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ORIGINAL ARTICLE

Hydrogeological and mixing process of waters in aquifers in arid regions: a case study in San Luis Potosi Valley, Mexico

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Abstract The climatic conditions of arid regions are characterized by high temperatures, low precipitation and high evapotranspiration rates that can explain the reduced recharge of aquifers. Thus, in these regions, there are some problems related to the groundwater quality and recharge that makes worse the problem of groundwater supply. A model, taking into account ternary mixtures, is presented and applied to a case study: the aquifer of San Luis Potosi valley located in the highlands of the central part of Mexico. In this valley, four hydrochemical facies were identified that correspond to the Ca–Na + K–HCO_3, Na + K–Ca–HCO_3, Ca–HCO_3 and Ca–SO_4 types. From this characterization, it was found out that the recharge area (known as Bledos Graben) is located at the SE of the valley; the deep water flow comes from there (Villa de Reyes and Alvarez Range) to the center of the valley. Mixture fractions were obtained by using chlorides and fluorides as conservative elements, from which it was possible to quantify the contribution of each member to the groundwater quality. According to these results, the contributions to the water extracted from this aquifer are as follows: shallow flows 50%, deep flows from Villa de Reyes 27%, and flows coming from the Alvarez Ranges about 15%.

Keywords Hydrochemistry · Mixing process · End-member · Groundwater

Introduction

The groundwater can be a mixture of waters of different chemical composition due to natural or anthropogenic processes (Harpaz and Bear 1964). To quantify the contributions of water mixtures to the underground flows one can make use of traditional hydrochemistry tools, particularly the conservative elements frequently considered as tracers. The mixtures can be binary or ternary; the first ones have been explained thoroughly in numerous publications and have been utilized to quantify the mixture of fresh and marine water (Apello and Postma 1996; Genereux et al. 2002; Ravenscroft and McArthur 2004; Wallick 1981; Lee and Krothe 2001; Abu-Jaber 2001; Skalbeck et al. 2002; Valentino and Stanzione 2002; Moise et al. 2000). However, models of ternary mixtures have been less identified and studied. For instance, Rice and Hornberger (1998) evaluated the contribution of peak flow to the groundwater in USA, and Genereux et al. (2002) evaluated the interbasin transfer in Costa Rica. Also, Laaksoharju et al. (1999) and Douglas et al. (2000) have reported that the mixture of three types of water with different chemical conditions can promote chemical reactions in an aquifer.

This manuscript describes the case of a ternary mixture in an arid zone in the central part of Mexico,

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San Luis Potosi. The study area is located south of San Luis Potosi, Mexico, in a wide valley bordered on to the West by the San Miguelito Range and to the East by a series of mountain chains including the Alvarez Range (Fig. 1). In this research, the mixing conditions of different groundwater flows in the graben of Villa de Reyes and San Luis Potosi were examined. The approach of this study is based on the hydrochemical characterization of the groundwater and the use of conservative elements to obtain the mixing fractions from which each end member contributes to the groundwater flow and chemical characteristics of water in the valley. Three end members were identified, two of which are associated with deep flows, one having a thermal component, and the other one being related to meteoric water of recent infiltration. These considerations were very important to establish the flow patterns and the mixture relations.

Study area

Because the study area is located in the intersection of the tectonic graben of San Luis Potosi, with preferential orientations N–S, and Villa de Reyes, from orientation NE–SW, a series of structures (graben and horst) are located in the valleys underground that can modify the flow direction in the valley. Another tectonic graben of fewer dimensions with orientation NW–SE (Bledos Graben) also intersects the Villa de Reyes Graben in the southern part of the valley. This valley is important because it supplies water to a thermoelectric plant located in Villa de Reyes (Carrillo et al. 1992). The valley originally had a hydrological system from SW to NW; however, since the colonial period, several small reservoirs were constructed that have modified the superficial runoffs. Nowadays the old reservoirs have been filled with sediments and are

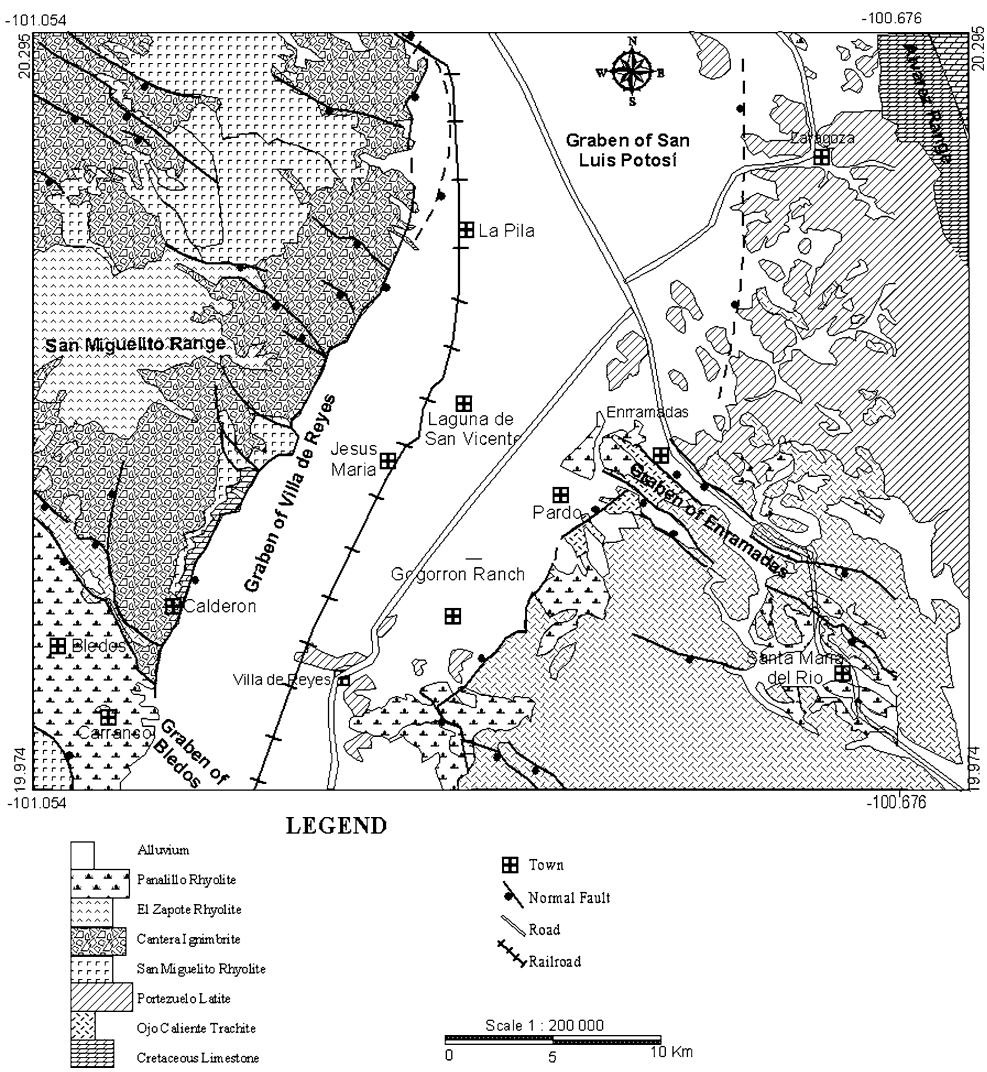


Fig. 1 Study area location

used as agriculture fields in Villa de Reyes (Carrillo et al. 1992). The annual precipitation mean is 400 mm and the average temperatures are 17.8°C, with monthly maximum temperatures in the month of May reaching up to 24.7°C (Moreno et al. 2004).

