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Articles

Water quality for agricultural irrigation in the Calera aquifer region in Zacatecas, Mexico

Calidad del agua para riego agrícola en la región del acuífero Calera en Zacatecas, México

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Abstract

In the region that includes the Calera, Zacatecas aquifer, the intensive production of chili (*Capsicum* ssp.) is of great economic importance, and depends entirely on groundwater. Being an overexploited aquifer in a karst and semi-arid zone, water availability becomes more limited and water quality is relevant. The objective of the research was to evaluate the impact on the chemical quality of the water and determine its aptitude for agricultural use through the criteria of salinity, sodicity and toxicity. For two consecutive cycles, a sampling was performed according to NOM-014-SSA1-1993 to wells that are frequently used for irrigation of chili. Five strata were designed whose depth ranges from 50 to 280 m above the static level. For the three criteria the water quality parameters were determined, their classification was shown on a

Richards diagram and their hydrogeochemistry using a Piper diagram. A statistical analysis of main components, a randomized complete block analysis and a cluster analysis were performed to identify the parameters that have a significant impact on water quality. The results showed that the cultivation of chili has not impacted the quality of the aquifer water and that the depth of the wells does not influence it, rather it depends on the region where each well is located, recharge processes, geology of the region , speed of underground currents and infiltration by the action of faults and geological fractures.

Keywords: Aquifer Calera, water quality, chili production.

Resumen

En la región que comprende el acuífero Calera, Zacatecas, la producción intensiva del cultivo de chile (*Capsicum* ssp.) es de suma importancia económica, y depende por completo del agua subterránea de un acuífero sobreexplotado en una zona cárstica y semiárida, donde la disponibilidad de agua se torna más limitada y la calidad del líquido es de relevancia. El objetivo de la investigación fue evaluar el impacto a la calidad química del agua y determinar su aptitud para uso agrícola mediante los criterios de salinidad, sodicidad y toxicidad. Durante dos ciclos consecutivos se llevó a cabo un muestreo, según la norma NOM-014-SSA1-1993, a los pozos que con más frecuencia se usan para irrigación de chile. De acuerdo con la profundidad resultaron cinco estratos, que van de 50 a 280 m sobre el nivel estático. Para los tres criterios se determinaron los parámetros de calidad de agua; su

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clasificación se mostró en un diagrama de Richards y su hidrogeoquímica mediante un diagrama de Piper. Se analizaron bloques completos al azar, así como los componentes principales y un clúster, a fin de identificar los parámetros que inciden de modo considerable en la calidad del agua. Los resultados evidenciaron que el cultivo de chile no ha impactado la calidad del agua de acuífero y que la profundidad de los pozos no influye en ésta; más bien depende de la región en donde se ubica cada pozo, procesos de recarga, geología de la región, velocidad de las corrientes subterráneas, y la infiltración por la acción de fallas y fracturas geológicas.

Palabras clave: acuífero Calera, calidad de agua, producción de chile.

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Introduction

Underground aquifers are one of the most important sources of fresh water for human supply, and their use has increased significantly as a consequence of the development and growth of the population that is demanding more and more food. The agricultural sector consumes about 70% of fresh water for irrigation of crops. In Mexico, more than half of the groundwater that is destined for agricultural use comes from overexploited aquifers or with the presence of brackish water. Most of them are located in the north and center of the country (Vivot *et al*., 2010; Díaz, Bravo, Alatorre, & Sánchez, 2013).

In the semi-arid areas of Mexico, intensive irrigation agriculture is characterized by a high use of fertilizers and agrochemicals to maintain high yields, competitiveness and quality of the products generated. However, of all human activities that influence water quality, agricultural activity is the most important because it can alter the chemical properties of water by the use of fertilizers and pesticides, since these depending on the transit time Through the unsaturated zone and the capacity of the soils to retard the movement of agrochemicals, they can leach into the aquifers causing an increase in the amount of total solids, and salts of nitrates, sulfates, chlorides and sodium (Bermejillo *et al*., 2012; Torres *et al*., 2014; Bedmar, Gianelli, Angelini, & Vigilianchino, 2015).

Among the most frequent salts in irrigation waters, calcium and magnesium carbonates and bicarbonates as well as calcium sulfate are the least soluble, therefore, the increase in the concentration of salts in the soil solution as a result of evapotranspiration is less than with highly soluble salts since those with less solubility are the first to reach their dissolution limit. If the percolation is low, the possibility of accumulation of salts at the bottom of the profile increases, and if sodium salts are abundant due to their wide solubility, the possibilities of their concentration in the soil solution with respect to those of calcium and magnesium rise and with it the risks of sodification, in this way the problems of salinity or accumulation of excess sodium cause losses in agricultural production, as well as an accelerated deterioration in the quality of the soils (Villafañe, 2011; Silva, Ochoa, Cristóbal, & Estrada, 2006).

The development of high-tech agriculture, in areas characterized by arid and semi-arid climates, depends on the availability of water for irrigation, which is sufficient in terms of quantity and acceptable in terms of quality, therefore, an intensive system of Agricultural exploitation has to assume sustainable characteristics, and to achieve it in the first instance, the availability of water must be measured from the economic, political and ecological point of view, with the aim of making it efficient, taking into account the conservation and preservation of water sources fresh water (Castellanos *et al*., 2002; Bermejillo *et al*., 2012).

Subsequently, the chemical quality of the water must be evaluated, since it is made up of the concentration of salts and the proportion of different ions in solution that could affect soil and crop resources, in their long-term use. Its knowledge allows determining if it can be recommended for agricultural use, since water plays an important role in the management of the irrigation and leaching fraction, as well as in the treatment of the water itself, in order to achieve an optimal level of production in situations where irrigation systems are used (Tartabull & Betancourt, 2016; Castellanos *et al*., 2002).

To estimate the suitability of water for agricultural irrigation, its salinity must be taken into account, since it is considered an important factor that affects crop yields, since it hinders the absorption of water by the plant. Another important aspect that must be taken into account is the sodicity of water, which originates when high concentrations of the sodium cation are present since it can displace calcium and magnesium or favor the precipitation of calcium and magnesium bicarbonates, causing that soil particles tend to disintegrate once sodium precipitates, causing a reduction in the rate of water infiltration, which may imply little availability of water in the soil (Vivot *et al*., 2010; Tartabull & Betancourt, 2016; Balmaseda & García, 2013).

Likewise, chlorine, phosphorous and boron ions must be evaluated, since these can accumulate in crops in concentrations high enough to reduce crop yield and facilitate the obstruction of some irrigation systems. However, the frequent problem in the case of agricultural irrigation is that it is generally not specified with what chemical quality the water should be used, but only importance is given to the agronomic quality determined by the crop to be irrigated, weather conditions, methods irrigation, soil drainage conditions and water, soil and plant management practices (Balmaseda & García, 2013; Castellón, Bernal, & Hernández, 2015). Therefore, the objective of the present study was to evaluate the impact on the chemical quality of groundwater and determine its suitability for agricultural use using the criteria of salinity, sodicity and toxicity in the region with the greatest productive intensification of the cultivation of chili (*Capsicum* ssp.), located on the Calera aquifer, in the state of Zacatecas.

Materials and methods

Location and characterization of the study area

The Calera aquifer belongs to Hydrological Region No. 37 El Salado, Fresnillo-Yescas basin, Fresnillo sub-basin, is located in the eastern portion of the state of Zacatecas with coordinates 22 ° 41 'and 23 ° 24' and 102 ° 33 'and 103 ° 01 ', with an approximate surface of 2,226 km² (Hernández *et al*., 2012). The aquifer is a closed basin and all the waterways are non-perennial streams, therefore there are no large reservoirs and rivers in the study area (Nuñez, Oesterreich, Castro, & Escalona, 2004).

The altitude of the Calera aquifer varies between 600 and 2000 m, which presents units of volcanic origin belonging to the Sierra Madre

Occidental, it is also formed by alluvial and lacustrine materials of clay, silt, sand and gravel cemented with calcareous clay. The lithology corresponds to igneous, limestone, dolomite and metamorphic rocks fractured by tectonic movements (Ávila *et al*., 2012; Hernández *et al*., 2012; Navarro *et al*., 2005). The most prevalent type of soil is the Catañozen luvico as it is the product of the dragging of the alluvial material that makes up the region (INEGI, 2014).

