribute to the mixing of water between the deep and upper aquifers. Such as differences in hydraulic heads between the two aquifers (the deep aquifer is associated with several springs), the existence of a fault system that would provide a route for rising flow and the hydraulic connection produced by wells at different levels of the aquifer (Flores-Márquez et al. 2006).

Brenes et al. 2009 reported the existence of pollution from nitrates in eight localities of the aquifer area, only three wells are located in study area of this work. However, in this analysis, in the urban area of Puebla aquifer, the concentrations of nitrates are in general low and only the increase in the nitrates content has occurred in 1997. There is a possibility that the depth to the groundwater

table of at least 80 m has reduced the impact of contaminants on the upper aquifer.

This type of process in which more mineralized water rises from the deep aquifers and then mixes with water in the shallow aquifers has been observed in other aquifers in the country that have been intensively exploited. One such example is the Independencia aquifer in Guanajuato (Ortega-Guerrero, 2009) where the deterioration in the water quality is related to the presence of As^- and F^-. The water quality problem in the San Luis Potosí aquifer (Carrillo-Rivera et al. 2002) is associated with the presence of F^- while the Toluca aquifer (Esteller et al. 2012; Martín del Campo et al. 2014) has high Fe and Mn contents. These elements are present in these aquifers because of the volcanic nature of the geological material that compose their deep

Fig. 6 Temporal evolution of water quality in the urban area of the Puebla Valley aquifer evaluated using the CCME-WQI, based on the NOM-127-SSA1–1994
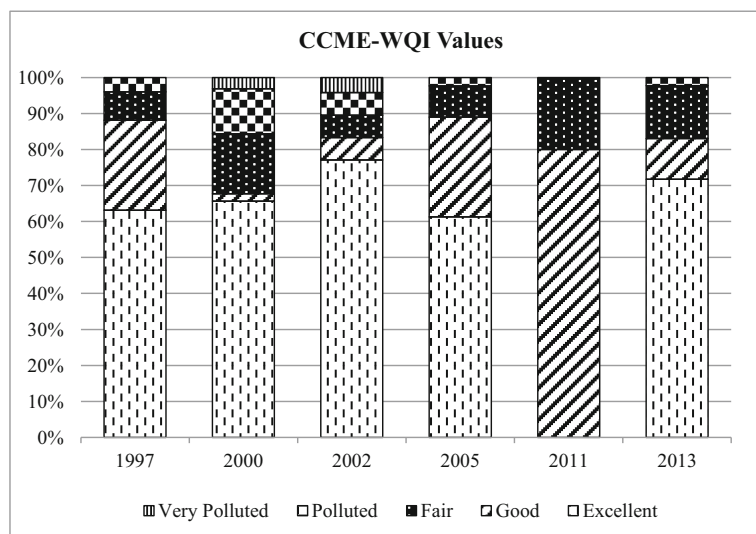
Fig. 7 Temporal evolution of water quality in the urban region of the Puebla Valley aquifer evaluated using the CCME-WQI, based on WHO criteria
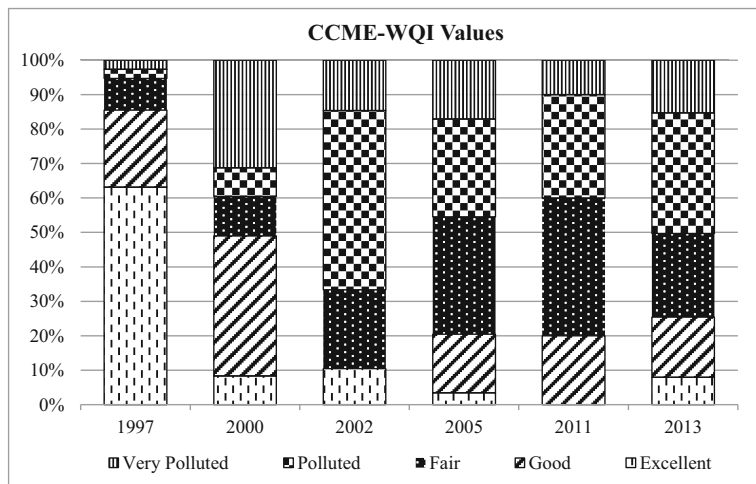