Hydrogeological background

The geology of the study area has been described by Labarthe et al. (1982). The rocky basement consists of volcanic rocks (rhyolites, trachites, and latites) of the Tertiary (Oligoceno), and a thick sedimentary packet fills the grabens that are composed of sandstones, siltstones, and conglomerates of Quaternary age (Fig. 2). Alluvial fans are distributed on both limits of the valley, for the most part carbonated fragments on the Alvarez ranges, whereas in the San Miguelito Range volcanic fragments predominate (Fig. 1).

The water table contour shows the saturation zone surface on the valley (Fig. 2), and the maps are based on the measurements of October 2003 (Martinez 2003). The groundwater levels vary from 45 to 163 m deep and the elevation ranges are between 1,653 and 1,881 m. The water table contour also shows that the flow is controlled by the topography of the valley.

The highest elevations are located in the left side of the valley and the lowest elevations are located in the drawdown toward the up right inside extreme of the area. The higher elevations are associated with the main recharge produced from the graben of Bledos to the W of the valley (Fig. 2).

In general, the direction of the regional flow is SW–NE, through the graben of Villa de Reyes (Carrillo et al. 1992), and because of this the structural control is very important in the aquifers hydrodynamic. The presence of clay-containing materials in the graben of San Luis Potosi toward the north part of the study area can also be contributing to the underground flow control. Induced recharge on the water table contour configuration can be observed due to some civil constructions such as reservoirs for water (Fig. 2).

Methods

Groundwater samples ($N = 25$) from the Villa de Reyes–San Luis Potosi grabens were collected in September 2003 at the near end of the dry season and the major cations and anions were determined. Figure 1 shows the distribution of well sampled.

All groundwater samples were collected in polyethylene bottles for the analysis of mayor ions. Briefly, high density linear polyethylene sample bottles (HDLP) were first triple washed with copious amounts of distilled–deionized water. Immediately after, samples were collected and acidified to pH < 2 with ultra pure nitric acid. Samples for the anions determination were not acidified. For each collected sample pH,

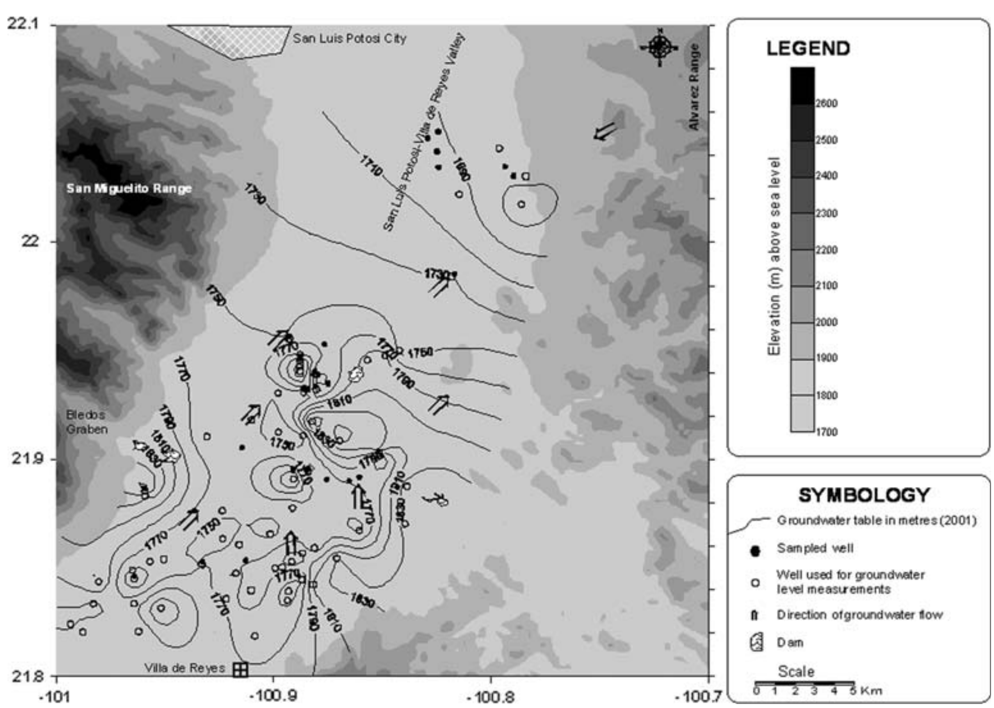


Fig. 2 Static level elevation and flow directions in the San Luis Potosi–Villa de Reyes valley

conductivity, and alkalinity were measured on site using standard field procedures (Martinez 2003).

Major ions and F were analyzed at the Laboratory of the National Water Commission (Comision Nacional del Agua, CNA). Concentrations of the major cations Ca, Mg, Na, and K were determined by ICP-OES and major anions (SO_4 and Cl) were analyzed using high performance liquid chromatography. Alkalinity and HCO_3 were determined on site by titration.

A graphical representation was used for detecting the mixture of water of different compositions and for identifying water chemical types and their genesis (see Figs. 6, 7, 8, and 9).

The saturation index (SI = logIAP/K where IAP is ion activity product and K is solubility product) with respect to calcite (SI_{CA}), aragonite (SI_{AR}), dolomite (SI_{DO}), gypsum (SI_{GY}), fluorite (SI_{FL}), and anhydrite (SI_{AN}) were calculated using the numerical model PHREEQE (Parkhurst and Apello 1999).

Water samples ($N = 47$) were collected during the sampling period from which only those that had an ionic balance error (electro neutrality) lower than 5%, 25 samples, were taken into account (Table 1).