The climate in the region is semi-arid, there is not enough water to recharge it since there are no continuous surface sources, which has caused it to be an over-exploited aquifer at the national level because it extracts 50% more than what is recharged and Most of this extraction is destined for agricultural activity, mainly for the irrigation of the chili crop (*Capsicum* ssp.). Likewise an average abatement rate of 1.90 m per year is registered (INIFAP, 2010; Hernández *et al*., 2012; Ávila *et al*., 2012; Conagua, 2015; Sagarpa, 2016).

Water sampling and analytical methods

Stratified sampling with proportional allocation was performed according to the guidelines of Sukhatme and Sukhatme (1970). A population of 592 active agricultural wells was defined, which are frequently used for irrigation of the chili crop. Five strata with a depth ranging from 50 to 280 m above the static level were designed. (E1 = Stratum 1 from 50 to 80 m; E2 = Stratum 2 from 81 to 110 m; E3 = Stratum 3 from 111 to 140 m; E4 = Stratum 4 from 141 to 170 m; E5 = Stratum 5 ≥ 171 m). For the location of wells with these characteristics, the database of the Public Registry of Water Rights (REPDA) (Conagua, 2014) and the database of the Program of Direct Supports to the Field (Procampo) from 2016 and 2017 were consulted, in this way 15 deep and shallow wells were selected and located using a GPS.

For the second sampling, two blanks were selected, which correspond to samples 16 and 17 since they are wells used for human use and consumption, white 1 supplies the town of Pozo de Gamboa, Pánuco, Zacatecas, in the same way the white 2, it supplies the municipality of Morelos, Zacatecas. In Figure 1, the location of each well is shown including the targets distributed in the region that encompasses the Calera aquifer. Regarding the taking of water samples, it was carried out based on the NOM-014-SSA1-1993 standard at the end of the 2016-2017 and 2017-2018 chili production cycles. Two samples were collected with sterile polyethylene containers. 250 mL in each well and each sample was subsequently analyzed in triplicate.

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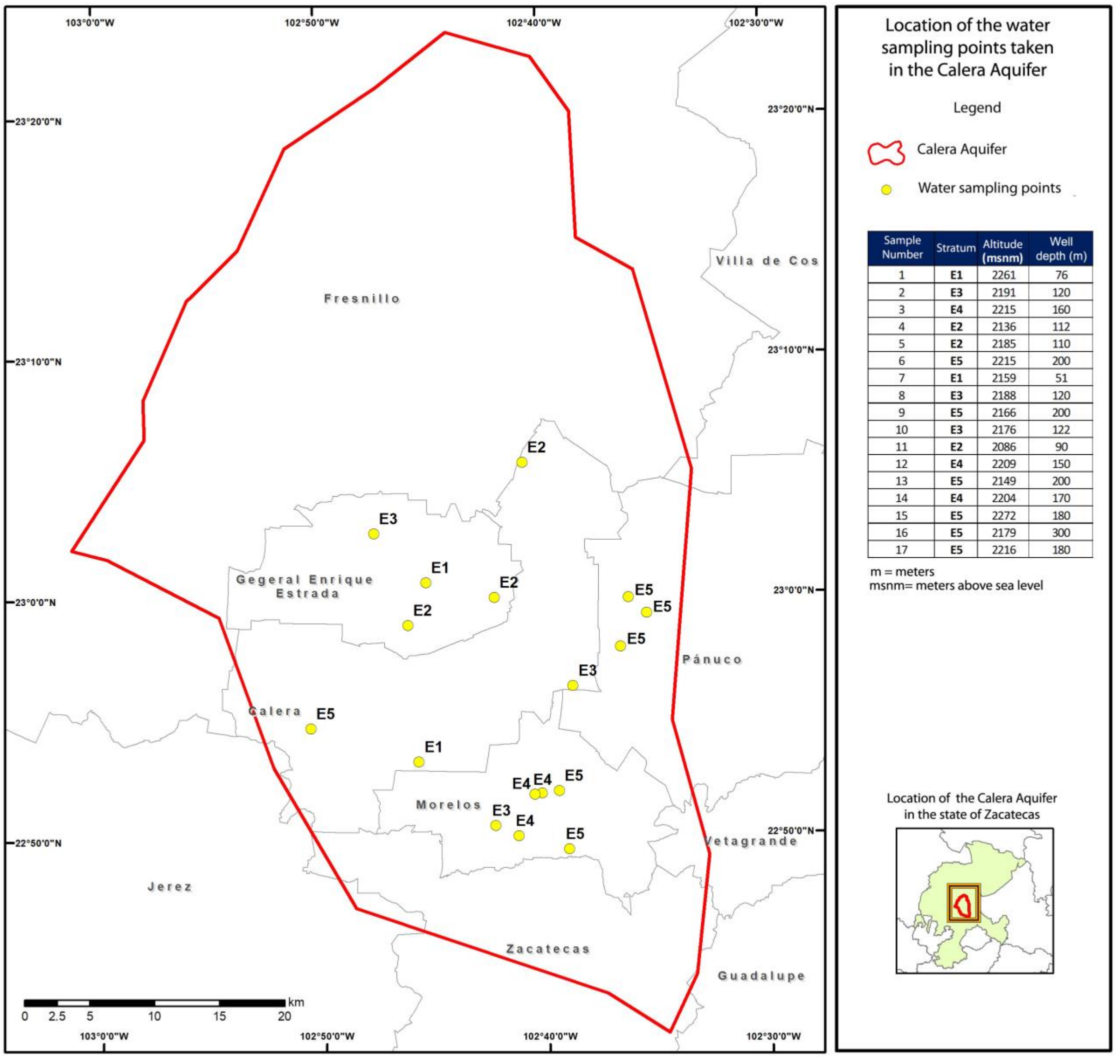

Figure 1. Location of the wells sampled by strata in the Calera aquifer.

To determine the quality of the aquifer water in each sample, the pH was measured and the concentrations in meq l^{-1} of the cations Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} and were determined the anions CO_3^{2-}, HCO_3^{-}, Cl^{-} and SO_4^{2-} as well as the electrical conductivity (EC) in µS cm^{-1}, boron (B), Nitrates (NO_3^-) and phosphorus (P) in mg l^{-1} (Table 1), then based on these parameters the indicators were estimated corresponding to evaluate the salinity, sodicity and toxicity criteria proposed by Ayers & Westcot (1987) and the hydrogeochemical classification of irrigation water was established.

Table 1. Applied techniques for the determination of the parameters in the groundwater of the Calera aquifer.

Determination	Method	References
pH	Potenciometric	NMX-AA-008-SCFI-2011
Electrical conductivity	Conductimetry	NMX-AA-093-SCFI-2000
Calcium and Magnesium	Volumetry	Richards, 1990
Sodium and potassium	Flamometry	NOM-021-SEMARNAT-2000
Carbonates and bicarbonates	Volumetry	NOM-021-SEMARNAT-2000
Chlorides	Volumetry	Richards, 1990
Sulfates	Turbidimetry	NOM-021-SEMARNAT-2000
Boron	Colorimetry	NOM-021-SEMARNAT-2000
Phosphor	Colorimetry	Rodier, 1990
Nitrate	Turbidimetry	Robarge, Edwards y Johnson, 1983

pH

According to Buccaro *et al*. (2006), cited by Medina *et al.* (2016), the pH is not a fundamental factor in determining water quality, but it does serve to assess the relative concentrations of dissolved carbonate species. Furthermore, Ortega *et al*. (2002) establishe that its values have important implications on the availability and management of nutrients, since the normal range of waters for agricultural use according to Ayers and Westcot (1987) is between 6.5 and 8.4.

Salinity, sodicity and toxicity criteria

Ayers and Westcot (1987), Richards (1990), Suárez (1981), and Wilcox (1948), indicate that they measure the amount of salts, sodium and soluble ions in irrigation water. Pérez and Pacheco (2004) point out that if they are found in excessive quantities they can accumulate in the soil or in the roots of the crop, reducing their yields and their presence comes mainly from agricultural fertilizers. To evaluate these criteria, the parameters of EC, total dissolved solids (TDS), effective salinity (ES), potential salinity (PS), normal sodium adsorption ratio (SAR), adjusted (SAR aj) and corrected (SAR°), residual sodium carbonate (RSC) and amount of B, P and NO_3^-. Based on the concentrations registered for SAR and EC, its classification was shown through a Richards diagram which was prepared with the QualiGraf program in its version 1.17.