aquifers. Meanwhile, since the Puebla Valley's deep aquifer consists of sedimentary material its water has high concentrations of sulfates, calcium and magnesium (which in turn is reflected in high TDS and hardness) resulting from the dissolution of sulfate mineral (gypsum and anhydrite) and carbonates (calcite) (Garfias et al. 2010).

The current scheme of groundwater abstraction has produced the decline of the piezometric head in the upper aquifer and the drawdown cone in the urban zone of the aquifer has become larger in area and deeper. This dynamic of the piezometric level increases the difference in the hydraulic potential between the upper aquifer and the deep aquifer and thereby contributes to the

Table 6 CCME-WQI calculations for specific standards

Year	Category, protocol or specific category-based standards	Sample size / Number. of variables	Total Number. of tests	% of failed tests	Parameters of failed test	WQI values and category based on specific standards	
						Mean + 2sd for all data	CCME-WQI category
1997	NOM-127-SSA, Drinking water	75 / 6	450	7.48	TDS, NO_3	92.4	Good
2000	NOM-127-SSA, Drinking water	97 / 6	485	15.05	TDS, TH $CaCO_3$	86.9	Good
2002	NOM-127-SSA, Drinking water	47 / 5	235	7.53	TDS, TH $CaCO_3$	92.5	Good
2005	NOM-127-SSA, Drinking water	179 / 6	1074	8.61	TDS, SO_4	92.7	Good
2011	NOM-127-SSA, Drinking water	10/ 6	60	18.30	SO_4, TDS	83.0	Good
2013	NOM-127-SSA, Drinking water	179/6	1062	2.42	TDS, TH $CaCO_3$	93.2	Good
1997	WHO, Drinking water	75 / 8	606	7.92	TDS, Ca, Mg	92.5	Good