Results and discussion

The central part of Mexico has a common tectonic evolution that gave origin to the formation of aquifers formed by wide valleys fillers with sedimentary material on a base of fractured volcanic rock. Some of these hydrogeological scenarios have been studied to the north of the study area (Carrillo 2000) and in neighbors valleys as that of Villa de Reyes (Carrillo et al. 1992), León Valley (Johannesson et al. 2005; Ramos et al. 2005), Aguascalientes Valley (Carrillo et al. 2001) and aquifer of The Independence (Mahlknecht et al. 2004). The mixture relationships among the shallow and deep aquifers are reported for each region in different contexts. The influence of regional and thermal flows on shallow aquifer is described by Carrillo (2000) and Carrillo et al. (2001), whereas Mahlknecht et al. (2004) identify as main cations source the meteorization of carbonates and albite.

The chemical analyses and saturation indexes for calcite, dolomite, anhydrite, aragonite and fluorite of the samples utilized in this work are reported in Table 1.

Hydrochemistry

The hydrochemistry of groundwater has been influenced by various factors that include the aquifers mineralogical composition, longitude and depth of the flows systems, underground temperatures, residence time and evaporation processes.

Figure 3 shows the hydrochemical behavior along two flow paths. Flow path A runs through the valley of

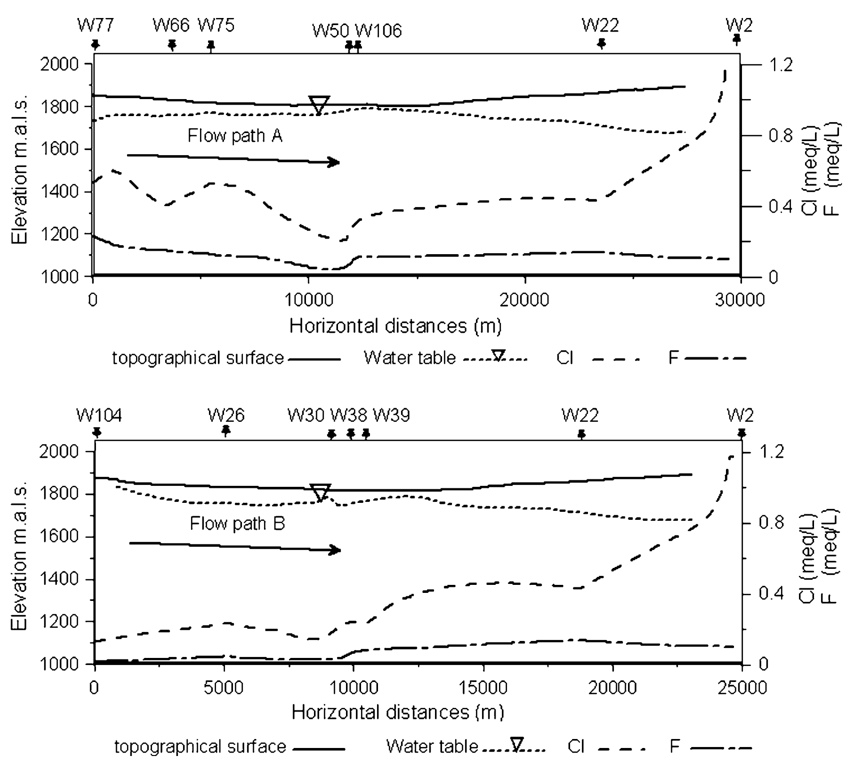


Fig. 3 Concentration of conservative constituents in groundwater samples in the San Luis Potosi–Villa de Reyes valley. The *arrows* indicate the direction of groundwater flow along flow paths

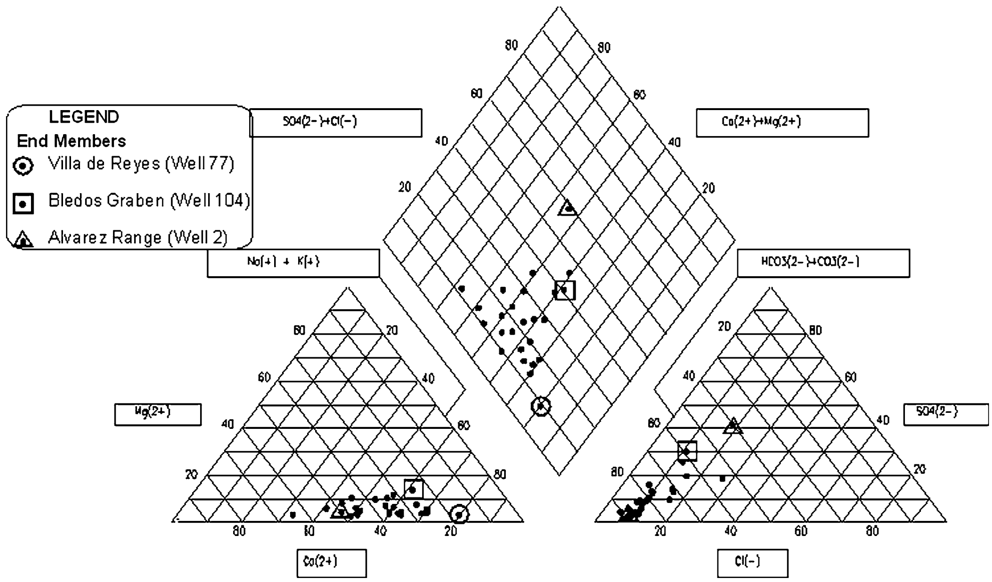


Fig. 4 Pipers diagram

Table 1 Hydrochemical data from the San Luis Potosi Valley aquifer, saturation indexes of calcite (SI_{CA}), aragonite (SI_{AR}), dolomite (SI_{DO}), gypsum (SI_{GY}), anhydrite (SI_{AN}) and fluorite (SI_{FL})