Hydrogeochemical classification of water

According to Can, Sánchez and Cruz (2014), Hydrochemical or hydrogeochemical evaluations help determine the origin of the chemical composition of water and the relationship between water and the chemical constitution of rocks. The classification of water families was made using the Piper diagram, which according to Peña, Santacruz and Charcas (2012), is made up of two equilateral triangles located on the sides and a rhombus in the center. The left triangle represents the concentrations of the cations, the right triangle those of the anions and the rhombus represents the intersection of the concentrations of the cations and anions to define the water family to which the sample belongs. The diagram was made with the program GW_Chart Water Resources - USGS in its version 1.29, for this the sum of the concentrations of the cations, anions and total dissolved solids was made, later they were graphed to determine the dominant ion and the families of the Water.

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Statistical analysis

The water quality information for both sampling cycles was analyzed according to a randomized complete block design, where each cycle is one block, with the SAS PROC GLM (Statistical Analysis System 9.2), for the variables where there were differences statistics ($p < 0.05$) a Tukey mean test was performed. In order to group and locate the wells according to the characteristics of the water, a Principal Components analysis and a Cluster analysis were carried out.

Results and discussion

Classification of water with respect to pH

In the analysis of the composition of water in two sampling cycles (2016-2017), differences ($p < 0.05$) are observed in most of the variables (Table 2); the pH of the water in the first cycle tended towards alkalinity, however, during the second cycle it was considerably reduced ($p < 0.05$), classifying as mildly alkaline to neutral.

Table 2. Parameters evaluated in the water samples of the Calera aquifer. Production cycles 2016-2017.

	Evaluation period			Evaluation period	
Parameter	**2016**	**2017**	**Parameter**	**2016**	**2017**
pH	8.1 ± 0.1 a	7.6 ± 0.1 b	**Ani.** (meq l^{-1})	6.9 ± 1.1 a	5.0 ± 1.2 b
EC (µS cm^{-1})	427 ± 123 a	502 ± 214 a	**B** (mg l^{-1})	-0.5 ± 0.3 a	0.3 ± 0.1 b
Ca^{2+} (meq l^{-1})	1.9 ± 0.5 a	1.9 ± 1.3 a	**P** (mg l^{-1})	3.9 ± 3.5 a	0.04 ± 0.05 b
Mg^{2+} (meq l^{-1})	1.8 ± 1.2 a	1.9 ± 1.4 a	**TDS** (mg l^{-1})	274 ± 79 a	326 ± 146 b
Na^{+} (meq l^{-1})	3.2 ± 1.3 a	1.5 ± 1.0 b	**SE** (meq l^{-1})	3.9 ± 1.2 a	2.3 ± 1.6 b
K^{+} (meq l^{-1})	0.5 ± 0.2 a	0.2 ± 0.1 b	**PS** (meq l^{-1})	0.9 ± 0.4 a	1.3 ± 0.7 b
Cat. (meq l^{-1})	7.5 ± 1.5 a	5.4 ± 2.5 b	**SAR** (meq l^{-1})	2.6 ± 1.4 a	1.1 ± 0.8 b
CO_3^{2-} (meq l^{-1})	1.0 ± 0.0 a	0.1 ± 0.2 b	**pHc** (meq l^{-1})	7.2 ± 0.1 a	7.4 ± 0.2 b
HCO_3^{-} (meq l^{-1})	4.7 ± 0.9 a	3.3 ± 0.7 b	**SARaj** (meq l^{-1})	5.4 ± 2.8 a	2.2 ± 1.7 b
Cl^{-} (meq l^{-1})	0.6 ± 0.4 a	1.2 ± 0.7 b	**SAR°** (meq l^{-1})	3.2 ± 2.0 a	1.3 ± 1.0 b
SO_4^{2-} (meq l^{-1})	0.5 ± 0.2 a	0.2 ± 0.1 b	**RSC** (meq l^{-1})	2.0 ± 1.9 a	-0.19 ± 1.9 b

The means with different literals are statistically different from one cycle to another ($p < 0.05$).

The alkalinity that was evidenced in the water during the first cycle, is due to the lithology of the Calera aquifer which is related to the presence of rocks with carbonates, such as limestones and dolomites, thus increasing the concentrations of hydroxides, carbonates and bicarbonates of the ions Ca^{2+}, Mg^{2+}, Na^{+} y K^{+} (Hernández *et al*., 2012; Pérez, 2016). For their part, Ortega *et al*. (2002) in the research that was carried out in the Independencia aquifer in Guanajuato found that alkalinity in water is also caused by high concentrations of carbonates and bicarbonates.

In the case of the evaluated wells, the variation of the pH from one cycle to another is linked to the reduction of the concentrations of Ca^{2+}, CO_3^{2-} and HCO_3^{-}, as shown in Tables 4 and 5, also this could be a consequence from the interaction of various factors that Tartabull and Betancourt (2016) and INIFAP (2006) point out, such as leaching from the application of excessive amounts of fertilizers.

According to INIFAP (2006), the cultivation of chili in the region requires 220N-100P-150K for groove-based nutrition and suggests 200N-75P-100K, through fertigation. High amounts were registered in the application of phosphorus and potassium, since they exceeded 958 and 492% respectively on their demand, due to the fact that 900 kg ha^{-1} of monoammonic phosphate and 900 kg ha^{-1} of potassium nitrate are destined. Thus, it is evident that the doses of phosphorus and potassium exceed the recommended nutrition for the cultivation of chili in the region. Criswell (1998) states that high concentrations of nutrients in the soil could reach the groundwater through its faults and geological fractures, gradually decreasing the alkalinity of the irrigation water.

It was observed that the farmers carry out this practice under the influence of the commercial agrochemical companies, since most of the technical advice received comes from them, in such a way that they make the recommendation with the aim of increasing their sales, and the producer due to ignorance of the real needs of the crop, it attends to its indications, pretending that excess fertilization can provide it with enough nutrients such as NPK to ensure its harvest, without considering that this dynamic, according to Tartabull and Betancourt (2016), it could generate a negative impact on long-term soil and water quality.

This information is similar to that reported in groundwater quality studies carried out by Medina *et al*. (2016) in the municipality of Tuxcacuesco in the state of Jalisco, Sánchez, Álvarez, Pacheco, Carrillo and Amílcar (2016) in the hydrological subregions Bahía de Chetumal and Cuencas Cerradas in the state of Quintana Roo; Castellón *et al*. (2015) in several municipalities in the state of Tlaxcala; Sandeep, Vinit, Minakshi and Anshu (2011) in the City of Jhansi, Bundelkhand region, India; and Castellanos *et al*. (2002) in the Bajío region in the state of Guanajuato where the pH of most of their samples were moderately alkaline. The water in the Calera aquifer is considered suitable for agricultural use in both periods since Ayers and Westcot (1987) mention that the normal pH values fluctuate between 6.5 and 8.4. However, an adaptation to a pH between 5.5 and 6.5, with acids, is necessary for fertigation.

Salinity criterion

Electric conductivity

Regarding the EC, there were no statistical differences ($p > 0.05$) from one cycle to another. Despite this, it was possible to identify a slight increase in its concentration in the second year (Table 3), this may be a consequence of several complex processes of redistribution of salts which according to Tartabull and Betancourt (2016), depend on natural conditions, characteristics of the system, agricultural practices, and irrigation and drainage management, so it is inferred that the excessive application of phosphorous and potassium fertilizers in the region could have a marked influence on variations in the ionic concentration of irrigation water, if These manage to move to the groundwater.

Table 3. Parameters with the highest incidence on the water quality of the Calera aquifer. Production cycles 2016-2017.