2000	WHO, Drinking water	97 / 7	679	35.80	TDS, TH $CaCO_3$, Ca, Mg	66.1	Fair
2002	WHO, Drinking water	48 / 7	336	37.5	TDS, TH $CaCO_3$, Ca, Mg	64.4	Polluted
2005	WHO, Drinking water	179 / 9	1611	52.1	TDS, TH $CaCO_3$, SO_4,Ca, Mg	64.2	Polluted
2011	WHO, Drinking water	10 / 9	90	34.00	TDS, TH $CaCO_3$, Ca, Mg	65.2	Fair
2013	WHO, Drinking water	179/9	1611	33.58	TDS, TH $CaCO_3$, Ca, Mg	65	Polluted
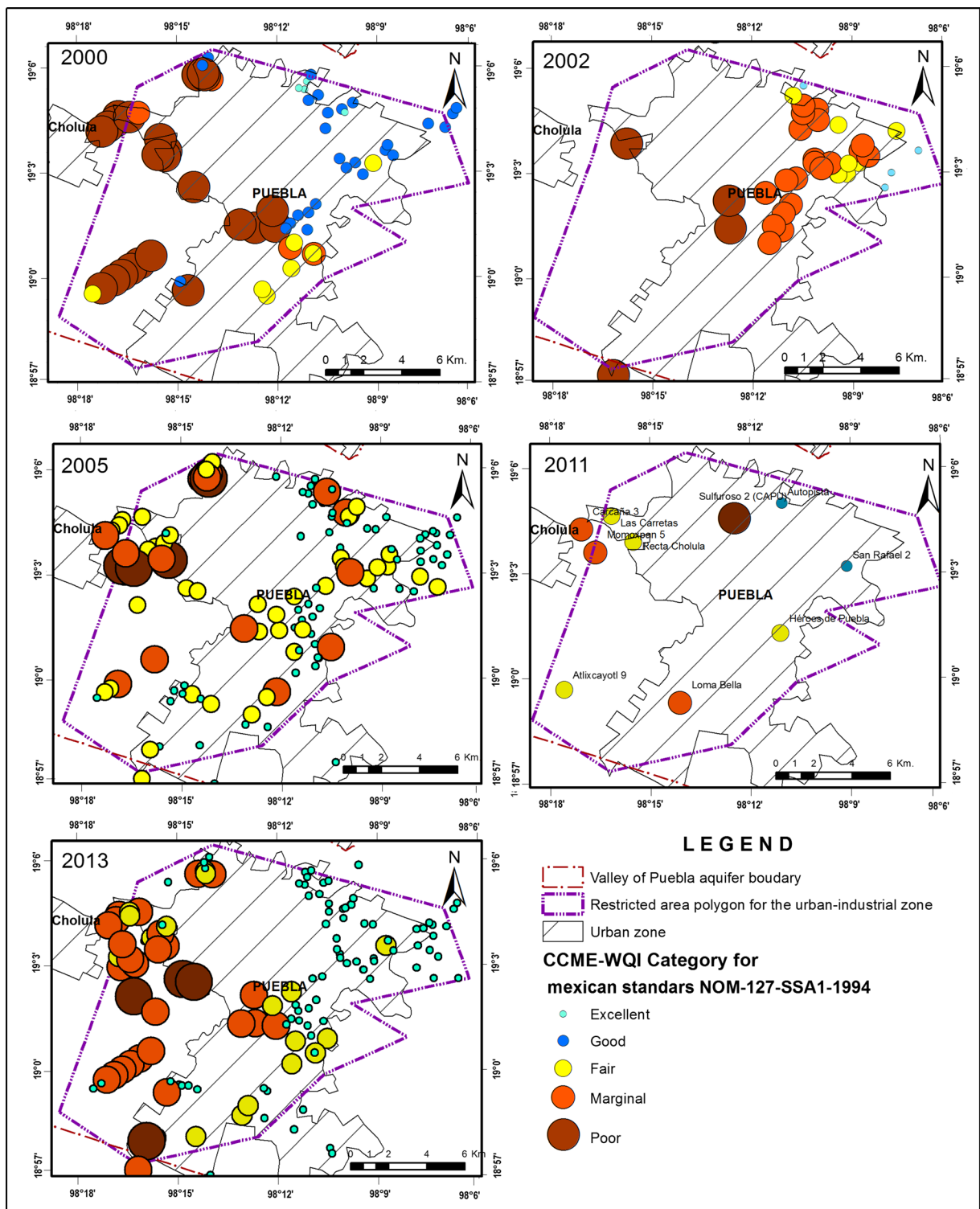
Fig. 8 Spatial and temporal distribution of the CCME-WQI classification in the urban region of the Puebla Valley aquifer based on Mexican standards (NOM-127-SSA1–1994)
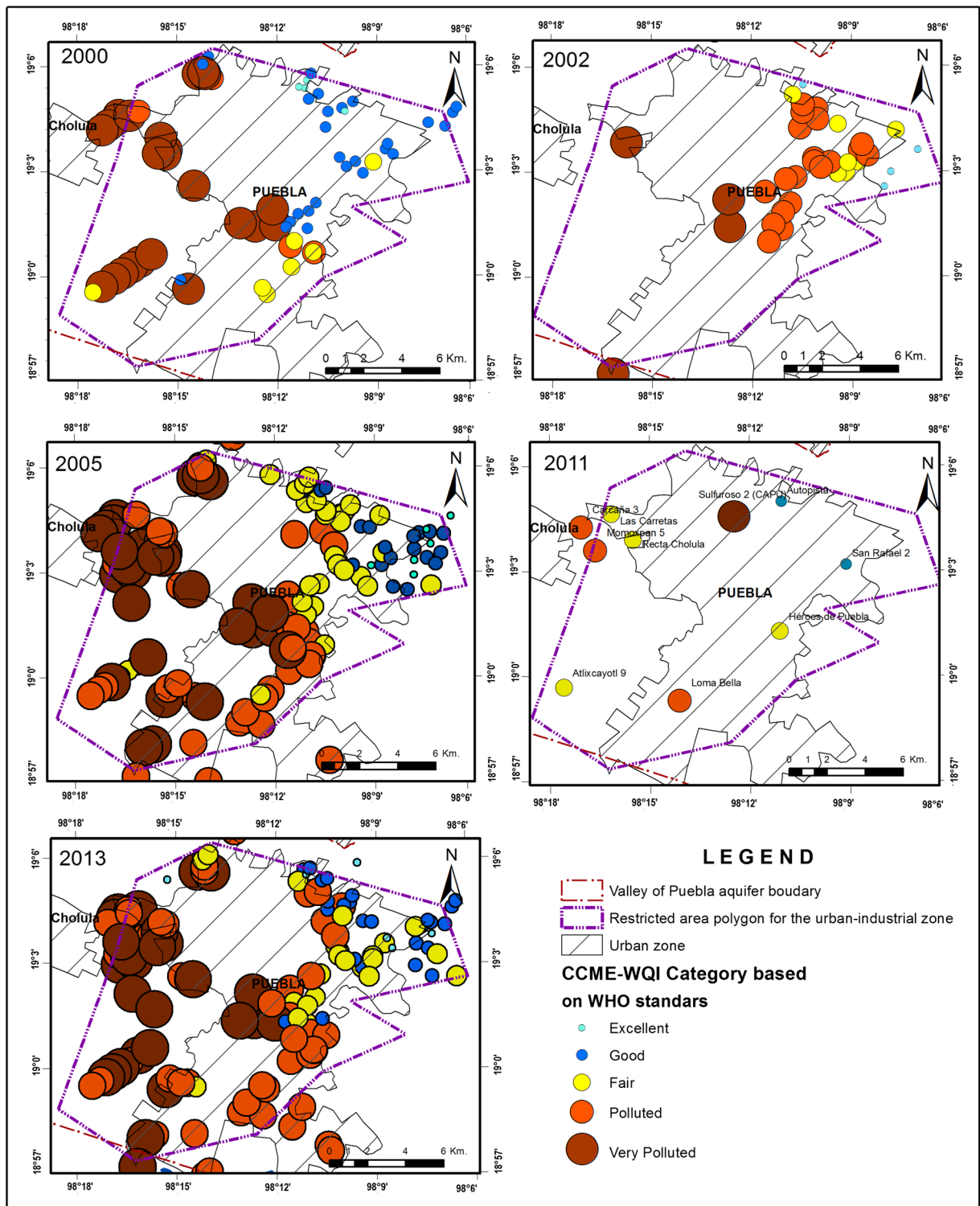
Fig. 9 Spatial and temporal distribution of the CCME-WQI classification in the urban region of the Puebla Valley aquifer based on WHO criteria