Well	Ca (meq/L)	Mg (meq/L)	Na (meq/L)	K (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	SO4 (meq/L)	F (meq/L)	SI_{CA}	SI_{DO}	SI_{AR}	SI_{GY}	SI_{AN}	SI_{FL}	Error (%)
1	1.2	0.12	2.02	0.18	2.5	0.53	0.47	0.12	0.44	0.1	0.3	–2.59	–2.76	–0.81	1.26
2	1.62	0.16	2.35	0.24	2.5	1.28	0.82	0.1	0.44	0.09	0.3	–2.26	–2.43	–0.84	3.53
6	1.86	0.2	1.76	0.22	2.55	0.64	0.76	0.06	0.59	0.34	0.44	–2.22	–2.44	–1.15	0.49
8	2.74	0.2	2.17	0.28	2.13	1.01	2.16	0.06	0.51	0.19	0.36	–2.2	–2.44	–1.16	0.28
9	1.66	0.14	2.37	0.26	2.7	0.53	1.1	0.12	0.65	0.35	0.5	–2.12	–2.34	–0.6	0.34
10	1.74	0.16	1.76	0.17	2.6	0.59	0.46	0.1	0.7	0.52	0.56	–2.46	–2.67	–0.74	1.19
18	1	0.16	1.13	0.57	1.98	0.45	0.24	0.06	0.05	–0.58	–0.1	–2.92	–3.15	–1.27	2.32
21	0.84	0.28	1.07	0.41	1.87	0.24	0.3	0.05	–0.03	–0.41	–0.18	–2.89	–3.11	–1.62	2.57
22	1.48	0.1	2.48	0.22	3.33	0.43	0.4	0.14	0.54	0.08	0.4	–2.59	–2.8	–0.52	0.12
26	1	0.28	1.17	0.43	2.08	0.24	0.19	0.05	–0.11	–0.64	–0.25	–3.01	–3.23	–1.53	5.88
27	0.8	0.08	1.64	0.3	2.29	0.29	0.14	0.11	–0.08	–0.97	–0.22	–3.23	–3.42	–0.99	0.18
30	0.64	0.08	1.03	0.65	1.87	0.21	0.07	0.04	–0.53	–1.83	–0.67	–3.59	–3.81	–1.96	4.57
33	2.66	0.4	1.79	0.6	4.21	0.43	0.82	0.03	0.6	0.47	0.45	–2.09	–2.32	–1.48	0.36
38	0.64	0.12	1.24	0.48	1.87	0.24	0.19	0.07	–1.02	–2.62	–1.16	–3.18	–3.4	–1.37	2.47
39	0.64	0.16	1.18	0.33	1.81	0.23	0.06	0.08	–0.81	–2.07	–0.95	–3.64	–3.85	–1.27	2.89
46	0.68	0.12	0.74	0.31	1.8	0.17	0.01	0.03	–1.36	–3.33	–1.5	–4.39	–4.61	–1.99	4.39
47	0.96	0.2	0.7	0.28	2	0.19	0.04	0.04	–1.15	–2.88	–1.3	–3.65	–3.87	–1.63	2.71
48	1.3	0.12	0.61	0.36	2.2	0.19	0.11	0.02	0.14	–0.69	–0.01	–3.14	–3.38	–1.96	2.65
50	1.24	0.04	0.43	0.17	1.8	0.19	0.04	0.06	–0.36	–2.14	–0.51	–3.53	–3.77	–1.19	5.29
66	2.2	0.08	1.91	0.28	3.9	0.4	0.41	0.15	–0.53	–2.35	–0.67	–2.43	–2.64	–0.28	4.18
69	0.88	0.2	0.91	0.28	2.2	0.27	0.07	0.06	–1.22	–2.96	–1.37	–3.52	–3.74	–1.37	6.58
75	2.16	0.12	2.06	0.26	3.9	0.53	0.58	0.13	–0.4	–1.93	–0.55	–2.29	–2.51	–0.39	5.54
77	1.56	0.2	6.09	0.81	8.5	0.53	0.31	0.24	–0.65	–1.85	–0.7	–2.79	–2.94	–0.19	5.10
104	0.32	0.16	0.48	0.28	0.7	0.13	0.35	0.02	–2.07	–4.33	–2.21	–3.16	–3.39	–2.78	1.64
106	1.56	0.12	1.74	1.02	3.8	0.35	0.37	0.13	0.35	–0.21	0.21	–2.61	–2.8	–0.62	2.31

Villa de Reyes and it goes by the end members of Villa de Reyes and Sierra de Alvarez (wells 77 and 2). The flows in the valley show high concentrations of F and Cl, and in well 2 the concentration of Cl increases even more whereas the concentration of F decreases a little. This behavior signifies that the end member two has different origin. On the other hand, flow path B goes by the end members of Bledos graben and Sierra de Alvarez (wells 104 and 2). At the beginning of this flow, the concentrations of Cl and F are low but these increase in direction of the groundwater flow although the concentration of F diminishes at the end member Alvarez Range, which is caused by the mixture with the local recharge.

Table 2 Field data and mixture fractions between three end members

Well	pH	EC (μS/cm)	T (°C)	F_{LR} (%)	F_{AR} (%)	F_{VR} (%)
Group I						
1	8.1	370	34.5	0.39	0.19	0.41
2	8	503	34	0.01	0.87	0.12
6	8.2	410	25	0.52	0.38	0.09
8	8.1	580	26	0.3	0.7	0
9	8.3	478	–	0.39	0.19	0.41
10	8.3	380	27	0.42	0.28	0.3
22	8.1	450	27.5	0.39	0.07	0.54
33	7.9	555	22	0.75	0.25	0
106	7.76	445	32	0.47	0.02	0.51
Group II						
18	8	280	24	0.64	0.22	0.14
21	8	260	25	0.8	0.05	0.15
26	7.8	288	25	0.8	0.05	0.15
27	7.8	300	31	0.57	0	0.43
48	7.98	231	20	0.93	0.06	0.01
Group III						
30	7.6	240	–	0.85	0.04	0.11
39	7.3	240	27	0.71	0	0.3
50	7.57	212	20	0.8	0	0.21
66	6.8	554	26	0.37	0.03	0.59
75	6.95	534	25	0.36	0.18	0.46
77	6.42	950	36	0	0	1
Group IV						
38	7.1	250	26	0.73	0.02	0.24
46	6.75	202	25	0.91	0.03	0.07
47	6.79	228	23.5	0.86	0.03	0.11
69	6.7	253	–	0.75	0.06	0.19
104	6.79	121	23	0.96	0.01	0.03

The hydrochemical results of the water samples are plotted in Piper's diagram (Fig. 4). Four facies were recognized in the groundwater of study area and the abundance order is as follows (Table 2): Na + K + Ca–HCO_3 > Ca + Na + K–HCO_3 > Ca–HCO_3 > Ca–SO_4 (Fig. 4).

The facies Ca–HCO_3 are associated mainly with the water circulation through fragments of volcanic rocks and carbonated minerals rich in calcium.

Some samples of group Na + K–Ca–HCO_3 show a change to the facie Ca–SO_4, which is one of the most evolved flows and manifest the carbonated material influence. Another observed change is the facie Ca–Na + K–HCO_3 to Na + K–Ca–HCO_3; this last facie is very evolved and it is characteristic of high temperatures (thermal).

The physicochemical parameters (pH, EC, T) show low values in the W zone of the study area (Fig. 5). This is related to an important water recharge diluted in chemical components, which is also observed in the water table contour (Figs. 2, 3) or to the low solubility of minerals (this related to the clays where they are present).

In general, the hydrochemical parameters increase in two big zones (Fig. 5, 6). The first one is located in the NE extreme where samples 2 and 8 are located. This zone coincides with the exit of the regional flow of the Villa de Reyes graben (Figs. 5, 6). The second zone is located to the south of the study area where sample 77 is located, and where some thermal wells are also situated (Carrillo et al. 1996). The contrast areas either with low or high concentrations are related to the end members definitions in the study area (Figs. 5, 6). Some diluted zones could be associated with the water infiltration from small superficial reservoirs (Figs. 2, 3).