	Principal components

	2016			2017		
	%					
Variables	**1**	**2**	**3**	**1**	**2**	**3**
Depht	-4	15	54	-8.5	-21	48
pH	-18	20	51	2	-4	66
EC	-6	-19	58	-6.8	-26	47
TDS	-26	43	-16	43	5	1
ES	-32	43	-16	43	5	1
PS	-29	35	8	37	24	5
SAR	-29	34	2	30	-6	12
pHc	35	27	6	-5.4	49	21
SAR aj.	32	-14	10	-38	9	0
SAR°	34	30	6	1	50	16
RSC	35	27	0.8	-2.9	51	12
P	-5	7	4	-10	0	4
B	-8	6	9	-2	0	0
NO_3^-				-39	20	1

Note: Each of the variables has a percentage incidence on the quality of the aquifer water, however they do not represent the percentage by component, which is obtained from the statistical program.

However, despite the increase observed in EC in most of the samples in both cycles, a C2 classification was reached, and being of this type Medina *et al.* (2016) establish that it can be used to obtain appropriate agricultural yields as long as there is a moderate degree of washing and sufficient drainage.

Only one sample during the second period was classified as C3, which is highly saline water, so INIFAP (2009) points out that even with adequate drainage, special salinity control practices may be required and only those species that are highly selected should be selected salt tolerant with an EC of 750 to 2,250 μS cm^{-1}, as is the case of cultivation, since according to Ayers & Westcot (1987) it can tolerate up to 850 μS cm^{-1}.

Based on the above, it can be established that the water of the Calera aquifer is suitable for irrigation of this crop, because, in general the samples from both cycles presented less than 750 μS cm^{-1}, these results coincide with those reported for groundwater by Ortega *et al*. (2002), Medina *et al.* (2016), and Castellón *et al*. (2015) in the states of Guanajuato, Jalisco and Tlaxcala, respectively, since they registered a C2 classification for most of their samples.

When using irrigation water for fertigation, the ionic concentration must be considered to adjust the content of the fertilizer to be dissolved, since by containing a good proportion of Ca^{2+} and Mg^{2+}, it can complement the nutritional requirement. For their part, the whites presented values of 426 and 466 μS cm^{-1}, which are within the acceptable scale for human use and consumption, according to the Ministry of Health (1994) in the NOM-127-SSA1-1994.

Total dissolved solids

Differences ($p < 0.05$) were found from one period to another in TDS concentrations, being higher during the second cycle. However even with the increase most of the samples were located between the admissible values for agricultural activities and human consumption, only sample 02 presented a slight degree of restriction, but in general the water of the Calera aquifer with respect to the TDS parameter is acceptable, since together with the EC they do not present a latent danger of salinity for the soil, however, its adequate drainage must be monitored.

Sandeep *et al*. (2011), and Oyedotun and Obatoyinbo (2012) in the cities of Jhansi, Uttar Pardesh, India and Akoko of Ondo, Nigeria, found that groundwater presented concentrations of 110 to 280 mg l^{-1} in TDS for the dry season, which did not show any type of restriction for agricultural use and human consumption, similar to the context of the Calera aquifer.

The increase in TDS from one period to another in the aquifer is due to its relationship with electrical conductivity, as according to Silva *et al.* (2006) the EC is directly proportional to the content of total dissolved solids in the water and these increase with the evolution of groundwater, or due to the effect of natural or anthropogenic contamination, and Porras, López, Álvarez, Fernández and Gimeno (1985) point out that temperature can influence the increase or decrease in the solubility of the substances present, specifically their electrical conductivity. Therefore, it is inferred that agricultural dynamics could be an important factor that can gradually contribute to the decrease in water quality in the region.

Effective and potential salinity

Regarding the effective salinity, statistical differences were identified ($p < 0.05$) from the first to the second evaluation cycle, observing that for 2017 most of the samples were not considered suitable for agricultural irrigation because in this period was higher concentrations of Na^+ than Ca^{2+} and Mg^{2+} therefore, there may be a risk of forming Na^+ salts as they are the last to precipitate, as Ortiz (1997).

In contrast, during the 2017 cycle, only two samples presented high levels of ES, placing the majority as acceptable for agricultural purposes, although, during this period, it was detected that the concentrations of Ca^{2+} y Mg^{2+} were lower than those of CO_3^{2-}, HCO_3^-, managed to exceed the Na^+ content and it can be inferred that there was a lower risk of forming carbonated and bicarbonate salts of Na^+ since, according to the NOM-O21-SEMARNAT-2000 (2000), they are classified as highly harmful for cultivation and favorable for the processes of salinization and deflocculation of clays in the soil since their saturation point is very high.

Silva *et al*. (2006), in the Ciénega de Chapala, recorded ES values between 1 to 15 meq l^{-1} for most of the groundwater samples, classifying them as conditioned for agricultural use as Balmaseda and García (2013) in the basin from the Naranjo river, Cuba. For their part, Castellón *et al*. (2015), in the state of Tlaxcala obtained concentrations of 0.4 to 4.2 meq l^{-1} which can be used for the irrigation of most crops, a situation that is similar to that of the Calera aquifer.

The potential salinity was different ($p < 0.05$) during its evaluation period, since in the first cycle it was observed that all the samples were within the acceptable scale for agricultural use despite the content of CO_3^{2-}, HCO_3^- and SO_4^2 was higher with respect to Ca^{2+} and Mg^{2+}, so the possibility of forming $CaSO^4$ salts in the soil could be presented, since Salgado, Palacios, Galvis, Gavi and Mejía (2012) in the Valle de Guadalupe aquifer observed that this situation is more frequent in soils of calcareous origin such as the Calera aquifer region, especially after having precipitated Ca^{2+} and Mg^{2+} from the soil with CO_3^{2-} y HCO_3^- from irrigation water.

For the second evaluation cycle, a wide increase ($p>0.05$) was observed in Cl^- concentrations with respect to SO_4^{2-}, so according to Castellón *et al*. (2015) there is a possibility that Cl^- salts gradually form and accumulate after precipitating.

Robles (2002) reports that in the Tehuantepec Irrigation District, Oaxaca, the potential salinity of the water was classified as acceptable since values of 1 to 3 meq l^{-1} were reported. The water in the Calera aquifer is in this range, and it also corresponds to the dry period, however, the parameter must be monitored frequently to avoid possible damage to the crop due to the accumulation of Cl^{-} salts. In general, the salinity criterion during both periods was acceptable for agricultural use.

Sodicity criterion

Sodium adsorption ratio

During the first period evaluated, most of the samples, regarding the three SAR variations, showed higher sodium content in 2016 than in 2017; and together with the EC, they were classified as C2-S1, water of medium salinity low in sodium with a moderate risk of soil salinization (Figure 2). For the second cycle, an increase in the concentrations of Ca^{2+} and Mg^{2+} and a decrease in the content of Na^{+} were identified, and consequently there was a reduction in the Sodium Adsorption Ratio, which allowed registering statistical differences ($p < 0.05$) of one cycle to another, however despite this the water classification was C2-S1 (Figure 3).