upward migration of the water from the deep aquifer, which is also facilitated by the existence of faults and fractures (Garfias et al. 2010).

After the mineralized water rises from the deep aquifer it mixes with the water in the upper aquifer, which has a lower saline content. The mixing proportions of each type of water differ depending on factors such as the depth of the catchment (depending on the water that can be extracted directly from the deep aquifer) and the location of the well (the effect on a well located near faults and fractures is not the same as one located further away, nor is it the same for wells near drawdown areas and those located at distances further away). These factors would explain the large spread found in the concentrations of the parameters that are affected by the mixing between the two types of water and, therefore, the water quality may vary depending on the characteristics (depth and location) of each well.

The geostatistical analysis was not able to predict a trend in the solute plume. This feature could be the result that water samples were obtained from the entire water column, that is, about 100 to 200 m. In this thickness of the subsurface, the geological units are made up of pyroclastic and volcanic flows produced by the main volcanoes that surround the study area (Popocatépetl, Iztaccíhuatl and Malinche volcanoes). The depositional directions of these materials vary from NE-SW, NW-SE and N-S directions, making almost impossible to detect the influence of the depositional facies on the possible anisotropy of a solute plume. The original groundwater flow direction that run from North to South has been changed in the City of Puebla due to the highly pumping activities for industrial and potable use. This groundwater abstraction has caused a series of drawdowns that basically overshadow a possible plume orientation, thus, resulting a complex mixing of the solutes that comes from the deeper aquifer with the shallow groundwater.

The isoconcentrations maps of TDS during the period 2000–2013 show the evolution of the water quality in the upper aquifer (Fig. 4). In 2000, the highest concentrations of TDS (2500 mg/L) were detected in the NW portion, whereas in the remainder of the zone, concentrations were less than 400 mg/L. In 2002, the highest TDS concentrations were found in the northern portion and the center of the City of Puebla, with values ranging from 1700 to 1300 mg/L. In 2005, the highest concentrations of TDS were identified in the NE and the central sector of the study zone (1200 mg/L). In 2011 the highest concentrations of TDS (1600 mg/L) were

detected in northern portion and the center of the City of Puebla. In 2013, the highest concentrations were located NW and central part of the study area, with maximum values of 1680 mg/L, whereas concentrations were less than 750 mg/L in the remainder of the zone. Puebla is one of the first industrial centers of Mexico. The textile industry came to Puebla with La Constancia factory, at north of the city, then a significant development of textile factories in the periphery of the historical center were located, in this area there is a high demand for water and the highest concentrations of TDS. The water quality represented through the CCME-WQI index (Figs. 8 and 9) confirms the trend of high concentrations of TDS; the deterioration of water quality is more visible in the northwest and center of the city, associated to areas of water depletion and upwelling of mineralized water.

Expansion of the urban zone in the central portion of the Puebla valley aquifer is a consequence of industrialization and migratory flow of population. Water needs are exclusively met by groundwater, causing an intense exploitation of the aquifer and water quality changes. The noticeable groundwater quality changes associated with intensive extraction, generally include the presence of two types of inputs, the induction of older groundwater with longer residence times and a distinctive chemical composition in the production zone; and the incorporation of shallow and younger waters that may be include anthropogenic components (Esteller et al. 2012). But the analysis suggests that chemical changes in the urban zone of Puebla Valley aquifer can be associated to alterations of local flow system and upwelling mineralized water with an induction natural water including elements at concentrations above drinking water standards (sulfates, magnesium and calcium).

Conclusions and recommendations

The quality of the water in the Puebla Valley aquifer is being negatively affected by the depletion of the upper aquifer, which is contributing to a decrease in piezometric levels. This in turn enables water from the deep aquifer to migrate up into the upper aquifer and mix with the water in that aquifer. The water in the deep aquifer has high concentrations of sulfates, calcium and magnesium (which in turn are reflected in high TDS and hardness) resulting from the dissolution of sulfated (gypsum, anhydrite) and carbonated (calcite) minerals

contained in the geological materials that make up the deep aquifer.

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

To acquire more precise knowledge about the evolution of the water quality the evolution of each well would have to be studied and the catchment depth of each would have to be considered since, for example, the quality would differ among wells that capture only the surface, middle or deep aquifer.

It is important to implement sustainable extraction and operating conditions for wells located in the urban zone. Controlling these conditions will help to decrease poor water quality and increase the useful life of the wells. Otherwise, if the current extraction volumes continue, the piezometric levels will continue to decrease, the drawdown cone would grow and the thickness of the freshwater in the upper aquifer would decrease as the proportion of sulfated water in the upper aquifer increases.

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