The pH of water samples varied from 6.42 to 8.3. Values lower than seven are mainly located in the SW zone of the valley, and are associated with water that have circulated generally in volcanic rocks. Wells with pH values between 7 and 8 are distributed in the central part of the graben, and are related with waters that have been spread through sedimentary filling mostly compose of fragments of volcanic rocks. Wells with pH values higher than 8 are distributed on the NE region of the valley, this high pH values show the interactions with sedimentary deposits of alluvial fans where carbonated fragments are predominant (Fig. 5).

The electrical conductivity varies from 121 to 950 μS/cm. The lowest values are distributed in the central part W of the valley. These values are related to important recharges to the aquifer through the graben of Bledos. Values higher than 450 μS/cm are located in the S, E, and NE of the valley and are related to the most evolved water of the system (Fig. 5).

Low values of temperature, <25°C, are located in the central and western parts of the valley. These are justified for both the natural recharge through the Bledos graben and for the induced recharge due to water reservoirs. High values are specifically located to the NE and SW of the valley (Fig. 5).

On the other hand, the chemical analyses report that the highest concentrations of F are located to the S, in the thermal zone, where sample 77 reached the highest value (0.24 meq/L). The lowest values are distributed in the central–west of the valley that is possible due to the diluted recharge (low in F) in the Bledos graben, sample 104 only reached 0.02 meq/L of this element. Another zone with low concentration of F was located to the NE of the valley; these low values are probably due to the flows coming from the alluvial fans rich in carbonated rocks (Figs. 2, 3, 6).

The low Cl concentrations are found in the central part and W of the valley; these values are related to the natural local recharge and to both the induced recharge by reservoirs. The high concentrations of this element are found in the NE and S of the valley

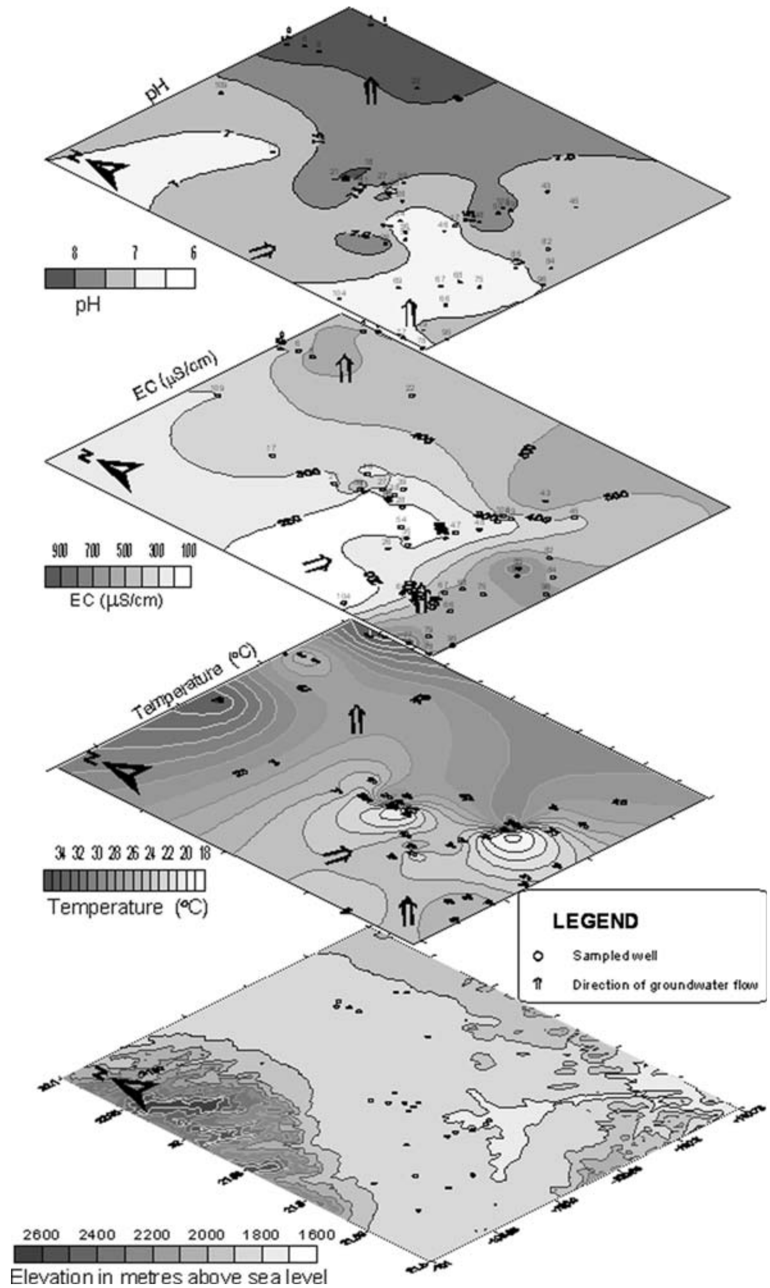


Fig. 5 Distribution of pH, EC and T in the San Luis Potosi–Villa de Reyes valley

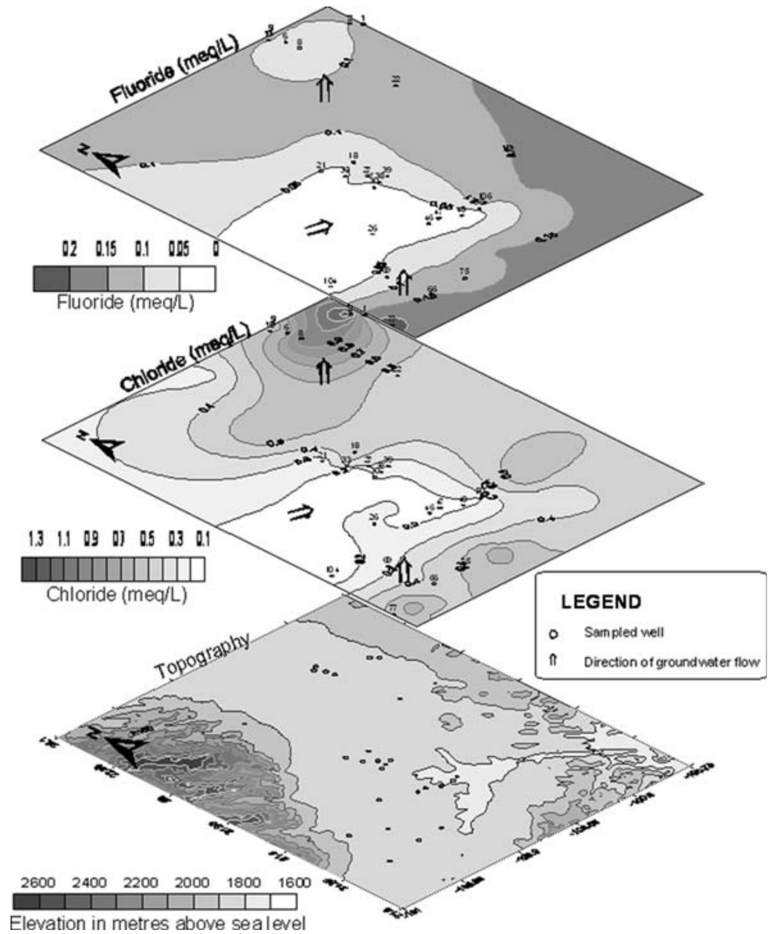
because these waters have circulated through the carbonated materials found in the Alvarez Range (Figs. 2, 3, 6).