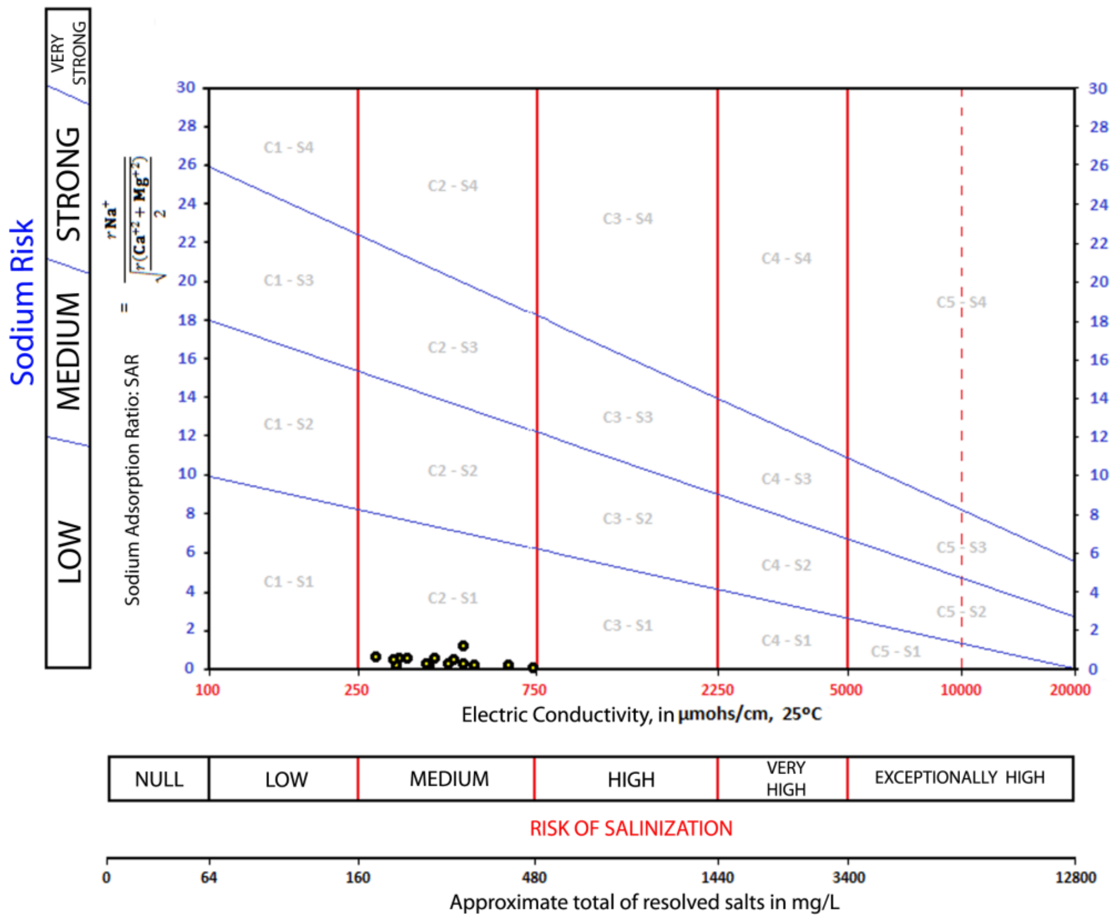


Figure 2. Classification of the Calera aquifer water in terms of its EC and SAR in the 2016 cycle.

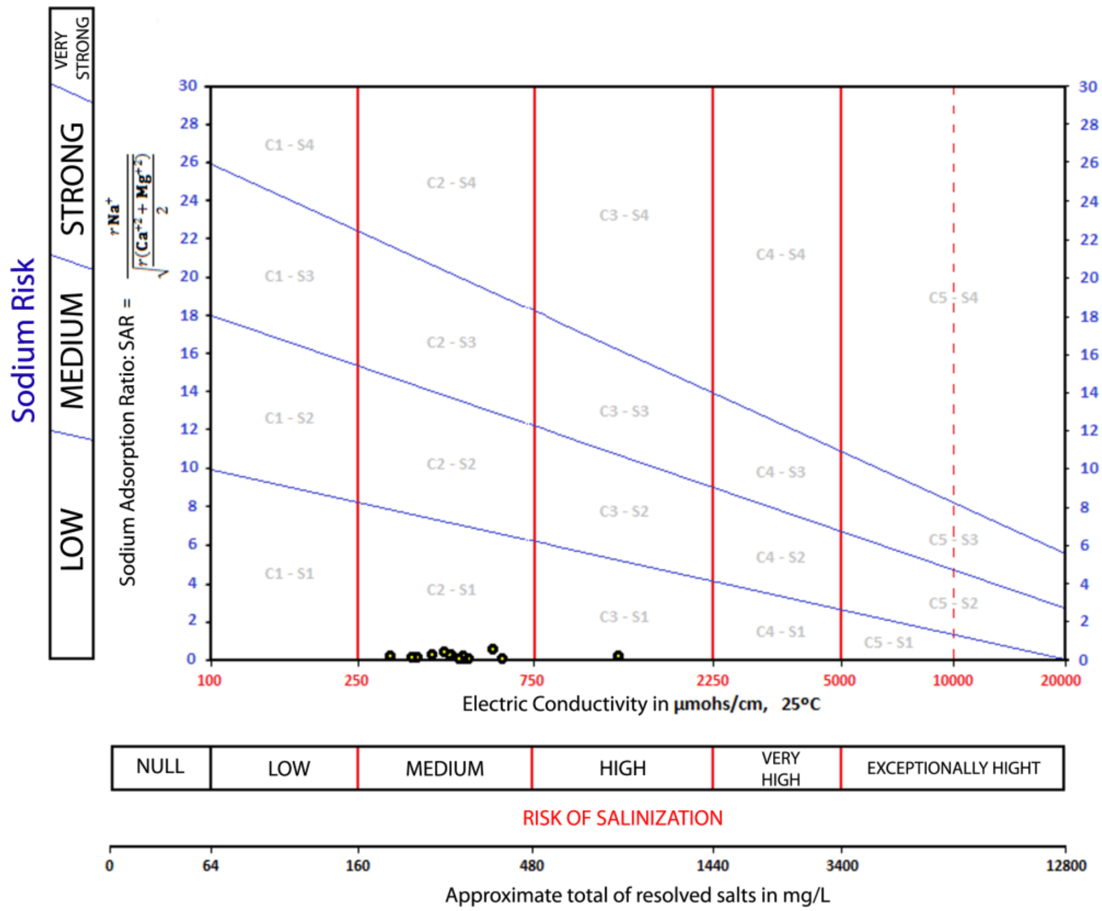


Figure 3. Classification of the Calera aquifer water in terms of its EC and SAR in the 2017 cycle.

Silva *et al*. (2013), in an evaluation of the chemical quality of ground and surface water in the Duero river basin, Michoacán, showed similar results and mention that water, being class C2-S1, can be used in almost any type of soil without high risk. to reach dangerous degrees of interchangeable sodium that affect its properties, as long as frequent washing is carried out to avoid possible salinization problems.

However, Can *et al*. (2011), in a study on the origin and quality of groundwater in the eastern basin of Mexico, emphasize that after carbonates, bicarbonates and sulfates have precipitated, sodium remains in solution and accumulates in the first layers of the soil, where it influences the stability of the aggregates and the structure of the soil for being the last salts to precipitate. Therefore, although the SAR was acceptable for the water samples of the Calera aquifer, it should be considered frequently analyze this parameter in the soils of the region to avoid its accumulation and possible damage to its structure, as mentioned by Castellanos *et al*. (2002) and Buccaro *et al*. (2006) in theirs researches on groundwater quality for agricultural use in the state of Guanajuato, México and Mar de Plata City, Argentina, found that groundwater is significantly increasing the concentration of sodium, SAR and pH over time, as well as potential damage to the soil structure.

Residual sodium carbonate

With regard to the residual sodium carbonate (RSC) parameter, during the first cycle evaluated it was evident that 13% of the samples were not suitable for agricultural use, and 86% were classified as conditioned since high HCO_3^- concentrations were detected with respect to those of Ca^{2+} and Mg^{2+}, a situation that according to Castellanos *et al*. (2002)

and Can *et al*. (2014) could have formed sodium carbonate salts due to its high solubility once calcium and magnesium as bicarbonates were precipitated into the soil, therefore greater care should be taken when using this water for agricultural irrigation in the Calera aquifer during the dry season, according to Cuellar, Ortega, Ramírez y Sánchez (2015), in an evaluation of the sodium adsorption ratio of the waters of the Mezquital Valley hydrographic network, Hidalgo found that water of this type is highly harmful to soil structure and infiltration processes.

Contrary to the above, for the period of 2017 it was observed that the concentrations of Na^+, CO_3^{2-} and HCO_3^- decreased considerably, evidencing statistical differences ($p < 0.05$) in the cycles analyzed, locating the majority of the samples as suitable for irrigation of the chili crop, this situation could be due to the interaction of the aquifer with its recharge before the evaluation cycle.

These values coincide with those reported by Can *et al*. (2014) in the Sierra Norte de Puebla, Mexico, since they indicate that samples of this type are calcium-magnesium and magnesium-calcium which show higher amounts of Ca^{2+} and Mg^{2+} with respect to CO_3^{2-} and HCO_3^-, and that the positive values indicate that calcium and magnesium precipitate into the soil as carbonates and bicarbonates, there being only sodium salts in solution, which must be taken into account when using these for irrigation, since they can form CO_3^{2-} and HCO_3^- of Na^+, salts that according to Cuellar *et al*. (2015) are highly damaging to the soil structure, since infiltration decreases with sodium concentrations. For their part, Nishanthiny, Thushyanthy, Barathithasan and Saravanan

(2010) mention that the main source of carbonates is the dilution of carbonate rocks and therefore the water in the Calera aquifer may contain higher concentrations of Ca^{2+} and Mg^{2+}, causing negative values in the RSC.