The distribution of SO_4 is very similar to other components. The low SO_4 concentrations are found in the central part and W of the valley; these values are also related to the natural local recharge and to the induced recharge by reservoirs. High concentrations of this element are found in the NE and S of the valley because these waters have circulated through the carbonated materials found in the Alvarez Range (Fig. 1).

The scatter plots of the different components show a ternary mixture mainly for the local recharge with the evolved end members, the mixture between the evolved end members is not very evident (Figs. 7, 8).

Two important processes of mixing and/or evolution based on different dispersion diagrams of hydrochemical parameters can be observed (F/Cl, HCO_3/Cl, EC/Cl, Na/Cl, Na/Ca, K/Cl, F/Ca, F/EC, Ca/SO_4, Ca/Mg, (SO_4/Cl)/HCO_3, EC/SO_4). The first one involves the local recharge and the mixture and/or evolution to the thermal end member, represented by sample 77. Samples with high fluoride concentrations are thermal;

Fig. 6 Distribution of F and Cl in the San Luis Potosi–Villa de Reyes valley



the enrichment of water with F can be related to the fluid interaction with fluorite or apatite (Fig. 7) found in volcanic rocks such as latites (Figs. 6, 7, 8). The second process includes the mixture of the local recharge and of a very evolved end member represented by samples 2 and 8 and the temperatures reach 34°C (Fig. 5).

Samples concentrated in Ca are associated with water circulation through alluvium that is made of conglomerates composed of $CaCO_3$ (Fig. 8e). The low Mg concentration is due to the hindered circulation of water through basaltic rocks and also to the precipitation of dolomite in some samples.

The water samples show high concentration of K that could be related to the flow circulation in trachites (Fig. 7). It is clearly observed that the two water evolved processes in the study area have low and high concentrations of K and Cl, respectively. The samples that present this tendency are mainly located in the NE extreme of study area where the water circulation occurs in sediments rich in carbonates (Fig. 1). In the other process, K is increased rapidly and Cl barely rises. This last group is mainly found in the NE zone of Villa de Reyes and its circulation happens in latites rich in K-feldspars. Another group low in Cl and K is also registered, but it is associated with the local recharge (Figs. 2, 5, 6, 7).

Four main groups are distinguished based on the saturation indexes (Figs. 9, 10)

Group I: Oversaturated for aragonite, calcite, and dolomite as shown in Figs. 9 and 10. This group is mainly distributed in the NE zone of the study area; it is rich in carbonates, has alkaline pH and it is influenced by flows coming from the NE that interact with alluvial fans with clast of carbonates (Figs. 2, 5).

Group II: Equilibrated with calcite, dolomite, and aragonite (Figs. 9, 10). This group is undersaturated with respect to anhydrite, gypsum, halite, and fluorite and it is distributed in the central part of the valley. It is formed with water that mainly moves in the sedimentary packet, which fills the Villa de Reyes and San Luis grabens (Figs. 1, 2). These fillings are made of volcanic rocks (latite).

Group III: Undersaturated with respect to calcite, dolomite, plaster, fluorite, halite, and aragonite (Figs. 9, 10), and it is located to the south of the valley.

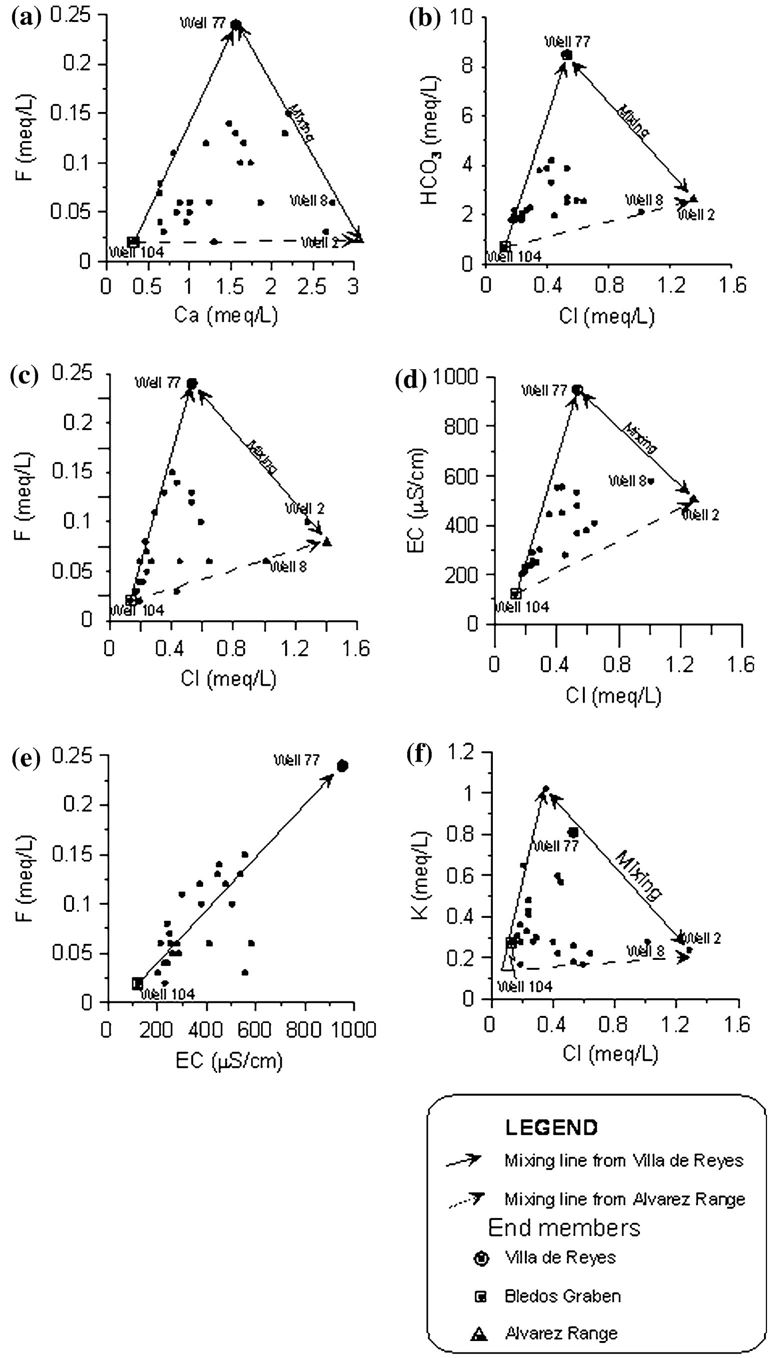


Fig. 7 Scatter plots for HCO_3/Cl, EC/SO_4, F/Cl, EC/Cl, F/EC, K/Cl

The groundwater moves through volcanic rocks such as latite (Figs. 1, 2).