The statistical analysis by main components shown that 88% of the water quality of the aquifer in the 2016 cycle was distributed in the first three components, which were related to the variables of the criteria of sodicity, salinity and environmental conditions (Table 3), likewise, it was observed that only 52% of the quality of the aquifer water in this period, depended on variables that met the criterion of sodicity, therefore, a negative correlation was identified for this period since at a lower concentration of the sodicity parameters, the water quality was mostly acceptable for agricultural use in the region.

For the 2017 cycle, the analysis observed that the percentage that evaluated the quality of the water in the Calera aquifer increased, and in the same way, it was strongly linked to the first three components, concentrating 90%, of which component one registered a greater presence with 43%, this was integrated by the variables of the salinity criterion, later the parameters referring to sodicity and environmental conditions contributed with 30 and 17%, respectively. Likewise, this situation again evidenced a negative correlation because, in general for this period, when observing lower concentrations of salinity, the quality of the water in the Calera aquifer was considered higher.

Both statistical analyzes agree with the results obtained in the evaluated periods since for the 2016 cycle higher values were registered in the concentrations of the sodium parameters and during the 2017 cycle an increase in some salinity parameters and a reduction were identified in those of sodicity, as previously mentioned according to Can *et al*. (2014) this situation could be due to various salt redistribution processes linked to the amount of river precipitation, mainly due to the fact that during the second period a 46% reduction in the amount of rain was detected.

Toxicity criteria

Boron

Through the two samplings it was detected that the boron content in the water was very low, for both periods the average of the concentrations was less than 0.67 mg l^{-1}, positioning the water of the Calera aquifer as suitable for semi-tolerant crops to this element (Table 3), since the chili crop according to Ayers and Westcot (1987) can support up to 2 mg l^{-1} of boron from irrigation water. The information generated in this study regarding this parameter coincides with the values recorded by Can *et al.* (2011) in the Eastern Basin of Mexico; Medina *et al.* (2016) in

Tuxcacuesco, Jalisco, and Castellón *et al.* (2015) in the state of Tlaxcala, Mexico, since they detected on average concentrations lower than 0.45 mg l^{-1} in groundwater, which can be used without any restriction.

Phosphorus

During the 2016 cycle, high amounts of phosphorus were found in the irrigation water of the Calera aquifer, since an average of 4 ± 3 mg l^{-1} was reached, because 50% of the samples had concentrations above 2 mg l^{-1}, classifying higher than normal values in irrigation water. According to Tunney, Csathó y Ehlert (2003) these values could be a consequence of the excessive phosphate fertilization applied in the Chilean plots in the region, surface runoff, leaching processes, the location of faults and geological fractures, and the movement of underground currents.

Contrary to the above, in 2017 the samples and even the blanks did not present high concentrations of phosphorus, on the contrary, an average of 0.04 ± 0.05 mg l^{-1} was registered, being within the acceptable range for agricultural use, therefore it is inferred that The quality of the water in the Calera aquifer is strongly linked to its recharge processes, especially those related to the amount of rain, since during the second cycle the rainfall recorded was almost 50% less than that of the 2016 and therefore statistical differences were evident ($p <$ 0.05).

The results of the second period coincide with those recorded by Oyedotun and Obatoyinbo (2012) during their hydrogeochemical assessment of groundwater quality in the local government area of Akoko Northwest of Ondo State, Nigeria, as they showed values below 2 mg l^{-1} which do not represent a degree of restriction for the irrigation of any crop, likewise, this parameter during the statistical analysis by main components did not present a wide incidence in the quality of the aquifer water in both cycles. So far, no studies have been identified where amounts greater than 2 mg l^{-1} of P are reported in groundwater.

Nitrate

The NO_3^- concentrations in the aquifer water were very low since an average of 2 ± 1 mg l^{-1} was observed, with a maximum value of 4 mg l^{-1} and a minimum of 0.5 mg l^{-1}, so the water Regarding this parameter, it does not represent a risk to human health according to the guidelines of the World Health Organization (WHO, 1985), Wakida and Lerner (2005), and the NOM-127-SSA1-1994, because the samples did not exceed the limit of 45 mg l^{-1} that are suitable for agricultural use, it was also observed that the amounts applied by producers of the Calera aquifer in terms of nitrogen fertilization were below what is recommended by INIFAP (2006) and by not present a surplus of this macroelement, so far they have not impacted the quality of the water in the Calera aquifer due to the effect of leaching and percolation of the water, as found by Saleem, Hussain and Mahmood (2016) in the Noida region of India. Furthermore, the amounts of NO_3^- found in the Calera aquifer are below those identified by Sarabia, Cisneros, Aceves, Duran and Castro (2011), and Peña *et al.* (2012), both works carried out in the San Luis Potosí valley aquifer; and Pérez and Pacheco (2004) in the state of Yucatan, therefore, showed average concentrations of 5.0, 6.2 and 21.3 mg l^{-1} respectively, all suitable for agricultural purposes.

Hydrogeochemical classification

During the 2016 sampling, two water families were recorded because 53% of the samples corresponded to non-dominant bicarbonated waters and the remaining 47 % were considered as bicarbonated sodium as shown in Figure 4, it should be noted that For the second evaluation period, Figure 5 shows four families in which bicarbonated non-dominant waters predominated with 47 %, followed by bicarbonated calcium waters with 24% and those of bicarbonated and sodium magnesium origin bicarbonated with 17 and 12 %, respectively.

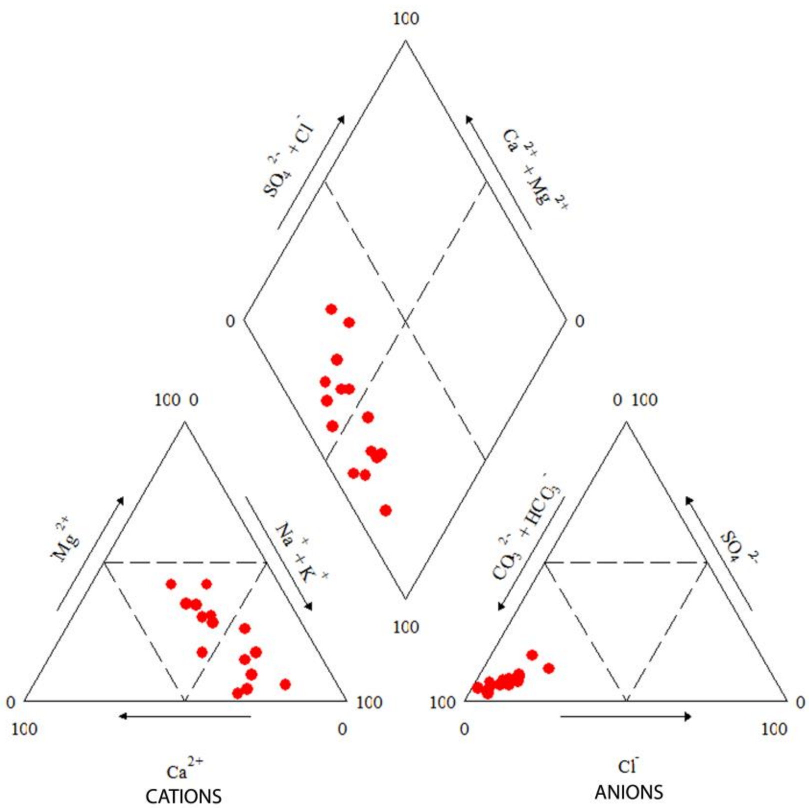


Figure 4. Hydrogeochemical classification of the Calera aquifer water in the 2016 cycle.