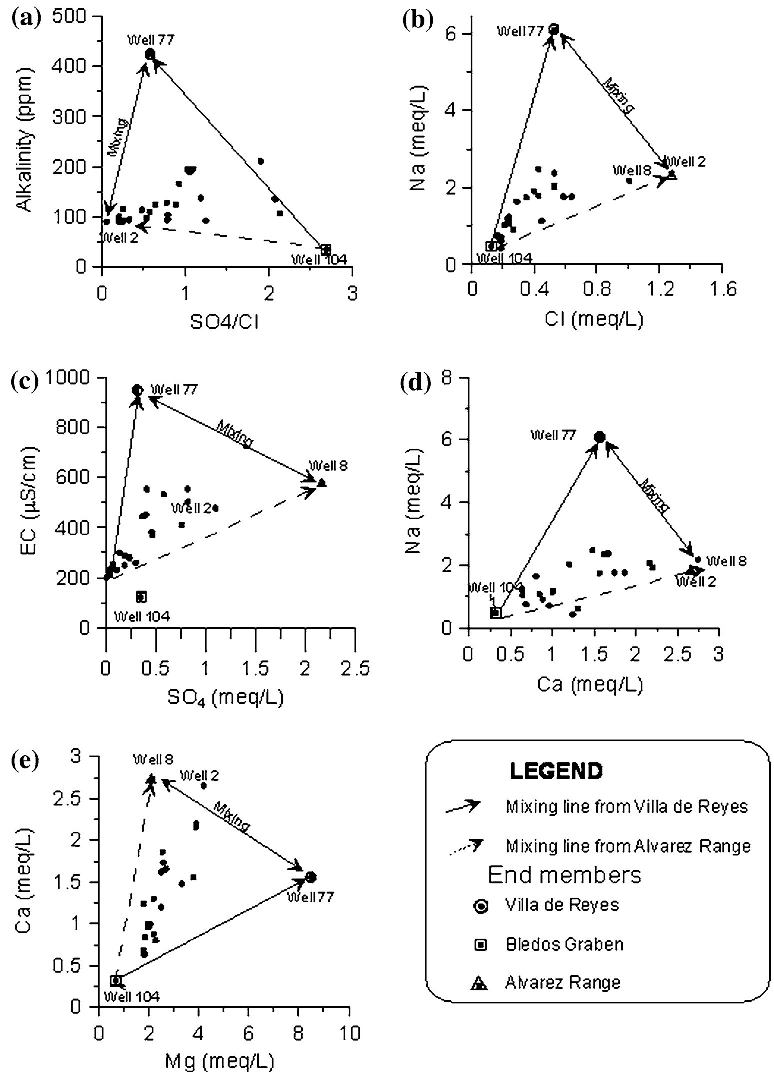
Group IV: Due to its low dissolved solid content, this group is the most diluted and because of this it is undersaturated with respect to different minerals. This group is distributed in the SW of the valley and it is related to shallow flows that move through the Bledos graben, which is filled with litic tuffs rich in silica (Figs. 9, 10).

Origin of end members

Three end members are observed, two very evolved and another one associated with the local recharge (Figs. 7, 8).

1. Graben of Bledos member (LR): This belongs to group IV, it is associated to the local recharge, it has low values of Cl, SO_4, and F, the lowest values

Fig. 8 Scatter plots for SO_4–Cl/Cl, F/Ca, Na/Cl, Na/Ca, Ca/SO_4, Ca/Mg



were found in sample 104 with 0.13 meq/L of Cl, 0.35 meq/L of SO_4, and 0.02 meq/L of F and the temperature is 23°C. The type of this member is Na + K–HCO_3 (Figs. 3, 7–10).

2. Villa de Reyes member (VR): It belongs to group III and it is represented by sample 77 located in the south part of the valley. This water sample represents regional flow, has high temperatures (36°C), and 0.53 meq/L of Cl, 0.31 meq/L of SO_4, and high F concentrations of 0.24 meq/L. This type of water is Na + K–HCO_3 (Figs. 3, 7–10).
3. Alvarez member (AR): It belongs to group I, it is represented by samples 2 and 8, and it is located in the left side of the Villa de Reyes valley. It represents a regional flow originated from the Alvarez Range. Sample 2 is the most representative of this member; it has a temperature of 34°C, and Cl, SO_4, and F concentrations of 1.28, 0.82, and 0.1 meq/L, respectively. The water type of this member is Na + K–HCO_3 with tendency to Na + K–SO_4 in sample 8 (Figs. 4, 7–10).

Mixing calculations

Based on the dispersion graphs behavior, ternary mixing processes were identified between end members (Figs. 7, 8). The composition of each sample can be expressed as a percentage of end members, and the water from wells was classified as a fraction of mixture of end members from hydrochemical parameters.

Dispersion graphs were obtained using different hydrochemical parameters on which three end members were always distinguished and the rest of water samples were delimited for these mixing lines.

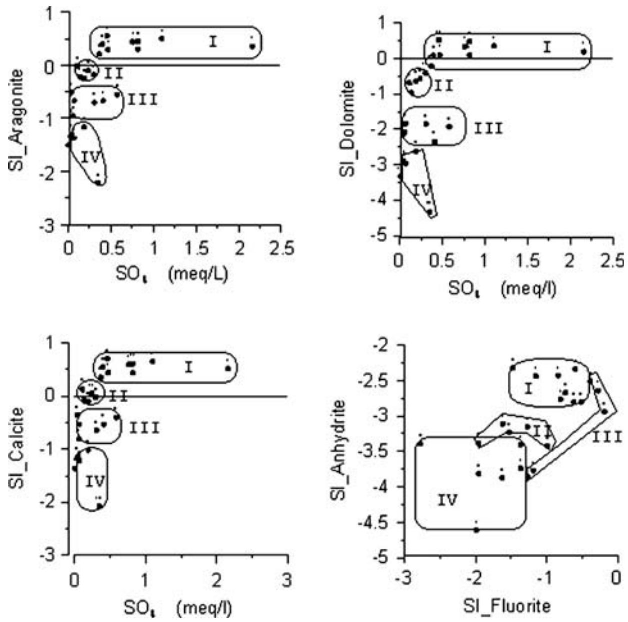


Fig. 9 Scatter plots for saturation indexes of aragonite/SO_4 (**a**), dolomite/SO_4 (**b**), calcite/SO_4 (**c**), anhydrite/fluorite (**d**)

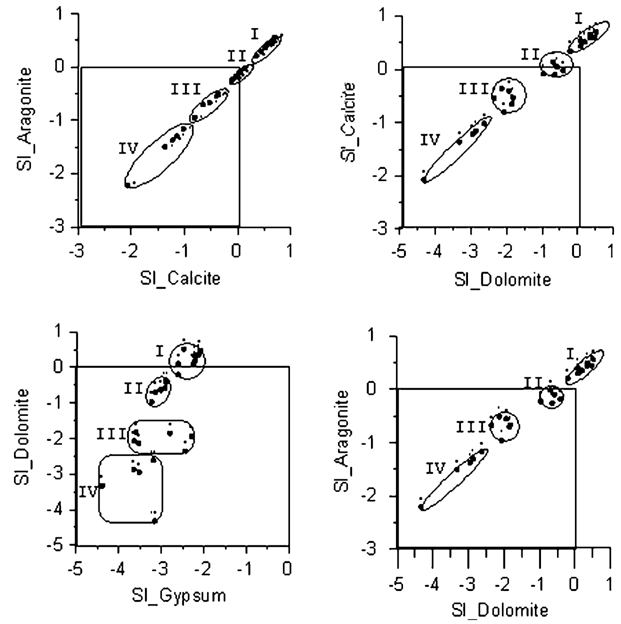


Fig. 10 Scatter plots for saturation indexes of aragonite/calcite (**a**), calcite/dolomite (**b**), dolomite/gypsum (**c**), aragonite/dolomite (**d**)

Conservative elements such as Cl, ^{18}O, δD, F, Li, and SO_4 have given good result in models of three components (Rice and Hornberger 1998; Douglas et al. 2000; Lee and Krothe 2001).

To obtain the mixing fractions, two conservative elements were utilized, Cl and F. The concentration ranges of Cl in groundwater in the Villa de Reyes graben varies from 0.13 to 1.28 meq/L and 0.02 to 0.24 meq/L for F.

The percentage calculation was obtained by using three equations with three unknown parameters. The mixture fraction sum, according to the volumetric balance equation, is represented as follows:

$$C_w = C_{LR} + C_{AR} - C_{VR} \quad (1)$$

where C_{LR} is the associated member to the local recharge, C_{AR} is the associated member to the Alvarez Range, and C_{VR} is associated with the flows of Villa de Reyes. C_{LR}, C_{AR}, and C_{VR} are unknown values and C_w is equal to 1.

These components were determined with the equations of the mass balance of two conservative elements Cl and F:

$$C_w Cl_w = C_{LR} \times Cl_{LR} + C_{AR} \times Cl_{VR} + C_{VR} \times Cl_{VR} \quad (2)$$

$$C_w F_w = C_{LR} \times F_{LR} + C_{AR} \times F_{AR} + C_{VR} \times F_{VR} \quad (3)$$

The next equation is obtained by substituting Eq. 2 in C_{VR} of Eq. 1:

$$C_{LR} = \frac{C_W(Cl_W - Cl_{VR}) + C_{AR}(Cl_{VR} - Cl_{AR})}{Cl_{LR} - Cl_{VR}} \quad (4)$$

Substituting C_{LR} from Eq. 3 to Eq. 1 it is obtained:

$$C_{VR} = \frac{C_W(F_W - F_{LR}) + C_{AR}(F_{AR} - F_{LR})}{F_{VR} - F_{LR}} \quad (5)$$

The only possible solution for C_{AR} is when $C_W = 1$. The other two components are calculated substituting C_{LR} and C_{VR} in Eq. 1. The obtained percentages from these mixture fractions for each considered sample are reported in Table 2. As it can be observed, the most prevalent mixture formed is between the members LR and VR.

Conclusions

In San Luis Potosí valley, four facies hydrochemistry types were identified that correspond to Ca–Na + K–HCO_3, Na + K–Ca–HCO_3, Ca–HCO_3 and Ca–SO_4; however, the most important seems to be Na + K–HCO_3. The recharge area (Bledos graben) and main deep flows, from Villa de Reyes and Alvarez Range, were identified as those that feed the San Luis Potosi valley. The direction of the regional flow is SW–NE, through the record of Villa of Reyes.

Group I is distributed mainly in the northeast portion of the study area, influenced by flows coming from the NE that interact with alluvial fans composed of clast of carbonates. This is supersaturated for aragonite, calcite, dolomite, carbonates, and it has alkaline pH. The material type that forms the filler is composed of volcanic rocks such as latite. Group II is in equilibrium with calcite, dolomite, and aragonite, but is subsaturated with anhydrite, gypsum, halite, and fluorite. Group III is located to the south of the valley; the groundwater circulates through volcanic rocks like latite. This group is subsaturated with regards to calcite, dolomite, gypsum, fluorite, halite, and aragonite. Group IV is distributed in the SW of the valley, it is related with shallow flows that circulate through the Bledos Graben, and it is filled with litic tuff rich in silica. This group is low in mineral content for what is subsaturated regarding the different minerals.

Of the characterized groups, three end members were identified. Two end members are much evolved chemically and one is associated with the local recharge. The fourth group corresponds to the ternary mixture of these end members.

The graben of Bledos member (LR) belongs to group IV, it is associated with the local recharge, it has low values of Cl and F, and the temperature is 23°C. The type of this member is Na + K–HCO_3.

The Villa de Reyes member (VR) belongs to group III and it is represented by sample 77 located in the south part of the valley. This water sample represents regional flow, has high temperatures (36°C), and 0.53 meq/L of Cl and high F concentrations of 0.24 meq/L. This type of water is Na + K–HCO_3.

The Alvarez Range member (AZ) belongs to group I, and is represented for samples 2 and 8, and it is located in the left side of the Villa de Reyes valley. It represents a regional flow originated from the Alvarez Range. Sample 2 is the most representative of this member; it has a temperature of 34°C, and Cl and F concentrations of 1.28 and 0.1 meq/L, respectively. The water type of this member is Na + K–HCO_3 with tendency to Na + K–SO_4 in sample 8.

It was possible to quantify the contribution of each end member to the aquifer using mixture fractions, obtained from the conservative elements Cl and F.

According to these results, the contributions to the extraction wells are as follows: shallow flows 50%, deep flows from Villa of Reyes 27%, and flows coming from the Alvarez Range about 15%.

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