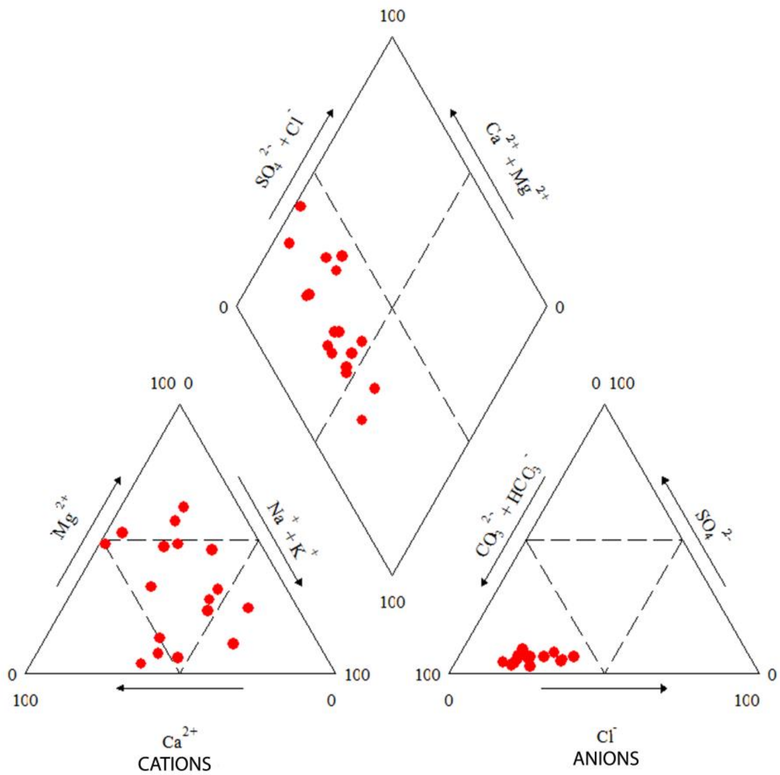


Figure 5. Hydrogeochemical classification of the Calera aquifer water in the 2017 cycle.

Contreras, Vargas and Badilla (2012), in a study on the hydrogeochemical and isotopic properties of groundwater in the middle part of the Tulián river basin, in Honduras, observed that mostly bicarbonate-type waters have a short residence time in the soil in the recharge areas, meanwhile Padilla and García (2012), and Morán, Ramos, López, Carranco and Santacruz (2013) in studies on hydrogeochemistry in the Quiscab river basins, Guatemala, and

Huasteca Potosina, Mexico, found that this type of water is characterized by interaction with sedimentary calcareous rocks.

Both situations are similar to that of the Calera aquifer, due to its geology of calcareous origin and the bicarbonate nature of its water could be due to its interaction with this type of rock and its hasty infiltration due to the action of faults and geological fractures in the region and a fast fluidity in the movement of underground currents, since the average displacement of water for the region is 64 cm. day^{-1}.

Subsequently Morán *et al*. (2013) recorded that bicarbonated magnesium-type waters are thus due to the incorporation of substances through the geological material with which they are in contact, in addition they have a longer travel time in the aquifer than bicarbonated calcium and finally according to Padilla and García (2012) according to the Chebotarev sequence, the water cationically evolves from the calcium type, going to the magnesium, and later ending in sodium, waters considered typical of volcanic geological environments.

According to Contreras *et al*. (2012), and Padilla and García (2012), the increase in water families from one period to another in the Calera aquifer may be a consequence of the interaction of water with the composition of the geological matrix with which it is in contact during its journey through the medium and by the reactions that are carried out as a water evolves, because during the first cycle a precipitation of 753 mm was recorded, far exceeding the average of this area which amounts to only 450 mm, for the second period evaluated, it was observed that the precipitation was slightly less than the average, registering 405 mm, thereby it is inferred that the waters interacted with the calcareous materials of the area, diluting the calcium and according to Can *et al*. (2014), this situation was the one that could originate the character of the bicarbonate calcium waters.

Sodium bicarbonate waters are associated with the presence of clay minerals that mainly affect the Na^{+}, Ca^{+}, and Mg^{2+} cations, because Contreras *et al*. (2012) exposes that the land gives Na^{+} ions and takes cations of Ca^{+} y Mg^{2+} from the water and as a result the water softens and tends to become sodium water. Therefore, throughout the flow of the Calera aquifer, a cation exchange is taking place that could be responsible for the waters sampled at some points being of the sodium bicarbonate type, which is considered to have the longest period of remained in the aquifer. However, more attention should be paid when using it since it shows high concentrations of Na^{+} that could precipitate in the soil, causing it to deflocculate.

In the Cluster analysis, three groups were obtained, which are not correlated by their depth, this classification was originated by the concentrations obtained in each parameter and by the region where the different evaluated wells are located, in this way during the period of 2016 it was identified that group one corresponded to the highest concentrations of ES, PS and RSC and the lowest in terms of EC and TDS, later in the other groups no other trend was observed in the distribution of concentrations for each of its parameters (Figure 6).

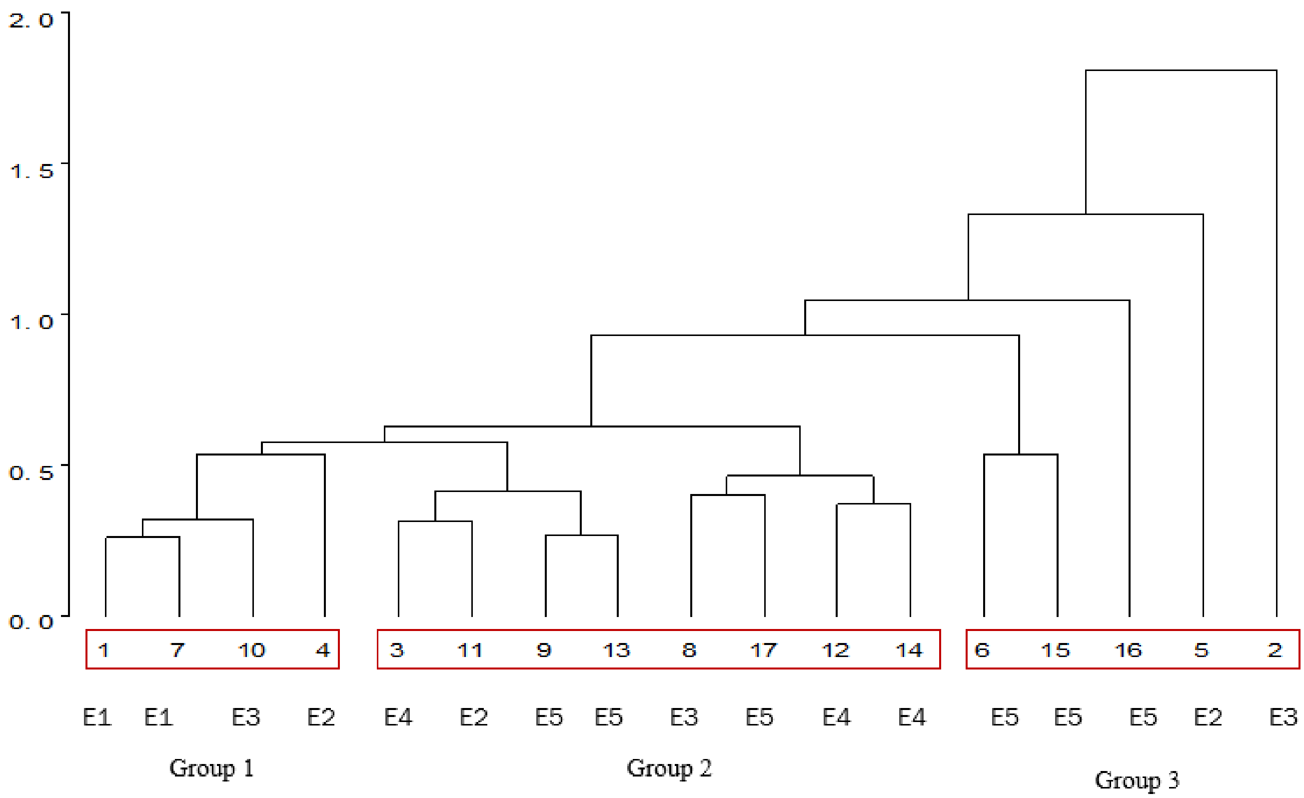


Figure 6. Grouping of Calera aquifer wells according to the evaluated parameters, 2016-2017 cycles. Note: Each evaluated well belongs to a stratum which is specified below the well number.

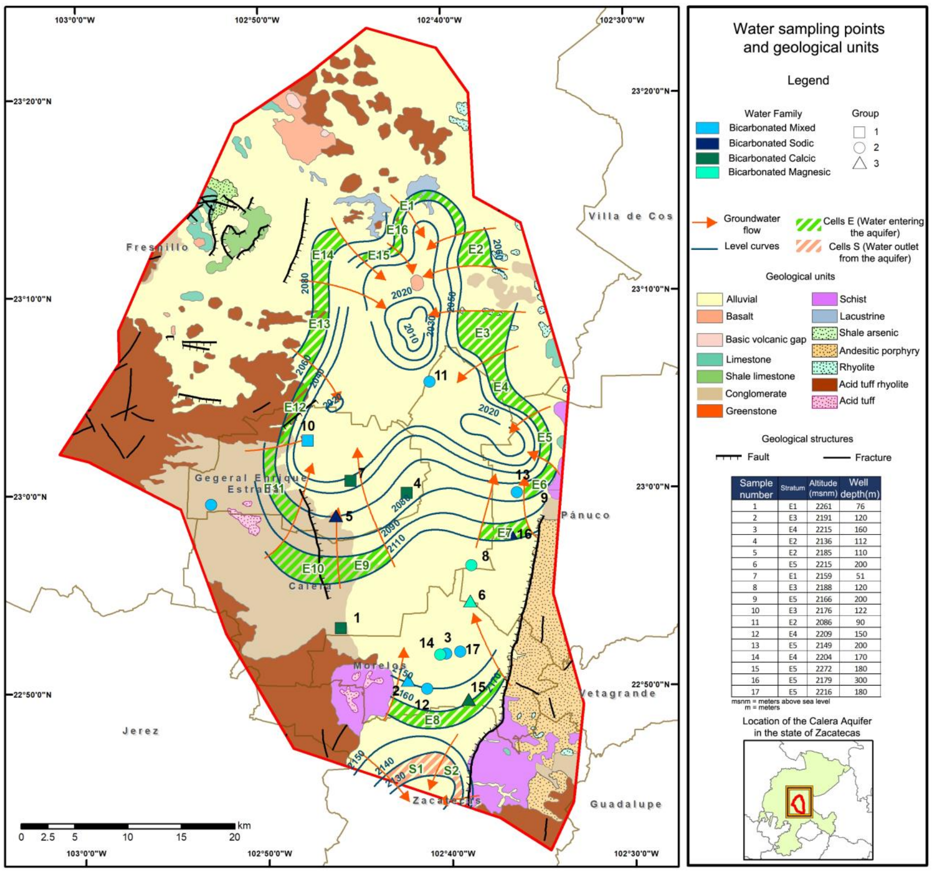
Regarding the period of 2017, it was found that in group one the lowest concentrations were found for EC, ES, PS, SAR and RSC, later in group two medium concentrations were located and in group three the presence of the higher concentrations in the same parameters (Table 4).

Table 4. Classification of EC, ES, PS, SAR and RSC according to the group of wells that was identified during the cluster statistical analysis.

Clúster	EC	ES	PS	SAR	RSC
Group 1	343 ± 26b	1.2 ± 0.02b	0.8 ± 0.2b	1.0 ± 0.1a	0.9 ± 0.1a
Group 2	453 ± 33ab	1.8 ± 0.5b	1.2 ± 0.3ab	1.1 ± 0.7a	0.01 ± 0.6a
Group 3	706 ± 316a	4.1 ± 2.1a	2.0 ± 0.9a	1.7 ± 1.5a	-1.2 ± 3.3a

The means with different literals per column are statistically different ($p < 0.05$).

The wells that made up group one in the 2017 cycle are located to the east of the Calera aquifer, the majority of group two is located to the west and the largest proportion of group three is in the southern portion of the aquifer. It should be noted that the wells that make up the three groups are the same for both evaluation cycles, which during the second period recorded the highest quality of water in the aquifer, the second group obtained an acceptable quality and the third conditional, which mostly Wells are located in the region with the highest altitude (Figure 7). However, all the parameters of the three groups proved adequate for agricultural irrigation, some can be used under certain restrictions or situations, but without any impediment for the production of chili to be affected.



Sample number	Stratum	Altitude (msnm)	Well depth(m)
1	E1	2261	76
2	E3	2191	120
3	E4	2215	160
4	E2	2136	112
5	E2	2185	110
6	E5	2215	200
7	E1	2159	51
8	E3	2188	120
9	E5	2166	200
10	E3	2176	122
11	E2	2086	90
12	E4	2209	150
13	E5	2149	200
14	E4	2204	170
15	E5	2272	180
16	E5	2179	300
17	E5	2216	180

Figure 7. Grouping of wells according to the values obtained in the evaluated parameters and their location in the region, 2017 cycle.

Likewise, the statistical analysis by strata during the evaluation cycles showed that the depth of each well is not related to the quality of the water in the Calera aquifer, since there are no statistical differences in the parameters of the shallower strata. Deeper ($p>0.05$), however, the pH, CO_3^{2-} and HCO_3^- are different from one cycle to another in all the strata ($p < 0.05$). Therefore, the depth of each well does not affect the quality of its water, it depends on the region where each well is located and its interaction with the elements of the geological material (Table 5).

Table 5. Analysis by strata in the ionic concentration, electrical conductivity (EC) and pH of the water in the Calera aquifer, Zacatecas. Production cycles 2016-2017.

	2016					2017					
	E1	**E2**	**E3**	**E4**	**E5**	**E1**	**E2**	**E3**	**E4**	**E5**	**EEM**
pH	8.1a	8.09a	8.21a	8.24a	8.24a	7.54b	7.46b	7.56b	7.58b	7.80b	0.07
EC μScm^{-1}	312.5a	377.7a	492.7a	399.7a	494.5a	354a	444.3a	682.7a	449.3a	550a	68.3
Ca^{2+}	1.67a	1.76a	2.44a	1.95a	1.99a	1.97a	1.68a	2.76a	1.60a	1.66a	0.38
Mg^{2+}	0.915a	0.46a	2.25a	2.20a	2.59a	0.30a	0.72a	2.72a	2.06a	2.65a	0.46
Na^{+}	2.5a	4.75a	2.67a	2.56a	3.54a	1.00b	2.33a	1.67a	1.00b	1.25b	0.61
K^{+}	0.67a	0.63a	0.56a	0.39ab	0.37ab	0.30a	0.30a	0.30a	0.21b	0.19b	0.06
Cations	5.75ab	7.59ab	7.79a	7.10a	8.50a	3.57b	5.03a	7.44b	4.86b	5.75ab	0.92
CO_3^{2-}	1.0a	1.0a	1.0a	1.0a	1.0a	0.12b	0.13b	0.31b	0.01b	0.28b	0.05
HCO_3^{-}	5.17a	5.28a	4.44a	4.67a	4.46a	3.04b	3.62b	3.55b	3.41b	3.24b	0.53
Cl^{-}	0.29a	0.48a	0.66a	0.71a	0.98a	0.90a	0.82a	1.63b	0.97a	1.54b	0.21
SO_4^{2-}	0.22a	0.37ab	0.73b	0.47ab	0.66b	0.13a	0.19a	0.33ab	0.33ab	0.35ab	0.08
Anions	6.68a	7.12a	6.83a	6.84a	7.10a	4.17b	4.76b	5.82ab	4.71b	5.41ab	0.68

SEM = Standard error of the mean. The parameters with different literals per row are statistically different ($p < 0.05$).

Conclusion

The excessive amount of nutrients applied for the production of chili has not impacted the quality of the water in the region through its infiltration by leaching and percolation movements, since the criteria of salinity, sodicity and toxicity evaluated revealed that the majority of its parameters were classified as acceptable for agricultural use, only during the 2016 cycle high concentrations of phosphorus were observed in 50% of the samples, however, in the period of 2017, these quantities were considerably reduced and can be used without any degree of restriction. Therefore, the water quality of the Calera aquifer presents a strong interaction with its recharge processes mainly due to the amount of river precipitation in each period, the geology of the region, the speed of underground currents and the infiltration by the action of geological faults and fractures. Thus, the chili production system in the region can be considered as a sustainable crop since, up to now, its processes have not had a significant impact on one of the resources on which it mainly depends, however, a new analysis is recommended. in the rainy season to contrast the results generated in this analysis and to be able to differentiate the amount of elements present in the irrigation water for both seasons.

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